

1 **A new high-performance proton-conducting electrolyte for next-generation**
2 **solid oxide fuel cells**

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19 **Abstract**

20 Conventional solid oxide fuel cells (SOFCs) are operable at high temperatures (700 –
21 1,000 °C) with the most commonly used electrolyte, yttria-stabilized zirconia (YSZ). SOFC
22 R&D activities have thus been carried out to reduce the SOFC operating temperature. At
23 intermediate temperatures (400 - 700 °C), barium cerate (BaCeO₃) and barium zirconate
24 (BaZrO₃) are good candidates for use as proton-conducting electrolytes due to their promising
25 electrochemical characteristics. Here, we combined two widely studied proton-conducting
26 materials with two dopants and discovered an attractive composition for the investigation of
27 electrochemical behaviors. Ba_{0.9}Sr_{0.1}Ce_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-δ} (BSCZYSm), a perovskite-type
28 polycrystalline material, has shown very promising properties to be used as proton-conducting
29 electrolytes at intermediate temperature range. BSCZYSm shows a high proton conductivity of

1 $4.167 \times 10^{-3} \text{ S cm}^{-1}$ in a wet argon atmosphere and peak power density of 581.7 mW cm^{-2} in Ni-
2 BSCZYSm | BSCZYSm | BSCF cell arrangement at $700 \text{ }^\circ\text{C}$, which is one of the highest in
3 comparison to proton-conducting electrolyte-based fuel cells reported till now.

4 *Keywords:* Proton-conducting electrolyte, Structural analysis, Electrochemical performance,
5 Power density, Solid oxide fuel cells.

7 **Introduction**

8 In the search for green energy resources, solid oxide fuel cells (SOFCs) have become a
9 promising alternative since these materials are practicable in a variety of fuels and have low
10 emission ^[1-3]. The state-of-the-art oxide ion-conducting electrolyte for SOFCs is yttria-stabilized
11 zirconia (YSZ), which operates at high temperatures ($700 - 1000 \text{ }^\circ\text{C}$). The high operating
12 temperature is a challenge in material selection and complex technology, resulting in high costs
13 and delayed SOFC commercialization. Although using oxide ion conductors in SOFCs is typical
14 at high temperatures, the challenges are still obvious in terms of mismatched materials, low
15 tolerance to operating conditions and low fuel efficiencies. Intermediate-temperature (IT)-SOFCs
16 are becoming increasingly attractive for energy generation. At intermediate temperatures ($400-$
17 $700 \text{ }^\circ\text{C}$), several perovskite electrolytes (general formula, ABO_3) exhibit good electrochemical
18 properties in terms of proton conductivity ^[4-8]. Enhanced proton conduction is a promising
19 method to improve the performance in operation. Higher efficiency can be achieved in proton-
20 conducting SOFCs (SOFC- H^+) than in oxide ion conducting SOFCs (SOFC- O^{2-}), although the
21 maximum voltage and power density are still lower ^[9].

22 Since Iwahara et al. ^[10] discovered protonic conductivity in SrCeO_3 ceramic oxides,
23 doped BaCeO_3 and doped BaZrO_3 have been extensively investigated as electrolyte materials for
24 proton-conducting SOFCs (SOFC- H^+) ^[4,11-14]. Yttrium-doped BaCeO_3 has been found to be one
25 of the best proton conductors but is unstable in CO_2 - and H_2O -containing atmospheres. On the
26 other hand, $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ shows excellent stability in CO_2 - and H_2O -containing atmospheres,
27 but its protonic conductivity is not sufficient for practical applications ^[15-17]. As there is a trade-
28 off between conductivity and chemical stability, solid solutions between BaCeO_3 and BaZrO_3 ,
29 e.g., $\text{Ba}(\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2})\text{O}_{3-\delta}$, have been found to possess a high ionic conductivity of 9×10^{-3} at
30 $500 \text{ }^\circ\text{C}$ and to show excellent chemical stability in a 2% CO_2 atmosphere at $500 \text{ }^\circ\text{C}$ (stored for

1 one week) and in an H₂O vapor atmosphere. Co-doping of the B-site (Ce/Zr site) with two
2 different trivalent cations is very beneficial for achieving high proton conductivity and good
3 stability in humid atmospheres^[18,19]. Several dopants have been studied to improve the stability
4 and conductivity of these materials. The A-site of perovskite can be doped with a large-ionic-
5 radius element, and the B-site can be doped with a small-ionic-radius element^[6]. In most
6 previous works, some percentage of Ce and/or Zr was substituted by trivalent cations such as Y,
7 Yb, Gd, Sc, Pr, and Sm at the B-site to generate oxygen vacancies to enhance the conductivity of
8 the material^[20–24]. For example, Ce was doped with Zr in a BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95} series to
9 increase proton conductivity and chemical stability, resulting in good chemical stability in steam
10 and carbon dioxide atmospheres^[22,23]. The percentage of Ce at the B-site also has a strong effect
11 on the proton concentration in perovskite materials^[25]. Sm-doped proton conductors show
12 promising performance for IT-SOFCs. Very little work has been done to substitute Ba with Sr or
13 Ca, which can also have a good effect on protonic conductivity^[26].

14 In this work, we prepared a novel composite electrolyte of
15 Ba_{0.9}Sr_{0.1}Ce_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-δ} (BSCZYSm) and carried out X-ray diffraction (XRD),
16 Rietveld refinement, particle size analysis, thermogravimetric analysis (TGA), electrochemical
17 impedance spectroscopy (EIS), fuel cell tests and scanning electron microscopy (SEM). An
18 anode-supported fuel cell with a thick anode layer and thinner electrolyte and cathode layers was
19 fabricated. A thin electrolyte is important to decrease the ohmic loss, thus increasing
20 performance and decreasing the operating temperature, which diminishes the degradation and
21 prolongs the lifetime of the cell. Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) is an excellent mixed ionic-
22 electronic conductor (MIEC) for IT-SOFC application because of its superior electrochemical
23 characteristics relative to other cathodes with a perovskite structure (ABO₃)^[27]. BSCF has a high
24 oxygen diffusion rate and oxygen vacancy concentration, resulting in an effective oxygen
25 reduction reaction (ORR) and high power production^[28]. Hence, we examined the novel
26 electrolyte (BSCZYSm) and fabricated an anode-supported fuel cell with BSCF as a cathode to
27 observe the electrochemical characteristics.

28

1 **Methods**

2 *Synthesis and characterizations of BSCZYSm*

3 $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$, a perovskite-type material, was prepared by the solid-
4 state reaction method. Stoichiometric amounts of BaCO_3 , SrO , CeO_2 , ZrO_2 , Y_2O_3 and Sm_2O_3
5 powders were mixed in ethanol and ground using an agate mortar and pestle. The mixed powders
6 were sintered in air at 950 °C for 8 hours. A hydraulic press was utilized to make 13 mm
7 diameter pallets by pressing at 4 psi and sintering at 1400°C and 1450°C for 6 hours and 8 hours,
8 respectively. XRD patterns were obtained on an Empyrean Alpha 1 X-ray diffractometer from
9 Malvern Panalytical ($\text{CuK}\alpha 1$, $\lambda = 1.5406 \text{ \AA}$) in air, and Rietveld analysis was performed using
10 FullProf software [29]. Particle size analysis was carried out using a HORIBA particle size
11 analyser to specify the grain size of the particle after manual grinding of the prepared material
12 with a mortar and pestle for 10-15 minutes. The hydration furnace was operated at 0.4 P_{N_2} at 800
13 °C, 600 °C, 400 °C, 200 °C and 150 °C with dwelling times of 2 hours, 2 hours, 48 hours, 2
14 hours and 55 hours, respectively. The heating and cooling rates were 200 °C/hour to reach 400
15 °C and 10 °C/h for cooling to 150 °C. The hydrated samples were prepared to examine the
16 chemical and thermal stability and proton intake capacity by using a NETZSCH
17 thermogravimetric analyser operated under a 20 ml/min constant flow of nitrogen. Pt paste was
18 painted on both sides of a 13 mm diameter pellet and sintered at 1000 °C for 2 hours. Impedance
19 spectroscopy was carried out by Solartron 1260 impedance analyzer in the frequency range of
20 100 mHz - 6 MHz and 1 V rms in signal amplitude from 1000 °C to 150 °C with the step of 50
21 °C at Chalmers University of Technology. This experiment was operated in wet and dry Argon
22 atmosphere. ZView (Scribner Associates Inc.) software was utilized to examine impedance data
23 for analyzing conductivity.

24

25 *Fabrication and performance test of fuel cells*

26 The fuel cell performance test was carried out at Sejong University, South Korea. The
27 anode supported cell, $\text{NiO-Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$ (BSCZYSm) | BSCZYSm |
28 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) as anode, electrolyte and cathode, was assembled. Anode layer
29 was made from mixing NiO (65 wt%), BSCZYSm (35 wt%), Solsperse, corn starch and ethanol
30 then ball milled with zirconia balls for 1 day. The ball milling rate was as low as 187 rpm.

1 Hence, the chance of getting impurities after milling is zero because firstly we use fresh zirconia
2 balls and secondly the milling rate was not so high so that does not cause any structural
3 deformation.

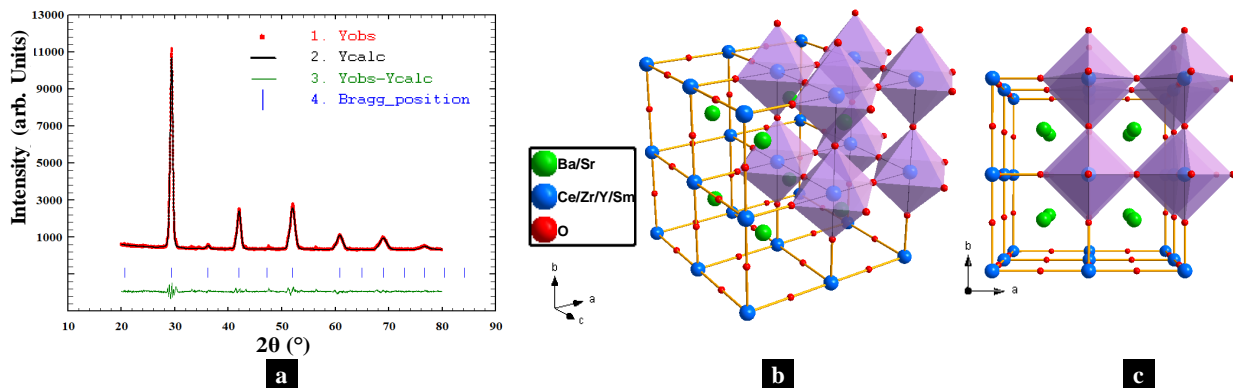
4 The mixture was dried and pressed at 2 tons for 1 minute to make pellets for sintering at
5 900 °C for 2 hours. Anode functional layer (AFL) was prepared by mixing NiO (65 wt%),
6 BSCZYSm (35 wt%), Solsperse and ethanol by ball milling for 1 day. The slurry was added with
7 Di-n-butyl phthalate (DBP) and polyvinyl butyral (PVB, B-98, Butvar) on the next day and ball
8 milled for one day. A side of the sintered anode was coated by AFL by drop coating and sintered
9 at 400 °C for 2 hours. Electrolyte slurry was made from mixing BSCZYSm, Solsperse and
10 ethanol by ball milling for one day. The slurry was added with DBP and Butvar on the next day
11 and continued ball milling for one day. The anode with AFL was coated with electrolyte by
12 dropping. The electrolyte layered cell was sintered at 1450 °C for 4 hours which was the final
13 sintering temperature of the electrolyte. The BSCF cathode (60 wt%) was made into ink by
14 mixing with BSCZYSm (40 wt%) and texanol. The cathode was painted on the cell with an area
15 of 0.2552 cm^2 ($\pi(0.285 \text{ cm})^2$) and sintered at 1,000 °C for 4 hours. The cathode area was pasted
16 with platinum paste and attached with silver mesh and gold wire. The fuel cell was connected
17 with the gold wire of the test station and placed on the alumina jig where the anode was at the
18 bottom side and the cathode was at the top. Ceramabond (100% Ceramabond-668, USA) was
19 used to seal the cell with the jig and close the gap to prevent gas mixing. Ceramabond-668, a
20 high temperature one-part alumina-silica based adhesive, was bought from Aremco.com (an
21 USA based commercial company). Ceramabond-668 is an excellent for heaters. It can make
22 bonds and seals ceramics to ceramics and ceramics to metals in applications up to 2500°F
23 (1371°C). At the anode, nitrogen gas was fed at 200 standard cubic centimeter per minute (sccm)
24 followed by feeding nitrogen/hydrogen (150/50 sccm, 100/100 sccm) and finally pure hydrogen
25 of 200 sccm while cathode was fed with an air of 200 sccm. The voltage, current and impedance
26 of fuel cell at 700 °C, 650 °C and 600 °C were recorded by the Potentiostat instrument of Bio-
27 Logic SP-240. The impedance was collected in a frequency range of 0.1 Hz - 1 MHz with a
28 signal amplitude of 10 mV under open-circuit voltage (OCV). The impedance spectra were fitted
29 with an equivalent circuit using EC-Lab software to calculate conductivity. Scanning electron
30 images from Hitachi SU8010 Field Emission scanning electron microscope (FE-SEM) was used
31 to examine the fuel cell micro-feature.

1 Results and discussion

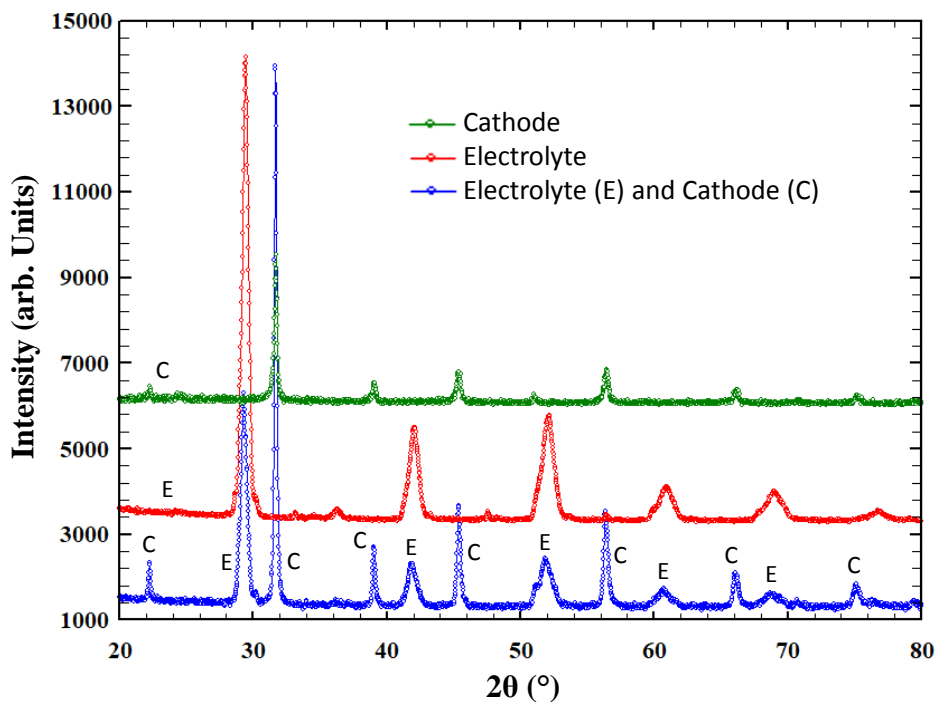
2 X-ray diffraction

3 Fig. 1a) shows the Rietveld refinement of the XRD data of the BSCZYSm electrolyte
4 material. Indexing of the pattern was performed using TREOR90 software, and subsequent
5 refinement of cell parameters was performed by using Checkcell. The Rietveld refinement shows
6 that BSCZYSm crystallizes in the cubic symmetry ($Pm-3m$ space group), and a schematic 3D
7 structure is shown in Fig. 1b) and c). In the perovskite ABO_3 structure, the central green atom
8 represents the A-site, the central blue atom of each octahedral BO_6 represents the B-site, and the
9 small red atom represents the O-site. The observed lattice parameter of 4.305 \AA was smaller than
10 that of $BaCeO_3$ ($a = 4.445 \text{ \AA}$)^[30] but larger than that of $BaZrO_3$ ($a = 4.193 \text{ \AA}$)^[31]. The phase
11 structure of $BaCeO_3$ - $BaZrO_3$ is highly dependent on the concentration of Ce/Zr at the B-site.
12 Typically, Y-doped $BaCeO_3$ is orthorhombic, and Y-doped $BaZrO_3$ is cubic. In fact, different
13 doped $BaCeO_3$ samples can have different symmetry and cell parameters depending on the B-site
14 cation ratio, synthesis route and final sintering temperature. $BaCe_{0.9-x}Zr_xY_{0.1}O_{3-\delta}$ shows an
15 orthorhombic structure for $x = 0.1$ and 0.2 and a cubic structure for $x \geq 0.3$ ^[23]. When the Y
16 percentage is slightly higher, e.g., $BaCe_{0.8-x}Zr_xY_{0.2}O_{3-\delta}$, the phase structure is orthorhombic for
17 $x = 0.1 - 0.5$ and cubic for $x = 0.6 - 0.8$ ^[22]. Sm- and Y-doped $BaCeO_3$ also shows an orthorhombic
18 crystal structure^[32]. Since the ionic radii of Y^{3+} and Sm^{3+} in 6-coordinate polyhedral, 0.90 \AA and
19 0.958 \AA , are very close to each other, the small percentage of Y and Sm co-doped
20 $Ba_{0.9}Sr_{0.1}Ce_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-\delta}$ shows cubic symmetry depending on the Ce/Zr concentration.
21 These studies show the influence of the preparation procedure and sintering temperatures on the
22 crystalline structure of the obtained materials. Higher sintering temperatures, which are normally
23 used for solid-state reactions, have an important effect on the symmetry of the crystal structure.
24 $Ba_{0.9}Sr_{0.1}Ce_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ were mixed and sintered at $1000 \text{ }^\circ\text{C}$
25 for 4 hours, and then XRD data were collected. XRD confirmed that the electrolyte and cathode
26 did not react with each other, as no additional phase was detected, which shows the compatibility
27 of the electrolyte and cathode in fuel cell operation. The XRD profiles of mixed
28 $Ba_{0.9}Sr_{0.1}Ce_{0.5}Zr_{0.35}Y_{0.1}Sm_{0.05}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ are shown in Fig. 2.

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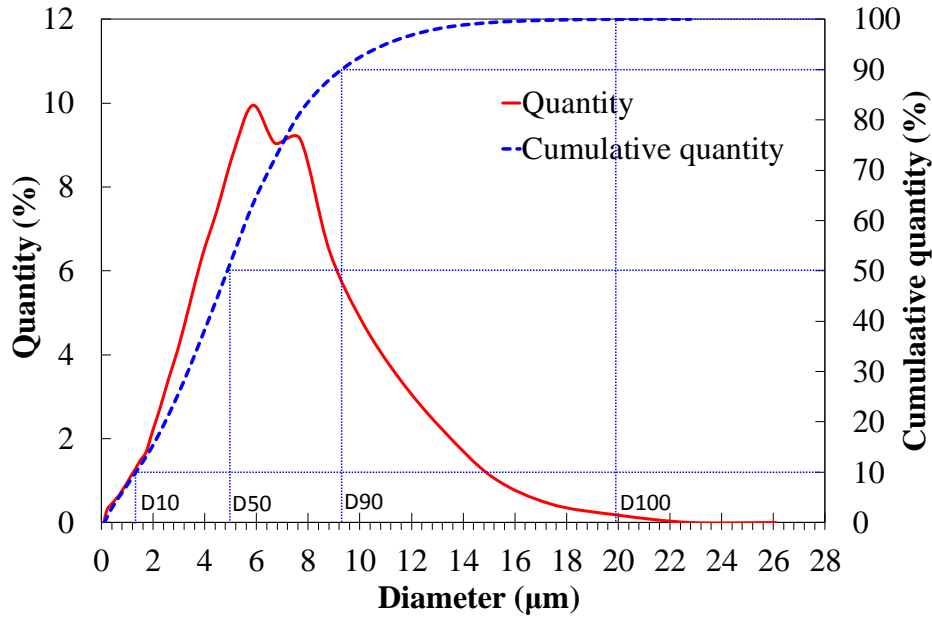


1
 2 **Fig. 1** a) Rietveld refinement profile of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$, where the observed
 3 data are represented by dots and the calculated data are represented by the continuous line. The
 4 short vertical lines represent the position of the Bragg reflections. The bottom line shows the
 5 difference of the plots ($I_{\text{obs}} - I_{\text{calc}}$), b) the 3D diagram of the perovskite (ABO_3) structure drawn by
 6 Diamond software in overall view and c) front view.



8
 9 **Fig. 2** The XRD profiles of pure BSCF cathode, pure BSCZYSm electrolyte and BSCZYSm-
 10 BSCF.

1 **Particle size analysis**



2
3 **Fig. 3** Particle size distribution of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$.

4
5 **Table 1** Particle size at various D-values of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$.

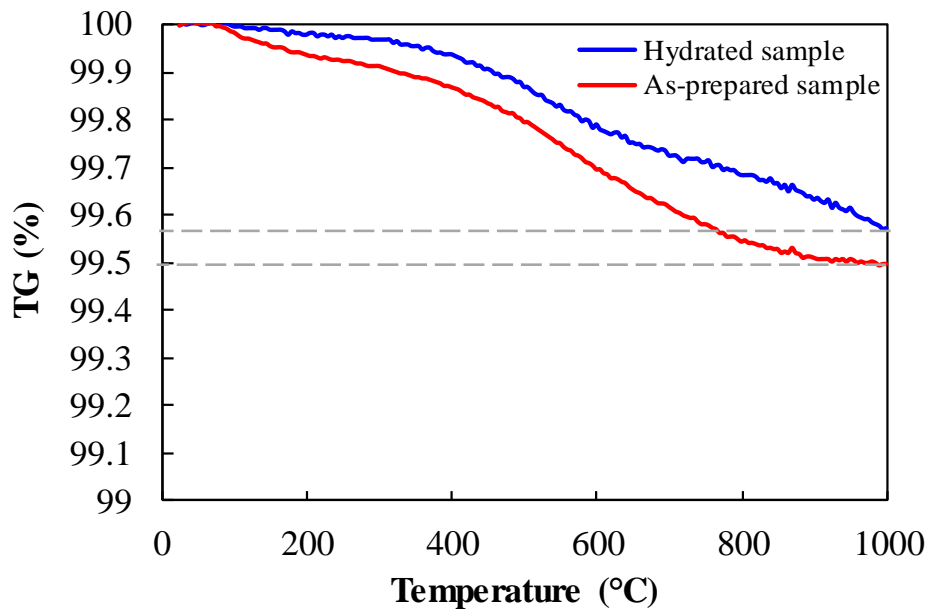
D-value	Particle size (μm)
D10	1.341
D50	4.878
D90	9.367
D100	19.90

6
7 The particle size distribution of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$ is shown in Fig. 3. The
8 powder sample was analysed after grinding with an agate mortar and pestle for 10-15 minutes.
9 Table 1 exhibits the particle size distribution in terms of the amount of particle. The particle size
10 of BSCZYSm has a median of 4.8674 μm , a mean of 5.195 μm and a mode of 5.490 μm . The D-
11 values represent the diameter of the particles indicated by a percentage. Overall, 10% of the
12 particles have a size smaller than 1.341 μm , and all other particles have a size not larger than
13 19.90 μm . However, the particle size of the material can be controlled during material
14 preparation by optimizing the ball milling time and sintering temperature, which can reduce the
15 porosity of the electrolyte material.

1

2 *Thermogravimetric analysis*

3 TGA was performed using the as-prepared and hydrated samples in the temperature range
4 of 20 – 1000 °C, as shown in Fig. 4. As the samples consist of moisture (water) by nature and as
5 a result of the hydration process, the moisture level is affected by elevated temperature, resulting
6 in a weight change. Oxygen is a component of water; hence, this weight loss results in a change
7 in oxygen occupancy ($3-\delta$). Oxygen vacancies were created by doping trivalent cations (Y and
8 Sm) at the B-site. For the as-prepared sample, the mass slightly increased at the beginning due to
9 the adsorption of gas and subsequently decreased by 0.5% at 1000 °C, which is equivalent to an
10 oxygen deficiency of 0.093 (oxygen occupancy of 2.907). In contrast, for the hydrated sample,
11 the mass loss was 0.425% at 1000 °C, which is equivalent to an oxygen deficiency of 0.079
12 (oxygen occupancy of 2.921). Hence, TGA was used to examine the oxygen vacancy
13 concentration. The oxygen occupancy of the hydrated material, 2.921, is closer to the theoretical
14 oxygen occupancy ($3 - \delta = 2.925$). For the hydrated sample, the mass loss indicates the loss of
15 the proton that was absorbed during the hydration process in the atomic structure by forming an
16 O-H bond. Hence, the mass loss of the hydrated sample represents the proton level, which is less
17 than that of the as-prepared sample. The location of protons in the structure can be observed
18 from neutron diffraction experiments ^[33,34].



19

20 **Fig. 4** Thermogravimetric profile of as-prepared and hydrated $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$.

1 *Electrochemical impedance spectroscopy*

2 Fig. 5 shows the Arrhenius plots of the total conductivity of
3 $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$ pellets in wet and dry argon in the temperature range of 400 –
4 700 °C in comparison with the conductivities of other similar proton conductors. BSCZYSm
5 exhibits notable electrochemical behavior, with a higher conductivity, $4.17 \times 10^{-3} \text{ S cm}^{-1}$ at 700
6 °C in wet Ar, and lower activation energy than the sample under dry conditions. This difference
7 is because of the introduced water in the wet experiment, which enhances proton conductivity.
8 The small activation energy is a favorable property that indicates the proton conduction ability of
9 the ceramic oxide. Table 2 shows the conductivity values and activation energies of BSCZYSm
10 in wet and dry Ar. At high temperatures, protons in proton-conducting perovskites are expected
11 to follow the Grotthuss mechanism ^[35] and transport in the following steps: i) a proton is
12 associated with a fixed oxygen atom; ii) the proton-oxygen bond reorients under the influence of
13 the neighboring oxygen atoms; iii) the proton starts to oscillate between the two oxygen atoms
14 and eventually moves to the neighboring oxygen ^[9]. The binding energy between OH^\bullet and $\text{M}_{\text{B}'}$
15 varies with the dopant. Simulation results show that the binding energies of $\text{OH}^\bullet\text{-M}_{\text{B}'}$ (hydroxyl–
16 dopant pairs at the nearest neighbor sites) for Y, Yb and In were -0.26, -0.35 and -0.58 eV,
17 respectively, which is in good agreement with the experimental results ^[36]. A more stable state
18 for the hydroxyl-dopant pair will be found for a more negative value of the binding energies. A
19 report on substitution of Sr for Ba in $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ ($x = 0.0 - 1.0$) shows that a higher
20 conductivity was achieved by $\text{Ba}_{1-x}\text{Sr}_x\text{Ce}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ ($x = 0.3$) than by Ba_{1-}
21 $x\text{Sr}_x\text{Ce}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ ($x = 0.0$), indicating that the small amount of Sr can enhance conductivity
22 ^[37].

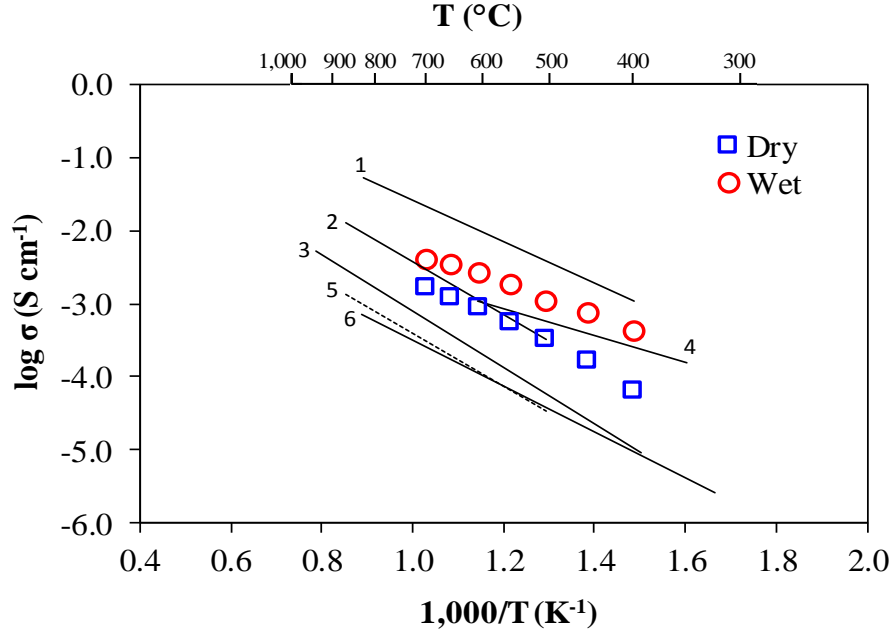
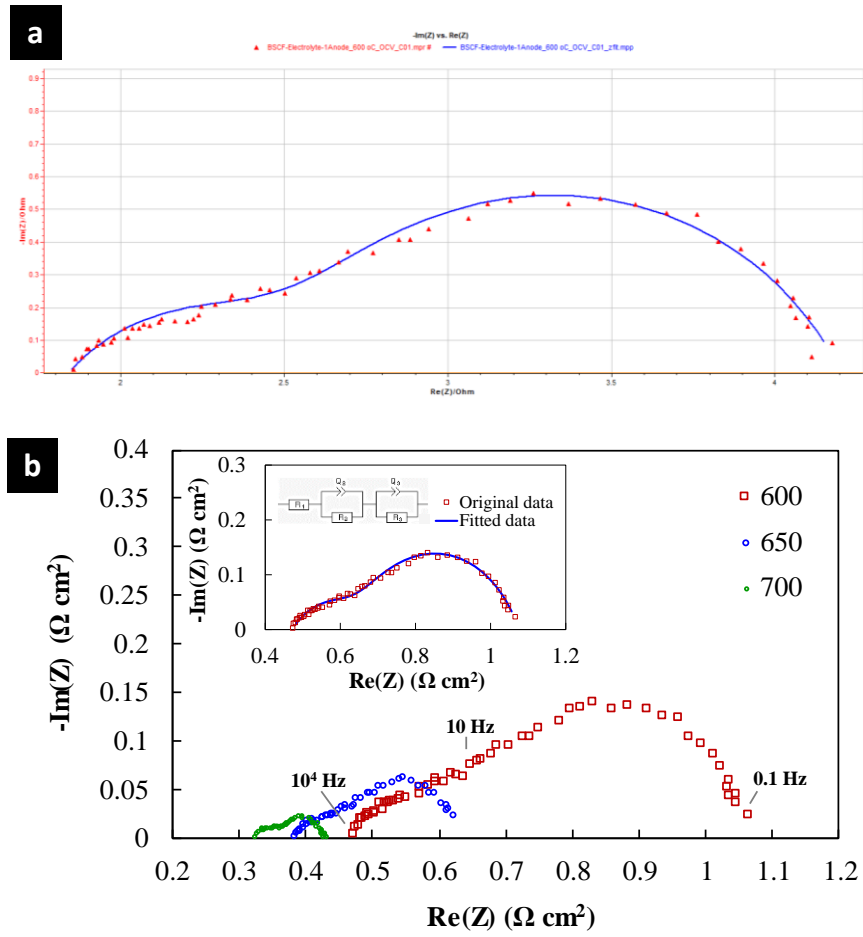


Fig. 5 Conductivity versus temperature plots of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$ in the range of 400-700 °C in wet and dry argon atmospheres. Our results (circle, O; square, \square) were compared with the conductivities of 1) $(\text{Ba}_{0.6}\text{Sr}_{0.4})(\text{Ce}_{0.75}\text{Zr}_{0.10}\text{Y}_{0.15})\text{O}_{3-\delta}$ in wet Ar^[38], 2) $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-\delta}$ ^[39], 3) $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Y}_{0.05}\text{Zn}_{0.05}\text{O}_3$ in wet Ar^[40], 4) $\text{BaZr}_{0.8}\text{Yb}_{0.2}\text{O}_{3-\delta}$ in wet N_2 ^[41], 5) $\text{Sr}_{0.995}\text{Ce}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ ^[39] and 6) $\text{BaCe}_{0.45}\text{Zr}_{0.45}\text{Sc}_{0.1}\text{O}_{3-\delta}$ in wet H_2 ^[18].

Table 2 Conductivities of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$ in wet and dry Ar atmospheres at different temperatures.

Temperature (°C)	Conductivity (S cm^{-1})	
	Wet Ar	Dry Ar
400	4.16×10^{-4}	6.43×10^{-5}
450	7.90×10^{-4}	1.66×10^{-4}
500	1.11×10^{-3}	3.31×10^{-4}
550	1.86×10^{-3}	5.68×10^{-4}
600	2.67×10^{-3}	9.16×10^{-4}
650	3.45×10^{-3}	1.23×10^{-3}
700	4.17×10^{-3}	1.71×10^{-3}
S.D.	1.42×10^{-3}	6.03×10^{-4}
Activation energy (eV) at 400 - 700 °C	0.44	0.61

1



2

3 **Fig. 6** Electrochemical impedance spectra of fuel cells at elevated temperatures in a) the original
 4 plot of the sample at 600 °C from EC lab and b) the area specific resistance. The fitting of the
 5 electrochemical impedance spectra with the equivalent circuit at 600 °C is shown in the insert.

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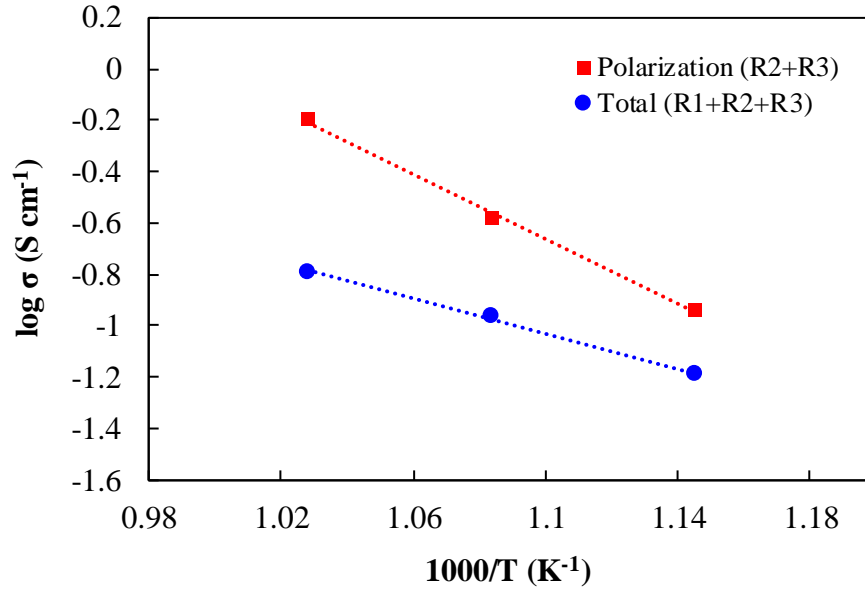


Fig. 7 Arrhenius plot of polarization and total conductivity of fuel cells at elevated temperatures.

Fig. 6a) shows the original impedance of the sample at 600 °C and Fig. 6b) presents the area specific resistance (ASR) of the fuel cell at 600 - 700 °C, and the impedance was recorded after the I-V measurement. At all temperatures, the first intercept represent the ohmic resistance (R_o) at a high frequency, which is correlated with the ionic resistance of the electrolyte and attributed to resistance at the interface of the electrode and electrolyte. The impedance spectra are attributed to electrochemical reaction or polarization resistance (R_p), which can be identified at i) the medium-frequency range of $\sim 10 - 10^4$ Hz involving the charge transfer mechanism of the oxygen ion and electron and ii) the low-frequency range of $\sim 0.1 - 10$ Hz related to the oxygen ion and mass transfer mechanism owing to the diffusion of the oxygen ions^{[42], [43]}. The obtained impedance at 600 °C was explained by an equivalent circuit where the ohmic resistance (R_1) is in parallel with two sub-circuits of polarization resistance (R_2 or R_3) and a constant phase element (Q_2 or Q_3), as shown in the insert of Fig. 6b). The R_o of fuel cell is attributed to electrolyte resistance, with values of 0.47 (0.077), 0.37 (0.077) and 0.32 (0.077) $\Omega \text{ cm}^2$ at 600, 650 and 700 °C, respectively, while the cell exhibited R_p values of 0.60 (0.253), 0.27 (0.253) and 0.11 (0.253) $\Omega \text{ cm}^2$ at 600, 650 and 700 °C, respectively. A greater porosity of the electrode microstructure is essential to achieve a lower R_p for cell performance enhancement^[44]. The smallest impedance at 700 °C patently denotes the highest conductivity. Impedance fitting of the sample was performed to determine the subsequent resistivity by conductivity calculations. The conductivities are

1 plotted in Fig. 7 according to the linear Arrhenius relation, where the highest conductivity was at
2 700 °C and the lowest conductivity was at 600 °C under the same conditions. The fuel cell
3 exhibited total conductivities of 0.06 (0.049), 0.11 (0.049) and 0.16 (0.049) S cm⁻¹ at 600, 650
4 and 700 °C, respectively, while the polarization conductivities were 0.12 (0.274), 0.26 (0.274)
5 and 0.64 (0.274) S cm⁻¹ at 600, 650 and 700 °C, respectively. The polarization conductivities
6 were higher than the total conductivity because the total conductivities consisted of ohmic and
7 polarization resistance in the calculation, where ohmic resistance was affected by the electrolyte
8 resistance.

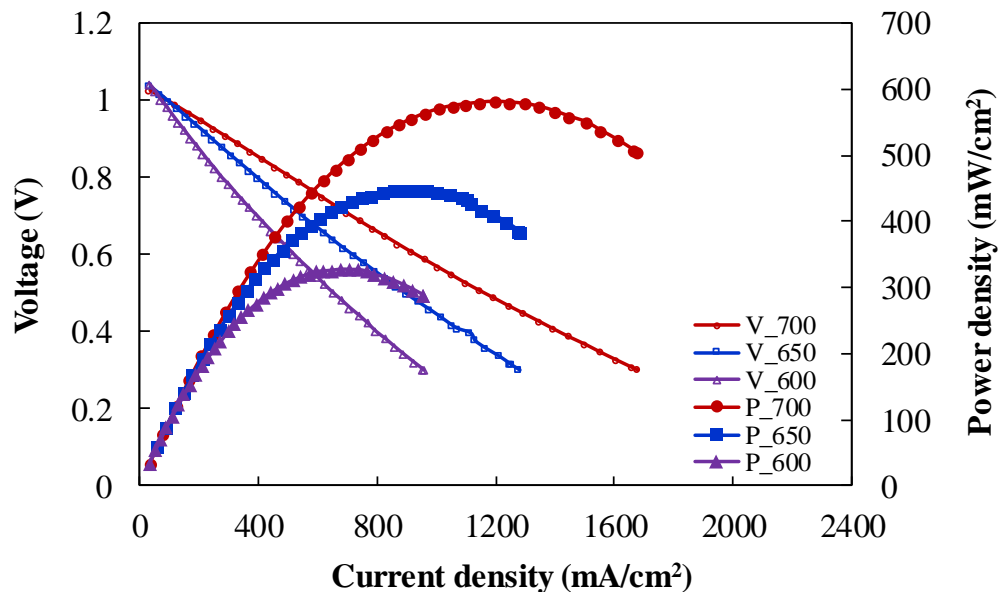
9

10 *Fuel cell performance*

11 BSCZYSm was further investigated as the electrolyte material in a complete fuel cell.
12 The cell was fabricated with a configuration of Ni-BSCZYSm | BSCZYSm | BSCF as the anode,
13 electrolyte and cathode. The cell was exposed to 200 sccm hydrogen as the fuel and 200 sccm air
14 as an oxidant at 600 - 700°C. Fig. 8 shows the voltage and power density versus current density
15 trends of the cells. The data were collected after the OCV was stabilized at 700 °C, which is
16 attributed to the appropriate mass transport property and good sealing of the fuel cell ^[42]. The
17 cell exhibited a maximum power density of 581.7 mW/cm² at 700 °C with an OCV of 1.025 V
18 and a power density of 327.8 mW/cm² at 600 °C with an OCV of 1.04 V. The cell performance
19 at 700 °C shows a higher power density than the reported values from similar cells, as shown in
20 Table 3. The obtained OCVs are in the range of 1.025 to 1.04 V. The increase in temperature
21 plays an important role in accelerating the electrochemical reaction, which decreases the OCV
22 consistent with the Nernst equation ^[45]. The obtained high OCV proved that the electrolyte is
23 dense, serving as a membrane to prevent gas leakage from the anode to the cathode or vice versa.
24 As the maximum power density is proportional to OCV², a high OCV could directly benefit the
25 performance ^[46]. The power density could be enhanced for greater performance by reducing the
26 ohmic resistance of the electrolyte and the polarization resistance of the electrodes, which
27 facilitates high ionic conductivity through the electrolyte ^[47]. A reduction in the thickness of the
28 electrolyte is also a key to enhancing performance ^[48]. The fuel cell operation of Ni-BSCZYSm |
29 BSCZYSm | BSCF released water at the cathode gas outlet, which proved that the proton-
30 conducting mechanism was dominant in this experiment at the examined temperature of 600 –

1 700 °C. According to the reported values in Table 3, the fuel cell performance varies with the
 2 material selection; precursor preparation method; heat treatment temperature of the material;
 3 fabrication of the fuel cell; layer multiplication of the anode, electrolyte or cathode; etc. A
 4 commonly used cell fabrication method is the typical dry-pressing anode substrate preparation,
 5 where the anode is fired alone or co-pressed and co-fired with the electrolyte layer, followed by
 6 painting of the cathode slurry onto the electrolyte layer ^[49–51]. Other cell fabrication methods
 7 have also been applied, such as tape casting, gel casting, phase inversion for anode preparation,
 8 spin coating, solution coating, pressurized spray coating of the electrolyte onto the anode layer
 9 and screen printing or painting of the cathode onto the electrolyte layer. In this report, we used a
 10 typical dry-pressing method to prepare the anode substrate, which revealed the greatest
 11 performance at 700 °C compared to the reported values based on dry-pressed anodes. However,
 12 Nguyen and Yoon ^[52] applied a spin-coating process to deposit an electrolyte onto the anode, and
 13 this process seems to be a better approach for controlling the electrolyte thickness to achieve
 14 higher performance. It is now evident that NiO can diffuse from anode to electrolyte and might
 15 change the sintering nature as well as conductivity of the materials ^[53]. We haven't used NiO as
 16 sintering aid of any of the materials and haven't observed any tress of Ni in the electrolyte.

17



18

19 **Fig. 8** Voltage and power density versus current density curves of the Ni-BSCZYSm |

20

BSCZYSm | BSCF single cell at 600, 650 and 700 °C.

21

1 **Table 3** Comparison of power density and OCV of Ni-BSCZYSm | BSCZYSm | BSCF cells
 2 with those of some reported fuel cells in the literature.

Cell	Power density (mWcm ⁻²)	Temperature (°C)	OCV (V)	Reference
NiO- Ba _{0.9} Sr _{0.1} Ce _{0.5} Zr _{0.35} Y _{0.1} Sm _{0.05} O _{3-δ} (BSCZYSm) BSCZYSm Ba _{0.5} Sr _{0.5} C o _{0.8} Fe _{0.2} O _{3-δ}	327.8	600	1.04	Present study
	448.8	650	1.035	
	581.7	700	1.025	
NiO-BaZr _{0.1} Ce _{0.7} Y _{0.2} O _{3-δ} BaZr _{0.3} Ce _{0.5} Y _{0.2} O _{3-δ} Sm _{0.5} Sr _{0.5} CoO _{3-δ} – Ce _{0.8} Sm _{0.2} O _{2-δ} (SSC–SDC)	396	600	1.02	[9]
	513	650	1.01	
NiO-BaZr _{0.1} Ce _{0.7} Y _{0.1} Yb _{0.1} O _{3-δ} (BZCYYb) BZCYYb BZCYYb- LSCF	470*	600	1.07*	[52]
	590*	650	1.04*	
	710*	700	1.00*	
	1000	750	0.94	
Ni– BaZr _{0.1} Ce _{0.7} Y _{0.2} O _{3-δ} (BZCY) BaCe _{0.7} In _{0.2} Yb _{0.1} O _{3-δ} La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} (LSCF) – BZCY	150	600	0.984	[54]
	218	650	0.981	
	280	700	0.963	
Ni–BaZr _{0.1} Ce _{0.7} Y _{0.1} Yb _{0.1} O _{3-δ} (BZCYYb) BZCYYb La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} (LSCF)– BZCYYb	260	600	1.01	[55]
Ni-BaZr _{0.1} Ce _{0.7} Y _{0.1} Yb _{0.1} O _{3-δ} (BZCYYb) BZCYYb PrBaCo ₂ O _{5+δ} (PBCO)	223	600	1.016	[56]
	358	650	1.007	
	490	700	0.983	
Ni- BaZr _{0.1} Ce _{0.7} Y _{0.1} Yb _{0.1} O _{3-δ} (BZCYYb) BZCYYb PrBaFe ₂ O _{5+δ} (PBFO)	179	600	1.034	[57]
	302	650	1.015	
	452	700	1.006	

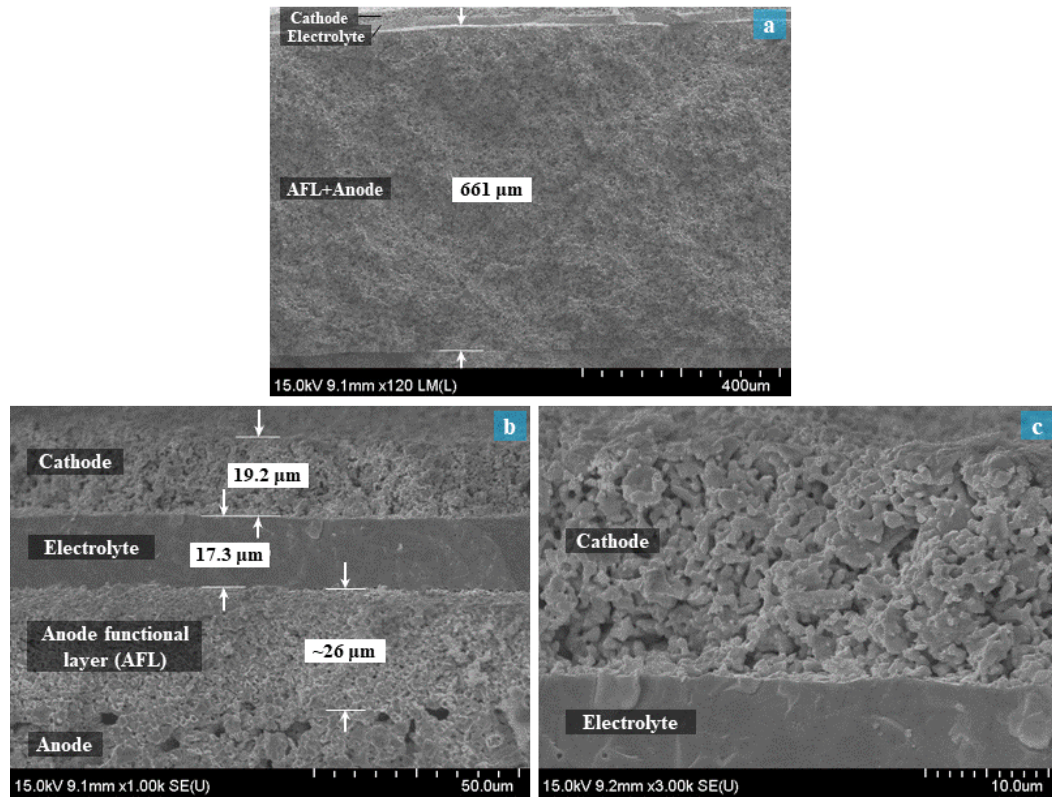
NiO-ScSZ ScSZ La _{0.8} Sr _{0.2} Sc _y Mn _{1-y} O _{3-δ} (y = 0.0-0.2)	80 (y = 0) 200 (y = 0.05)	650		[58]
BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ} (BCZYZ) - NiO BCZYZ LaSr ₃ Co _{1.5} Fe _{1.5} O _{10-δ} (LSCF)	175 250 275	600 650 700	1.02 1.00 0.95	[59]
NiO- BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ} (BCZYZ) BCZYZ Sm _{0.5} Sr _{0.5} CoO _{3-δ} (SSC) - BCZYZ	246 364 528	600 650 700	1.049 1.039 1.015	[60]
Ni- BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ} (BCZYZ) BCZYZ PrBaCo ₂ O _{5+δ} (PBCO)	194 266 361	600 650 700	1.042 1.021 1.007	[61]
Ni- BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ} (BCZYZ) BCZYZ Ba _{0.5} Sr _{0.5} Zn _{0.2} Fe _{0.8} O _{3-δ} (BSZF)- BCZYZ	201 323 387	600 650 700	1.042 1.021 1.007	[62]
Ni-BaZr _{0.1} Ce _{0.7} Y _{0.2} O _{3-δ} (BZCY7) BZCY7 Ba _{0.5} Sr _{0.5} Zn _{0.2} Fe _{0.8} O _{3-δ} (BSZF) -BZCY7	277 415 486	600 650 700	1.062 1.041 1.015	[63]
Ni- BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ} (BCZYZ) BCZYZ GdBa _{0.5} Sr _{0.5} Co ₂ O _{5+δ} (GBSC)	210 290 350	600 650 700	1.044 1.024 1.009	[64]
NiO-BaCe _{0.5} Zr _{0.3} Y _{0.2} O _{3-δ} (BCZY) -Z- C ₂ -starch NiO-BCZY-Z-C ₂ BZCY-Z-C ₂ Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} (BSCF)	102 190* 237* 302	500 600 650 700	1.094 1.014	[65]
NiO-BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ} (BCZYZ) BCZYZ	178 242	600 650	1.021 1.015	[66]

SmBa _{0.5} Sr _{0.5} Co ₂ O _{5+δ} (SBSC)	306	700	1.007	
NiO– BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3–δ}	241	600	1.005	[67]
(BZCYZn) BZCYZn	281	650	0.992	
SrCo _{0.9} Sb _{0.1} O _{3–δ} (SCS)	364	700	0.987	
NiO–BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3–δ}	122	600	1.06	[68]
(BCZYZn) BCZYZn	185	650	1.03	
Ba _{0.5} Sr _{0.5} Zn _{0.2} Fe _{0.8} O _{3–δ}	236	700	1.00	
Ni–BaZr _{0.1} Ce _{0.7} Y _{0.2} O _{3–δ} (BZCY)	74	600	1.01	[69]
BZCY BaZr _{0.8} Y _{0.2} O _{3–δ} (BZY)	131	650	1.00	
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3–δ} (LSCF)–BZY	181	700	0.98	

1 * Indicates the value estimated from the graph

2 **Scanning electron microscopy**

3



4

5 **Fig. 9** SEM cross-sectional image of the BSCF | BSCZYSm | Ni-BSCZYSm fuel cell at
 6 magnifications of a) 120, b) 1,000 and c) 3,000.

7

1 Microstructure plays a very important role in the properties of materials ^[70]. More
2 importantly, in the case of a fuel cell, we need to optimize the dense electrolyte and porous
3 electrodes. Electrolytes need to be gas tight to prevent the mixing of gaseous reactants. In
4 proton-conducting oxides, grain boundary resistance is detrimental to the total conductivity, and
5 an increase in the grain size decreases the number of grain boundaries, which obviously results in
6 a reduction in grain boundary resistance and hence an increase in the total ionic conductivity.
7 Fig. 9a) –c) show the SEM cross-section images of the Ni-BSCZYSm | BSCZYSm | BSCF fuel
8 cell with a total thickness of 697.5 μm . The cathode and anode appear as porous layers with a
9 dense electrolyte layer. The cathode and electrolyte layers were attached well with no
10 delamination, which demonstrates the good chemical compatibility and stability of the cathode-
11 electrolyte layer at the deposition temperature of 1,000 $^{\circ}\text{C}$, and the compatibility of these two
12 layers was examined by XRD (see Fig. 2). The electrolyte membrane exhibited a dense
13 microstructure with no visible cracks or holes, which confirms the prevention of fuel cross-over
14 from the anode and oxidant from the cathode. In this study, the drop coating of the electrolyte
15 onto the anode was sufficient to achieve a thickness of $\sim 17 \mu\text{m}$. Even though the electrolyte
16 thickness is slightly higher than those reported by Ding et al. ^[56], ^[57] and He et al. ^[69], the
17 achieved performance is higher than those of similar electrolyte-based fuel cells.

18

19 **Conclusions**

20 A proton-conducting perovskite electrolyte, $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$
21 (BSCZYSm), exhibited unique characteristics in fuel cell application, showing a high power
22 density at intermediate temperatures. BSCZYSm showed cubic symmetry in the $Pm-3m$ space
23 group and good proton conductivity. BSCZYSm was successfully synthesized by using a solid-
24 state sintering method with microscale particle sizes. The oxygen deficiency was determined by
25 TGA and was consistent with the theoretical value, showing the potential to achieve good ionic
26 conductivity. The proton conductivity of BSCZYSm was $4.167 \times 10^{-3} \text{ S cm}^{-1}$ at 700 $^{\circ}\text{C}$ in a wet
27 argon atmosphere, which is higher than those of other similar proton conductors. BSCZYSm was
28 utilized as an electrolyte layer in the fuel cell in the $\text{NiO-Ba}_{0.9}\text{Sr}_{0.1}\text{Ce}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.1}\text{Sm}_{0.05}\text{O}_{3-\delta}$
29 (BSCZYSm)||BSCZYSm|| $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ arrangement. The cell exhibited a peak power
30 density of 581.7 mW/cm^2 at 700 $^{\circ}\text{C}$ as a proton-conducting fuel cell, which was confirmed by
31 the presence of condensed water at the cathode outlet. The OCV of the fuel cell at 700 $^{\circ}\text{C}$ was

1 1.025 V, which was higher at a lower temperature, as predicted by the Nernst equation. Notably,
2 we have used only one device technology to obtain results. Different cell arrangements can be
3 employed to achieve even better performance.
4

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11

12 **Author contributions**

13 A.K.A. got the idea, designed the experiments and supervised the project. N.R. did the sample
14 preparation, characterization and prepared the first draft. A.A. and A.M.A. helped during XRD
15 and SEM experiments and refinement. M.S. and J.Y.P. helped to prepare fuel cell and test. J.Z.,
16 J.I. and J.H.K. have supervised the project, helped to write the manuscript and to edit it.
17

18 **Competing interest**

19 There is no competing interest in this work.
20

21 **Materials & Correspondence**

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25

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