

Continuous hydrothermal synthesis in supercritical conditions as a novel process for the elaboration of Y-doped BaZrO3

Mélanie François, Frédéric Demoisson, Mohamed Sennour, Gilles Caboche

► To cite this version:

Mélanie François, Frédéric Demoisson, Mohamed Sennour, Gilles Caboche. Continuous hydrothermal synthesis in supercritical conditions as a novel process for the elaboration of Y-doped BaZrO3. Ceramics International, 2021, 47 (12), pp.17799-17803. 10.1016/j.ceramint.2021.03.044 . hal-04027055

HAL Id: hal-04027055 https://hal.science/hal-04027055

Submitted on 9 May 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Version of Record: https://www.sciencedirect.com/science/article/pii/S0272884221007070 Manuscript_83abaa328af8f747e10f0b93f939ed37

1	Continuous hydrothermal synthesis in supercritical
2	conditions as a novel process for the elaboration of Y-doped
3	BaZrO ₃
4	Mélanie François ^{*1} , Frédéric Demoisson ¹ , Mohamed Sennour ² and Gilles Caboche ¹
5	¹ Laboratoire Interdisciplinaire Carnot de Bourgogne, FCLAB, ICB-UMR6303, CNRS – Université de
6	Bourgogne Franche-Comté, 9 Avenue Savary, BP47870 21078 DIJON Cedex, France
7	² Centre des matériaux – MINES ParisTech, 63-65 rue Henri Auguste Desbruères, BP 87 91003 Evry
8	Cedex, France
9	* Correspondence : melanie.francois@u-bourgogne.fr
10	Abstract: The present work describes a novel process for the elaboration of a ceramic material
11	Y-doped barium zirconate, an electrolyte material for Protonic Ceramic Fuel cell, was synthesized
12	by a continuous hydrothermal process in supercritical conditions (410°C/30.0MPa) using nitrate
13	precursors and NaOH reactants. The use of supercritical water allowed the formation of particles of
14	about 50 nm in diameter with a narrow size distribution. X-Ray Diffraction examination revealed
15	that a major perovskite phase with few $BaCO_3$ and $YO(OH)$ impurities was obtained. $BaCO_3$ is
16	assumed to form due to faster kinetics than Y-doped $BaZrO_3$ resulting in a Ba-deficient perovskite
17	phase. The Ba-deficiency limits the incorporation of yttrium into the perovskite structure. However
18	a thermal treatment at 1000 °C for 1 hour allows to homogenize the composition and thus to obtain
19	the compound $Ba_{1.01}Zr_{0.85}Y_{0.15}O_{3-\delta}$.
20	Keywords: Hydrothermal synthesis; Protonic Ceramic Fuel Cell; Nanoparticles; Supercritical

21 water; Y-doped BaZrO₃.

https://creativecommons.org/licenses/by-nc/4.0/

22 **1. Introduction**

Finding new clean and efficient ways to generate energy has become a major global challenge. For a few years now, Protonic Ceramic Fuel Cells (PCFCs) have attracted much attention in the field of hydrogen energy. Contrary to Solid Oxide Fuel Cells that operate at a temperature above 600 °C and where the oxygen ions are the charge carriers, PCFCs use protons. Indeed, the lower activation energy of proton diffusion compared to that of the oxygen ion allows to decrease the operating © 2021 published by Elsevier. This manuscript is made available under the CC BY NC user license temperature down to the 400 - 600 °C range[1]. Among the different electrolyte materials for
PCFCs, BaCeO₃ and BaZrO₃ have attracted much attention [2–4].

30 BaCeO₃-based oxides are currently the most commonly chosen electrolyte material for PCFC 31 [5,6]. It is generally reported that doped-BaCeO₃ exhibits the highest protonic conductivity among 32 the perovskite-type materials [7-9]. However, BaCeO₃-based perovskites exhibit low stability in 33 H_2O and/or CO_2 containing atmosphere which limits their practical application [10,11]. On the 34 contrary, doped BaZrO₃ exhibits excellent chemical stability [12]. The substitution of zirconium by 35 yttrium allows to achieve acceptable electrical conductivity up to 10⁻³ S.cm⁻¹ [13,14]. However, the 36 highly refractive nature of BaZr_{1-x}Y_xO_{3-δ} (noted BZY) leads to the requirement of a high synthesis 37 temperature (1400 °C) for the classical solid state reaction method and to an even higher (1600 – 38 1700 °C) sintering temperature [15,16].

39 In this work, a continuous hydrothermal process developed at the ICB laboratory is proposed 40 to elaborate the electrolyte material [17]. The supercritical hydrothermal synthesis of metal oxide 41 particles using a continuous flow reactor was first proposed by Adschiri et al. in 1992 [18]. This 42 process presents several advantages such as a precise control of the morphology and the size of the 43 particles with a narrow size distribution [19–21]. Furthermore, in supercritical water, inorganic 44 compounds become insoluble leading to the formation of hydroxide nuclei which are immediately 45 dehydrated to form ultrafine particles [22]. Another important advantage of using supercritical 46 water with a continuous flow is the short reaction time leading to the possible formation of 47 metastable and highly doped structures [23,24].

The synthesis of BaZrO₃ by the continuous hydrothermal process was investigated by several groups in the past decade. For example, Aimable *et al.* studied the influence of the nature of the precursors, the pH and the temperature on the synthesis of BaZrO₃ [25]. Yoko *et al.* studied the formation mechanism of BaZrO₃ in supercritical water. They suspected the formation of Ba-deficient particles with a shell of ZrO(OH) at the early stage of the precipitation followed by an uptake of Ba²⁺ up to Ba/Zr=1 [26]. In 2016, the same group used *in situ* X-ray diffraction to study and support the previous mechanism [27].

55 However, few studies focus on doped BaZrO₃ material elaborated by this method, and, to the 56 authors' knowledge, no studies on Y-doped BaZrO₃ have been conducted. Then, this work aims to 57 investigate the feasibility of the elaboration of $BaZr_{1-x}Y_xO_{3-\delta}$ by supercritical hydrothermal process 58 using a continuous flow reactor.

59 2. Materials and Methods

60 2.1. Continuous process

61 The continuous process can be used up to 600 °C/35.0 MPa. Indeed, for water, the critical 62 temperature/critical pressure values are 374 °C/22.1 MPa, this set-up can work in supercritical 63 conditions. For the experiments, the syntheses were carried out at 410 °C/30.0 MPa. A solution of metallic precursors (Ba(NO₃)₂, ZrO(NO₃)₂·6H₂O and Y(NO₃)₃·6H₂O purchased from Sigma-Aldrich) 64 65 is prepared by following the stoichiometry of the target composition by dissolution in deionized 66 water and homogenized with an ultrasonic rod, the concentration is 5×10^{-2} mol L⁻¹ for Ba²⁺, 4×10^{-2} 67 mol L⁻¹ for Zr^{4+} and 1×10^{-2} mol L⁻¹ for Y^{3+} . A second solution composed of sodium hydroxide at 68 3×10^{-1} mol L⁻¹ was employed in order to avoid the formation of ZrO₂ [25]. Figure 1 shows the 69 scheme of the continuous set-up. Container (a), at the beginning of the process, holds the aqueous 70 solution of metal cations, container (b) holds the solution of sodium hydroxide and the third 71 container (c) holds the distilled water. The reactor consists of a "pipe to pipe" cylinder with a total 72 volume of 25 mL, the inner diameter of the external pipe is 10 mm. Pressurized solutions (a) and 73 (b) are brought to the reactor inlet at room temperature by high-pressure pumps. Pressurized 74 demineralized water is pre-heated and brought counter-currently through the internal pipe of the 75 reactor so that the three solutions meet at the mixing zone. The resulting solution is evacuated 76 through the external pipe where the reactions leading to the formation of metal oxides take place. 77 The flow rate of the three solutions is set to around 10 mL min⁻¹ per solution, the final flow 78 measured at the end of the set-up (after the back pressure regulator) varies between 30 and 35 79 mL.min⁻¹. The residence time into the reactor under supercritical conditions is of the order of few 80 seconds (determined by Computational Fluid Dynamics calculations) [28]. At the reactor outlet, a 81 cooling system stops the germination and growth stages. A filtration system at the end of the device 82 captures the agglomerated particles that are added to the suspension obtained after the 83 back-pressure regulator. The particles sediment at the bottom of the beaker, the surfactant is 84 siphoned off and distilled water is added to wash the particles. This operation is repeated until a

neutral pH is obtained. The supernatant water is siphoned off one last time and the suspension is
dried in an oven at 80 °C for three days to obtain a powder.

87 2.2. Characterization methods

88 X-Ray Diffraction (XRD) analysis was conduct on a Bruker D2 Phaser coupled with linear 89 detector Lynxeye XE T using Cu K α radiation. The obtained XRD pattern was refined by the 90 Rietveld method using the Fullprof software. The microstructure was investigated by transmission 91 electron microscopy (TEM) on a ThermoFisher FEI Tecnai F20. The chemical composition was 92 analyzed by scanning electron microscopy (SEM) on a Hitachi SU1510 coupled with a Bruker 93 XFlash6I10 energy-dispersive X-ray (EDX) analyzer. The collected peaks for EDX quantification 94 were the L-series of Ba, Zr and Y and the K-series of O. EDX investigations were conducted on 16 95 different agglomerates with an area of measurement from 2.5 μ m \times 2.5 μ m to 5 μ m \times 5 μ m. The 96 Brunauer, Emmett and Teller (BET) measurement was carried out on a Micromeritics TriStar 3020. 97 Particle size distribution (PSD) was evaluated using the Dynamic Light Scattering method using Mie 98 theory calculation with a Malvern Microsizer 2000 laser granulometer coupled with a hydro 99 2000MU dispersion unit using ultrasound.

100 3. Results and discussion

Among the Y-doped BaZrO₃ materials, BaZr_{0.8}Y_{0.2}O_{3- δ} appears to be the best composition. The protonic conductivity increases with the Y content up to a substitution of 20 % before decreasing due to structural distortion and proton trapping [29,30]. Thus, BaZr_{0.8}Y_{0.2}O_{3- δ} was the target composition. The chemical reaction yield varies from 60.5 % to 70 % with an average value of 66.5 %, the productivity depends on the final flow measured after the back pressure regulator and varies from 5.5 to 6.8 g.h⁻¹, about 23.5 g was produced per synthesis.

Figure 2 shows the volume and number PSD of the synthesized powder. The volume PSD (Figure 1.a) exhibit a quadrimodal distribution with mean sizes at around 0.1 μ m, 1.7 μ m, 14 μ m and 210 μ m. The obtained D₁₀, D₅₀ and D₉₀ are 0.817 μ m, 4.570 μ m and 35.73 μ m respectively suggesting that the elementary grains are highly agglomerate. **Figure 3** shows the TEM micrograph of the synthesized powder. As suggested by the PSD analysis, the particles with a nearly spherical morphology are agglomerated. The particle size varies from 10 nm to 315 nm on this micrograph with a median value of 48 nm (evaluation on 50 particles). 114 The X-ray diffractogram of the obtained powder is shown in Figure 4. The major phase 115 obtained has a perovskite cubic structure with Pm-3m space group. BaCO₃, with an orthorhombic 116 Pnma structure, and YO(OH), with a monoclinic $P2_1/m$ structure as secondary phases were 117 detected. Rietveld refinement was performed on the diffractogram, the determined phase 118 percentages are 86.2, 10.6 and 3.1 wt% for BZY, $BaCO_3$ and YO(OH) respectively. The average 119 crystallite size of the perovskite phase was evaluated from the integral width of the diffraction 120 peaks and is 53 nm. This value is in agreement with the 48 nm obtained from TEM analysis and 121 with the 47.3 \pm 0.2 nm calculated from the 20.74 \pm 0.06 m² g⁻¹ specific surface area obtained by BET 122 measurement. The refined lattice parameter for the perovskite cubic phase is 4.2015 Å, this value is 123 lower than those reported in the literature for $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ suggesting that a part of Y is not in the 124 perovskite phase leading to the formation of YO(OH). As a comparison, Sun *et al.* obtained a lattice 125 parameter of 4.2048 Å for BaZr_{0.8}Y_{0.2}O_{3- δ} prepared by combustion method, Nuñez et al. obtained a 126 lattice parameter of 4.2067 Å for BaZr $_{0.8}$ Y $_{0.2}$ O₃₋₆ prepared by a modified Pechini method and Sazinas 127 et al. obtained a lattice parameter of 4.2151 Å for BaZr_{0.8}Y_{0.2}O₃₋₆ prepared by spray pyrolysis and 128 sintered at 1600 °C [31-33]. In order to investigate the origin of lattice parameter deviation, a 129 comparison with undoped BaZrO₃ elaborated by the same method was carried out. The refined 130 lattice parameter is 4.1939 Å, this value agrees well with the 4.1930 Å and the 4.1943 Å obtained by 131 the Nuñez group and the Akbarzadeh group [32,34]. Then, this synthesis method does not appear 132 to particularly generate defects or nano-size effects that affect the lattice parameter. Moreover, the 133 increase in the lattice parameter for Y-doped BaZrO₃ compared to the non-doped sample well 134 evidence the Y doping. However, the amount of Y cannot be quantified by XRD since the synthesis 135 route implement several defects or structural distortions that affect the lattice parameter value, for 136 example, values of lattice parameter for BaZr_{0.9}Y_{0.1}O_{3-δ} differ from 4.193 Å to 4.2101 Å [33,35–38].

In order to determine the composition of the BZY powder as-synthesized, EDX investigations were conducted on several agglomerates. Ba, Zr, Y and O elements were detected, for the following interpretation, Ba is assumed to belong to the A-site of the perovskite while Zr and Y are supposed to occupy the B-site of the perovskite. **Figure 5** shows a) the obtained A-site/B-site ratios and b) the obtained Y/(Zr+Y) ratios and the corresponding number of agglomerates per interval. The as-synthesized powder exhibits a wide range of A-site/B-site ratio, from 0.70 to 1.33, with a strong tendency for the Ba-deficient composition. In order to homogenize the composition, a heat

144 treatment at 1000 °C for 1 hour was applied to the powder. The resulting distribution of 145 A-site/B-site ratio is narrower, the lower value is 0.92 and the biggest value is 1.08 with an average 146 value equal to 1.01. Then, the thermal treatment at 1000°C effectively homogenizes the 147 composition. Moreover, a study of Haile group showed that BaCO₃ decomposition leads to the 148 compensation of the Ba sub-stoichiometry during sintering [39]. Since $BaCO_3$ decomposition 149 (reaction 1) occurs at around 1000 °C [40], it can reasonably be assumed that the increase of the 150 A-site/B-site ratio in the annealed powder is due to the Ba uptake from BaCO₃. The integration of 151 Ba in the BZY structure is described in Kröger – Vink notation in reaction 2.

Reaction 1

152 $BaCO_3 \rightarrow BaO + CO_2$

153
$$BaO + V_{Ba}'' + V_0^{\bullet \bullet} \rightarrow Ba_{Ba}^{\times} + O_0^{\times}$$
 Reaction 2

154 The Y/(Zr+Y) ratio values of the as-synthesized powder cover an interval of 0.08 to 0.25 with 155 an average value of 0.14, this ratio is lower than the expected 0.20. Yamazaki et al. and Magrez et al. 156 have shown that yttria exsolution in Ba-deficient BZY compounds during sintering is due to the Ba 157 sub-stoichiometry [41,42]. It can then be assumed that, in hydrothermal synthesis, the 158 Ba-deficiency caused by the kinetics of the BaCO₃ formation faster than the BZY formation hinders 159 the incorporation of more than 14 % of Y in the BZY structure. After thermal treatment, the 160 distribution of Y/(Zr+Y) is substantially the same as before, covering an interval from 0.07 to 0.24 161 with an average value of 0.15. Because of the high occupancy rate of the B-site of the perovskite, 162 yttrium from YO(OH) cannot integrate the perovskite structure and react at 450 °C to form Y_2O_3 163 according to reaction 3 [43]:

164 2 $YO(OH) \rightarrow Y_2O_3 + H_2O$ Reaction 3

165 4. Conclusions

166 The hydrothermal synthesis of $BaZr_{1-x}Y_xO_{3-\delta}$ was carried out in supercritical water (410 167 °C/30.0 MPa) using a continuous flow reactor. This process allows the elaboration of nanoparticles 168 of about 50 nm in diameter with great productivity (5.5 – 6.8 g h⁻¹), an average chemical reaction 169 yield of 66.5 % and high reproducibility. XRD characterization revealed the presence of BaCO₃ and 170 few YO(OH) impurities. It is assumed that BaCO₃ formation occurs due to faster kinetics compared 171 to that of BZY formation. EDX study showed the obtaining of highly Ba-deficient perovskite and a 172 substitution rate of Zr by Y of about 14%. However, a thermal treatment at 1000 °C for 1 hour allowed the homogenization of the composition resulting in a $Ba_{1.01}Zr_{0.85}Y_{0.15}O_{3-\delta}$ perovskite phase.

174 In summary, this continuous hydrothermal synthesis in supercritical conditions is highly promising

175 and extensive research on controlling the synthesis parameters would greatly broaden the

176 possibilities for elaborating advanced ceramic materials at low temperature.

Funding: This research was funded in part by the Regional Council of Bourgogne
Franche-Comté, the FEDER and the Graduate School EIPHI (Contract ANR-17-EURE-0002).

179 **Acknowledgments:** The authors thank the ESIREM Engineering college for the SEM

- 180 experimentations.
- 181 **Conflicts of Interest:** The authors declare no conflict of interest.

182 References

- 183 [1] Y. Meng, J. Gao, Z. Zhao, J. Amoroso, J. Tong, K.S. Brinkman, Review: recent progress in
 184 low-temperature proton-conducting ceramics, J Mater Sci. 54 (2019) 9291–9312.
 185 https://doi.org/10.1007/s10853-019-03559-9.
- 186 [2] S. Hossain, A.M. Abdalla, S.N.B. Jamain, J.H. Zaini, A.K. Azad, A review on proton conducting
 187 electrolytes for clean energy and intermediate temperature-solid oxide fuel cells, Renewable
 188 and Sustainable Energy Reviews. 79 (2017) 750–764.
 189 https://doi.org/10.1016/j.rser.2017.05.147.
- A. Nowick, High-temperature protonic conductors with perovskite-related structures, Solid
 State Ionics. 77 (1995) 137–146. https://doi.org/10.1016/0167-2738(94)00230-P.
- 192 [4] H. Dai, H. Kou, H. Wang, L. Bi, Electrochemical performance of protonic ceramic fuel cells with
 193 stable BaZrO3-based electrolyte: A mini-review, Electrochemistry Communications. 96
 194 (2018) 11–15. https://doi.org/10.1016/j.elecom.2018.09.001.
- 195[5]X. Xu, L. Bi, Proton-conducting electrolyte materials, in: Intermediate Temperature Solid196OxideFuelCells,Elsevier,2020:pp.81–111.197https://doi.org/10.1016/B978-0-12-817445-6.00003-X.
- 198 [6] L. Bi, Z. Tao, C. Liu, W. Sun, H. Wang, W. Liu, Fabrication and characterization of easily
 199 sintered and stable anode-supported proton-conducting membranes, Journal of Membrane
 200 Science. 336 (2009) 1–6. https://doi.org/10.1016/j.memsci.2009.03.042.
- [7] K.D. Kreuer, Proton-Conducting Oxides, Annual Review of Materials Research. 33 (2003) 333 359. https://doi.org/10.1146/annurev.matsci.33.022802.091825.
- [8] K.H. Ryu, S.M. Haile, Chemical stability and proton conductivity of doped BaCeO3-BaZrO3
 solid solutions, Solid State Ionics. 125 (1999) 355-367.
 https://doi.org/10.1016/S0167-2738(99)00196-4.
- S. Wang, J. Shen, Z. Zhu, Z. Wang, Y. Cao, X. Guan, Y. Wang, Z. Wei, M. Chen, Further
 optimization of barium cerate properties via co-doping strategy for potential application as
 proton-conducting solid oxide fuel cell electrolyte, Journal of Power Sources. 387 (2018) 24–
 32. https://doi.org/10.1016/j.jpowsour.2018.03.054.

- [10] H. Matsumoto, Y. Kawasaki, N. Ito, M. Enoki, T. Ishihara, Relation Between Electrical
 Conductivity and Chemical Stability of BaCeO[sub 3]-Based Proton Conductors with Different
 Trivalent Dopants, Electrochemical and Solid-State Letters. 10 (2007) B77.
 https://doi.org/10.1149/1.2458743.
- [11] W. Münch, Proton diffusion in perovskites: comparison between BaCeO3, BaZrO3, SrTiO3,
 and CaTiO3 using quantum molecular dynamics, Solid State Ionics. 136–137 (2000) 183–189.
 https://doi.org/10.1016/S0167-2738(00)00304-0.
- [12] J.-H. Kim, Y.-M. Kang, M.-S. Byun, K.-T. Hwang, Study on the chemical stability of Y-doped
 BaCeO3-δ and BaZrO3-δ films deposited by aerosol deposition, Thin Solid Films. 520 (2011)
 1015-1021. https://doi.org/doi:10.1016/j.tsf.2011.08.013.
- [13] E. Fabbri, L. Bi, D. Pergolesi, E. Traversa, Towards the Next Generation of Solid Oxide Fuel
 Cells Operating Below 600 °C with Chemically Stable Proton-Conducting Electrolytes,
 Advanced Materials. 24 (2012) 195–208. https://doi.org/10.1002/adma.201103102.
- [14] D. Yun, J. Kim, S.-J. Kim, J.-H. Lee, J.-N. Kim, H. Yoon, J. Yu, M. Kwak, H. Yoon, Y. Cho, C.-Y. Yoo,
 Structural and Electrochemical Properties of Dense Yttria-Doped Barium Zirconate Prepared
 by Solid-State Reactive Sintering, Energies. 11 (2018) 3083–3099.
 https://doi.org/10.3390/en11113083.
- [15] L. Bi, E. Traversa, Synthesis strategies for improving the performance of doped-BaZrO 3
 materials in solid oxide fuel cell applications, J. Mater. Res. 29 (2014) 1–15.
 https://doi.org/10.1557/jmr.2013.205.
- 230 [16] F.J.A. Loureiro, N. Nasani, G.S. Reddy, N.R. Munirathnam, D.P. Fagg, A review on sintering 231 technology of proton conducting BaCeO3-BaZrO3 perovskite oxide materials for Protonic 232 Ceramic Fuel Cells, Journal of Power Sources. 438 (2019) 226991. 233 https://doi.org/10.1016/j.jpowsour.2019.226991.
- [17] D. Aymes, M. Ariane, F. Bernard, H. Muhr, F. Demoisson, Counter-current flow reactor with
 heat transfer for hydrothermolytic synthesis, WO 2011010056A1, 2011.
- [18] T. Adschiri, K. Kanazawa, K. Arai, Rapid and Continuous Hydrothermal Crystallization of Metal
 Oxide Particles in Supercritical Water, J American Ceramic Society. 75 (1992) 1019–1022.
 https://doi.org/10.1111/j.1151-2916.1992.tb04179.x.
- [19] F. Demoisson, R. Piolet, F. Bernard, Hydrothermal Synthesis of ZnO Crystals from Zn(OH) 2
 Metastable Phases at Room to Supercritical Conditions, Crystal Growth & Design. 14 (2014)
 5388–5396. https://doi.org/10.1021/cg500407r.
- [20] C. Pighini, D. Aymes, N. Millot, L. Saviot*, Low-frequency Raman characterization of
 size-controlled anatase TiO2 nanopowders prepared by continuous hydrothermal syntheses,
 Journal of Nanoparticle Research. 9 (2007) 309–315.
 https://doi.org/10.1007/s11051-005-9061-6.
- 246[21]G. Philippot, E.D. Boejesen, C. Elissalde, M. Maglione, C. Aymonier, B.B. Iversen, Insights into247BaTi1-yZryO3 ($0 \le y \le 1$) Synthesis under Supercritical Fluid Conditions, Chemistry of248Materials. 28 (2016) 3394-3400. https://doi.org/DOI: 10.1021/acs.chemmater.6b00635.
- [22] F. Demoisson, Influence of the pH on the ZnO nanoparticle growth in supercritical water:
 Experimental and simulation approaches, Journal of Supercritical Fluids. 95 (2014) 75–83.
 https://doi.org/10.1016/j.supflu.2014.08.007.

- 252 [23] Y. Zhu, G. Seong, T. Noguchi, A. Yoko, T. Tomai, S. Takami, T. Adschiri, Highly Cr-Substituted 253 CeO 2 Nanoparticles Synthesized Using a Non-equilibrium Supercritical Hydrothermal 254 Process: High Oxygen Storage Capacity Materials Designed for a Low-Temperature Bitumen 255 Upgrading Process, ACS Appl. Energy Mater. 3 (2020)4305-4319. 256 https://doi.org/10.1021/acsaem.0c00026.
- [24] A. Yoko, G. Seong, T. Tomai, T. Adschiri, Continuous Flow Synthesis of Nanoparticles Using
 Supercritical Water: Process Design, Surface Control, and Nanohybrid Materials, KONA. 37
 (2020) 28-41. https://doi.org/10.14356/kona.2020002.
- [25] A. Aimable, B. Xin, N. Millot, D. Aymes, Continuous hydrothermal synthesis of nanometric
 BaZrO3 in supercritical water, Journal of Solid State Chemistry. 181 (2008) 183–189.
 https://doi.org/10.1016/j.jssc.2007.11.015.
- [26] A. Yoko, M. Akizuki, Y. Oshima, Formation mechanism of barium zirconate nanoparticles
 under supercritical hydrothermal synthesis, Journal of Nanoparticle Research. 16 (2014).
 https://doi.org/10.1007/s11051-014-2330-5.
- [27] A. Yoko, M. Akizuki, N. Hirao, S. Kohara, M. Kumar, N. Umezawa, T. Ohno, Y. Oshima, In situ
 X-ray diffraction for millisecond-order dynamics of BaZrO 3 nanoparticle formation in
 supercritical water, The Journal of Supercritical Fluids. 107 (2016) 746–752.
 https://doi.org/10.1016/j.supflu.2015.08.002.
- 270 [28] F. Demoisson, M. Ariane, A. Leybros, H. Muhr, F. Bernard, Design of a reactor operating in 271 supercritical water conditions using CFD simulations. Examples of synthesized 272 nanomaterials, The Journal of Supercritical Fluids. 58 (2011)371-377. 273 https://doi.org/10.1016/j.supflu.2011.07.001.
- [29] D. Han, N. Hatada, T. Uda, Chemical Expansion of Yttrium-Doped Barium Zirconate and
 Correlation with Proton Concentration and Conductivity, J. Am. Ceram. Soc. 99 (2016) 3745–
 3753. https://doi.org/10.1111/jace.14377.
- [30] E. Fabbri, D. Pergolesi, S. Licoccia, E. Traversa, Does the increase in Y-dopant concentration
 improve the proton conductivity of BaZr1-xYxO3-δfuel cell electrolytes?, Solid State Ionics.
 181 (2010) 1043-1051. https://doi.org/doi:10.1016/j.ssi.2010.06.007.
- [31] W. Sun, M. Liu, W. Liu, Chemically Stable Yttrium and Tin Co-Doped Barium Zirconate
 Electrolyte for Next Generation High Performance Proton-Conducting Solid Oxide Fuel Cells,
 Adv. Energy Mater. 3 (2013) 1041–1050. https://doi.org/10.1002/aenm.201201062.
- [32] G. Nuñez, M.J. Balanay, R.B.M. Cervera, Preparation of Y-Doped BaZrO₃ Proton Conducting
 Solid Electrolyte via Modified Low Temperature Pechini Method, AMR. 1098 (2015) 86–91.
 https://doi.org/10.4028/www.scientific.net/AMR.1098.86.
- [33] R. Sažinas, C. Bernuy-López, M.-A. Einarsrud, T. Grande, Effect of CO 2 Exposure on the
 Chemical Stability and Mechanical Properties of BaZrO 3 -Ceramics, J. Am. Ceram. Soc. 99
 (2016) 3685–3695. https://doi.org/10.1111/jace.14395.
- [34] A.R. Akbarzadeh, I. Kornev, C. Malibert, L. Bellaiche, J.M. Kiat, Combined theoretical and
 experimental study of the low-temperature properties of BaZrO 3, Phys. Rev. B. 72 (2005)
 205104. https://doi.org/10.1103/PhysRevB.72.205104.
- [35] M.F. Hoedl, E. Makagon, I. Lubomirsky, R. Merkle, E.A. Kotomin, J. Maier, Impact of point
 defects on the elastic properties of BaZrO3: Comprehensive insight from experiments and ab

- 294
 initio
 calculations,
 Acta
 Materialia.
 160
 (2018)
 247-256.

 295
 https://doi.org/10.1016/j.actamat.2018.08.042.

 247-256.
- [36] S.B.C. Duval, P. Holtappels, U.F. Vogt, U. Stimming, T. Graule, Characterisation of BaZr 0.9 Y 0.1 O
 3-δ Prepared by Three Different Synthesis Methods: Study of the Sinterability and the
 Conductivity, Fuel Cells. 9 (2009) 613–621. https://doi.org/10.1002/fuce.200800170.
- [37] T. Schober, Water vapor solubility and electrochemical characterization of the high
 temperature proton conductor BaZr0.9Y0.102.95, Solid State Ionics. 127 (2000) 351–360.
 https://doi.org/10.1016/S0167-2738(99)00283-0.
- 302 [38] Tsvetkov, Ivanov, Malyshkin, Sereda, Zuev, Thermoelectric Behavior of BaZr0.9Y0.103-d
 303 Proton Conducting Electrolyte, Membranes. 9 (2019) 120.
 304 https://doi.org/10.3390/membranes9090120.
- 305 [39] Y. Yamazaki, R. Hernandez-Sanchez, S.M. Haile, High Total Proton Conductivity in
 306 Large-Grained Yttrium-Doped Barium Zirconate, Chem. Mater. 21 (2009) 2755–2762.
 307 https://doi.org/10.1021/cm900208w.
- I. Arvanitidis, D. Sichen, S. Seetharaman, A Study of the Thermal Decomposition of BaC03,
 Metallurgical and Materials Transactions B. 27B (1996) 409-416.
- 310 [41] Y. Yamazaki, R. Hernandez-Sanchez, S.M. Haile, Cation non-stoichiometry in yttrium-doped
 311 barium zirconate: phase behavior, microstructure, and proton conductivity, Journal of
 312 Materials Chemistry. 20 (2010) 8158–8166. https://doi.org/DOI: 10.1039/c0jm02013c.
- A. Magrez, T. Schober, Preparation, sintering, and water incorporation of proton conducting
 Ba0.99Zr0.8Y0.203Àd: comparison between three different synthesis techniques, Solid State
 Ionics. 175 (2004) 585–588. https://doi.org/doi:10.1016/j.ssi.2004.03.045.
- T. Sato, S. Imaeda, K. Sato, Thermal transformation of yttrium hydroxides to yttrium oxides,
 Thermochimica Acta. 133 (1988) 79–85. https://doi.org/10.1016/0040-6031(88)87140-5.
- 318 [44] F. Demoisson, R. Piolet, F. Bernard, Hydrothermal growth of ZnO nanostructures in 319 supercritical domain: Effect of the metal salt concentration (Zn(NO3)2) in alkali medium 320 (KOH), The Journal Supercritical Fluids. 97 (2015)268-274. of 321 https://doi.org/10.1016/j.supflu.2014.12.012.
- 322





323

325

Figure 1. Schematic of the continuous hydrothermal set-up (adapted from[44]) (*Not colored*

for the print version)



Figure 2. Particle size distribution by volume of the powder synthesized by the continuous

hydrothermal process



326

329





330	<u>0.2 μm</u>
331	Figure 3. TEM micrograph of the BZY powder synthesized by continuous hydrothermal
332	process
333	





Figure 4. X-ray diffractogram of the BZY powder synthesized by continuous hydrothermal

337 process (Not colored for the print version)

338





