Continuous hydrothermal synthesis of doped barium zirconate powder for PCFC (Protonic Ceramic Fuel Cell) application

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Protonic Ceramic Fuel Cell

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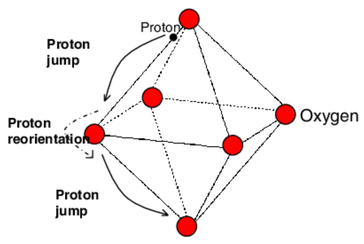
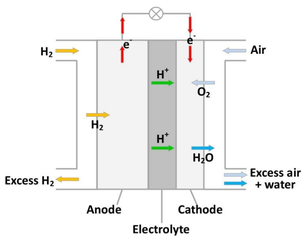




Abstract

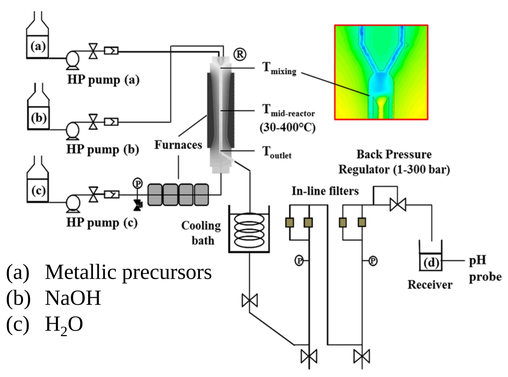
$BaZr_{1-x}M_xO_{3-\delta}$ (M=Ce and/or Y) perovskite materials are good potential candidates for Protonic Ceramic Fuel Cell (PCFC) electrolyte due to their remarkable property of protonic conduction at intermediate temperature (400-600°C). Fabbri et al. have reported a protonic conductivity of 2.10^{-2} S.cm^{-1} at 600°C for $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ [1]. However, the synthesis of these materials requires high temperature (1500°C) by solid state reaction. The hydrothermal synthesis in supercritical water appears then as a way to synthetize perovskite materials at a temperature as low as 400°C. Furthermore, this process allows the formation of nanometric powder. Finally the continuous hydrothermal process offers many advantages such as: "soft-chemistry" route, low cost and sustainable elaboration.

Synthesis process

Continuous hydrothermal process developed at ICB laboratory

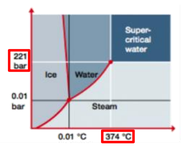
Particles in solution → washing → lyophilization → Powder

- T = 300 – 500 °C
- P = 250 – 300 bar
- Productivity : 3 – 10 g.h^{-1}

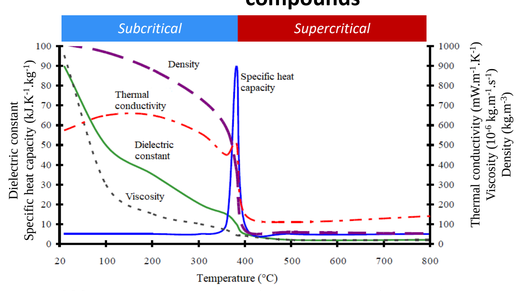


Diagrammatical representation of the process [2]

Supercritical water contribution



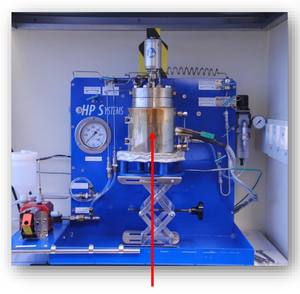
ρ ↘ and η ↘ ⇒ rapid and homogeneous mixing
κ ↘ ⇒ less heat exchanges
ε ↘ ⇒ affect solubility ⇒ **precipitation of inorganic compounds**

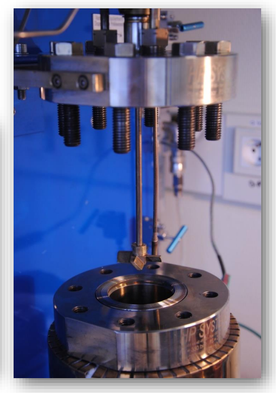


Water properties change in sub- and supercritical conditions [3]

Batch process

- T = 300 – 400 °C
- P = 200 – 300 bar
- Productivity : 0.5 g.h^{-1}

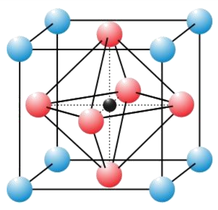




Synthesized powders

$BaZrO_3$ (BZ)
$\sigma_{bulk,600°C,wet\ H2}$ = 5x10^{-3} S.cm^{-1} [4]
$\sigma_{total,600°C,wet\ H2}$ = 2.1x10^{-6} S.cm^{-1} [5]
$T_{sintering}$ > 1700 °C
High stability

$BaZr_{1-x}Y_xO_{3-\delta}$ (BZYx)
↗ Protonic conductivity
BZY20
$\sigma_{bulk,600°C,wet\ H2}$ = 2.5x10^{-2} S.cm^{-1} [4]
$\sigma_{total,600°C,wet\ H2}$ = 6.3x10^{-3} S.cm^{-1} [6]



$BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$ (BZCYx)
$T_{sintering}$ < 1500 °C
High stability
BZCY172
$\sigma_{total,600°C,wet\ H2}$ = 2.2x10^{-2} S.cm^{-1} [8]

$BaCeO_3$ (BC)
$\sigma_{total,600°C,wet\ H2}$ = 1.6x10^{-2} S.cm^{-1} [7]
$T_{sintering}$ > 1700 °C
High stability

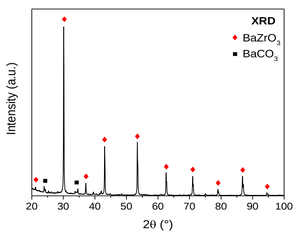
$BaZr_{1-x}Ce_xO_{3-\delta}$ (BZCx)
↗ Stability

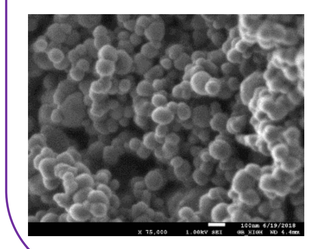
Precursors:
$Ba(NO_3)_2$
$ZrO(NO_3)_2{\cdot}xH_2O$
$Ce(NO_3)_3{\cdot}6H2O$
$Y(NO_3)_3{\cdot}6H2O$

Solvent:
H_2O, NaOH

$BaZrO_3$ (BZ)

$BaZrO_3$ prepared by the continuous process (500°C – 300 bar)

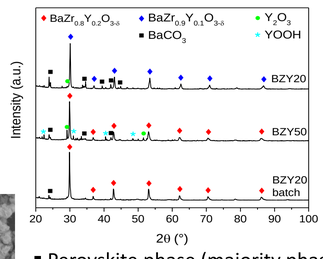


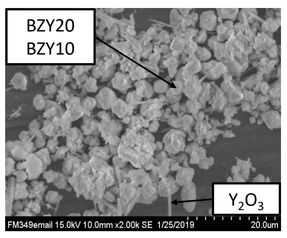


- Well crystallized perovskite phase
- Few impurities ($BaCO_3$) < 4 wt%
- Spherical particles of 95 ± 15nm

$BaZr_{1-x}Y_xO_{3-\delta}$ (BZYx)

$BaZr_{1-x}Y_xO_{3-\delta}$ prepared by the continuous process (500°C – 300 bar) and by the batch process (400°C – 300 bar)

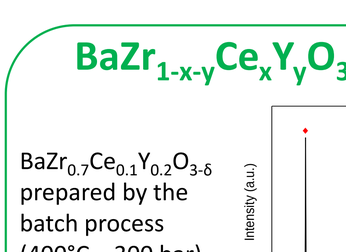




- Perovskite phase (majority phase)
- Formation of BZY20 for a ratio Zr/Y 50/50 in the continuous process
- Impurities : $BaCO_3$, Y_2O_3 et YOOH
- Few impurities ($BaCO_3$) < 3 wt% for the batch synthesis
- Particles of about 50nm (BET) in agglomerates of 3 to 6µm

$BaCeO_3$ (BC)

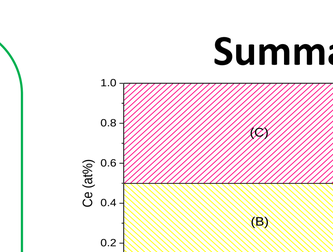
Attempt to synthesize $BaCeO_3$ prepared by the continuous process (500°C – 300 bar)



- Formation of almost pure CeO_2
- Kinetics of CeO_2 precipitation faster than BC formation
- Impossible to synthesize BC by hydrothermal process

$BaZr_{1-x}Ce_xO_{3-\delta}$ (BZCx)

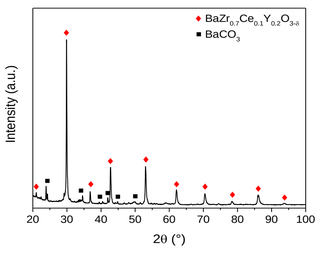
$BaZr_{1-x}Ce_xO_{3-\delta}$ prepared by the continuous process (500°C – 300 bar)



- Formation of $BaZr_{0.92}Ce_{0.08}O_{3-\delta}$ and CeO_2 for x=0.10
- Formation of CeO_2, $BaZrO_3$ and $BaCO_3$ for x=0.90
- Kinetics of CeO_2 precipitation faster than BZC formation
- Only a small proportion of Ce enter into the perovskite structure

$BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$ (BZCYxy)

$BaZr_{0.7}Ce_{0.1}Y_{0.2}O_{3-\delta}$ prepared by the batch process (400°C – 300 bar)



- Well crystallized perovskite phase
- Few impurities ($BaCO_3$) < 8 wt%

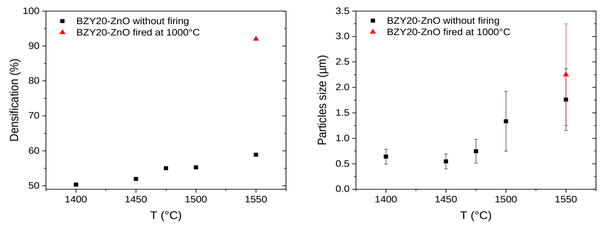
Summary

(A) Possible synthesis
(B) Not tested
(C) Impossible synthesis

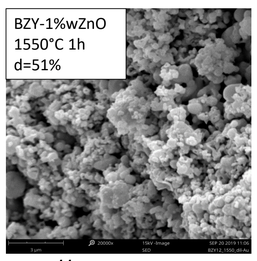
Diagrammatical representation of the accessible composition of $BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$ by hydrothermal process.

Application as electrolyte for PCFC

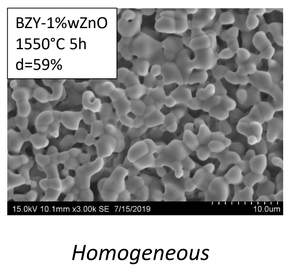
Densification



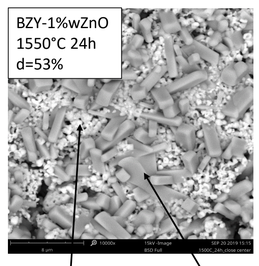
- Necessary to add sintering aid (ZnO 1wt%)
- Sintering for 24h cause the evaporation of Ba and a segregation of phases
- Thermal treatment at 1000°C promotes densification and avoid segregation of phases
- Densification max = 92%
- Average particles size max = 2.25µm



Homogeneous composition
$Ba_{0,96}Zr_{0.78}Y_{0.22}O_{3-\delta}$

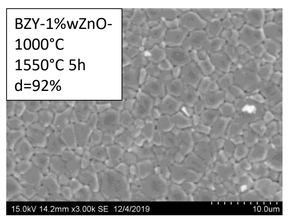


Homogeneous composition
$Ba_{0,96}Zr_{0.79}Y_{0.21}O_{3-\delta}$



$Y_{1.82}Zr_{0.18}O_{3+\delta}$

$Ba_{0.71}Zr_{0.74}Y_{0.26}O_{3-\delta}$



Homogeneous composition
$BaZr_{0.80}Y_{0.20}O_{3-\delta}$

Electrochemical Impedance Spectroscopy

Principle:
Applying a small quantity of sinusoidal voltage (or current) to perturb a system a measuring the response of the system (a oscillating current or voltage with a certain amplitude and shift depending on the frequency of the applied signal.

Set up:
Norec Probostat™
Metrohm Autolab™
Different atmospheres : dry H_2, wet H_2 (3%), dry O_2, wet O_2 (3%), dry N_2.
Temperature range : from 400 to 600°C

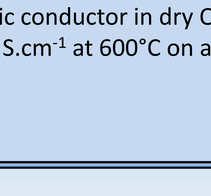
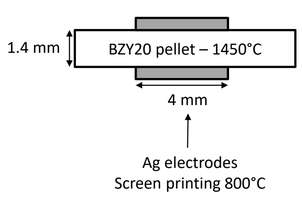
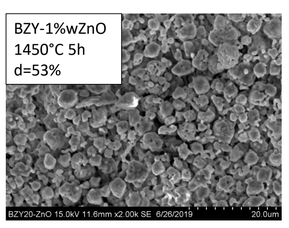


Fig. 11. Apparent transport numbers of ions in $BaCe_{1-x}Sm_xO_{3-x}$ under fuel cell condition. (○●) $x = 0.05$; (△▲) $x = 0.10$; (□■) $x = 0.15$.[9]

Sample:

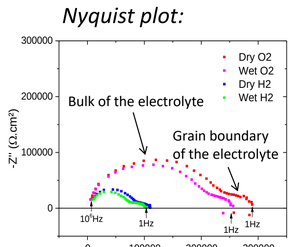


Microstructure:

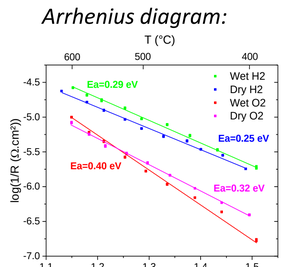


Homogeneous composition :
$Ba_{0.96}Zr_{0.82}Y_{0.18}O_{3-\delta}$

Nyquist plot:



Arrhenius diagram:



Atmosphere	Dry O_2	Wet O_2	Dry H_2	Wet H_2
Activation energy (eV)	0.40	0.32	0.25	0.29
Charge carriers	Holes	H^+, O^{2-}, holes	H^+	H^+
Conductivity at 600°C (S.cm^{-1})	3.18x10^{-6}	3.40x10^{-6}	3.32x10^{-6}	3.69x10^{-6}

Conclusion

Synthesis

- BZY20 powder obtained by both continuous and batch process
- Less impurities with batch process but less production
- Synthesis of Ce-based compounds impossible by hydrothermal way due to the poor stability of BaCeO3 against water containing atmosphere

→ Synthesis of BZY20 and BZCY712 by the continuous process trying to reproduce the conditions of the batch reactor

Sintering

- Using nanosized powder synthesized by hydrothermal process allows to reduce the sintering temperature from 1700°C to 1550°C
- Long sintering time causes the formation of undesirable phase
- Necessary to fire the powder at 1000°C in order to stabilize the crystal structure and promote a better densification without any secondary phase.

Electrochemical performances

BZY20 is a protonic conductor and became electronic conductor in dry O_2
Best total conductivity obtained in wet H_2 : 3.3x10^{-6} S.cm^{-1} at 600°C on a non-dense sample

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[1] E. Fabbri et al. *Adv. Mater.*, 24 (2012) 195-208
[2] F. Demoisson et al., *Cryst. Growth Des.*,14 (2014) 5388-5396
[3] R; Piolet, PhD thesis, 2014, Université de Bourgogne
[4] Kreuer, *Annu. Rev. Mater. Res.*, 33 (2003) 333-359
[5] Morishita et al., *J. Mater. Sci. Eng.*, 6 (2018) 19-27
[6] Tao et al., *J. Solid State Chem.*, 180 (2007) 3493-3503
[7] Shi et al., *Appl. Mater. Interfaces*, 6 (2014) 5175-5182
[8] Zuo et al., *Adv. Mater.*, 18 (2006) 3318-3320
[9] Iwahara, *Solid State Ionics*, 77 (1995) 289-298