



HAL
open science

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

Mélanie François, François Maeght, Frédéric Demoisson, Gilles Caboche

► **To cite this version:**

Mélanie François, François Maeght, Frédéric Demoisson, Gilles Caboche. Continuous hydrothermal synthesis of doped barium zirconate powder for PCFC (Protonic Ceramic Fuel Cell) application. C'NANO (Le congrès commun SFNano C'Nano 2019), Dec 2019, DIJON, France. hal-03169162

HAL Id: hal-03169162

<https://hal.science/hal-03169162v1>

Submitted on 15 Mar 2021

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.

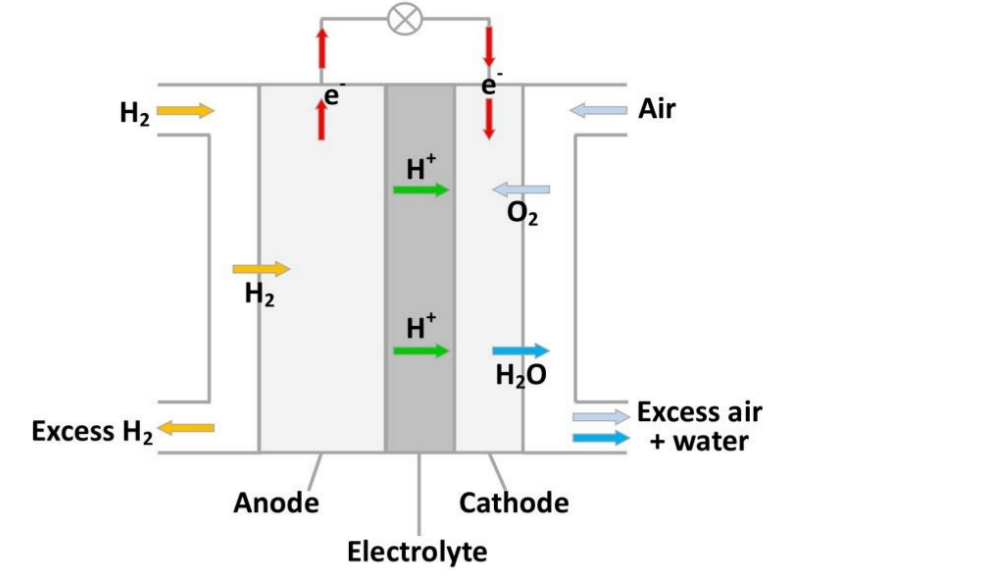
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Continuous hydrothermal synthesis of doped barium zirconate powder for PCFC application

Protonic Ceramic Fuel Cell

Mélanie François¹, François Maeght¹, Frédéric Demoisson¹, Gilles Caboche¹

¹ Laboratoire Interdisciplinaire Carnot de Bourgogne, Université de Bourgogne Franche-Comté, Dijon, FRANCE
melanie_francois@etu.u-bourgogne.fr

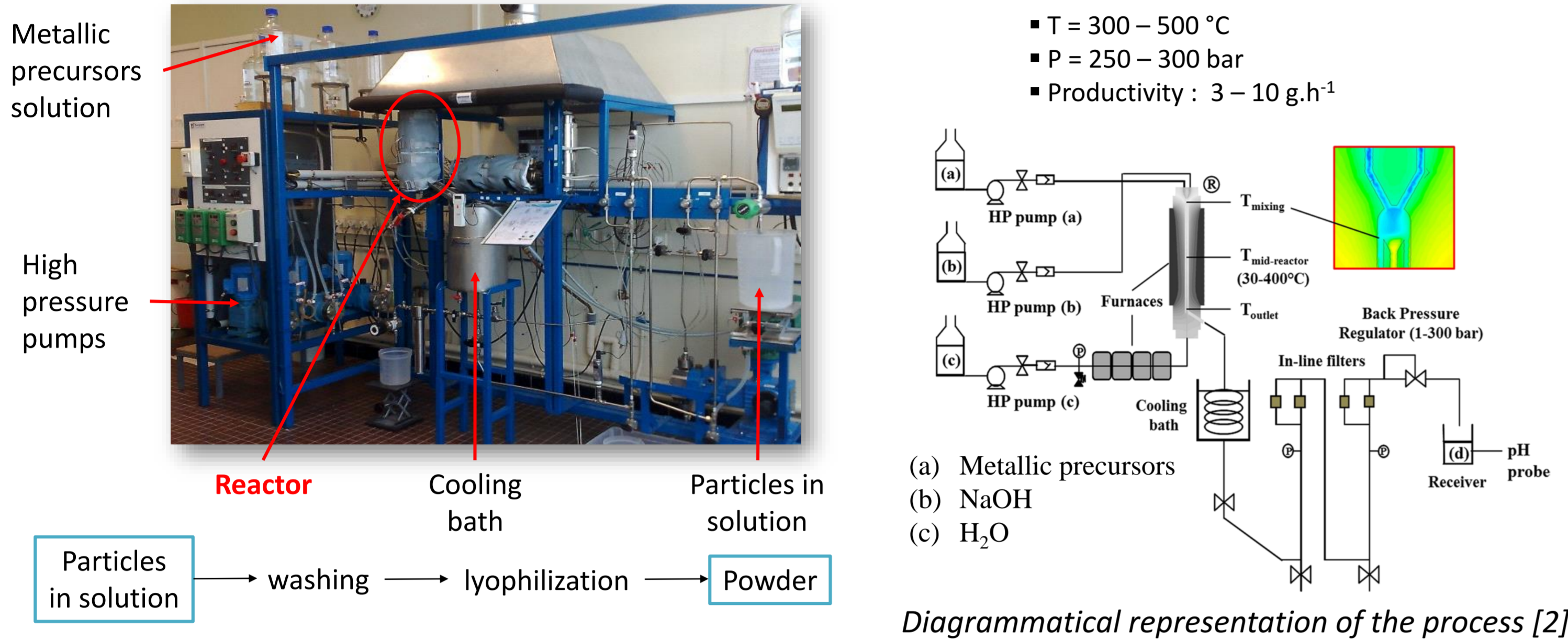


Abstract

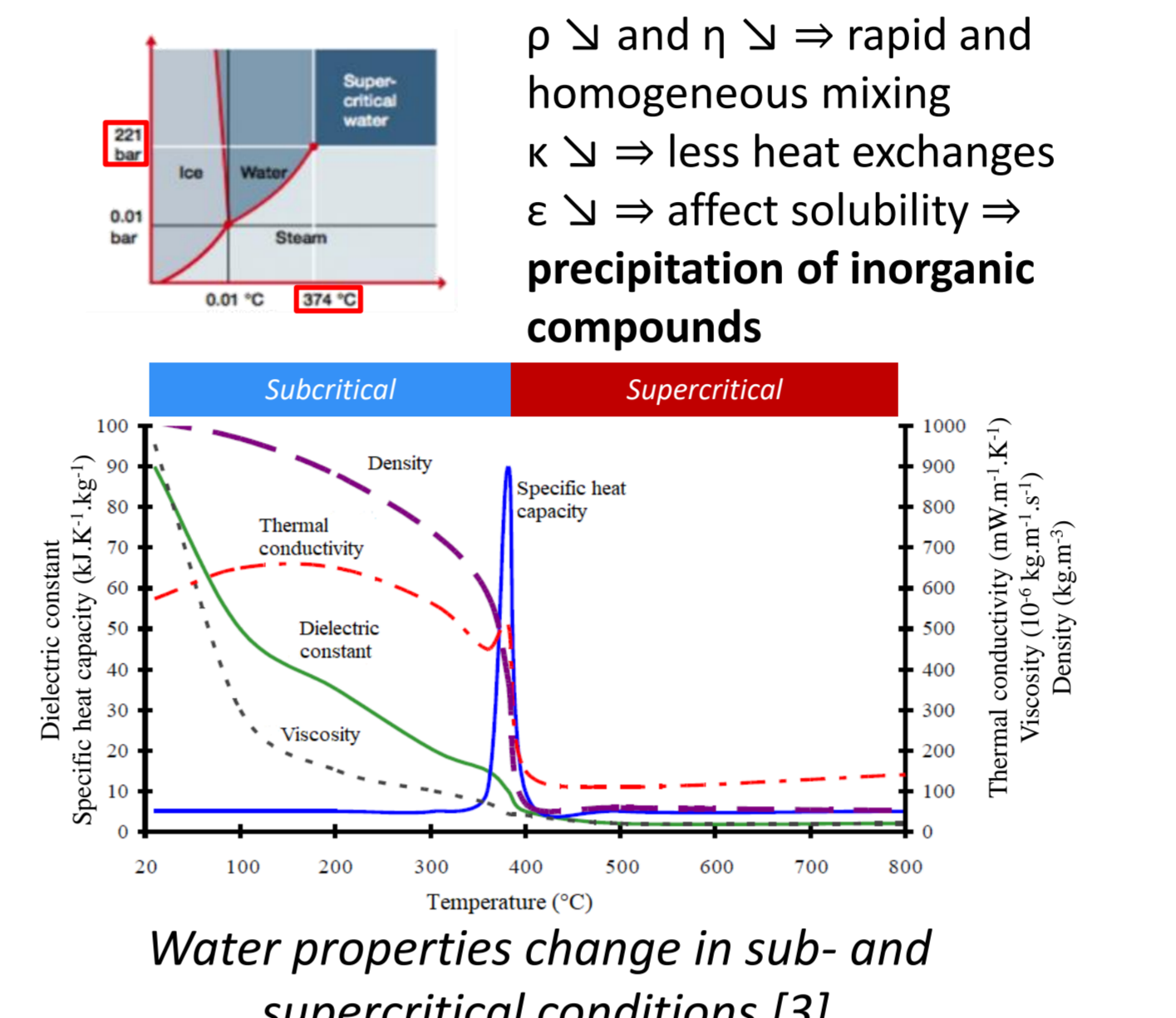
BaZr_{1-x}M_xO_{3-δ} (M=Ce and/or Y) perovskite materials are good potential candidates for Protonic Ceramic Fuel Cell (PCFC) electrolyte due to their remarkable property of protonic conduction at intermediate temperature (400-600°C). Fabbri et al. have reported a protonic conductivity of 2.10⁻² S.cm⁻¹ at 600°C for BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} [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 synthesize 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

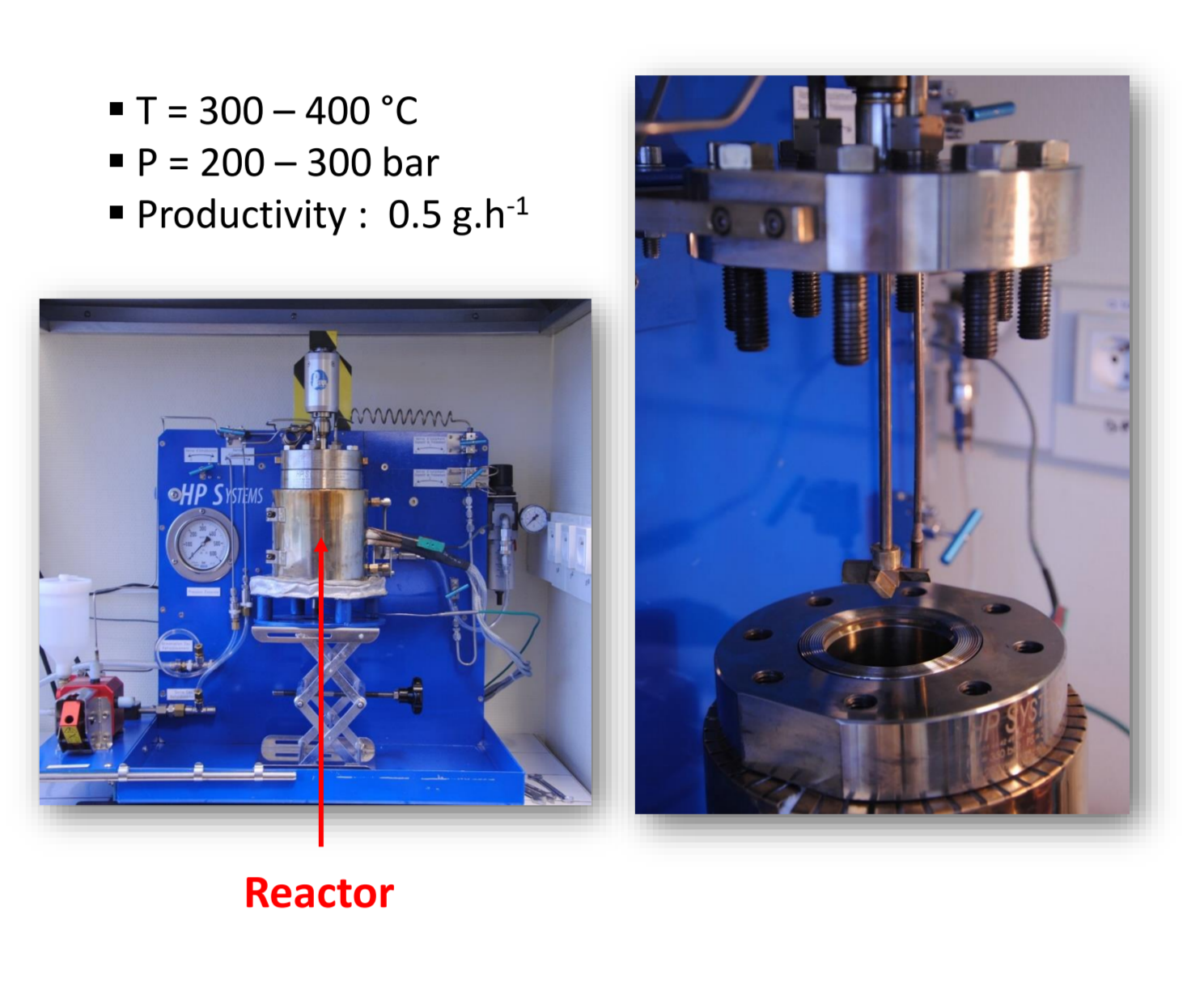
Continuous hydrothermal process developed at ICB laboratory



Supercritical water contribution



Batch process



Synthesized powders

BaZrO₃ (BZ)
σ_{bulk,600°C,wet H2} = 5x10⁻³ S.cm⁻¹ [4]
σ_{total,600°C,wet H2} = 2.1x10⁻⁶ S.cm⁻¹ [5]
T_{sintering} > 1700 °C
High stability

BaCeO₃ (BC)
σ_{total,600°C,wet H2} = 1.6x10⁻² S.cm⁻¹ [7]
T_{sintering} > 1700 °C
High stability

BaZr_{1-x}Ce_xO_{3-δ} (BZCx)
σ_{total,600°C,wet H2} = 2.2x10⁻² S.cm⁻¹ [8]

BaZr_{1-x}Y_xO_{3-δ} (BZYx)
σ_{total,600°C,wet H2} = 2.5x10⁻² S.cm⁻¹ [4]
σ_{total,600°C,wet H2} = 6.3x10⁻³ S.cm⁻¹ [6]

BaZr_{1-x-y}Ce_xY_yO_{3-δ} (BZCYx)
T_{sintering} < 1500 °C
High stability
BZCY172

BaZr_{1-x-y}Ce_xY_yO_{3-δ} (BZCYxy)
σ_{total,600°C,wet H2} = 2.2x10⁻² S.cm⁻¹ [8]

BaZrO₃ (BZ)
BaZrO₃ prepared by the continuous process (500°C – 300 bar)
SEM image showing spherical particles of 95 ± 15nm.
XRD plot showing well crystallized perovskite phase with few impurities (BaCO₃) < 4 wt%.

BaZr_{1-x}Y_xO_{3-δ} (BZYx)
BaZr_{1-x}Y_xO_{3-δ} prepared by the continuous process (500°C – 300 bar) and by the batch process (400°C – 300 bar).
SEM image showing particles of about 50nm (BET) in agglomerates of 3 to 6µm.
XRD plot showing perovskite phase (majority phase) and formation of BZY20 for a ratio Zr/Y 50/50 in the continuous process. Impurities: BaCO₃, Y₂O₃ et YOOH. Few impurities (BaCO₃) < 3 wt% for the batch synthesis.

BaCeO₃ (BC)
Attempt to synthesize BaCeO₃ prepared by the continuous process (500°C – 300 bar).
XRD plot showing almost pure CeO₂ precipitation faster than BC formation. Kinetics of CeO₂ precipitation faster than BZC formation. Impossible to synthesize BC by hydrothermal process.

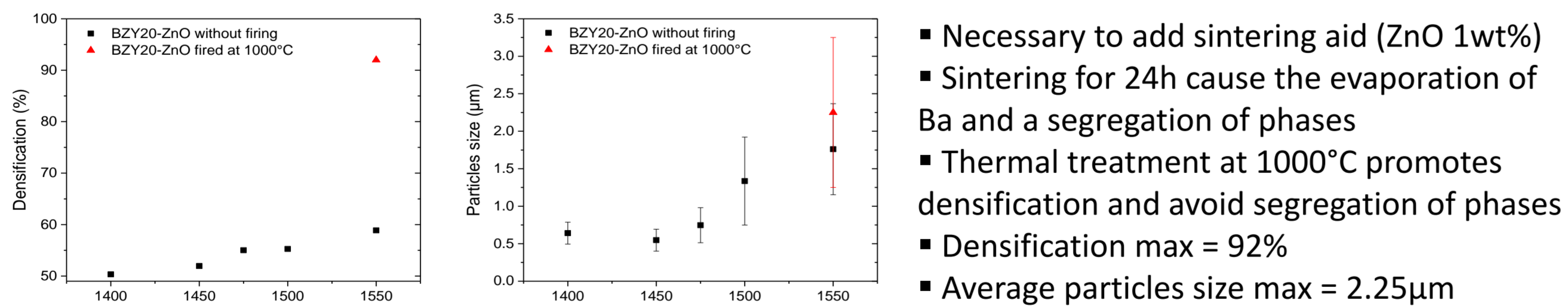
BaZr_{1-x}Ce_xO_{3-δ} (BZCx)
BaZr_{1-x}Ce_xO_{3-δ} prepared by the continuous process (500°C – 300 bar).
XRD plot showing formation of BaZr_{0.92}Ce_{0.08}O_{3-δ} and CeO₂ for x=0.10. Formation of CeO₂, BaZrO₃ and BaCO₃ for x=0.90. Kinetics of CeO₂ precipitation faster than BZC formation. Only a small proportion of Ce enter into the perovskite structure.

BaZr_{1-x-y}Ce_xY_yO_{3-δ} (BZCYxy)
BaZr_{0.7}Ce_{0.1}Y_{0.2}O_{3-δ} prepared by the batch process (400°C – 300 bar).
XRD plot showing well crystallized perovskite phase with few impurities (BaCO₃) < 8 wt%.

Summary
Diagrammatical representation of the accessible composition of BaZr_{1-x-y}Ce_xY_yO_{3-δ} by hydrothermal process.
(A) Possible synthesis
(B) Not tested
(C) Impossible synthesis

Application as electrolyte for PCFC

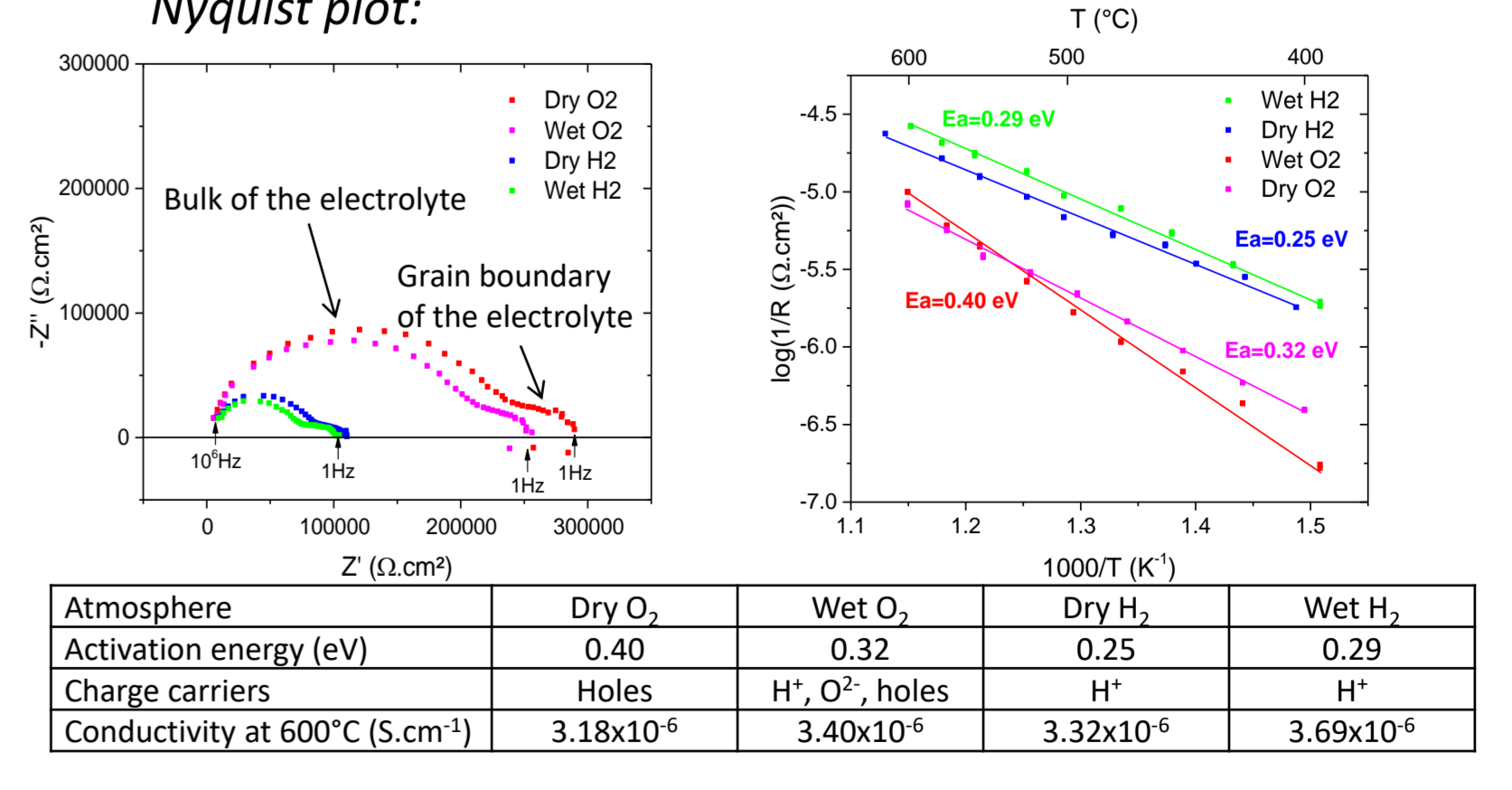
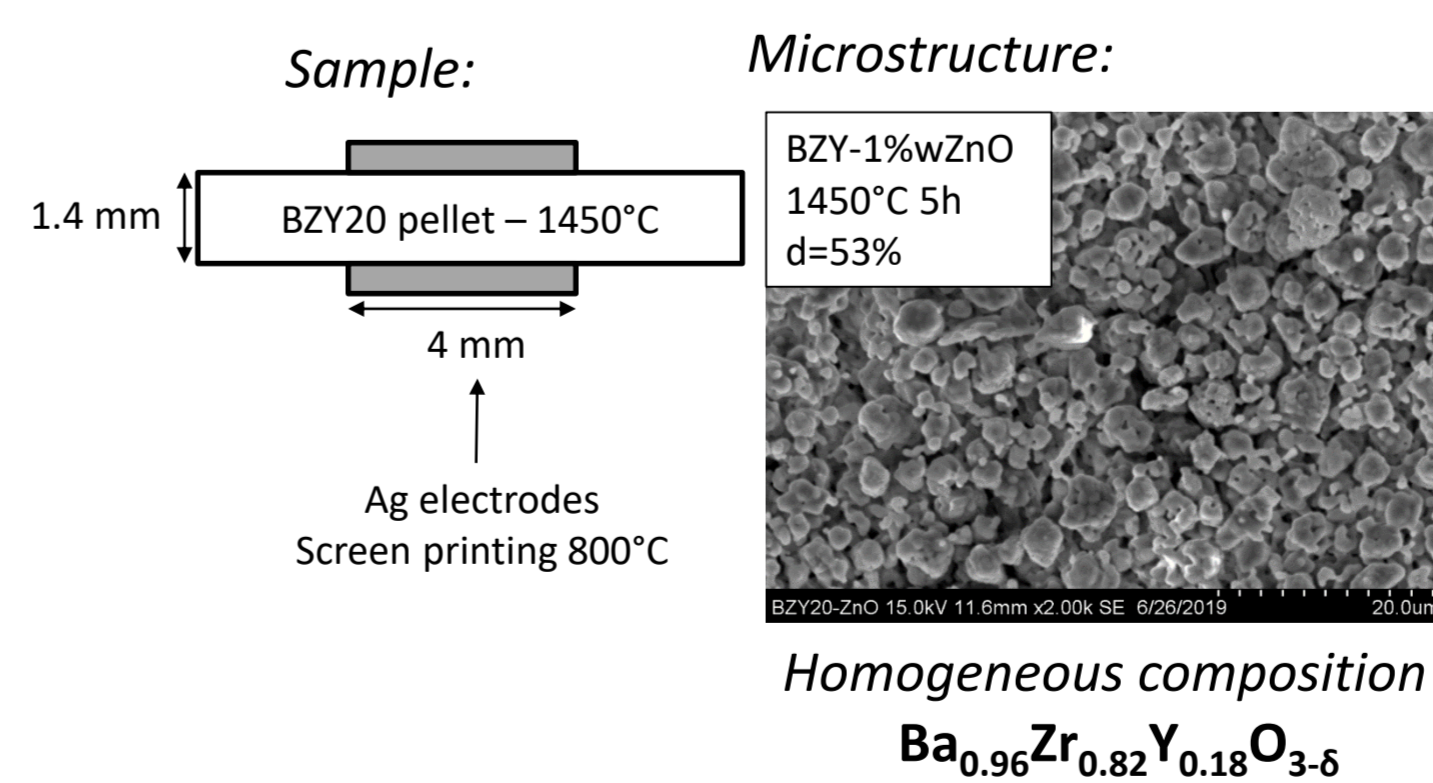
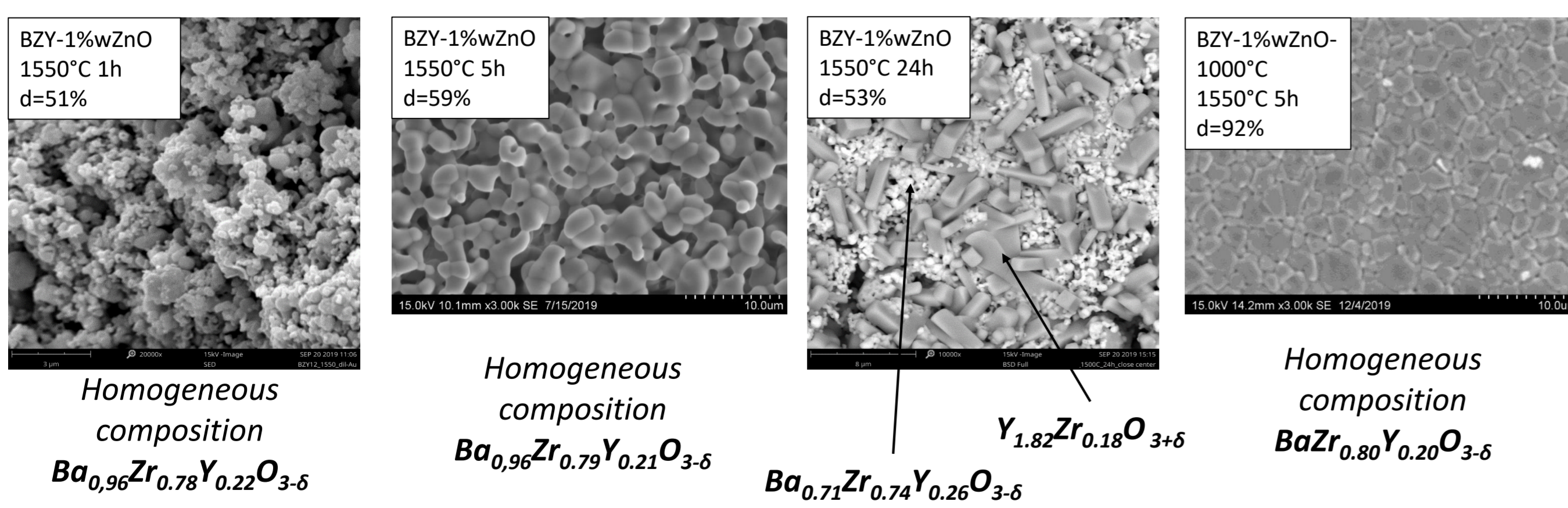
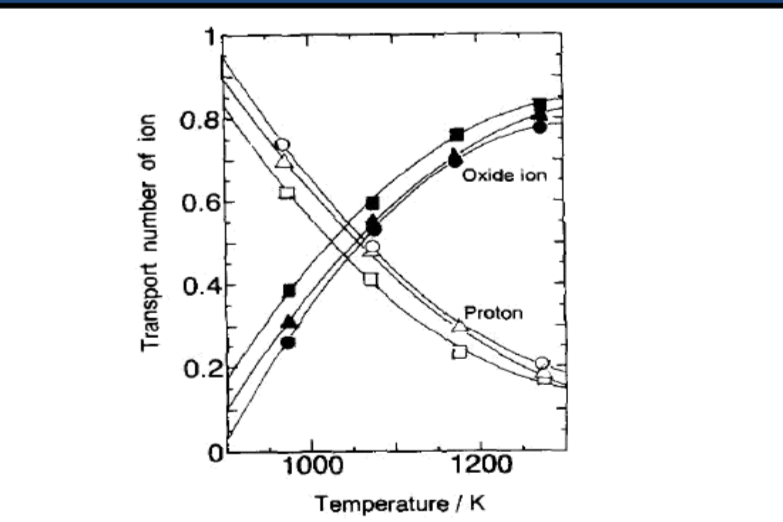
Densification



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 Probatat™ Metrohm Autolab™
Different atmospheres : dry H₂, wet H₂ (3%), dry O₂, wet O₂ (3%), dry N₂.
Temperature range : from 400 to 600°C



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 BZCY172 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 O₂. Best total conductivity obtained in wet H₂ : 3.3x10⁻⁶ S.cm⁻¹ at 600°C on a non-dense sample