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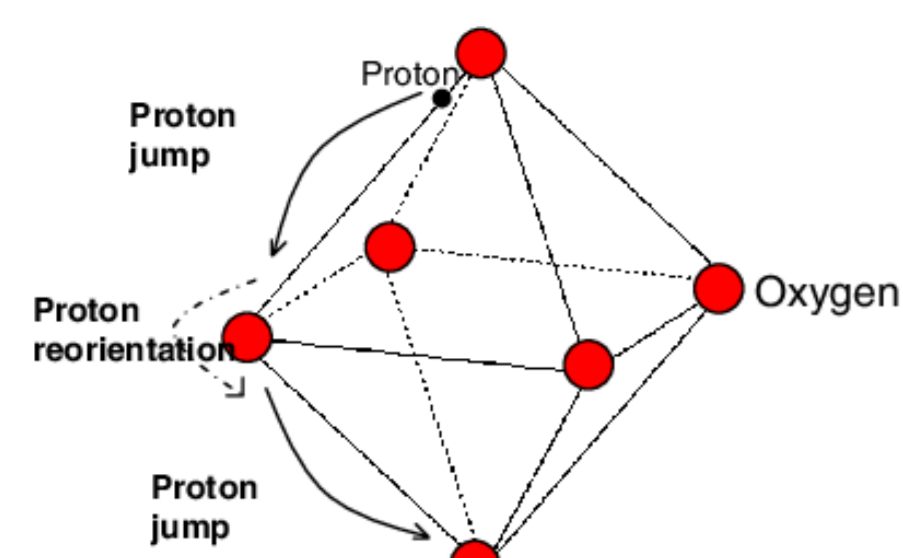
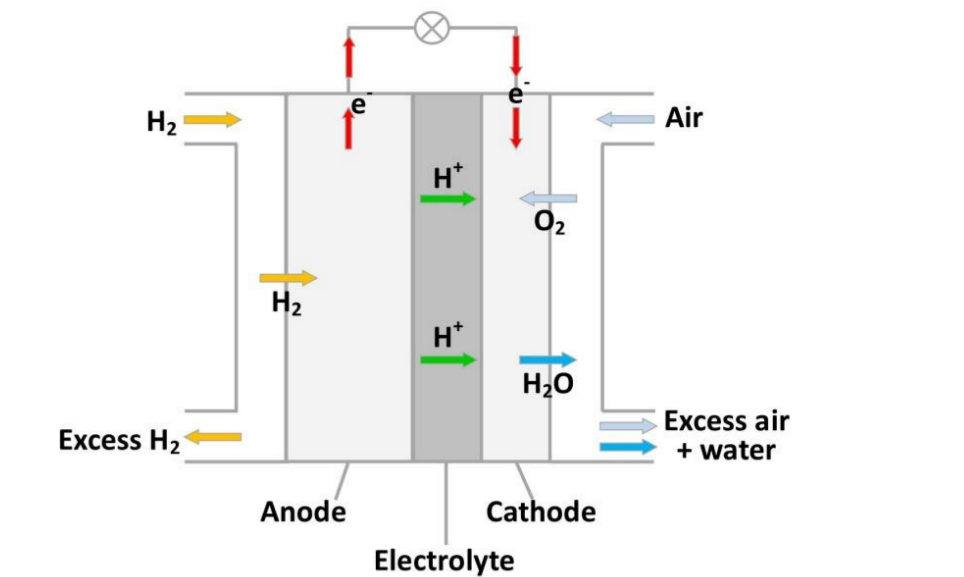
Continuous hydrothermal synthesis of doped barium zirconate powder for PCFC application

Protonic Ceramic Fuel Cell

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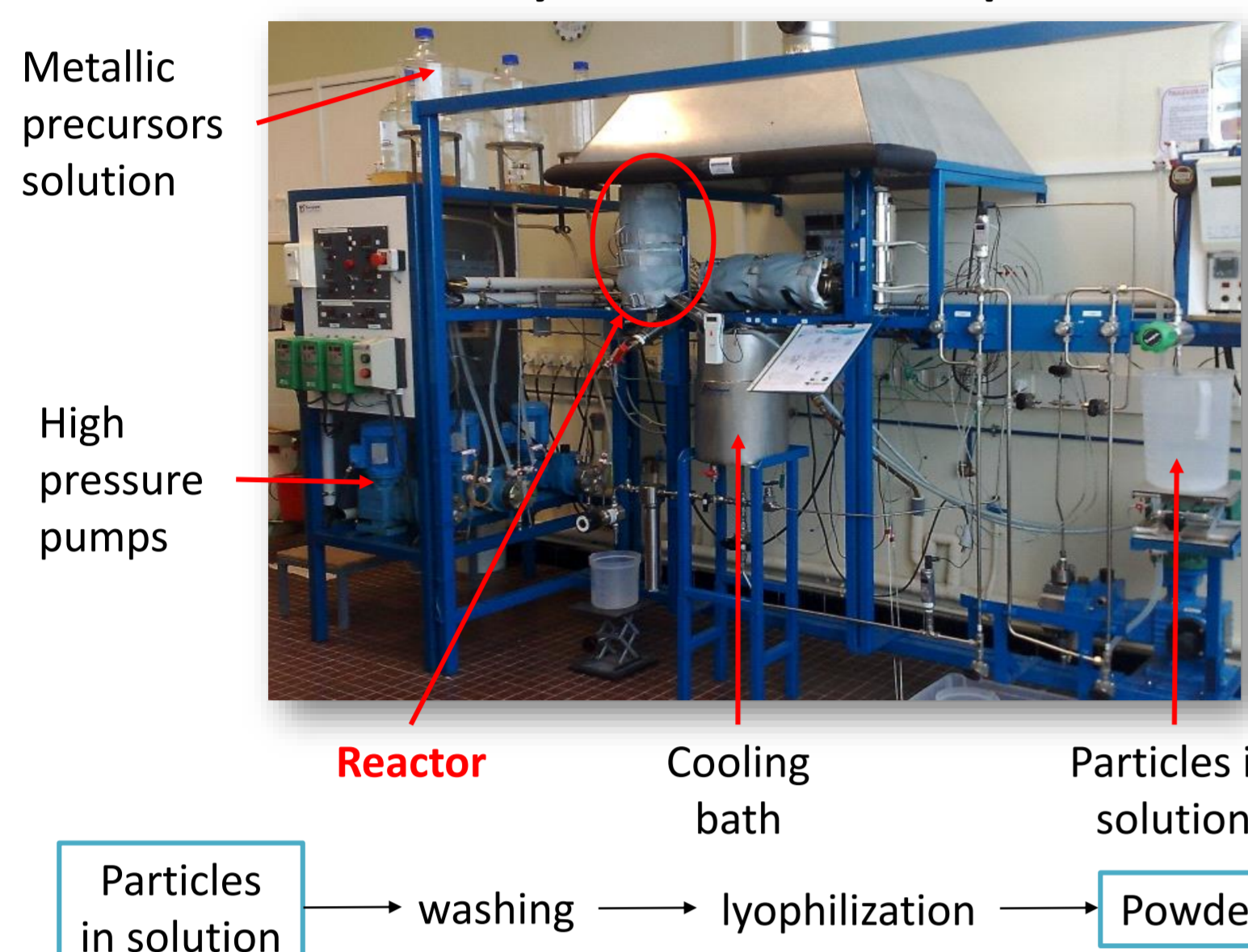


Abstract

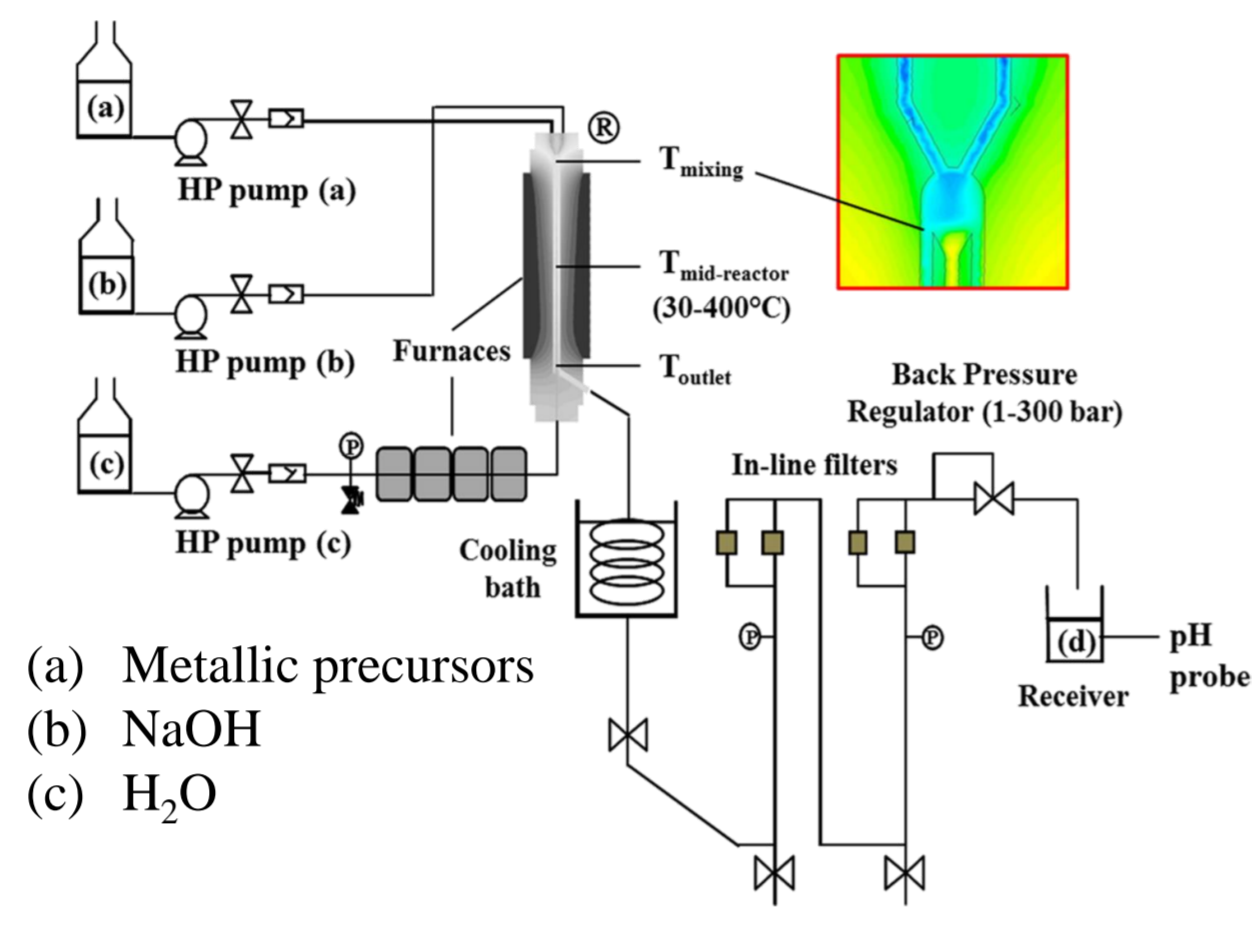
BaZr_{1-x}M_xO_{3-δ} (M=Ce and/or Y) perovskite materials are good potential candidates for Protonic Ceramic Fuel Cell (PCFC) electrolyte due to their remarkable property of protonic conduction at intermediate temperature (400-600°C). Fabbri et al. have reported a protonic conductivity of 2.10⁻² S.cm⁻¹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

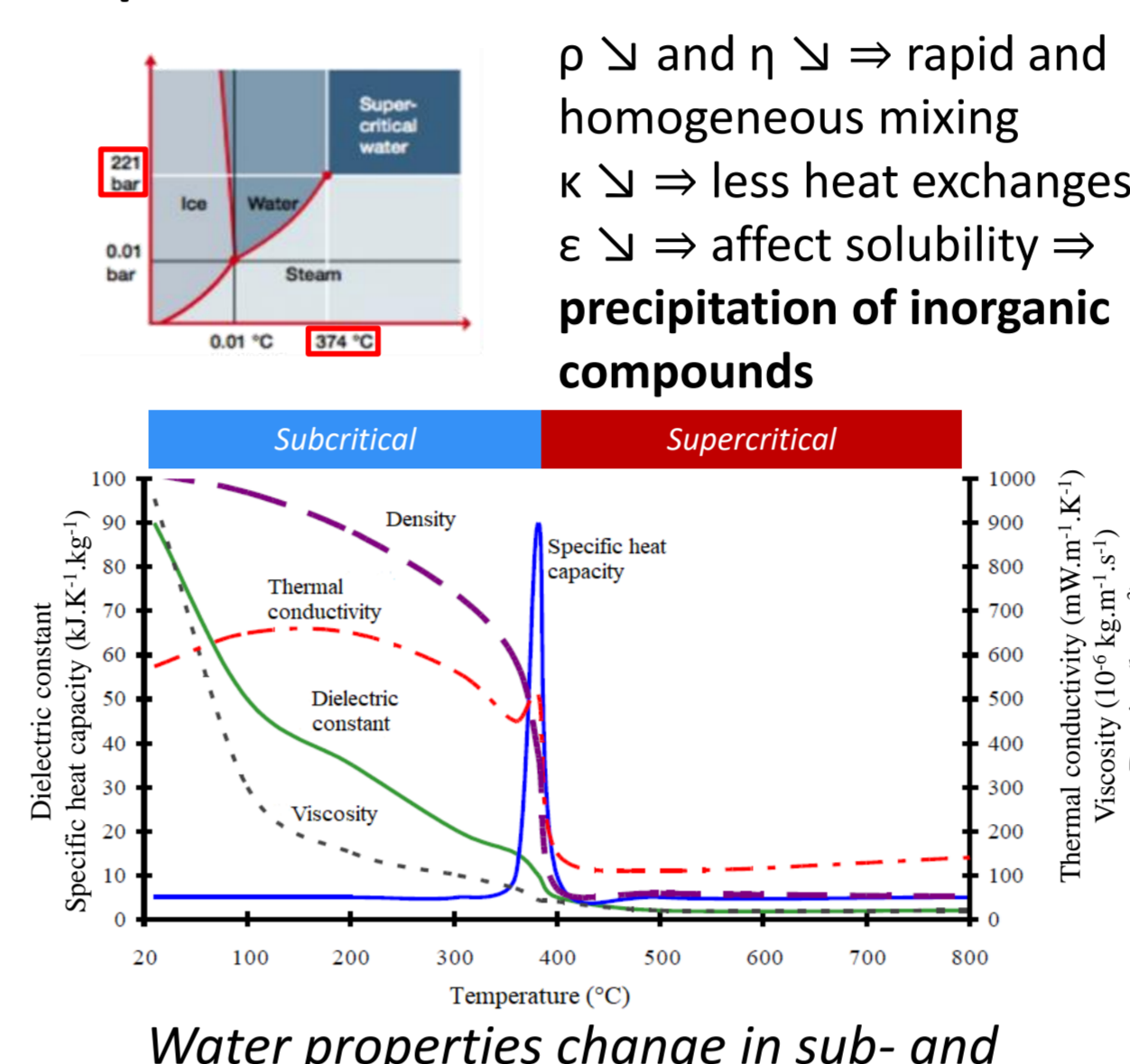


- T = 300 – 500 °C
- P = 250 – 300 bar
- Productivity : 3 – 10 g.h⁻¹



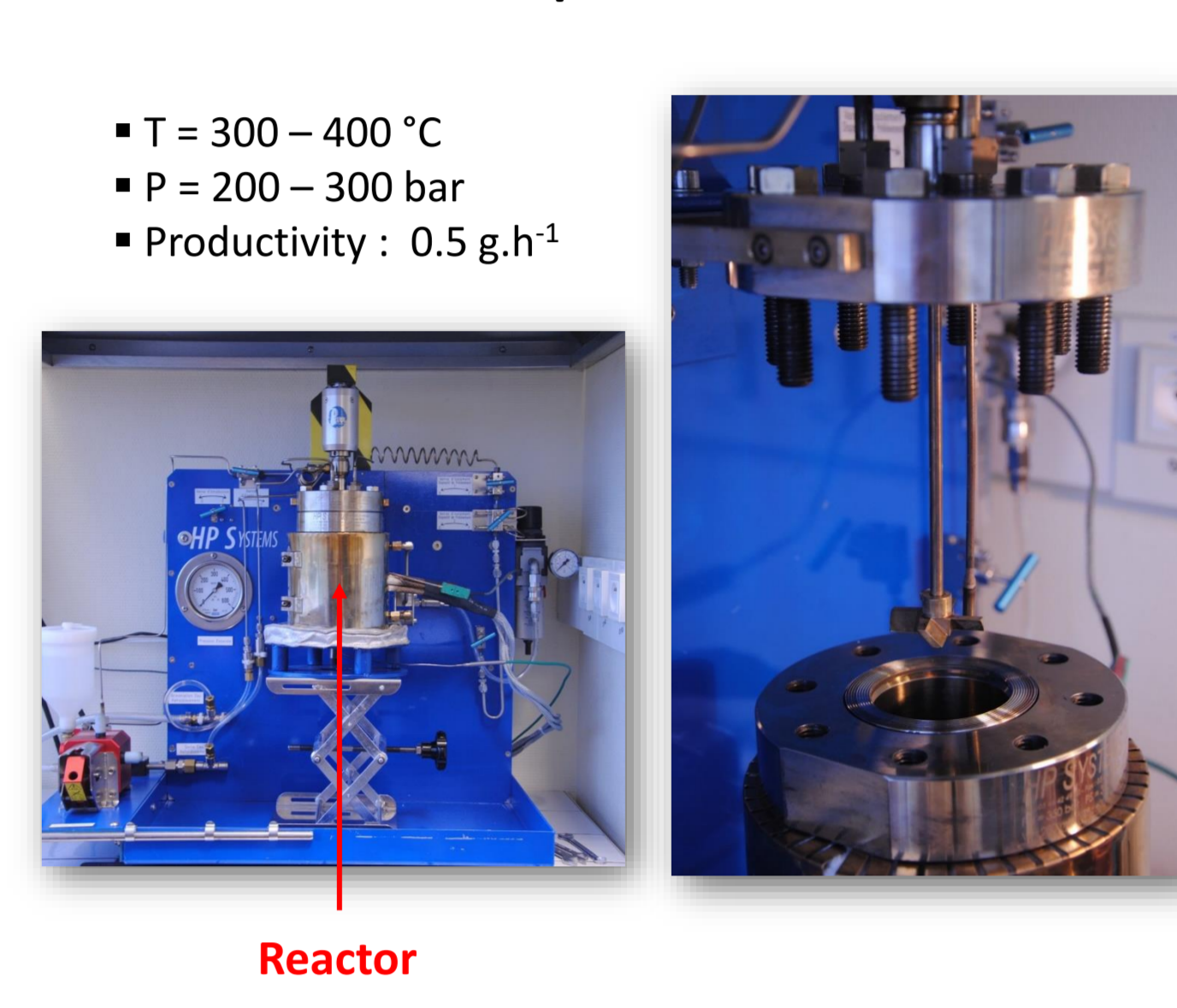
Diagrammatical representation of the process [2]

Supercritical water contribution



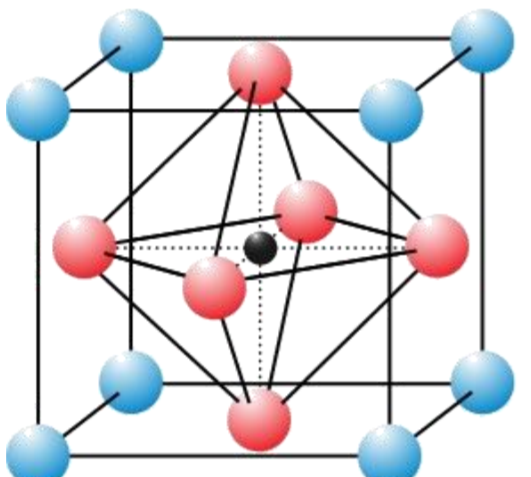
Water properties change in sub- and supercritical conditions [3]

Batch process



Synthesized powders

BaZrO₃ (BZ)
 $\sigma_{\text{bulk},600^\circ\text{C,wet H}_2} = 5 \times 10^{-3} \text{ S.cm}^{-1}$ [4]
 $\sigma_{\text{total},600^\circ\text{C,wet H}_2} = 2.1 \times 10^{-6} \text{ S.cm}^{-1}$ [5]
 $T_{\text{sintering}} > 1700^\circ\text{C}$
High stability



BaZr_{1-x}Y_xO_{3-δ} (BZYx)
Protonic conductivity
BZY20
 $\sigma_{\text{bulk},600^\circ\text{C,wet H}_2} = 2.5 \times 10^{-2} \text{ S.cm}^{-1}$ [4]
 $\sigma_{\text{total},600^\circ\text{C,wet H}_2} = 6.3 \times 10^{-3} \text{ S.cm}^{-1}$ [6]

BaZr_{1-x-y}Ce_xY_yO_{3-δ} (BZCYx)
 $T_{\text{sintering}} < 1500^\circ\text{C}$
High stability
BZCY172
 $\sigma_{\text{total},600^\circ\text{C,wet H}_2} = 2.2 \times 10^{-2} \text{ S.cm}^{-1}$ [8]

BaCeO₃ (BC)
 $\sigma_{\text{total},600^\circ\text{C,wet H}_2} = 1.6 \times 10^{-2} \text{ S.cm}^{-1}$ [7]
 $T_{\text{sintering}} > 1700^\circ\text{C}$
High stability

Precursors:
 Ba(NO₃)₂
 ZrO(NO₃)₂·xH₂O
 Ce(NO₃)₃·6H₂O
 Y(NO₃)₃·6H₂O

Solvent:
 H₂O, NaOH

BaZr_{1-x}Ce_xO_{3-δ} (BZCx)
Stability

BaCeO₃ (BC)
 Attempt to synthesize BaCeO₃ prepared by the continuous process (500°C – 300 bar)

- Formation of almost pure CeO₂
- Kinetics of CeO₂ precipitation faster than BC 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)

- 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

BaZrO₃ (BZ)
 BaZrO₃ prepared by the continuous process (500°C – 300 bar)

- Well crystallized perovskite phase
- Few impurities (BaCO₃) < 4 wt%
- Spherical particles of 95 ± 15nm

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)

- Perovskite phase (majority phase)
- 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
- Particles of about 50nm (BET) in agglomerates of 3 to 6µm

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)

- Well crystallized perovskite phase
- Few impurities (BaCO₃) < 8 wt%

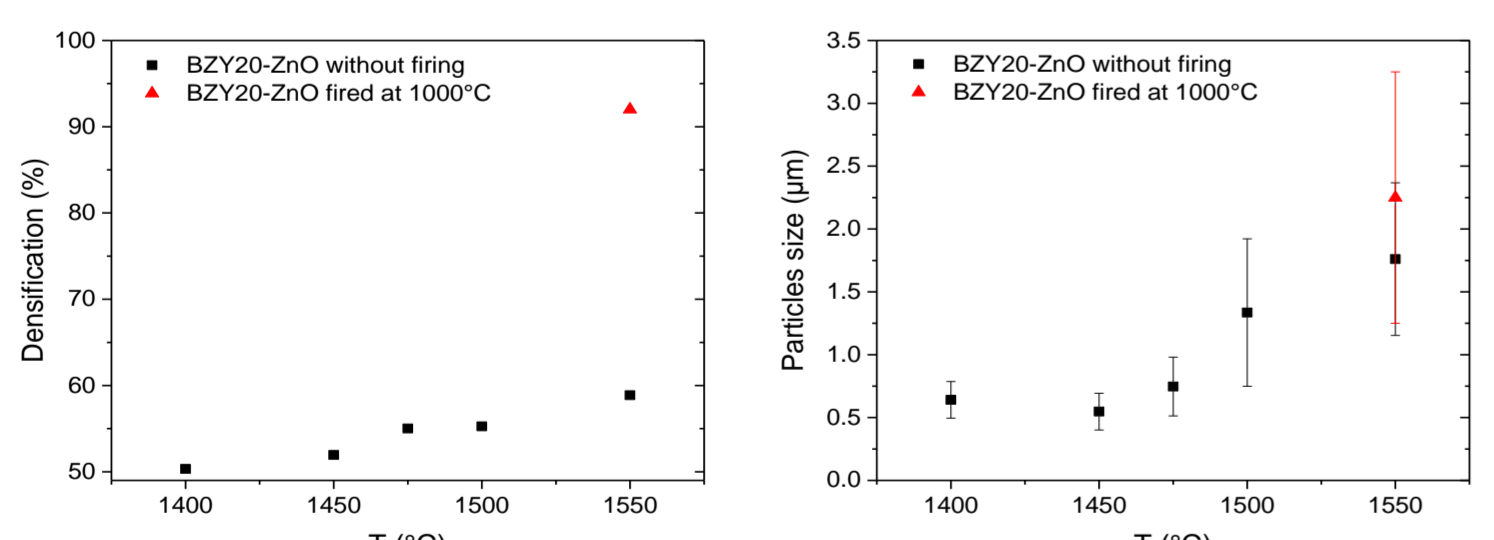
Summary

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

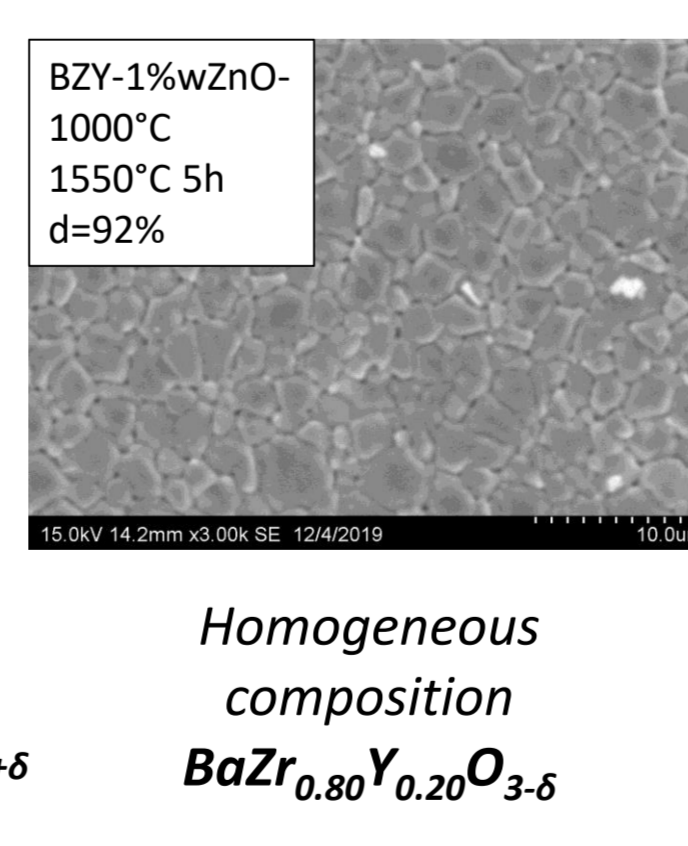
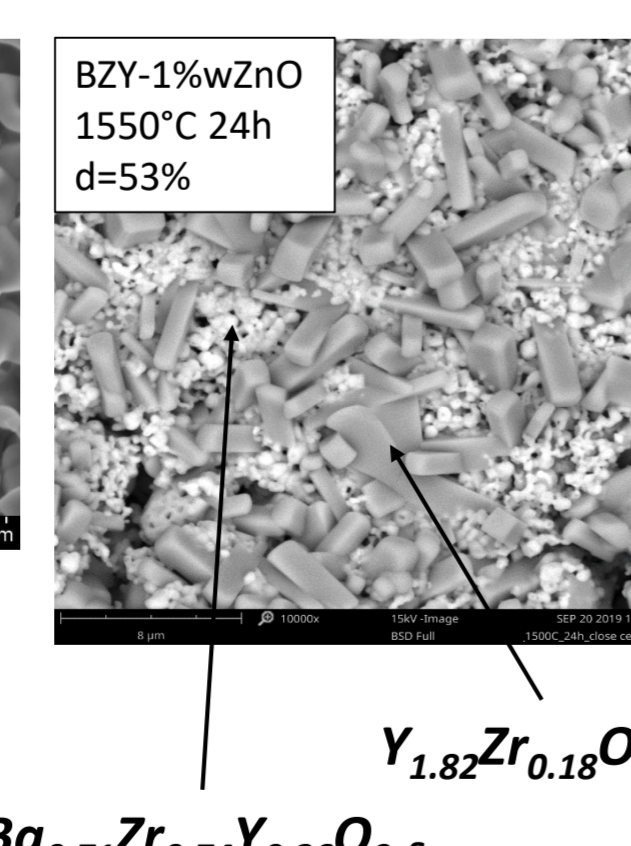
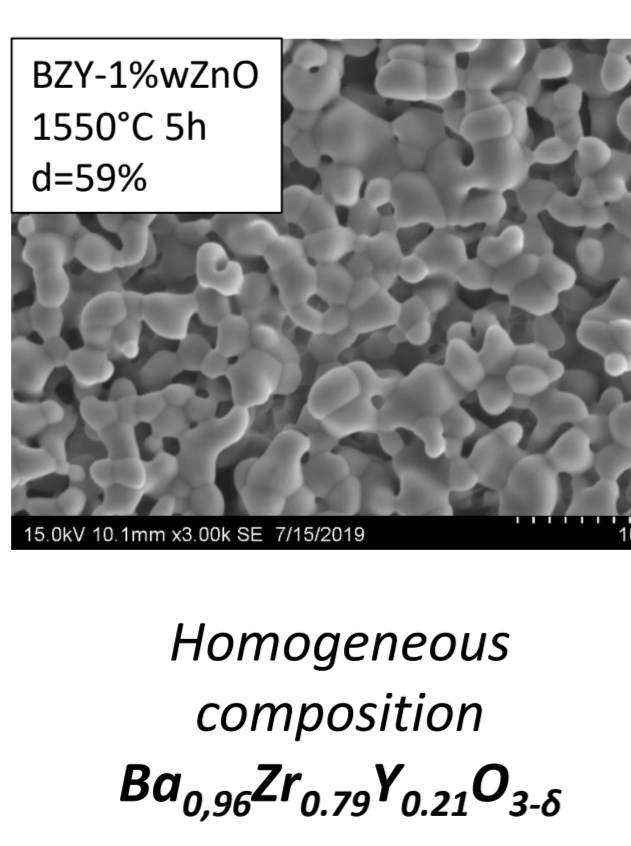
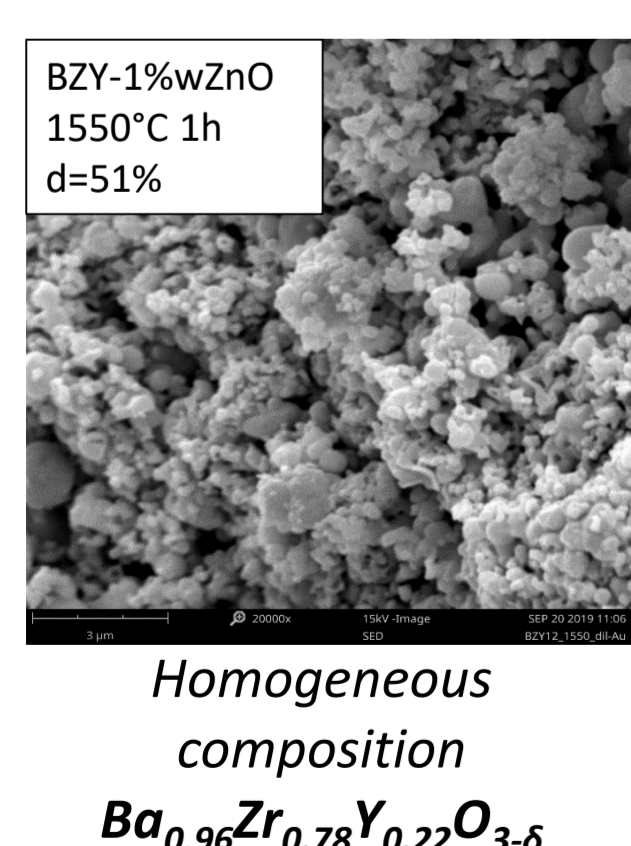
Diagrammatical representation of the accessible composition of BaZr_{1-x-y}Ce_xY_yO_{3-δ} by hydrothermal process.

Application as electrolyte for PCFC

Densification



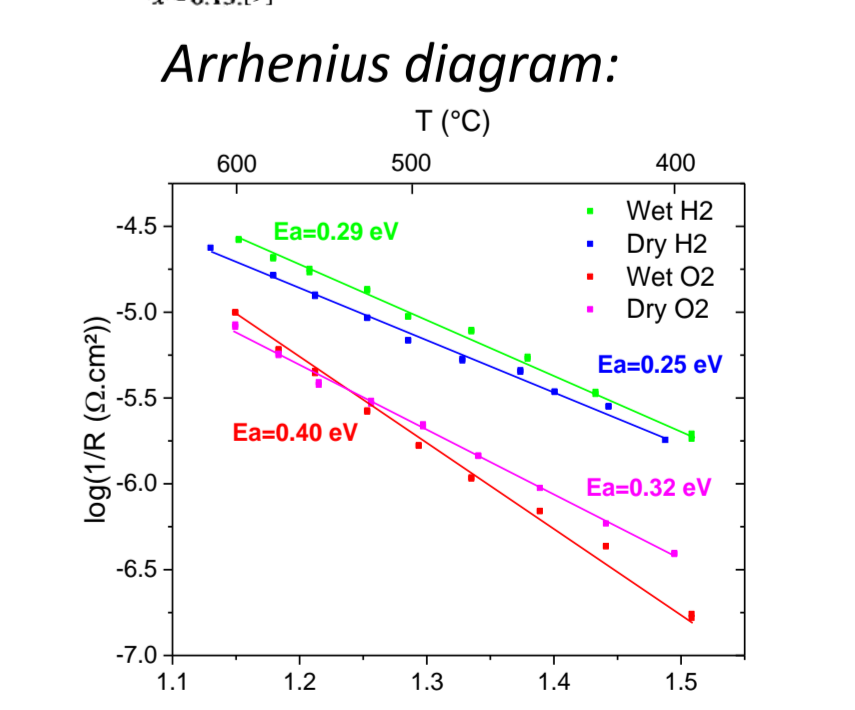
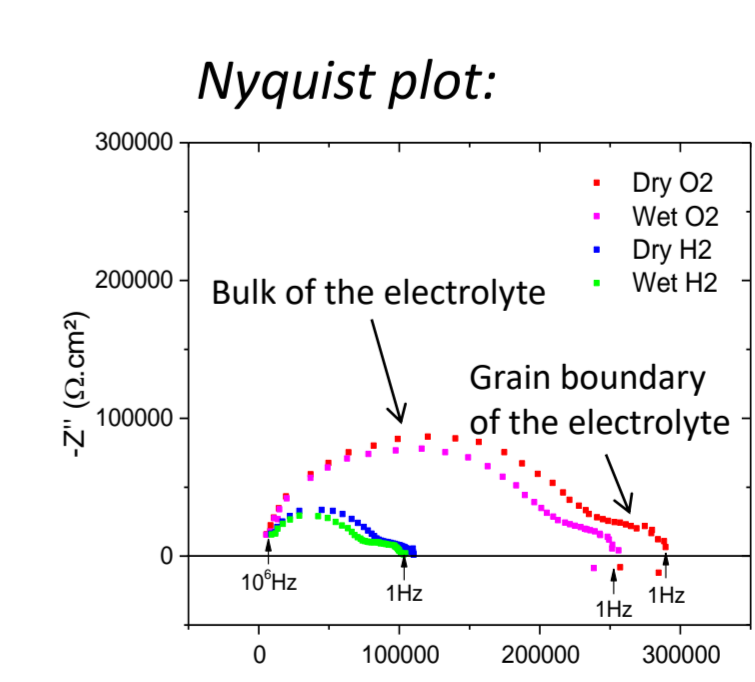
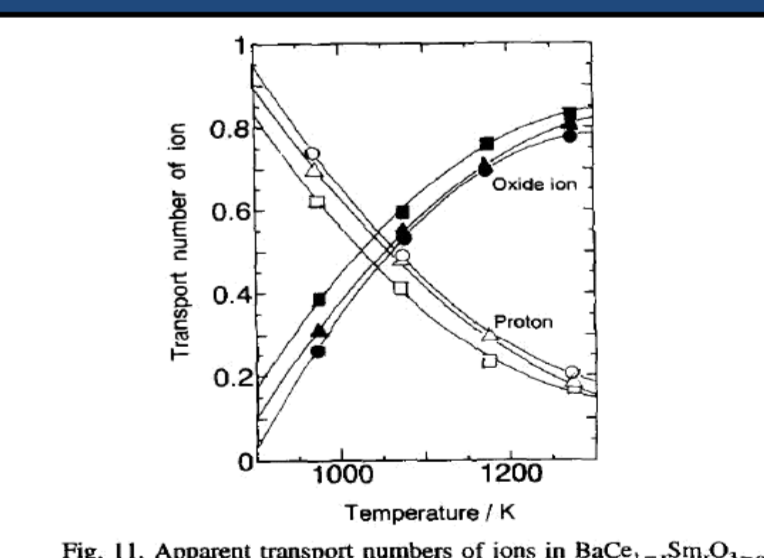
- Necessary to add sintering aid (ZnO 1wt%)
- Sintering for 24h cause the evaporation of Ba and a segregation of phases
- Thermal treatment at 1000°C promotes densification and avoid segregation of phases
- Densification max = 92%
- Average particles size max = 2.25µm



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



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 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