Synthesis and characterization of $BaCe_{1-x}Y_xO_{3-\delta}$ protonic conductor

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In recent years, doped perovskite such as barium cerates ($BaCeO_3$), strontium cerates ($SrCeO_3$) and barium zirconates ($BaZrO_3$) have been studied as ceramic proton conductors for several technological applications: protonic membranes, hydrogen separation, catalytic support and solid oxides fuel cell components. Among those compounds, yttrium doped barium cerates have the best performances in terms of protonic conductivity at lowest temperature [1].
In this activity, variously doped BCY oxide powders were synthesized via a novel soft chemical route. The method is based on the formation of a metallorganic xero-gel at room temperature. The structural phase of powders and the dense pellets were analyzed using X-ray diffraction (XRD), while the morphology was investigated by field emission scanning electron microscopy (FE-SEM). The results of the XRD analysis (figure 1) show a pure perovskite phase both for the BCY powders and pellet, and the SEM microghaphs revel dense microstructure. Electrochemical impedance spectroscopy (EIS) measurement were performed on dense pellet under synthetic air flux at a temperature range between 200-750°C and frequency range between 10mHz-10MHz. EIS measurements were also performed at the same frequency range in wet hydrogen atmosphere. Figure 2 shows the Arrhenius plot of BCY_{20}, the activation energy is 0.40eV, in agreement with the values reported in literature [2].

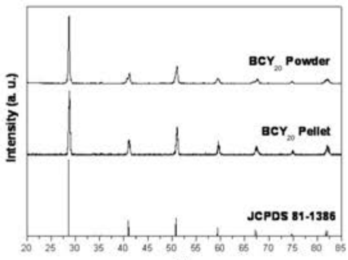

Figure 1. XRD patterns of BCY_{20} powder calcined at 900 °C for 6h, BCY_{20} pellet sintered at 1450 °C for 8h.

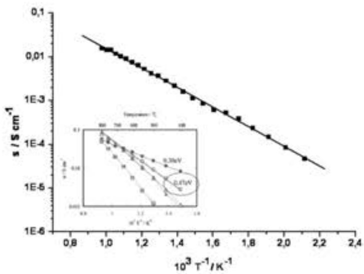

Figure 2. Arrhenius plot for BCY_{20}.

[1] Bin Zhu, Xiangrong Liu, Electrochemistry Communications, 6, 378-383 (2004).

[2] A. Tomita, T. Hibino Journal of Materials Science, 39, 2493-2497 (2006).

SYNTHESIS AND CHARACTERIZATION OF $BaCe_{1-x}Y_xO_{3-\delta}$ PROTONIC CONDUCTOR

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High Temperature Proton Conductors

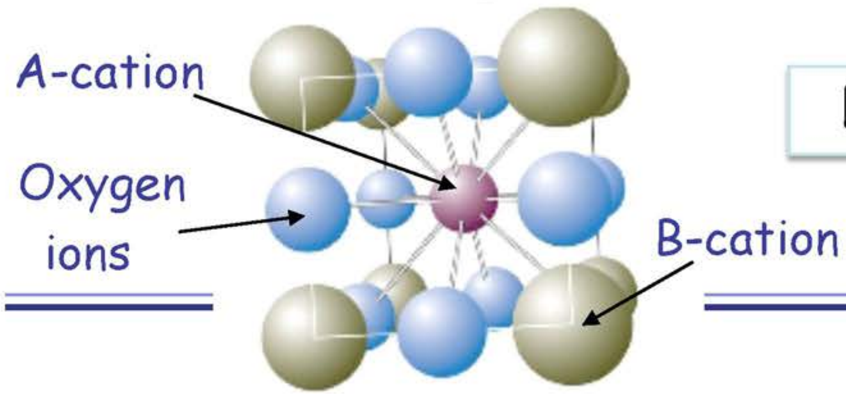
HTPCs came in the early 1980s when Iwahara and co-workers showed that some ceramic perovskite-related oxides presented proton conduction in hydrogen or vapor containing atmosphere at high temperatures

The most investigated HTPCs belong to the families of:

- ✓ $SrCeO_3$
- ✓ $BaCeO_3$
- ✓ $BaZrO_3$

Perovskite Structure

ABO_3



Doping →

Modified Perovskite Structure (rare earth: Y,Eu,Gd…)

$AB_{1-x}O_{3-\delta}$

Oxygen Vacancies

Proton Conduction Mechanism

Why oxygen vacancies?

$AB_{1-x}O_{3-\delta}$

Oxygen Vacancies

with
x = concentration of dopant
δ = oxygen vacancies

The proton conduction mechanism in HTPCs involves two different steps, they are:

- ✓ **Proton Incorporation**
- ✓ **Proton Mobility**

Mechanism: Proton Incorporation

The most important reaction related to the formation of protonic defects is the dissociative adsorption of water

$$H_2O \rightarrow H^+ + OH^-$$

Proton

Form a covalent bond with a lattice oxygen

Idroxyde Ion

Fill the oxygen vacancies ($V_O^{\bullet\bullet}$)

Using a Kroeger-Vink notation

$$H_2O + V_o^{\bullet\bullet} + O_o^x \rightarrow 2(OH)_o^{\bullet}$$

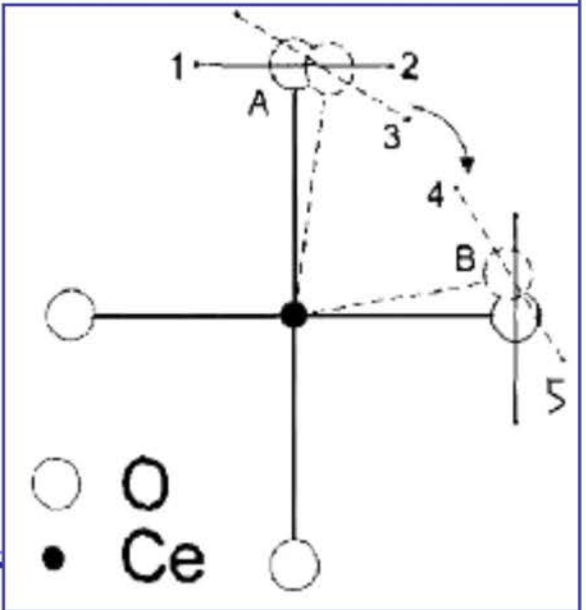
The saturation value of the protons uptake is equal to twice the initial oxygen vacancy concentration

Mechanism: Proton Mobility

Grotthuss Mechanism → hopping mechanism

- **the H-bonded protons form an OH group ($OH_o^{\bullet}$)**
- **protons move around O_o^x and jump to the neighbour O_o^x**

Quantum molecular dynamics (MD) symulations and IR spectra analysis → possible proton diffusion path.

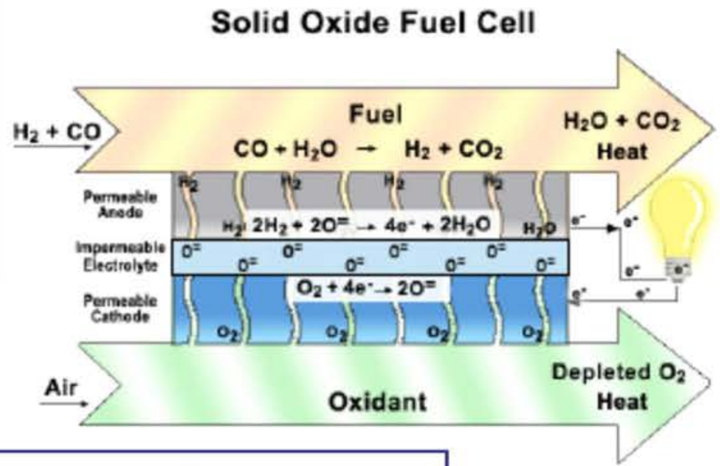


a. The proton moves from position 1 to position 2 by its rotational motion around oxygen atom A.
b. Upon bending of the Ce-O bond, the proton can reach position 3, where a hydrogen bond to oxygen atom B can be formed.
c. At this position the proton can move to position 4 if the energetic barrier for proton transfer is reduced by shortening the bond length between A and B.
d. After a successful transfer, the Ce-O bending motion eventually breaks the hydrogen bond and the proton ends up in position 5.

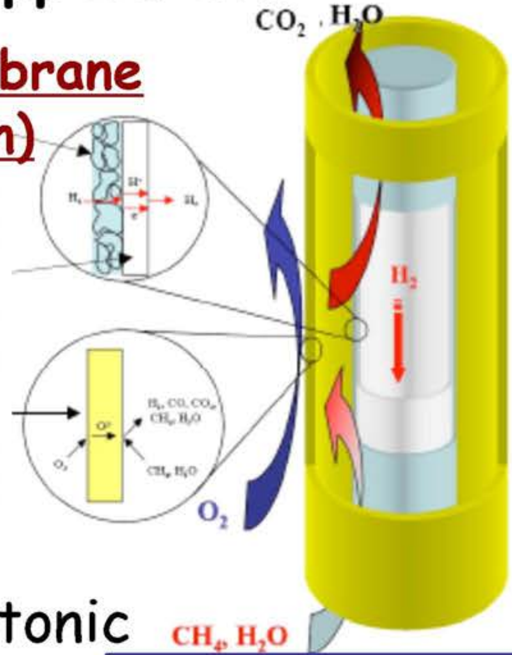
Applications

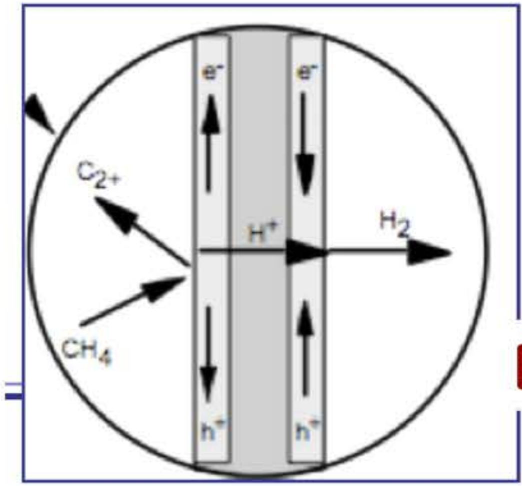
Proton conductor materials have received many attentions as promising materials for several applications

Fuel Cell technology



Hydrogen Membrane (Gas separation)

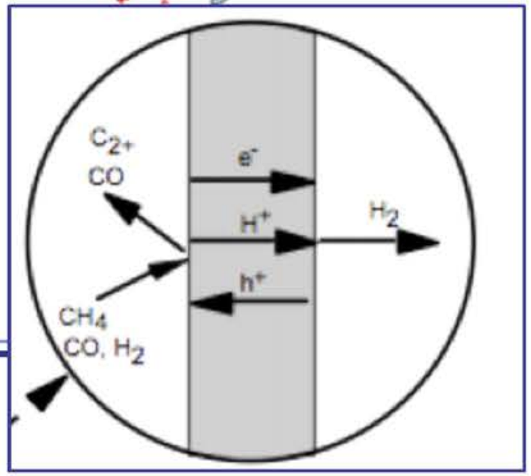




Pure protonic conductivity

$BaCe_{0.8}Y_{0.2}O_{3-\delta}$

Mixed protonic electronic conductivity



Processing of proton conductors (Y-doped $BaCeO_3$)

Solid state reaction

In general those oxides were synthesized by the conventional solid state reaction in which the oxide precursors are milled and calcined at high temperature

Several drawbacks → **the high sintering temperature creates inhomogeneities in the chemical composition**

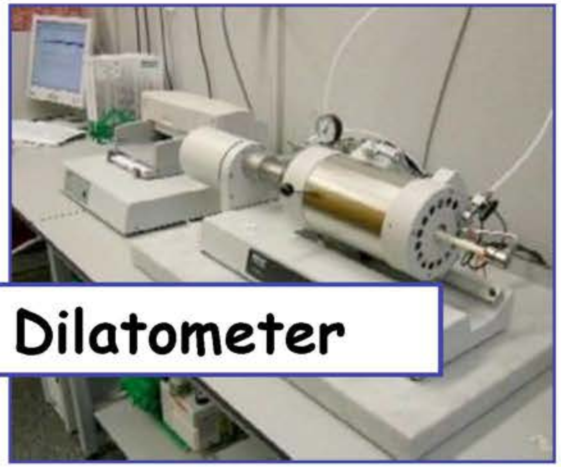
Soft chemical processes

- decrease the sintering temperature and processing time
- good control of morphology and chemical composition
- high purity and ultrafine powders

Characterization of Y-doped $BaCeO_3$

✓ Chemical Composition → XRD analysis

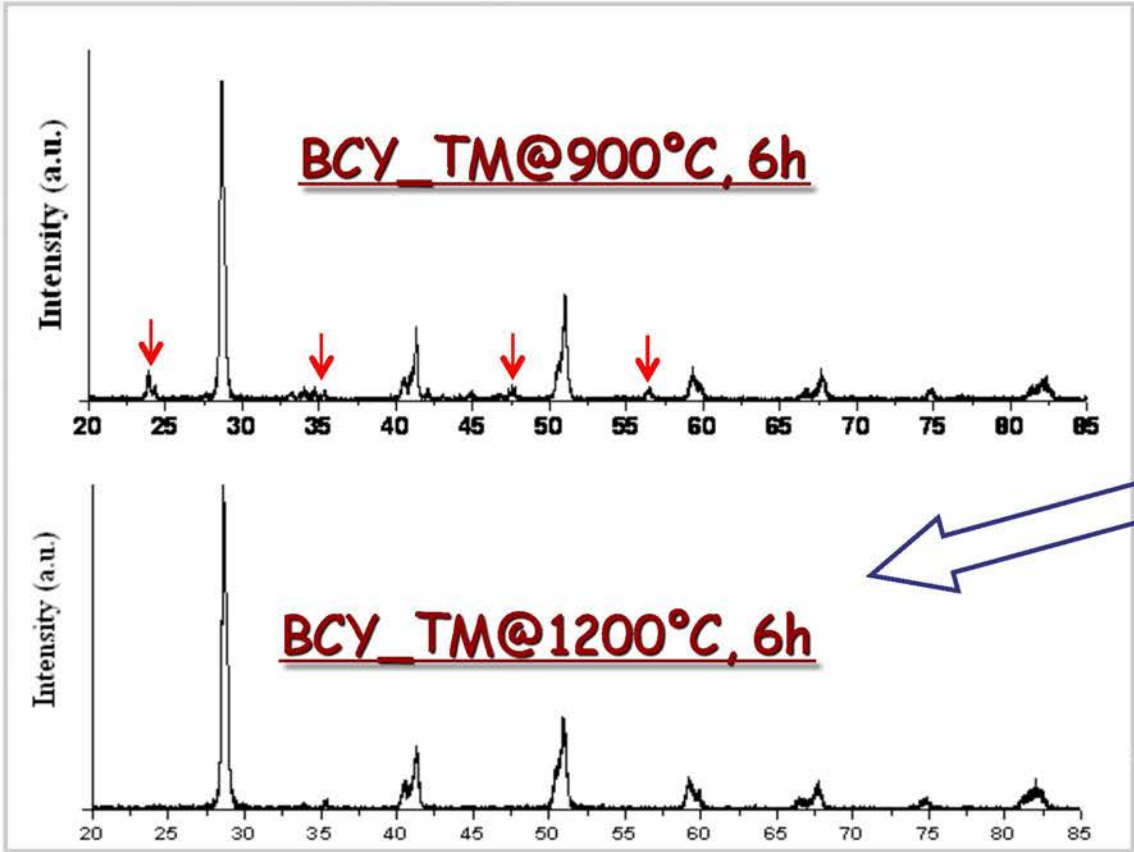
✓ Morphological Composition → FE-SEM



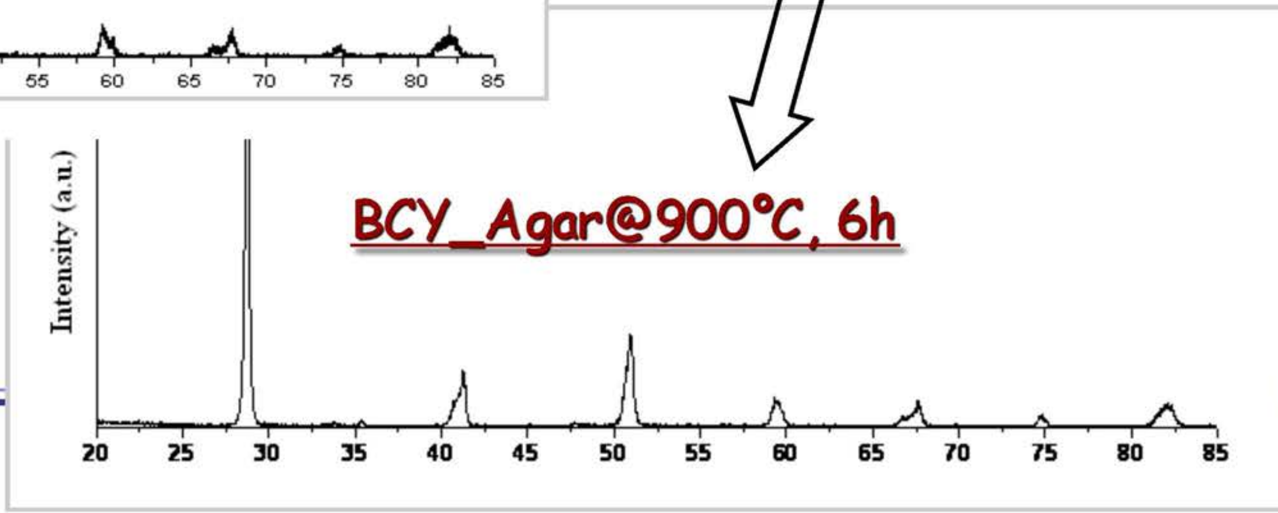
✓ Mechanical Behavior → Dilatometer

✓ Electrical Behavior → Electrochemical Impedeace Spectroscopy (EIS)

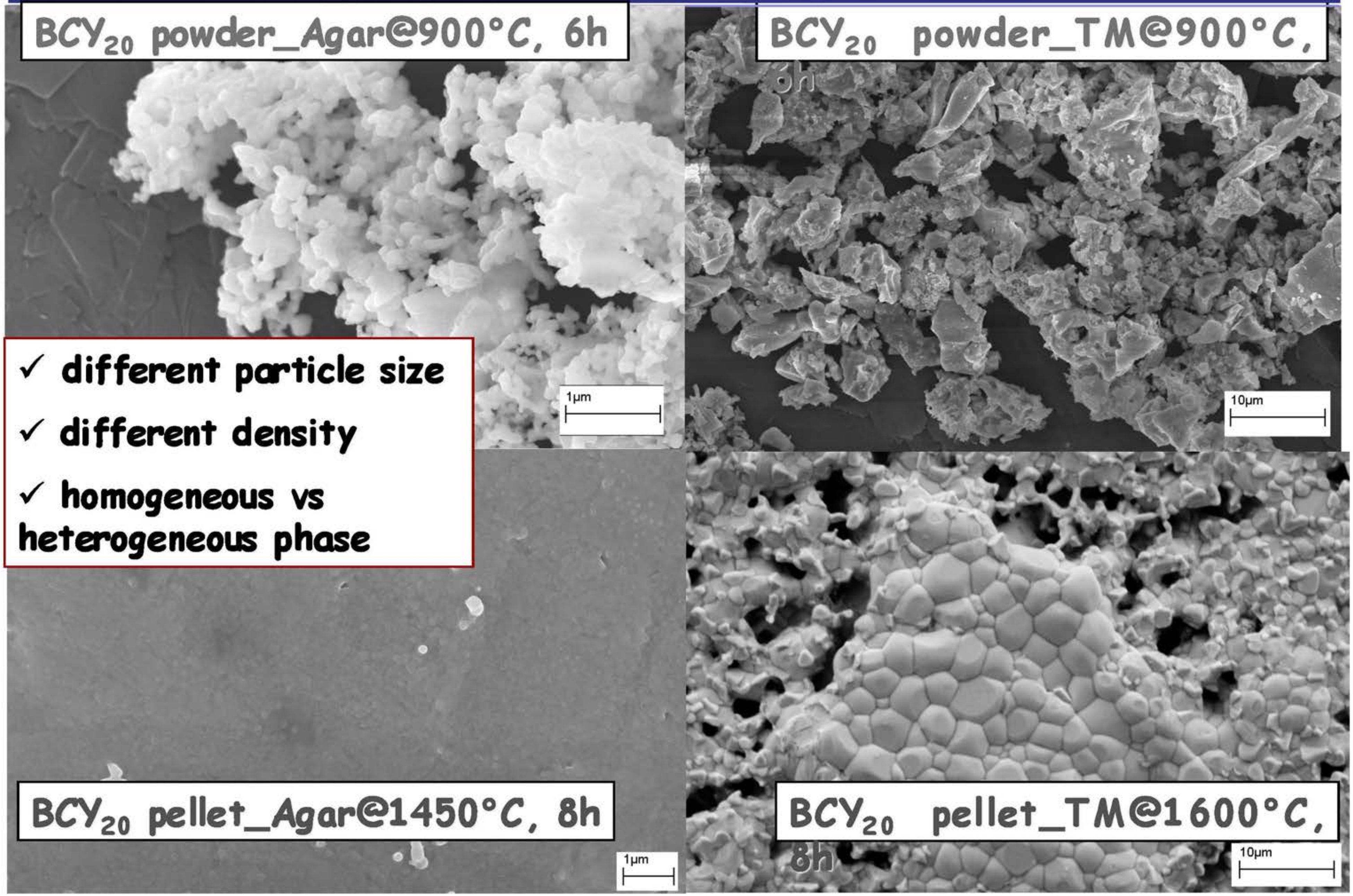
X-ray diffraction patterns BCY_{20} powders



With both methods is possible to achieve the pure phase, but it is obtained at different temperatures

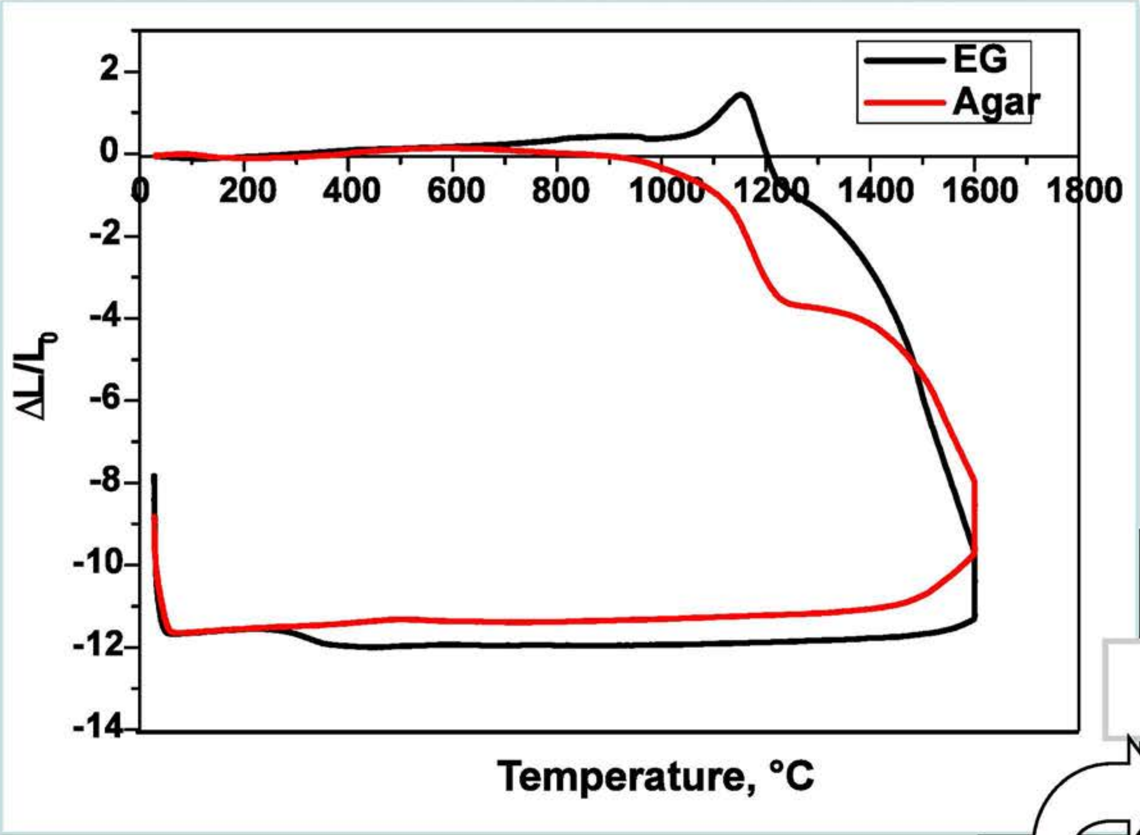


SEM micrographs of BCY_{20} powders

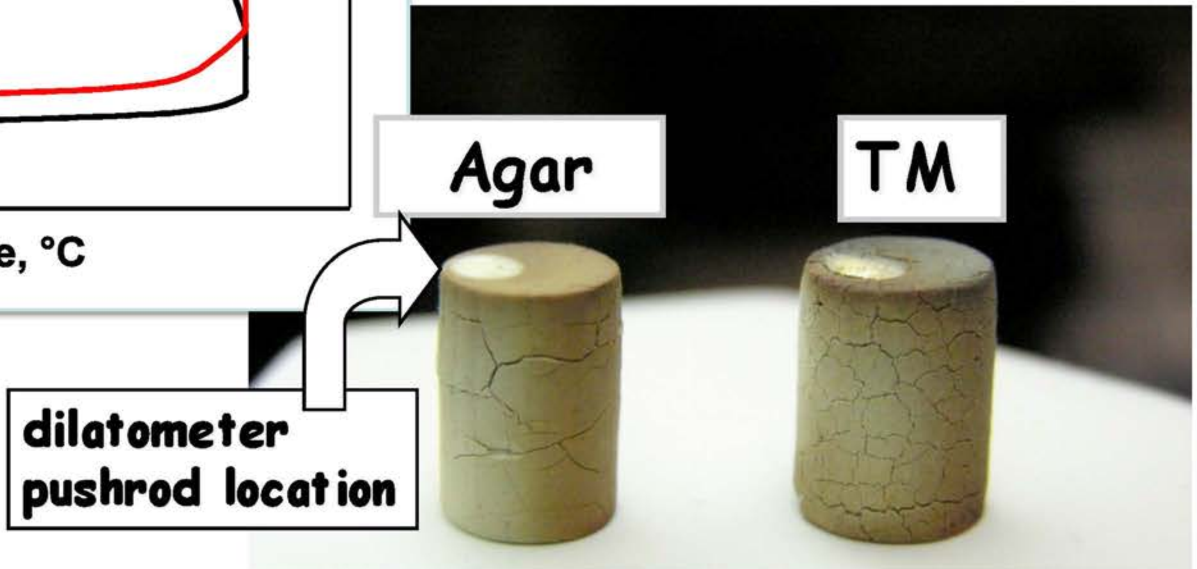


- ✓ different particle size
- ✓ different density
- ✓ homogeneous vs heterogeneous phase

Dilatometric Measurement

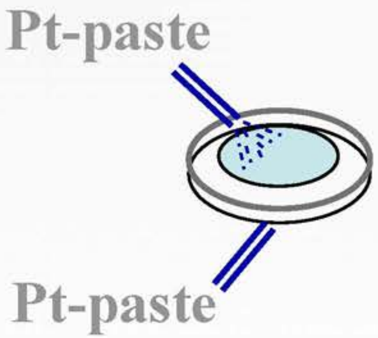


- The samples start to shrinkage at different temperatures



⇨ **The samples are cracked, but in the TM sample the cracks are more!**

EIS of the BCY_{20}_with Agar method

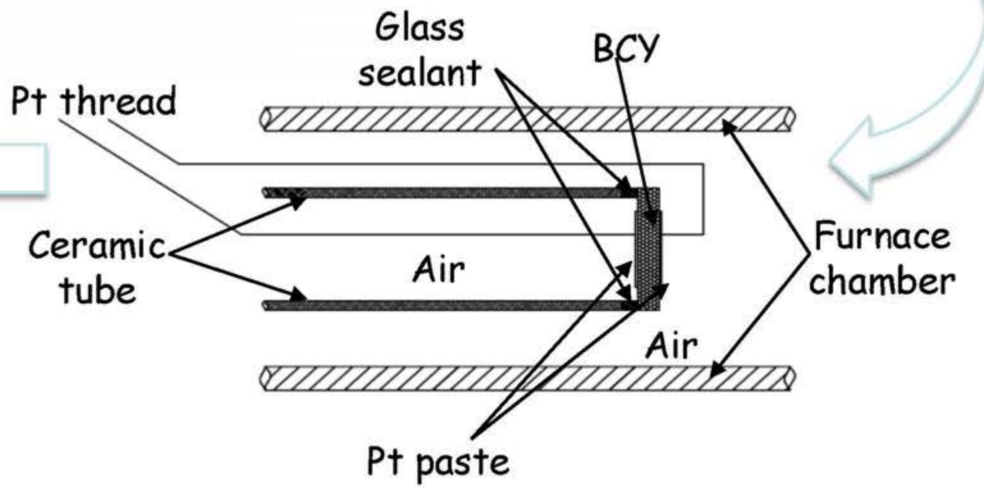


Simmetrical Cell

Pt – BCY - Pt

Electrode – Electrolyte - Electrode

Frequency Response Analyzer



Electrochemical Impedance Spectroscopy (EIS)

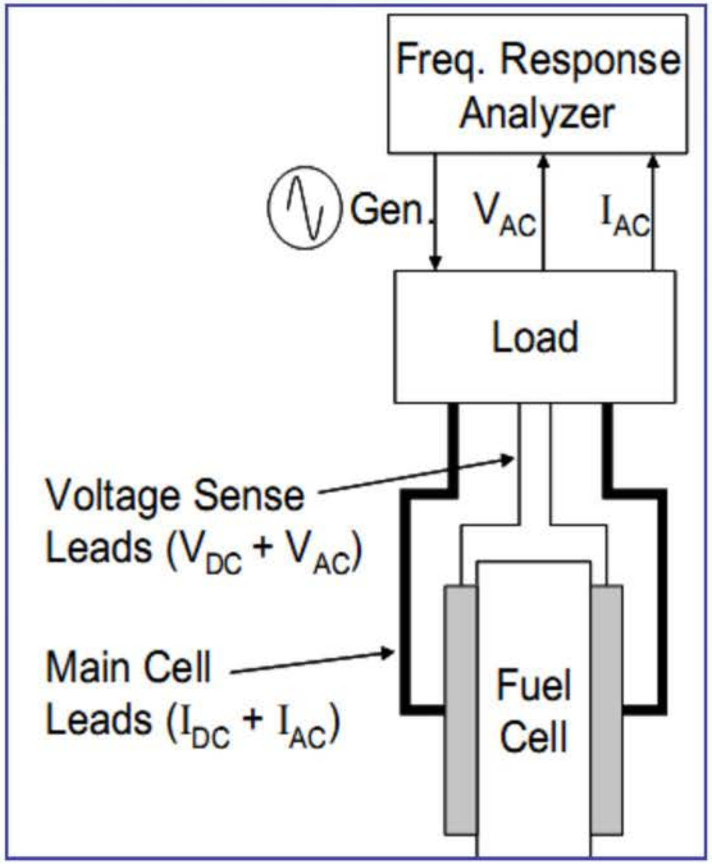
EIS is a very versatile tool to characterize intrinsic electrical properties of any material and its interface

Definition

- impedance (Z) is a general circuit parameter that measure the ability of a circuit to resist the flow of the electrical current
- is usually measured using small excitation signal
- is represented as a complex number

$$Z(\omega) = Z' + jZ'' = Z_{Re} + jZ_{Im}$$

EIS – Basics in FC application



- A frequency response analyzer (FRA) is used to improve a small amplitude AC signal to the fuel cell via the load.
- The AC voltage and current response of the fuel cell is analyzed by the FRA to determine the impedance of the cell at that particular frequency.
- **Physical and chemical processes occurring within the cell** (such as electron and ion transport) **have different characteristic time-constants** and therefore are exhibited at different AC frequency
- When conducted over a broad range of frequencies, **impedance spectroscopy can be used to identify and quantify the impedance associated with these various processes.**

EIS – Basics in FC application

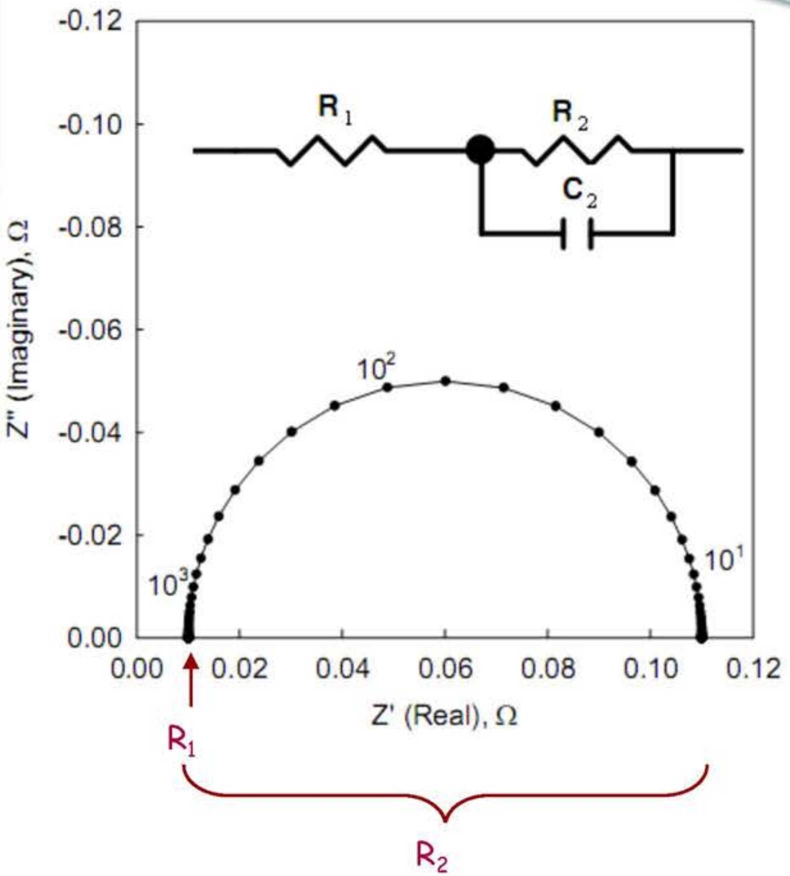
The EIS data are analyzed using **equivalent circuit**, that are essentially composed by

		Defining Relation	Impedance
Resistor		$V = I \times R$	$Z_R = R$
Capacitor		$I = C\frac{dV}{dt}$	$Z_C = \frac{1}{j\omega C} = -\frac{j}{\omega C}$
Inductor		$V = L\frac{dI}{dt}$	$Z_L = j\omega L$

- **the resistors usually describe the bulk** (bulk + grain boundary) **resistance of the material** to charge transport such as the resistance of the electrolyte to ion transport or the resistance of a conductor to electron transport → Z_{Re}
- **capacitors and inductors are associated with space-charge polarization regions**, such as the electrochemical double layer, and adsorption/desorption processes at an electrode, respectively → Z_{Im}

Representation of Impedance Data

EIS data for electrochemical cells are most often represented in Nyquist plot



The Nyquist plot is a complex plane that reports the **imaginary impedance**, which is indicative of the capacitive and inductive character of the cell, versus the **real impedance** (resistive part)

Conclusions

- HTPCs are promising material for several applications

- With the Agar procedure we are able to synthesized BCY at lower temperature
- A complete characterization of the material has been performed
  - high purity metal-oxides compounds
  - almost fully dense pellet
  - very good protonic conduction (10^{-2} Siemens/m)

Acknowledgments

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Thank you for your attention!