THE ROLE OF DRYING IN WATER BASED SEQUENTIAL TAPE CASTING PROCESSING FOR THE SIZE SCALE-UP OF PLANAR SOFC CELLS

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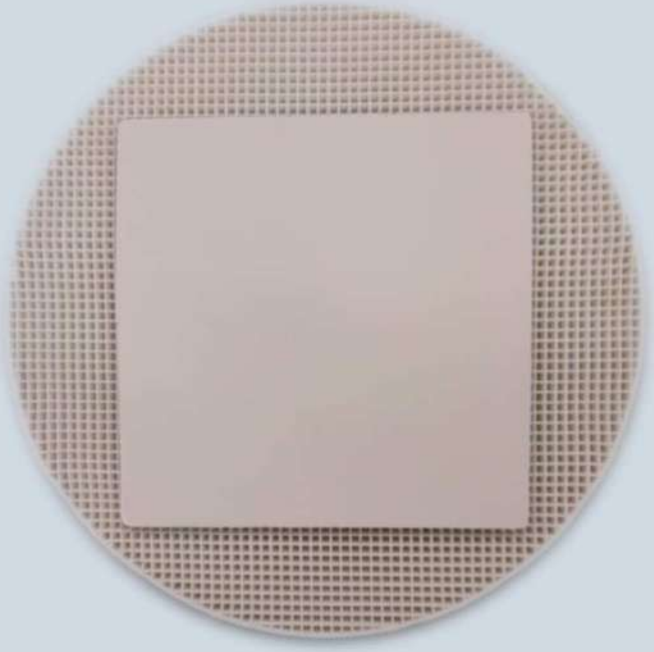
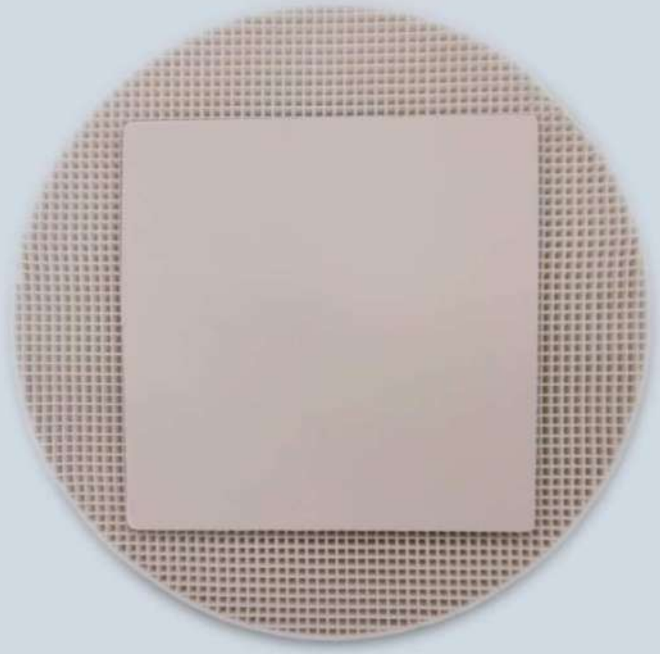
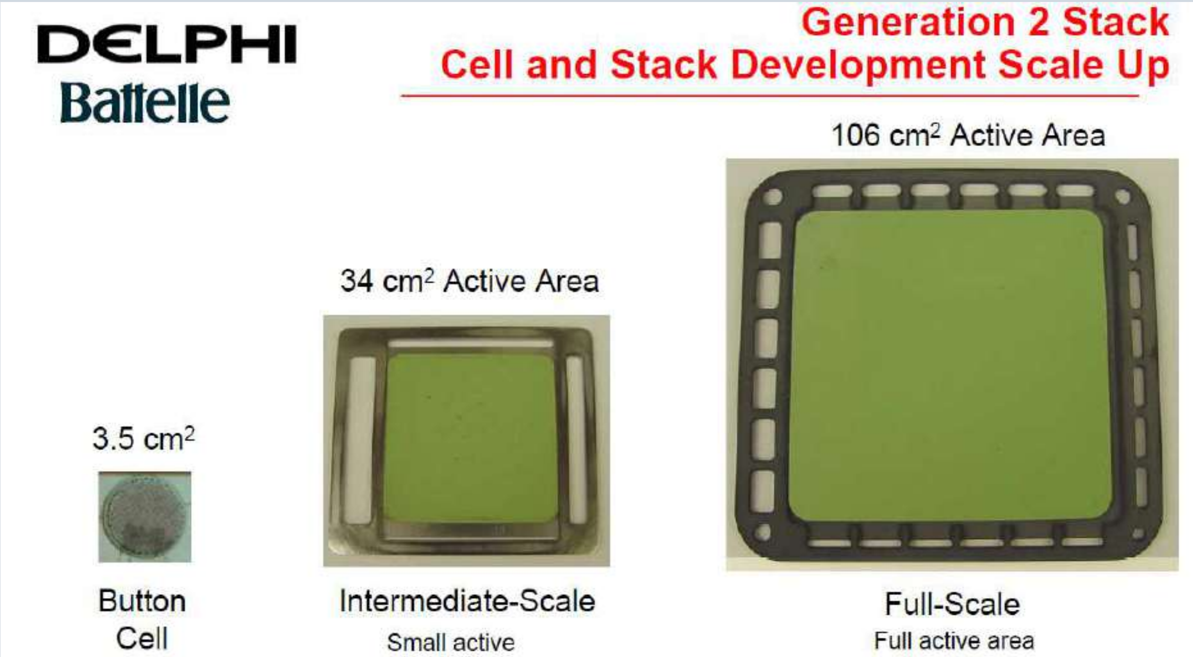
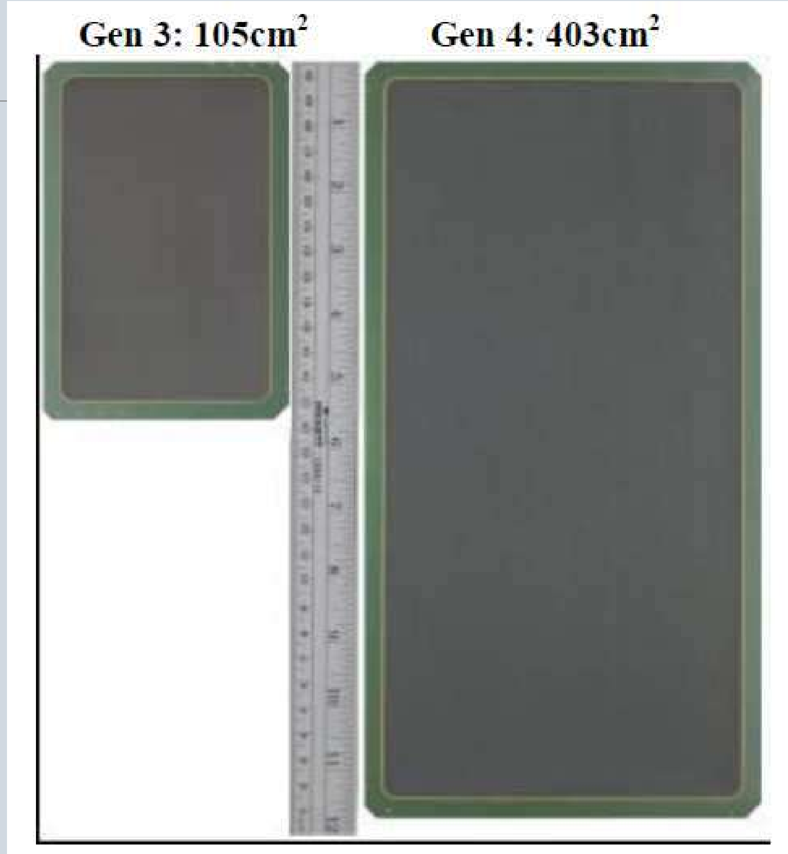


INTRODUCTION



SCALE-UP PLANAR SOFC

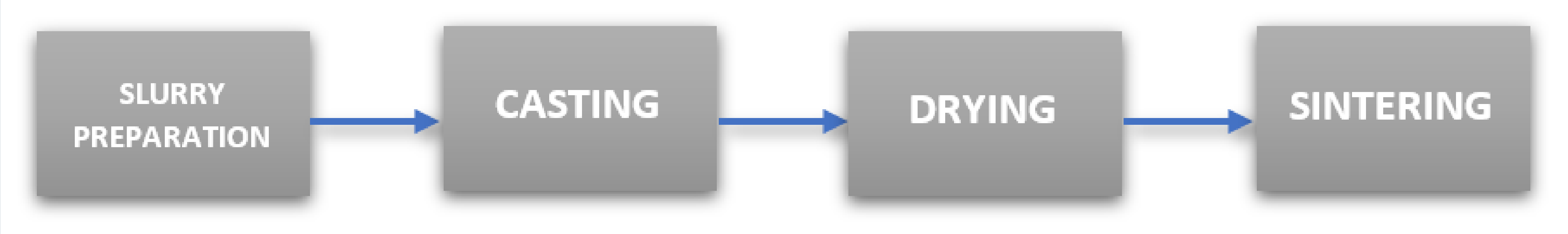




https://doi.org/10.2172/1084477

Solid State Energy Conversion Energy Alliance (SECA) developed in the United States between 1999 – 2013.

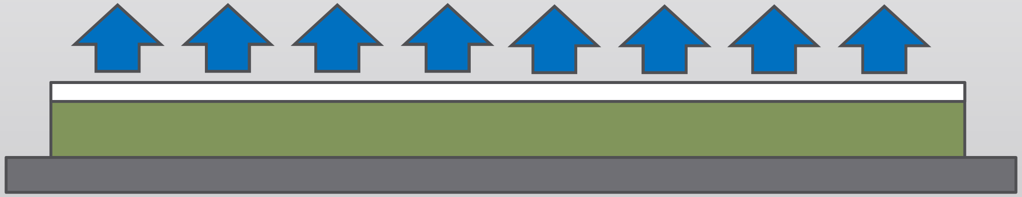
SOFC PRODUCTION PROCESS



Typical steps for the production of Solid Oxide Fuel Cells

DRYING GREEN BODIES

Typical drying profiles for humidity and temperature along drying.

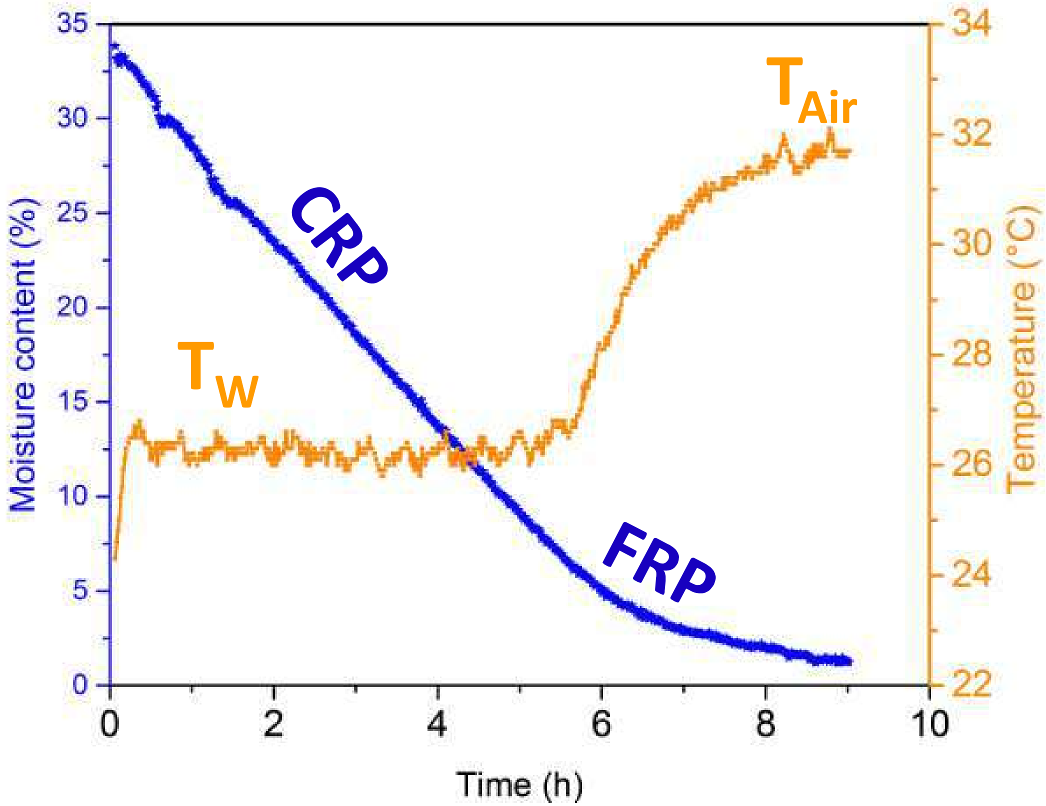


CRP

Constant Rate Phase

FRP

Falling Rate Phase



Tw: wet bulb temperature, depends on air RH.

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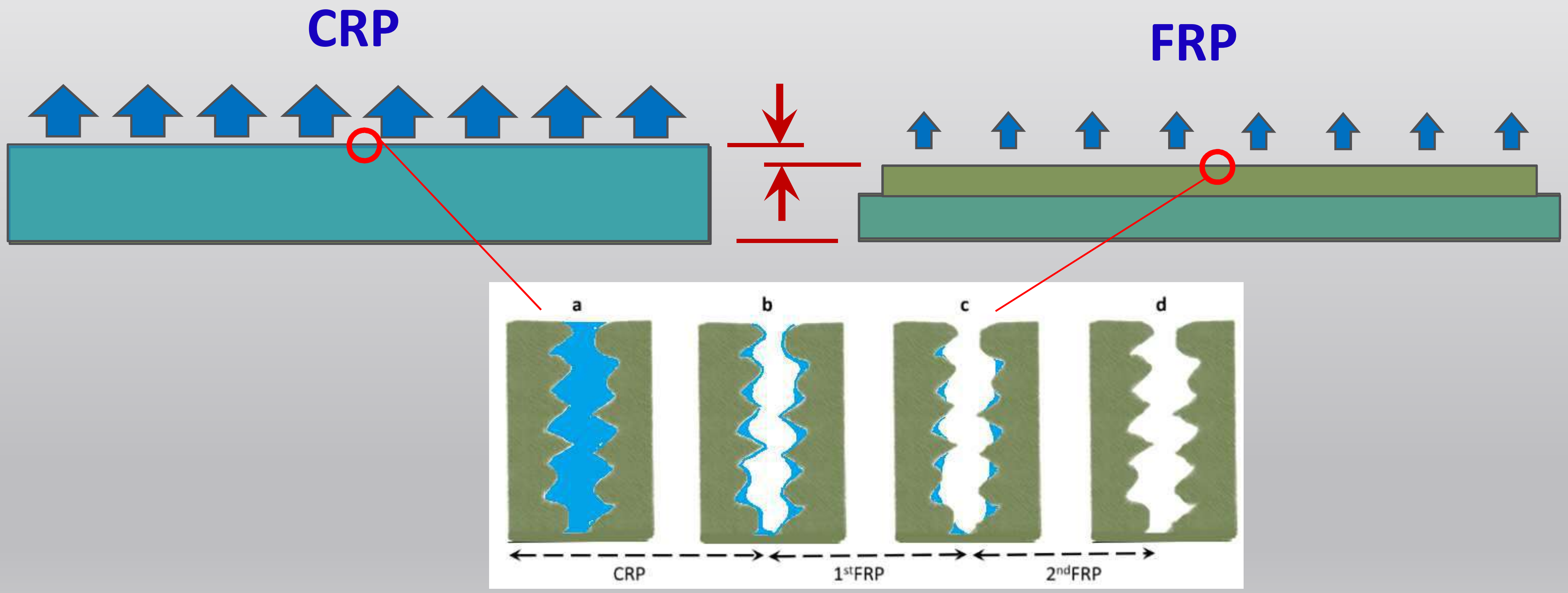
DRYING GREEN BODIES



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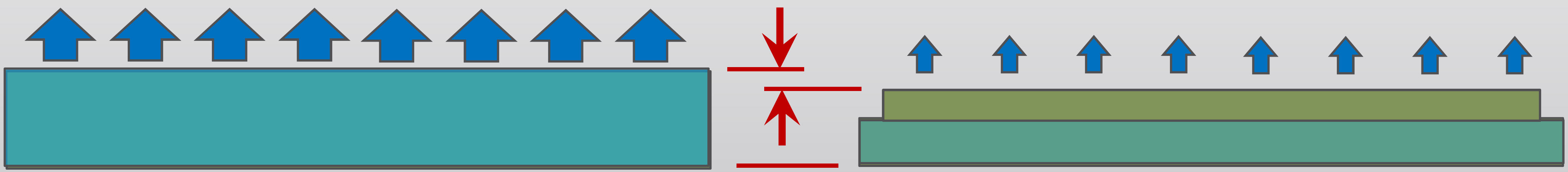
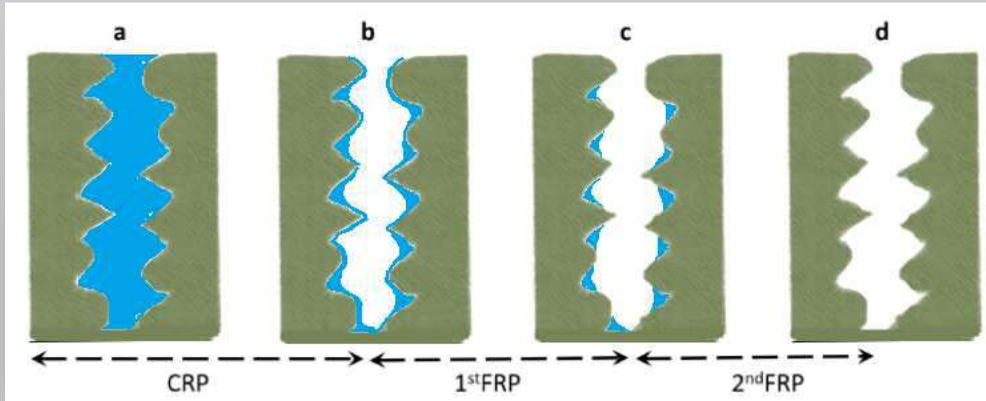
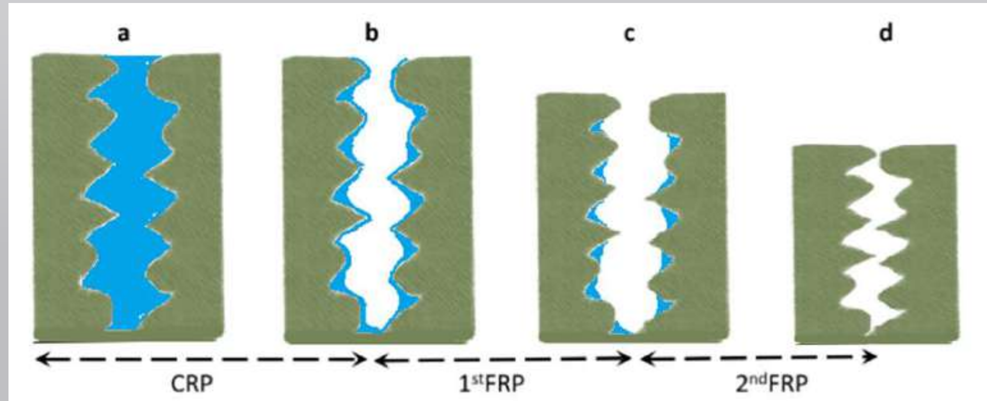
DRYING GREEN BODIES

Retraction is mainly produced affecting the thickness of the tape, while not much over the surface.

CRP **FRP**







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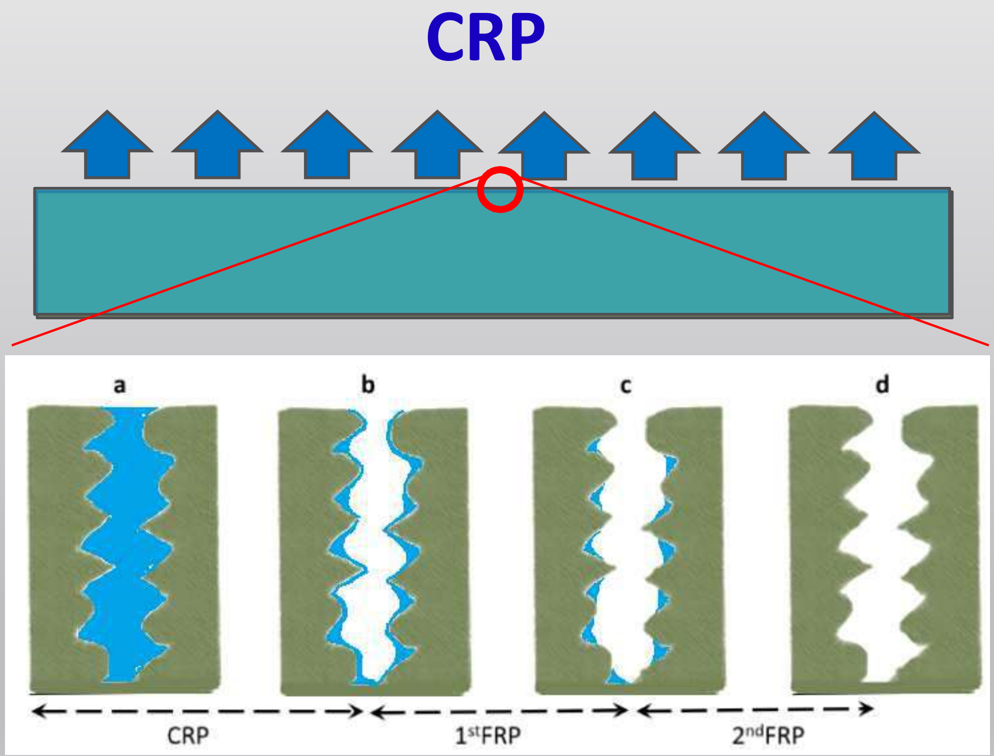
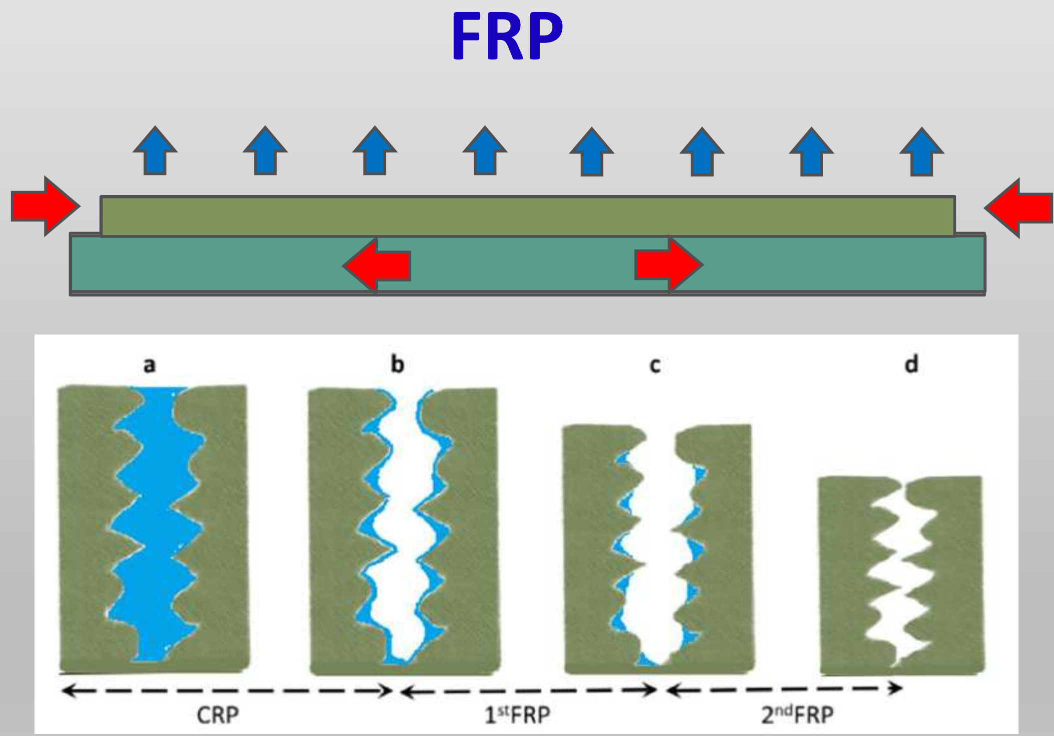
DRYING GREEN BODIES

Surface dryness produces humidity gradients and differential retraction, giving rise to residual stresses.





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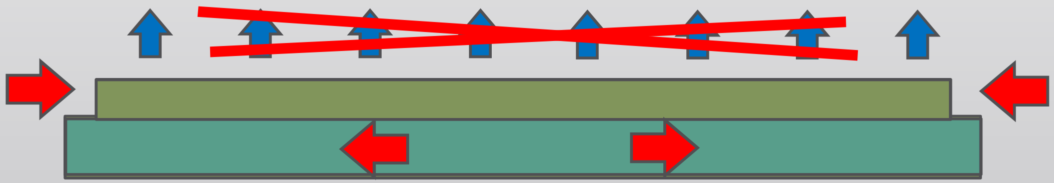
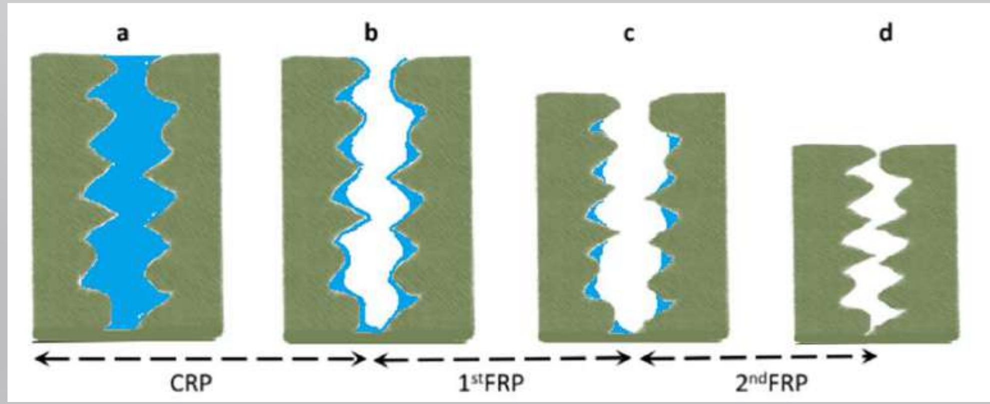
MANAGEMENT OF DRYING

Drying in the FRP is not left to develop with freedom .

FRP





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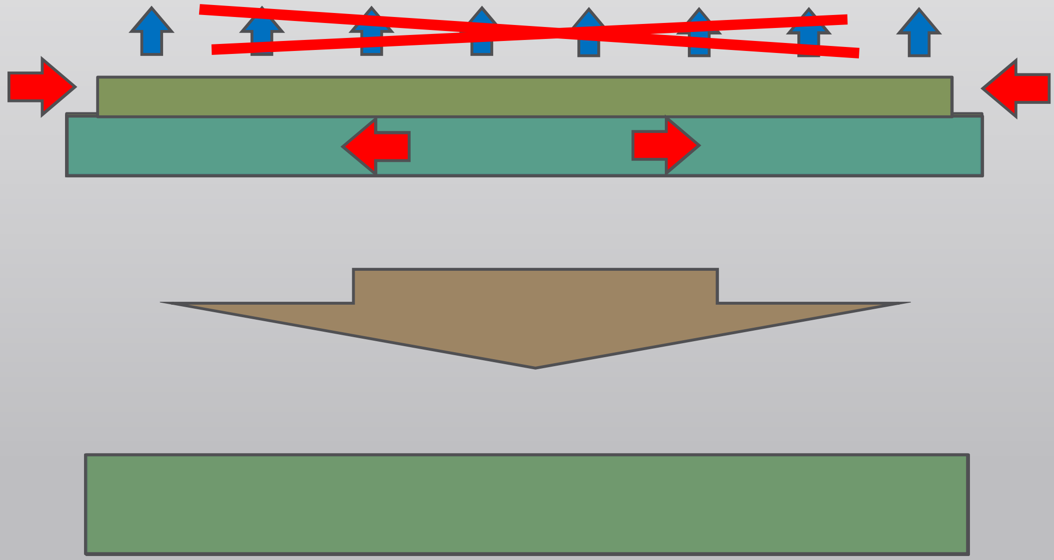
RELAXING RESIDUAL STRESS

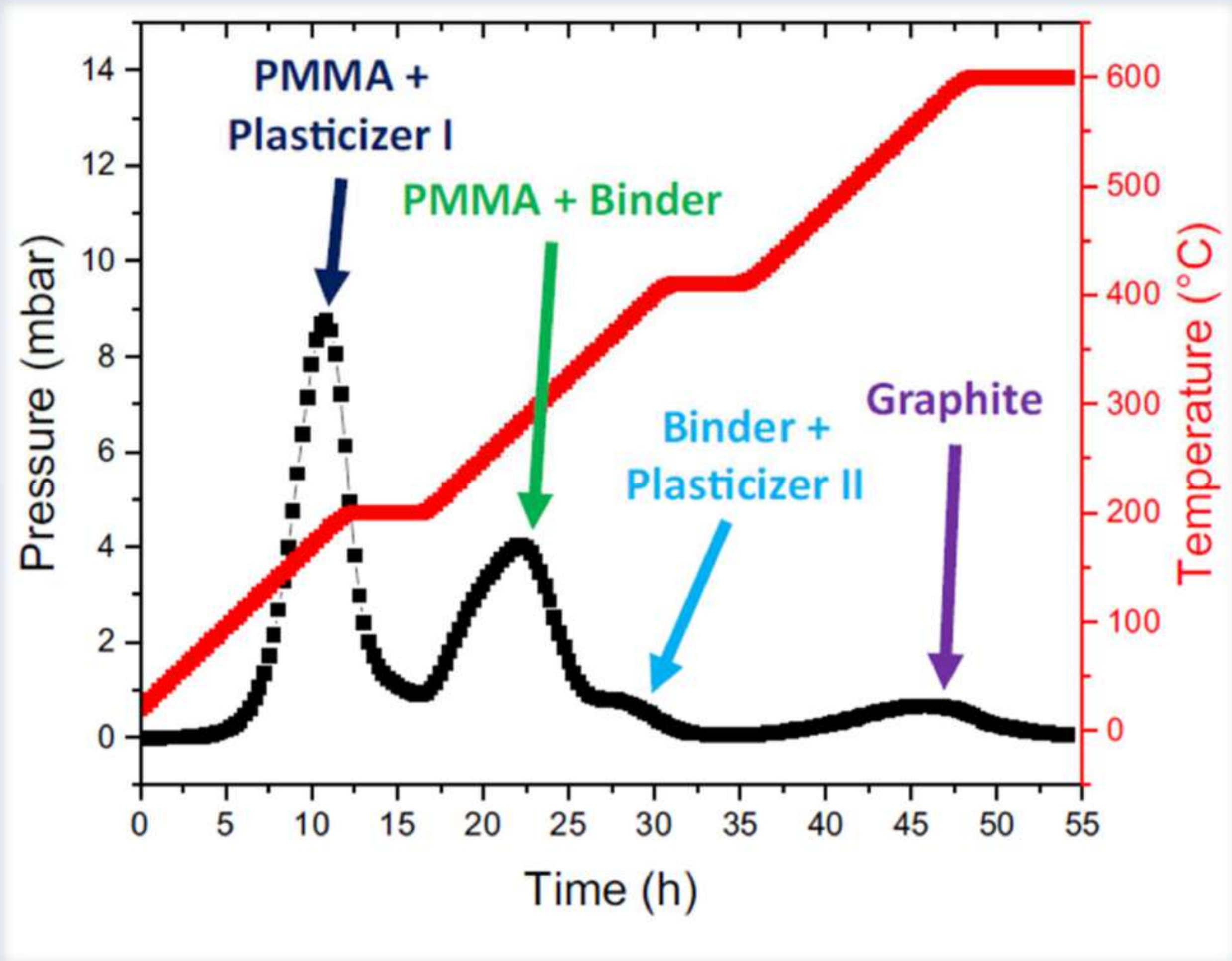
Reducing the rate of drying is possible to let the tape to relax the stresses.

Humidity is retained around 11%.



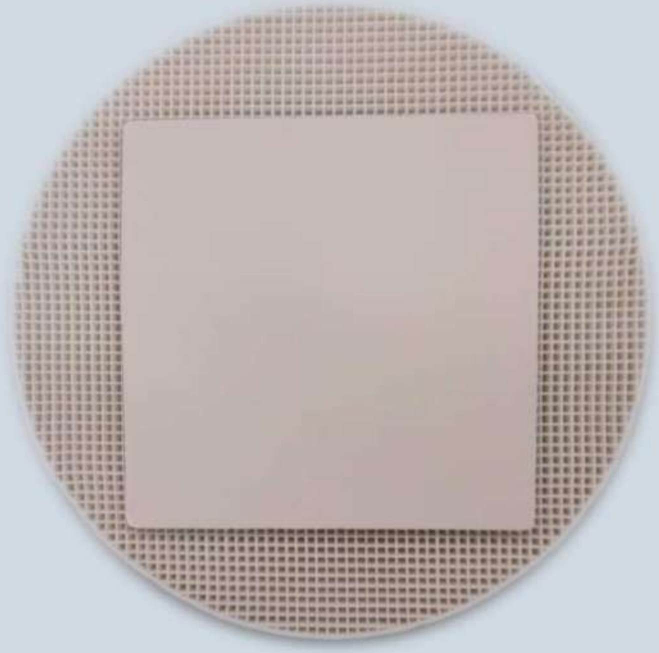
SINTERING PROFILE

Heat treatment is attained using TGA results as basic information mainly for the temperatures of dwells. Rates of heating and time of dwells are found by considering the amount of each component and their ease for removal.



doi:10.1038/s41467-022-28970-w

MATERIALS AND METHODS



SLURRIES COMPOSITIONS

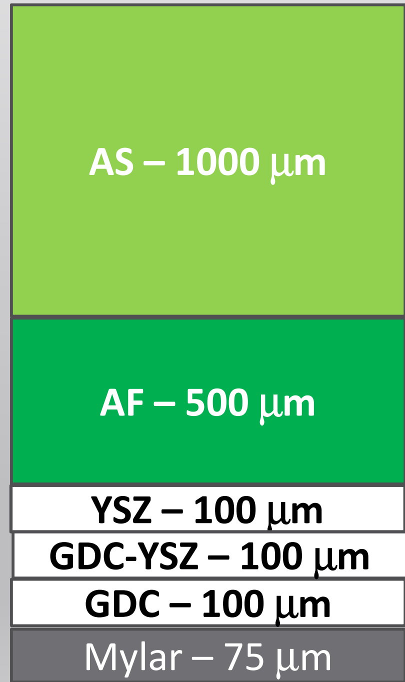
Water-based slurries (AS, AF, YSZ, GDC) were prepared as described by PARVAIX[1].

COMPONENT	ELECTROLYTE E24 (%m)	F. ANODE AF4 (%m)	BARRIER CGO3 (%m)	INT. LAYER CGO-YSZ3 (%m)
YSZ Powder (TOSOH)	47.0	19.3	0.0	15.9
NiO	0.0	28.9	0.0	0.0
CGO	0.0	0.0	47.0	15.9
Flour	0.0	0.0	0.0	0.0
Water	33.8	32.0	33.8	22.9
Dispersant (Darvan CN)	0.5	0.5	0.5	0.3
Binder (PVA)	8.5	8.7	8.5	5.7
Plastifiant (PEG400)	8.5	8.7	8.5	5.7
T-A (PEG20)	1.4	1.4	1.4	1.0
Antimousse (octanol)	0.4	0.4	0.4	0.3

SEQUENTIAL TAPE CASTING

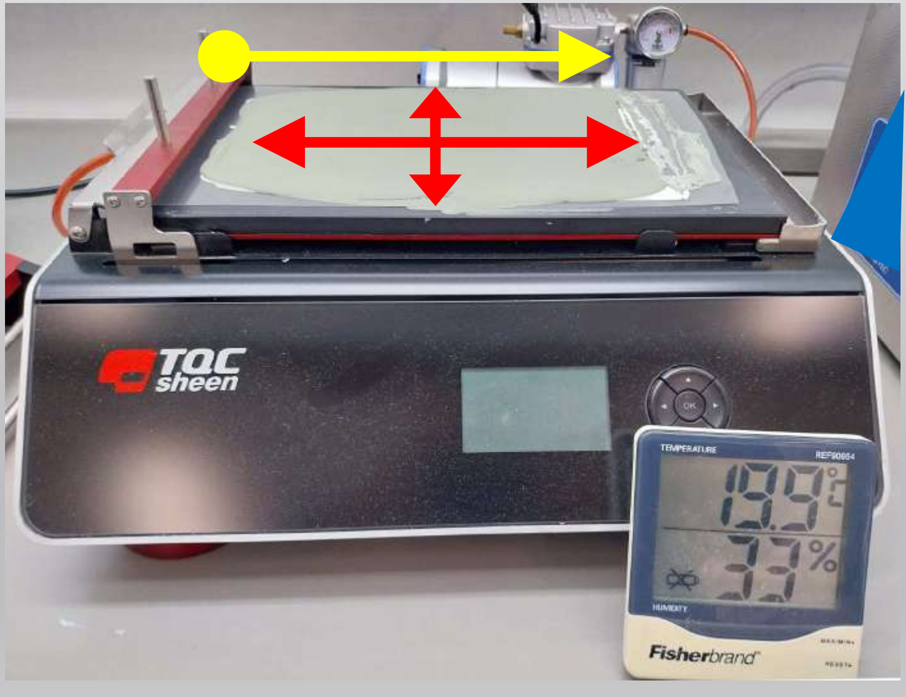
Structural anode was developed in this work in order to increase the amount of flour as pore former.

The drying was monitored registering time, weight, temperature and relative humidity of the air.
Doctor blade speed was 10 mm/s, gaps are shown for sequential casting.

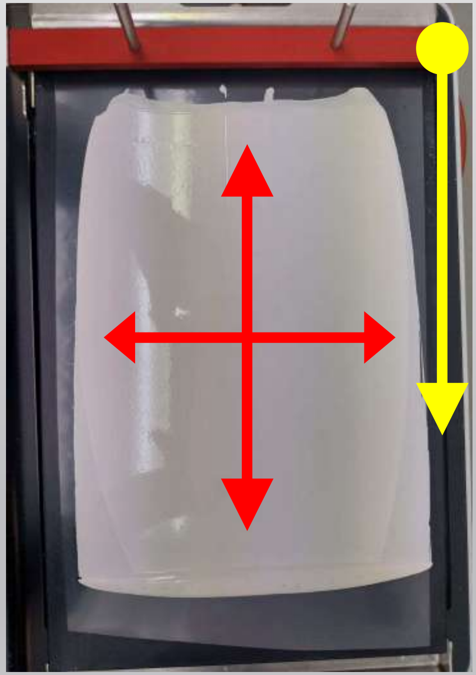


RESUDUAL STRESSES

Humidity gradients rising in the FRP, together with the orientation induced by the passage of the Doctor Blade in the Tape Casting, combine to give resultant stresses.



Surface stresses



Doctor Blade passing

FALLING RATE PHASE

After tape is partially dried, to the FRP, having about 11% humidity, can be placed in a flat closed box, for stress relief and planarity fixation.
Time must be at least 12h, and can be extended for several days for stock.

SECONDARY DRYING UNDER LOAD

Partially dried stocked tapes were cut using a squared die-cut and let to dry for 72h, using loads between 400 and 600 Pa.

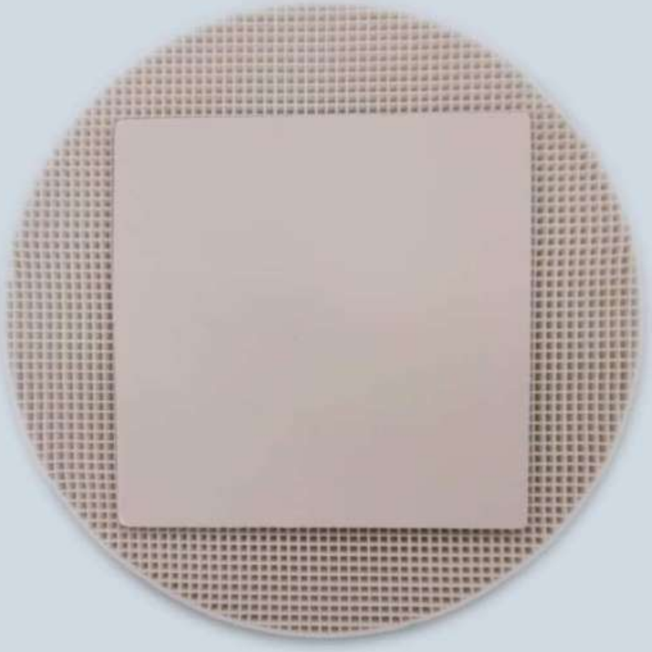
SINTERING

A well tuned program for sintering is to be determined.

The sintering program is set based on:

- Temperatures of boiling and decomposition of the components.
- Proportional composition.
- Heating behavior of the furnace.

EXPERIMENTAL RESULTS



STRUCTURAL ANODE SLURRY COMPOSITION – IMPACT ON DRYING

Component	AS-I	T_{decomp}/T_b, °C
YSZ	18.1	
NiO	27.2	
Flour	5.0	
Solvent	35.1	96.0
Dispersant	0.5	
Binder	4.5	420-450
Plasticizer	9.1	190
Surfactant	0.5	
Antifoam	0.1	
Total	**100**	

The structural anode composition was developed by previous experience and sintering tests.

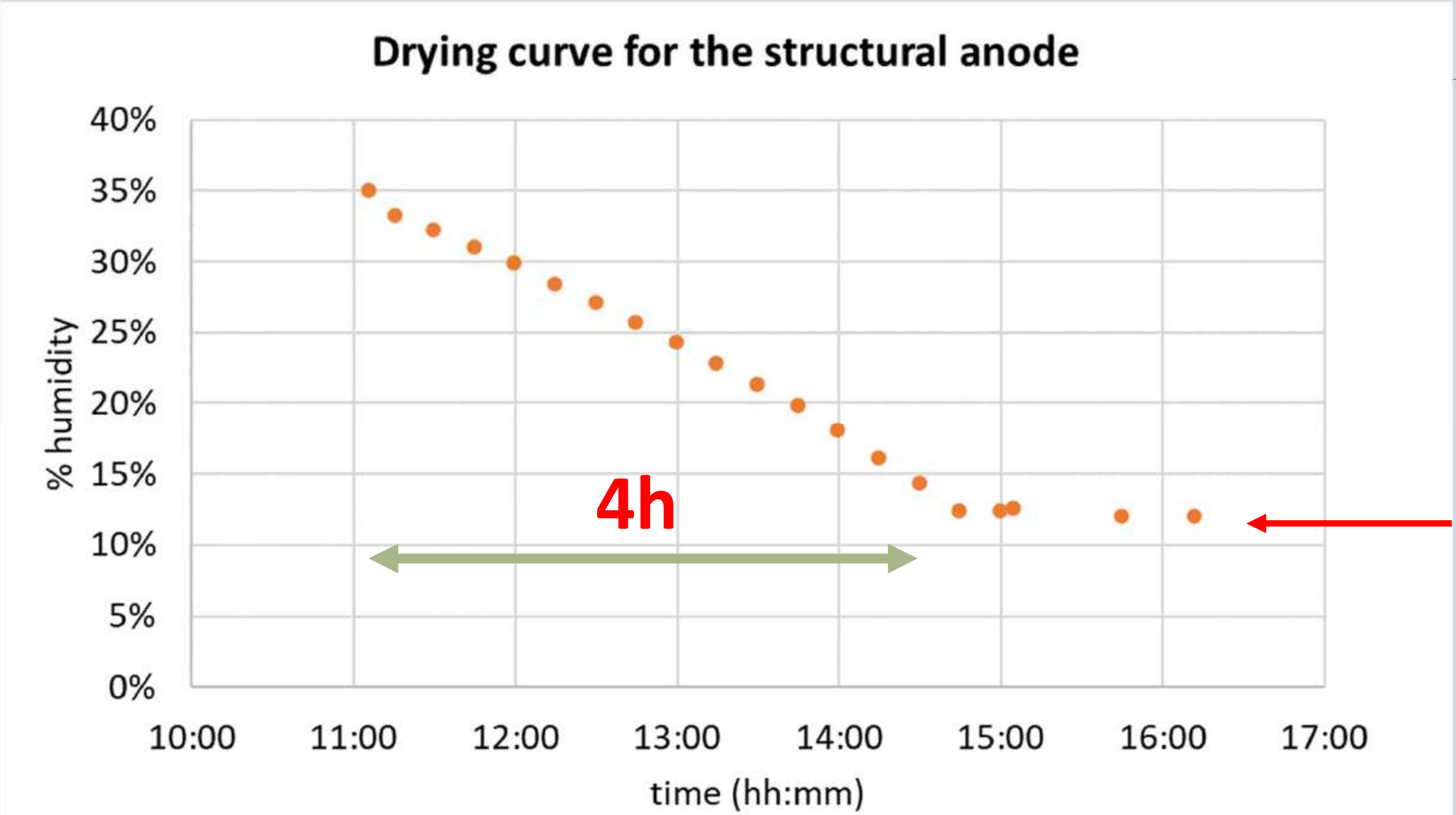
Temperatures of boiling or decomposition determine the temperature dwells for the sintering program: 85, 150, 410 °C.

Composition and size determines the time for dwells, and rates of heating.

SEQUENTIAL TAPE CASTING

From casting to the end of CRF, there is some retraction.

1^{st} DRYING PHASE - CRF



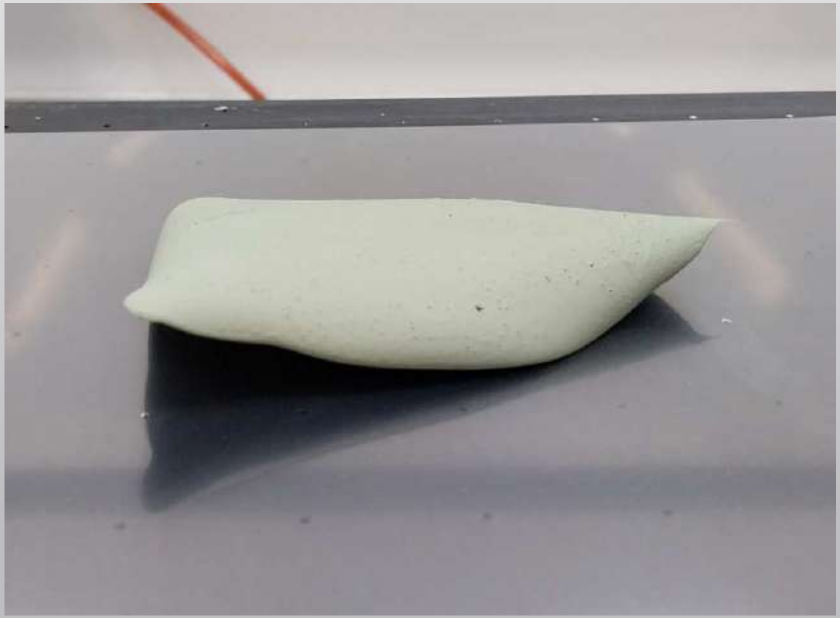
The mass loss is about 4g/h

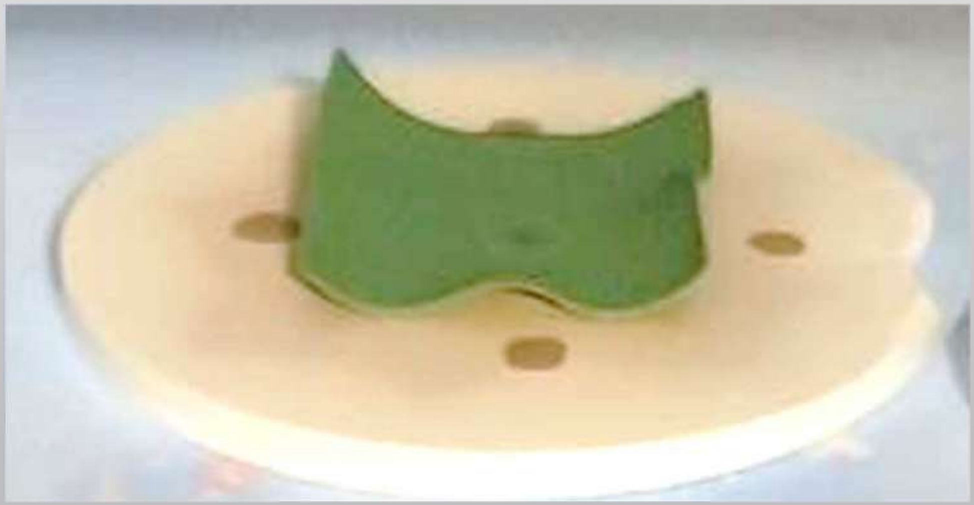
11% hum

This stage finish at about 11% humidity.

FREELY DRYING - BEHAVIOR UPON STRESSES

This combination of shear stress and tensorial stress to net resultant stresses explain the behavior of freely dried tapes.



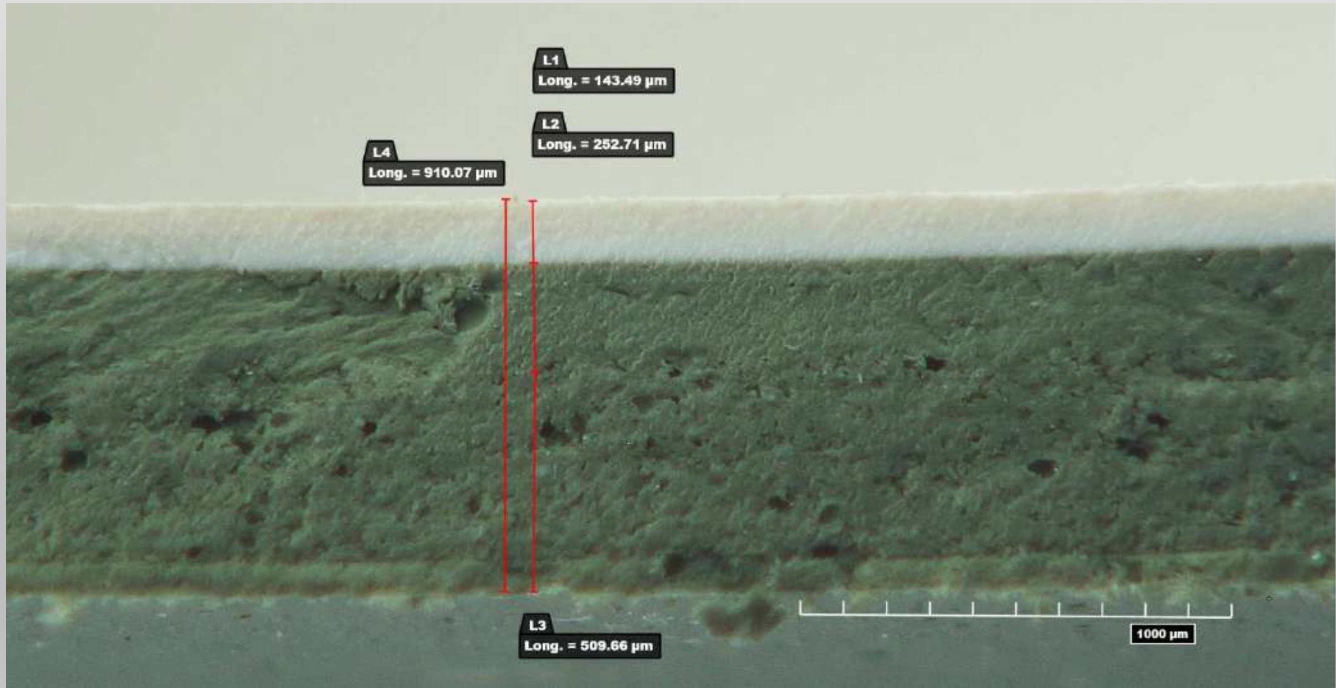


FREELY DRYING - BEHAVIOR UPON STRESSES

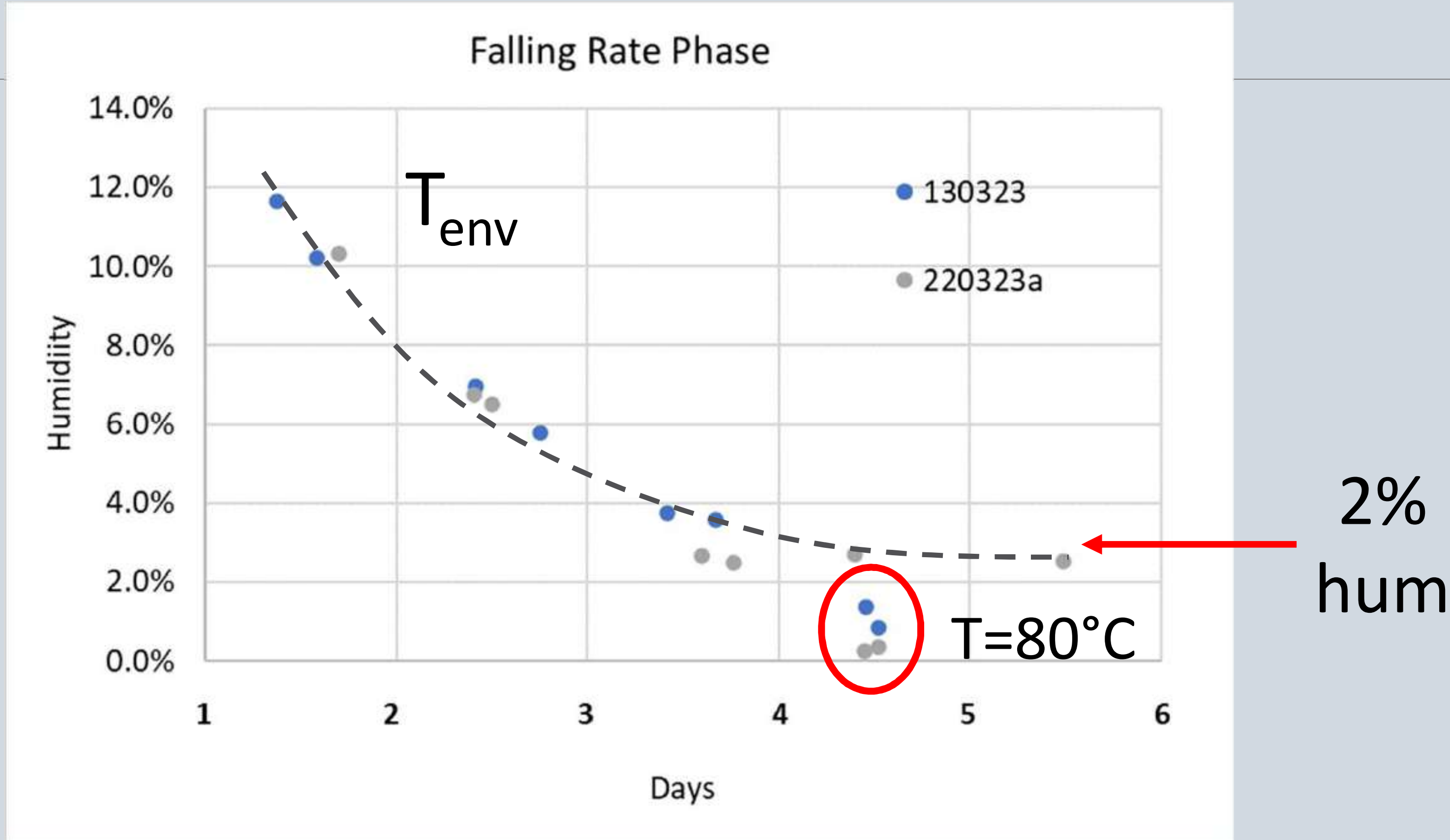
This combination of shear stress and tensorial stress to net resultant stresses explain the behavior of freely dried tapes.

CONTROLLED DRYING TAPE

Image of the dried tape in the Falling Rate Phase.

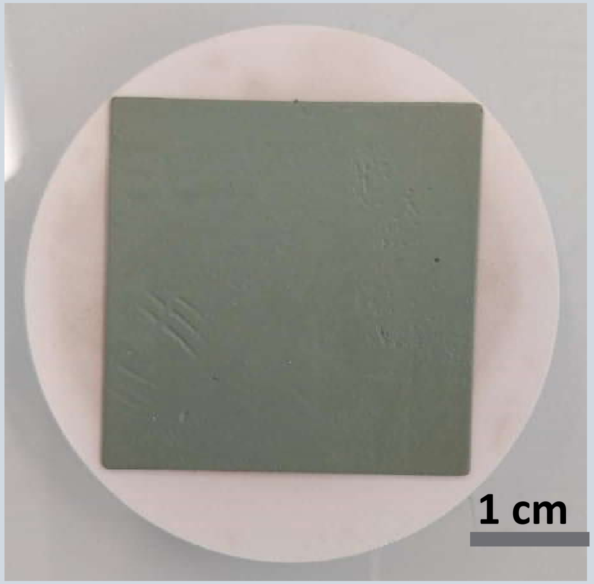


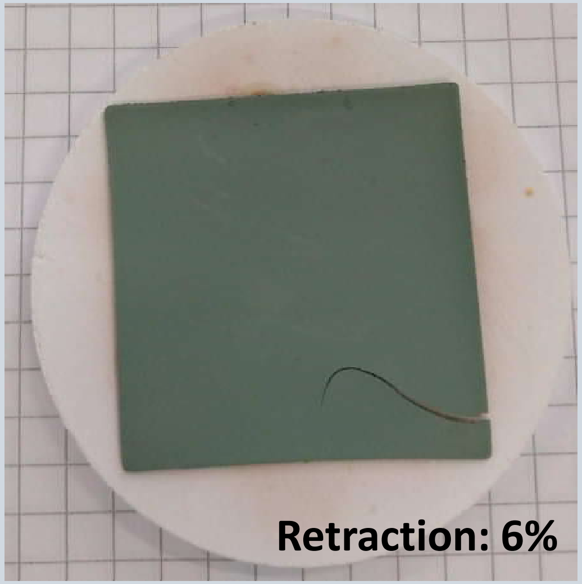
FALLING RATE PHASE



Le séchage entre ~12% et ~3% doit être fait très lentement.

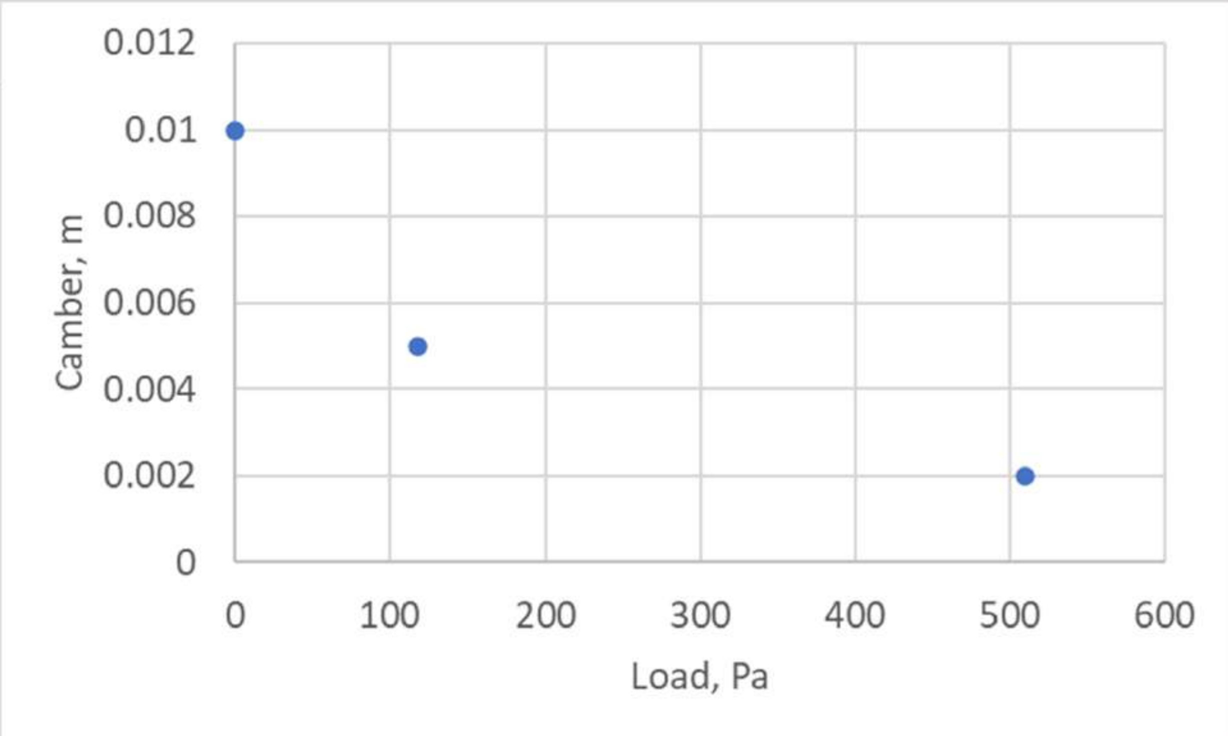
DRYING UNDER LOAD





Drying must be done very slowly to avoid strong tensions and fracture of the tape. The load must be over 900 Pa.

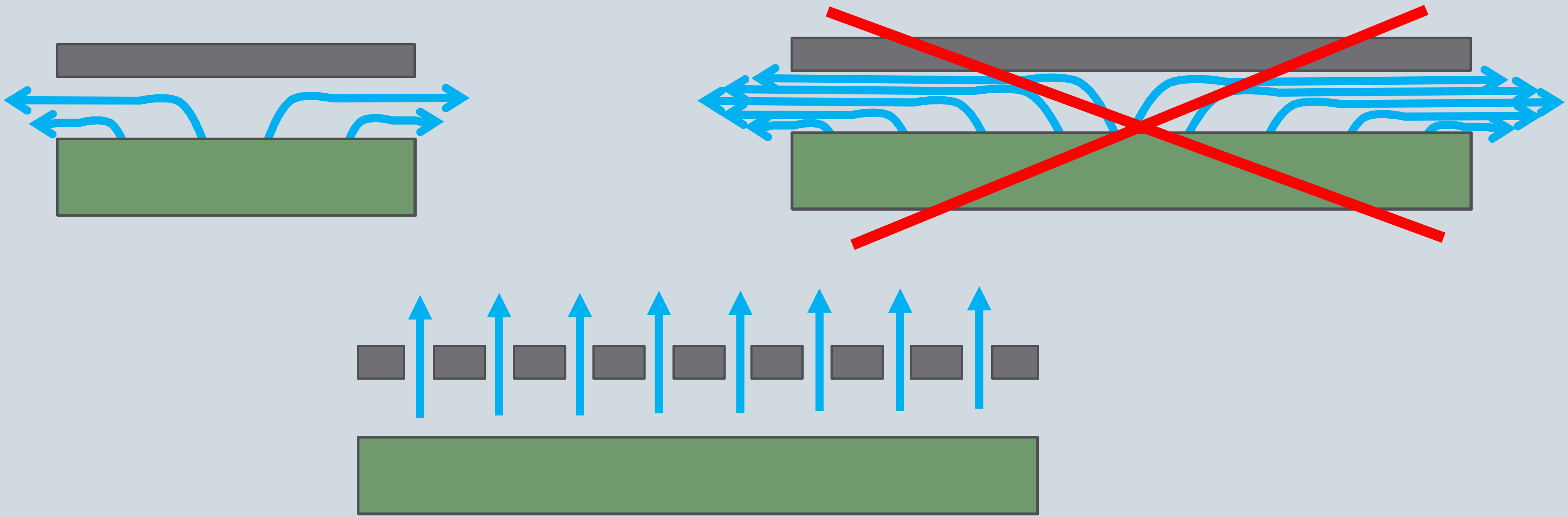
DRYING UNDER LOAD



Drying must be done very slowly to avoid strong tensions and fracture of the tape. The load must be over 900 Pa.

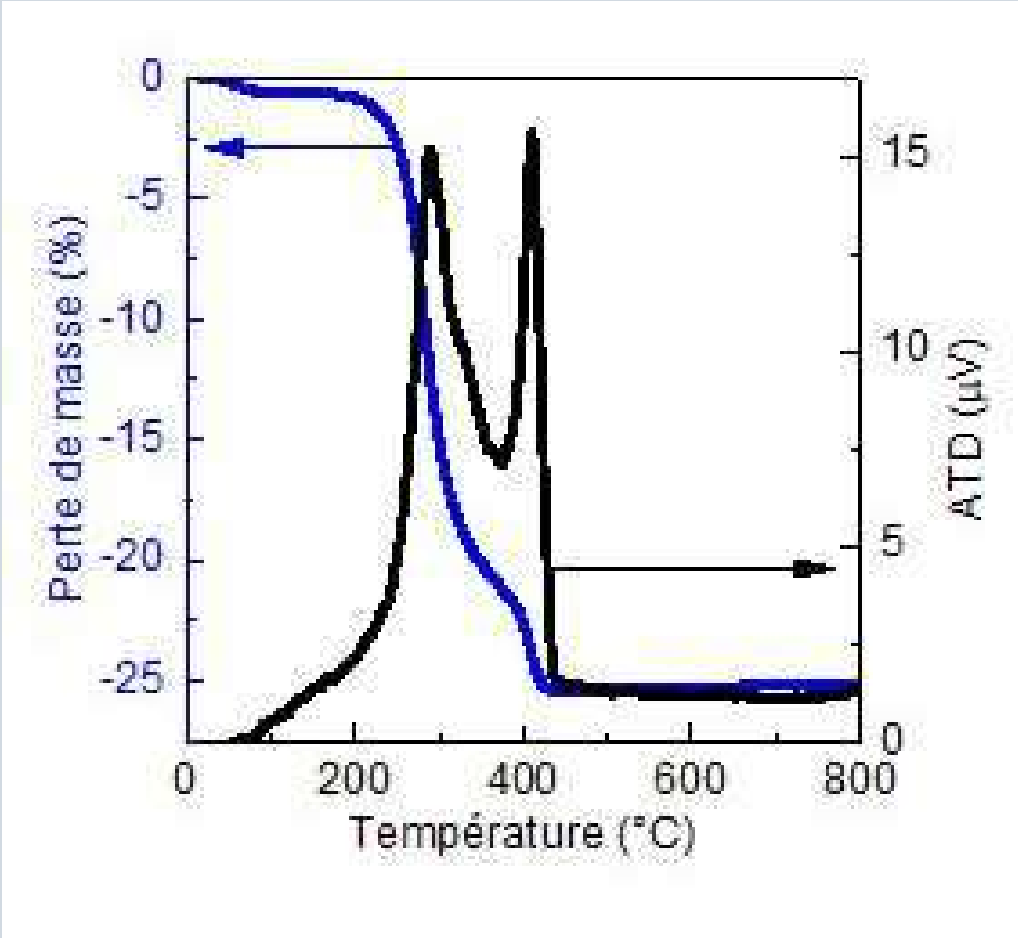
ORGANICS REMOVAL DYNAMICS: SIZE

Bigger samples have different dynamics for drying, and organics removal, requiring different heat treatments and loads design.



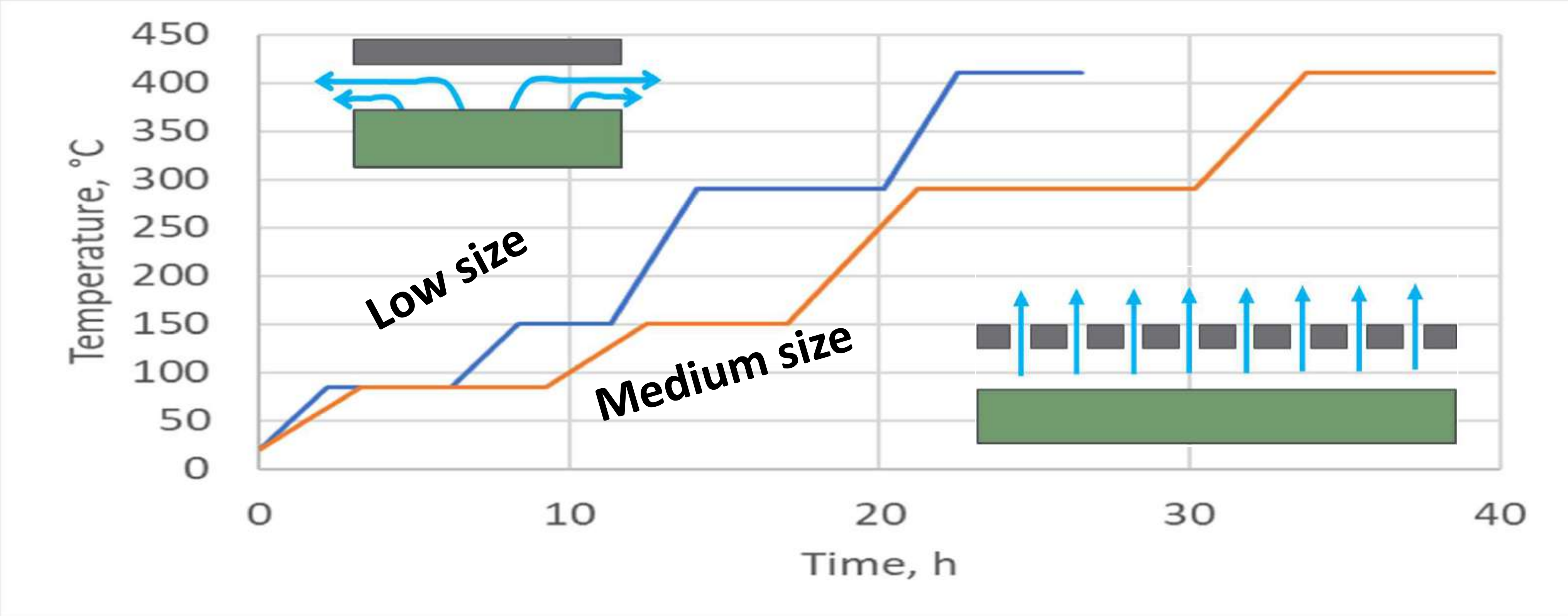
TGA RESULTS

TGA results are useful for determining temperatures for the dwells in the sintering program. However, the conditions for the little sample in the TGA are so different for the large samples.



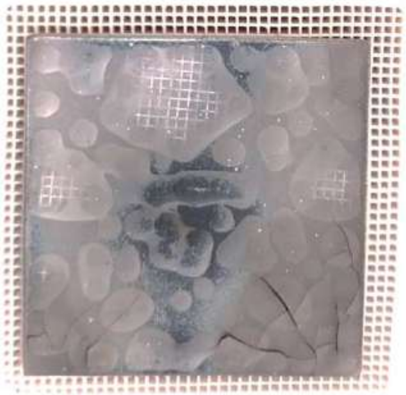
ORGANICS REMOVAL DYNAMICS: SIZE

TGA results are not enough to find an adequate sintering program.

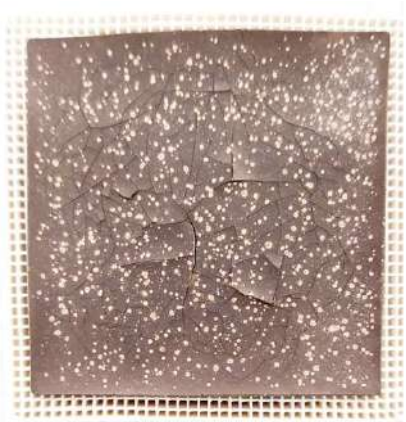


PLASTIFIER REMOVAL

FINE TUNING FOR ADEQUATE REMOVAL

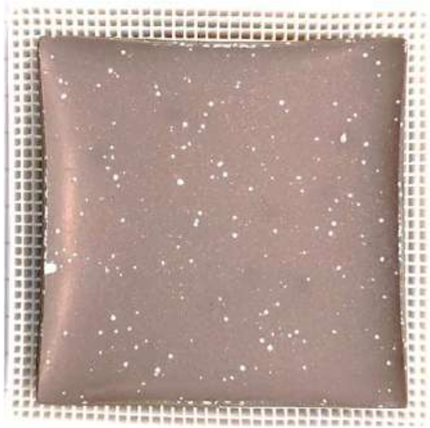


290°C



240°C

210°C
30°C/min

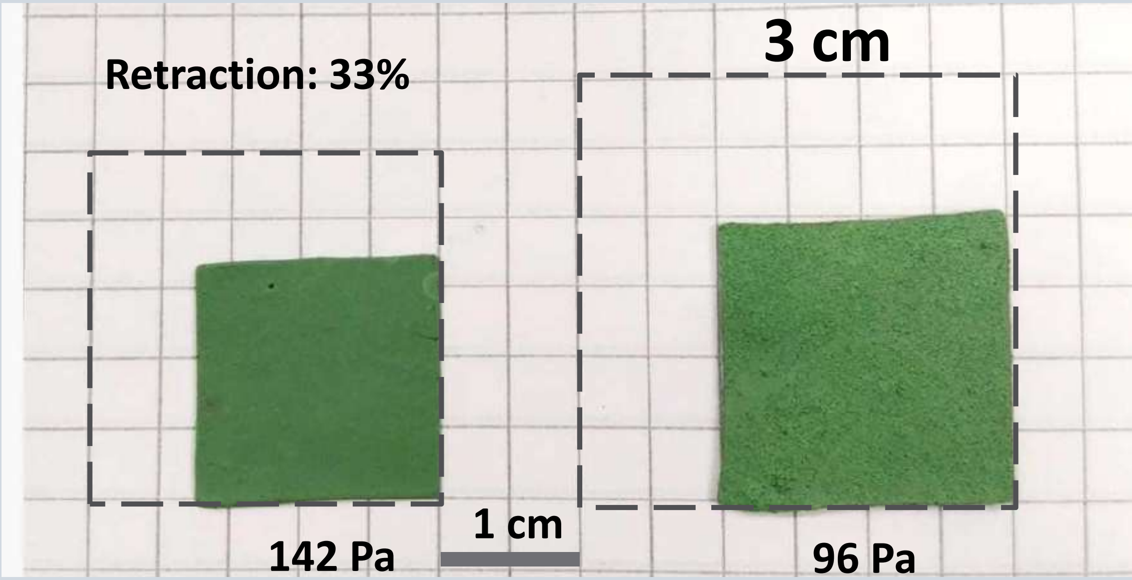


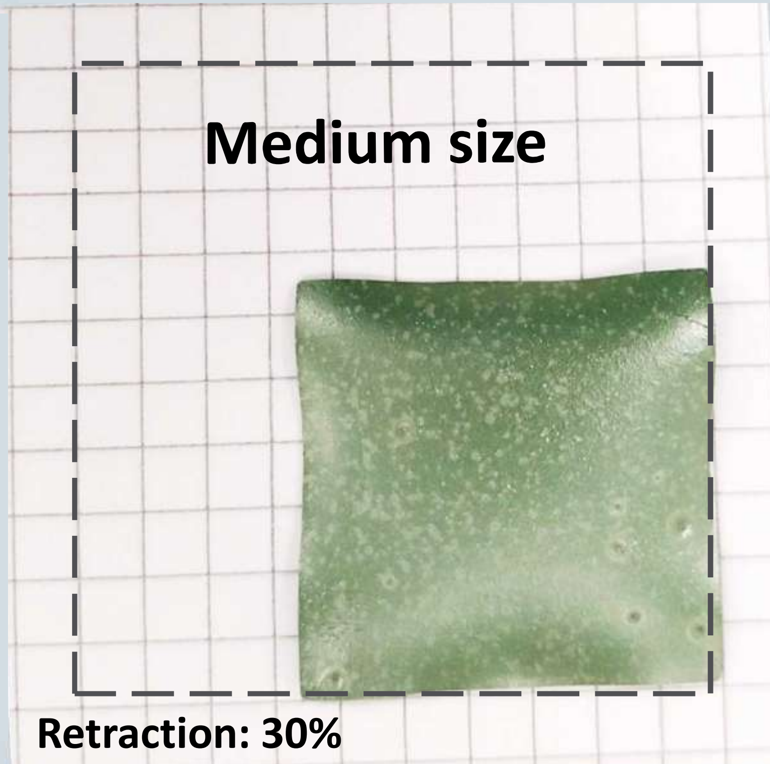
210°C
20°C/min

SINTERING RESULTS

Densification temperature: 1500°C, 2h

Low size





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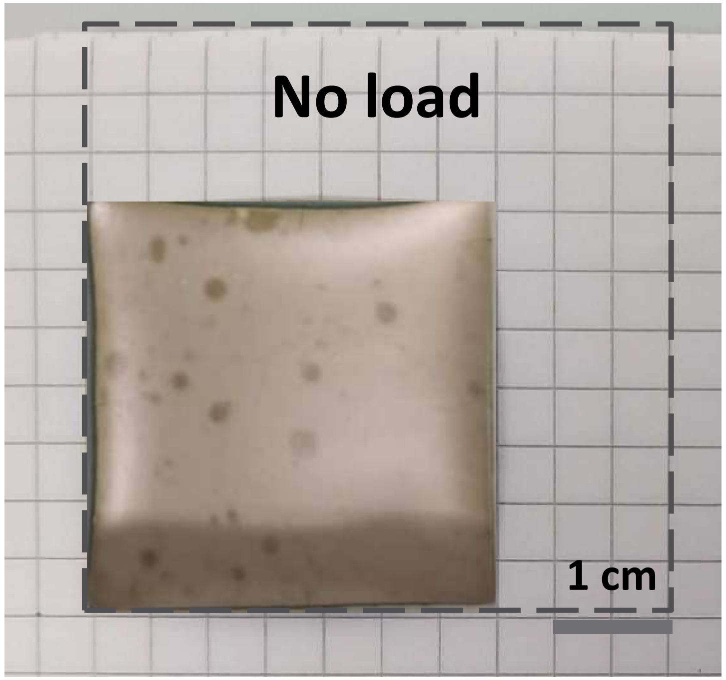
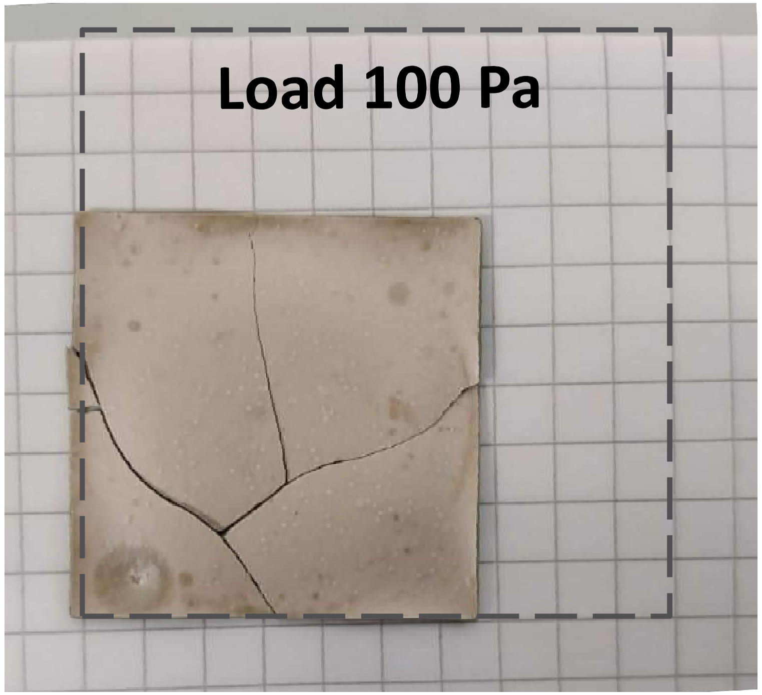
SINTERED HALF CELLS

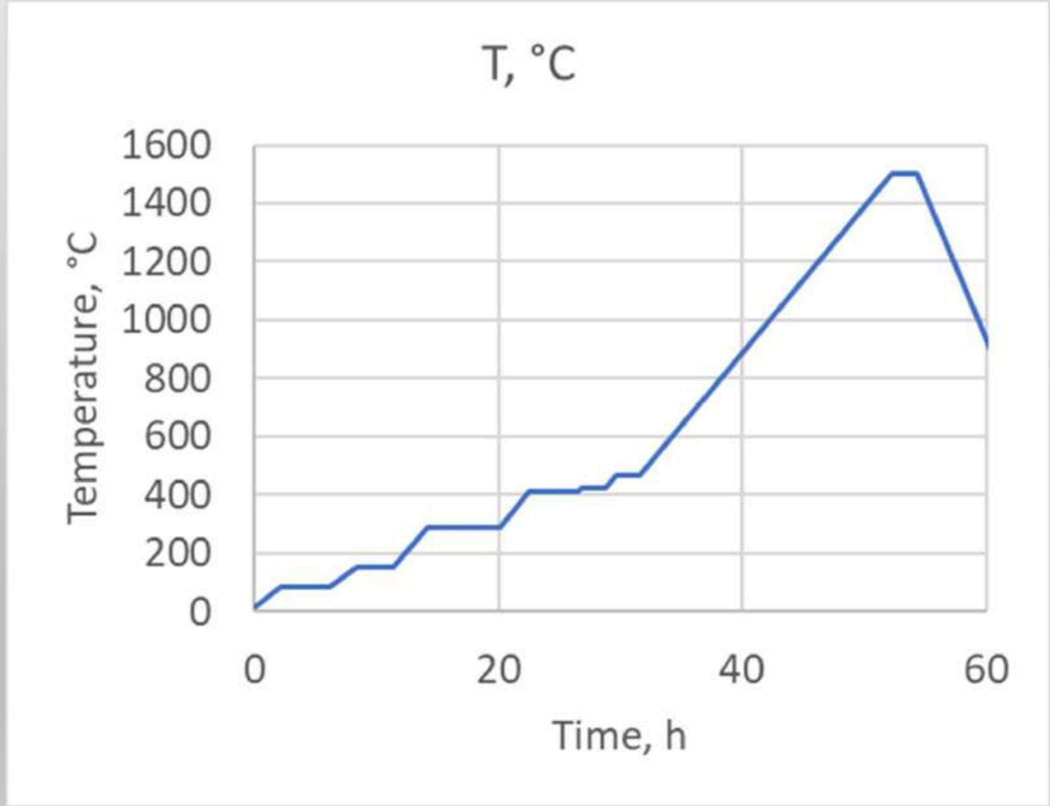
Preliminary results for half cells sintered at 1500°C, 2h





SINTERING PROGRAM

The sintering program is shown in the image, it is currently under development.

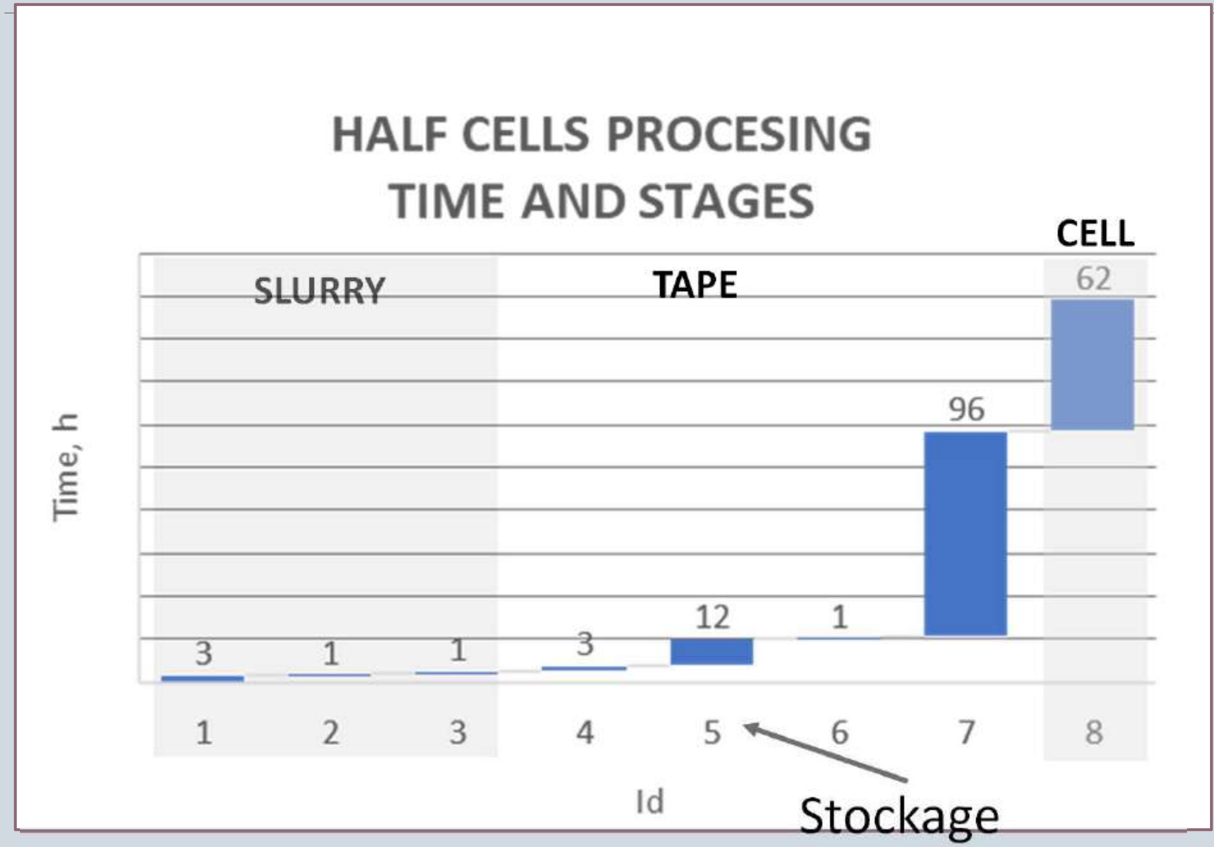


STAGES FOR THE HALF CELLS PROCESS

Id	State	Stage		Time, h	Humidity	Load, Pa / T, °C
1	Slurry	Preparation		3	35%	-- / Tamb
2		Rest		1	35%	-- / Tamb
3		Casting		1	35%	-- / Tamb
4	Tape	Drying	1e étape	3	35% -> 11%	-- / Tamb
5		Drying	2e étape	12	11%	10 / Tamb
6		Lamination		1	11%	500 / Tamb
7		Drying	3e étape	96	11% -> 2%	100 - 200 / Tamb
8	**Solid**	Sintering		62	0%	50 - 100 / 1500
		Total time, h		**179**		

Each half cell requires 179h, 7.3 jours, but they are processed in parallel.

TIMETABLE FOR PROCESSING HALF CELLS



Id	Stage	
1	Preparation	
2	Rest	
3	Casting	
4	Drying	1st stage
5	Drying	2nd stage
6	Lamination	
7	Drying	3rd stage
8	Sintering	

PERSPECTIVES

Obtained results provide valuable information for optimizing the process that can be used for obtaining medium sized Solid Oxide Fuel Cells.

Current activities are focused on:

- Use of special designed loads
- Optimize the sintering program

Completing these tasks, it is expected to validate the full production process for SOFC and continue to the performance tests.

MERCI BEAUCOUP
THANK YOU
MUCHAS GRACIAS