



# Development of proton conducting electrolyser cells

Marie-Laure Fontaine, Christelle Denonville, Jonathan Polfus,  
Wen Xing, Paul Inge Dahl, Tor Olav Sunde, Rune Bredesen

SINTEF Materials and Chemistry

Thin Film and Membrane Technologies Department





# Solid State Reactive Sintering (SSRS)

Wet milling of precursor powders:  
 $\text{NiO} + \text{BaCO}_3, \text{Y}_2\text{O}_3, \text{ZrO}_2, \text{CeO}_2$



Drying of powders in oven



Pressing and sintering at  $T > 1400^\circ\text{C}$

**BZCY based dense pellets  
with 1 wt. % NiO**



Limited number of processing steps



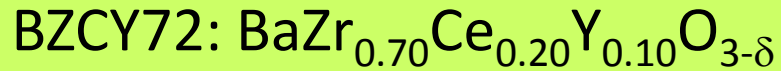
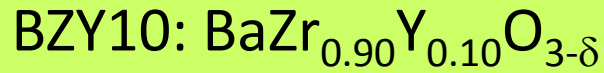
Fine Homogeneous microstructure  
Fast sintering



- Cost effective
- Lower  $\text{CO}_2$  emissions

- G. Coors 2011, [www.intechopen.com](http://www.intechopen.com)
- J. Tong, Ryan O'Hayre et al., *J. Mater. Chem.*, 2010, 20

# SSRS for enabling cells production in ELECTRA



Fuel electrode:  $\text{NiO} + \text{BaCO}_3, \text{Y}_2\text{O}_3, \text{ZrO}_2$

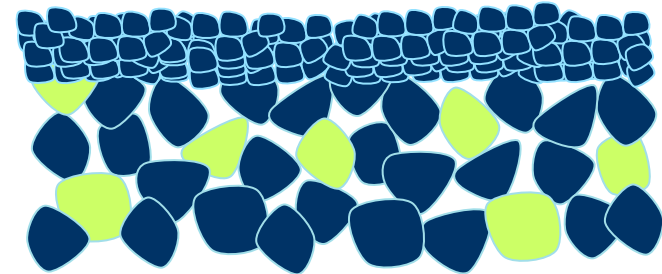
Electrolyte:  $\text{BaCO}_3, \text{Y}_2\text{O}_3, \text{ZrO}_2$

and

Fuel electrode:  $\text{NiO} + \text{BaSO}_4, \text{Y}_2\text{O}_3, \text{ZrO}_2$ ,  
*with and without  $\text{CeO}_2$*

Electrolyte:  $\text{BaSO}_4, \text{Y}_2\text{O}_3, \text{ZrO}_2$ , *with and without  $\text{CeO}_2$*

BZY10 or BZCY72



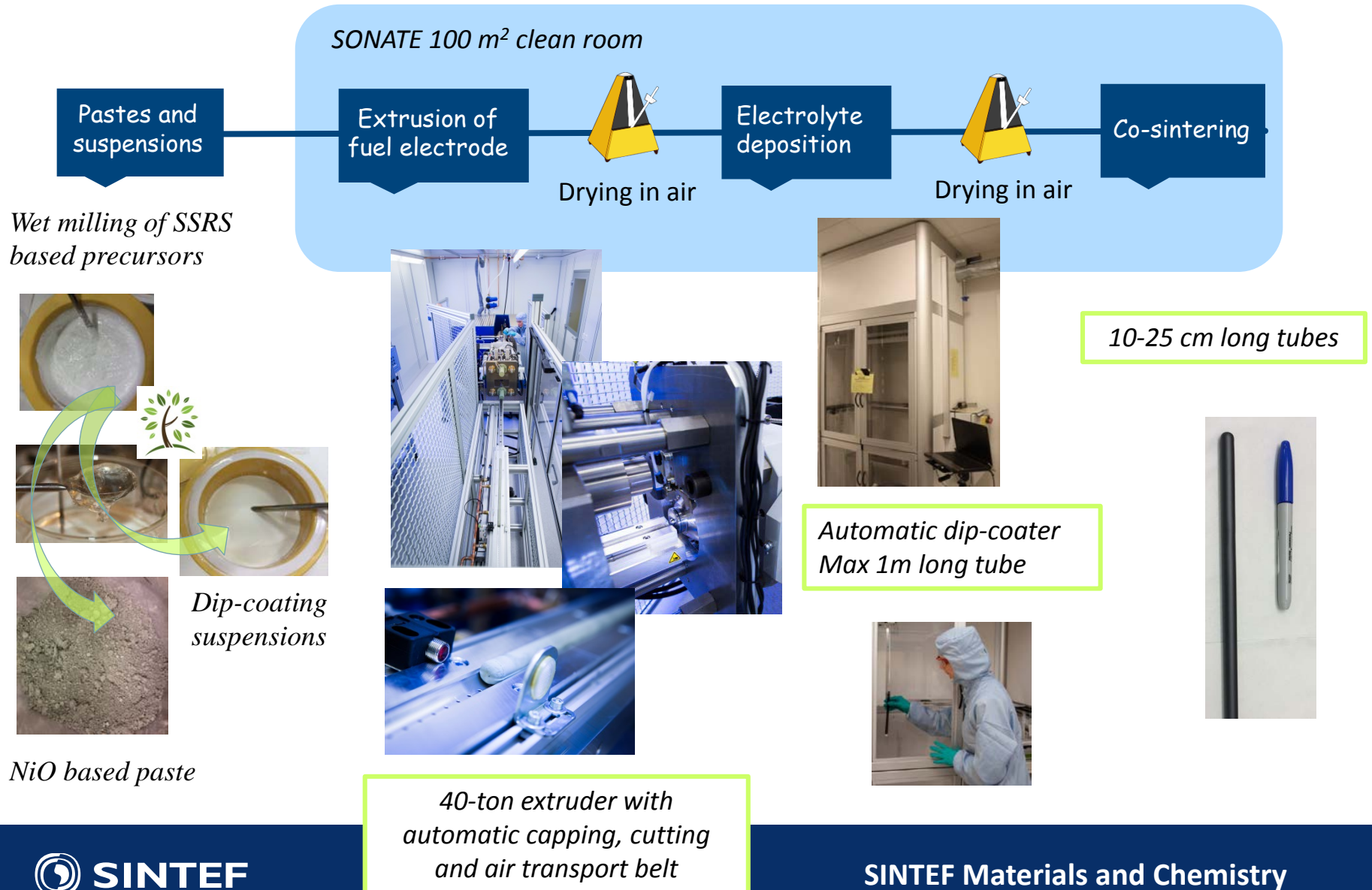
NiO+ BZY10 or NiO + BZCY72  
(60/40 vol. %)

Notation: BZY10 // BZY10-NiO

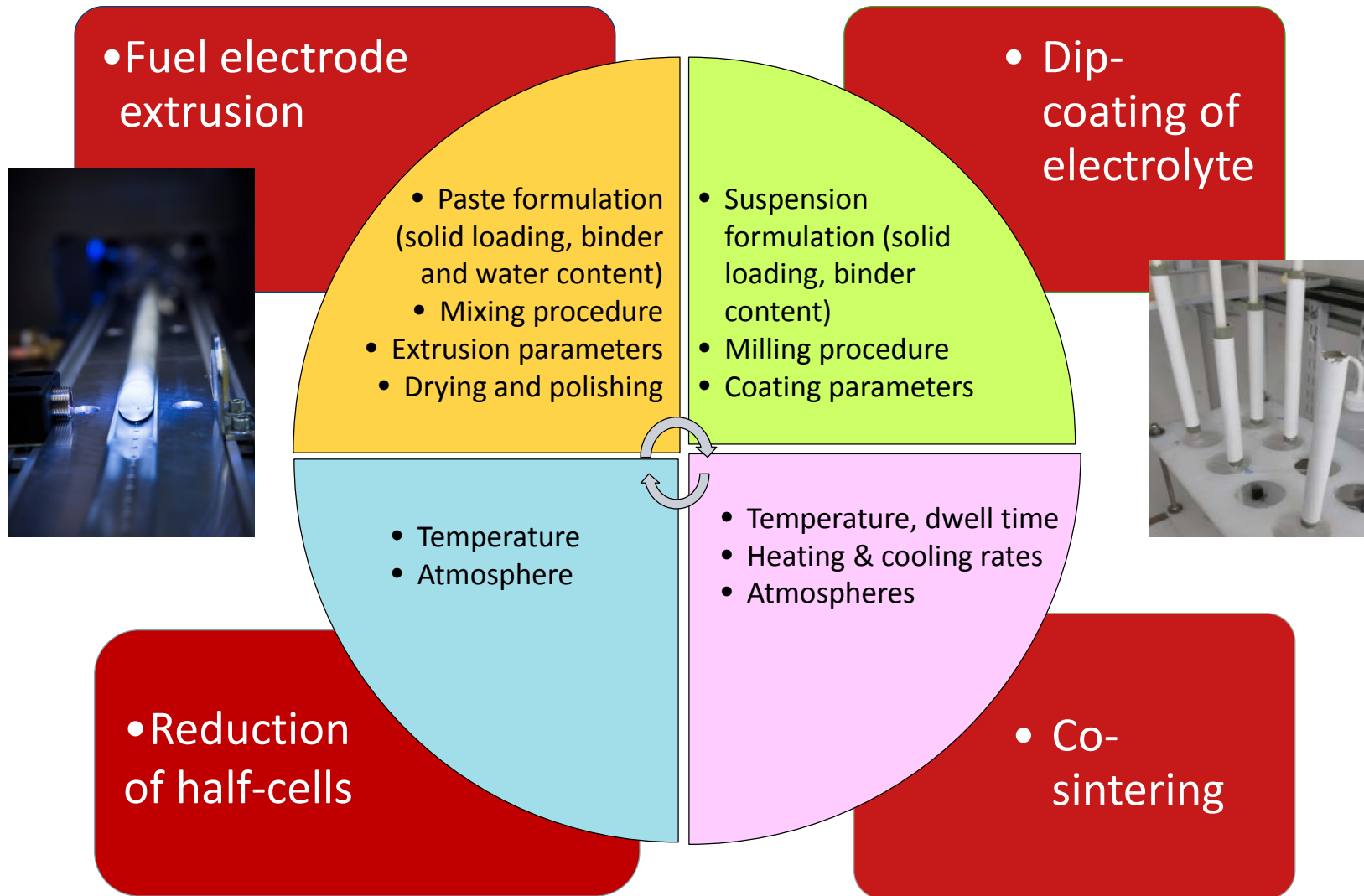
Electrolyte

Electrode

# Solid state reactive sintering for BZY based cell production



# Investigated parameters



# Drying and polishing



*"Green" tubes after coating*

Close end from capping system →

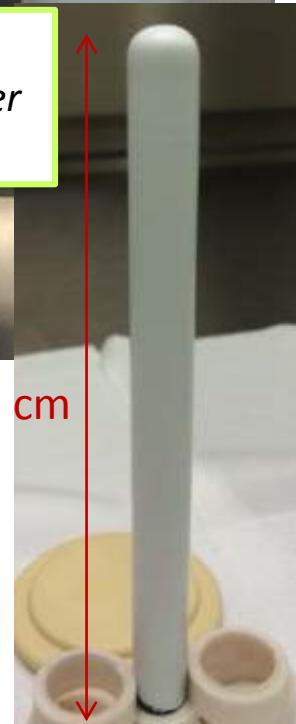


*Tubes after extrusion and roll-drying in air for 24h*

*Dried tubes after polishing with wet clean room tissue*



15 cm



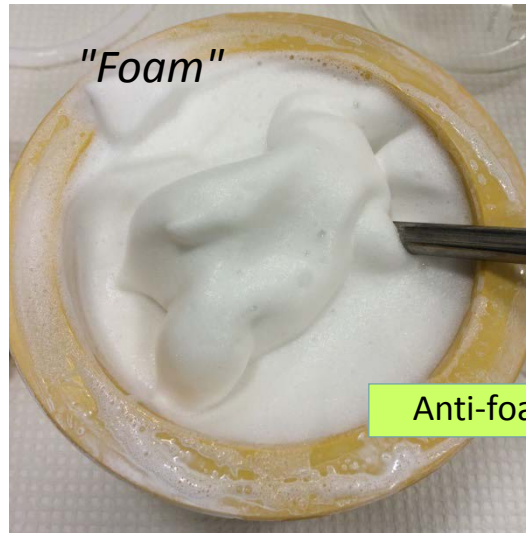
# SSRS-based suspensions

- Water-based suspension  
(cellulose based binder)

$BaSO_4$ ,  $Y_2O_3$ ,  $ZrO_2$ ,  $CeO_2$

- Organic-based suspension

$BaCO_3$ ,  $Y_2O_3$ ,  $ZrO_2$ ,  $CeO_2$



*Viscosity 110-175 cP at 60 rpm with LV2 spindle*

## Protocol:

Planetary milling of powders + binders +  
water or solvent @ 300 rpm – 2h

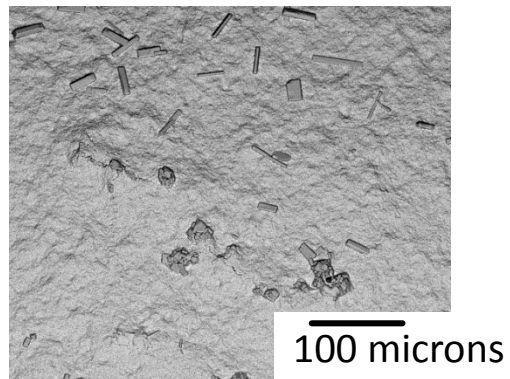


*Viscosity around 19 cP at 60 rpm  
using LV2 spindle*

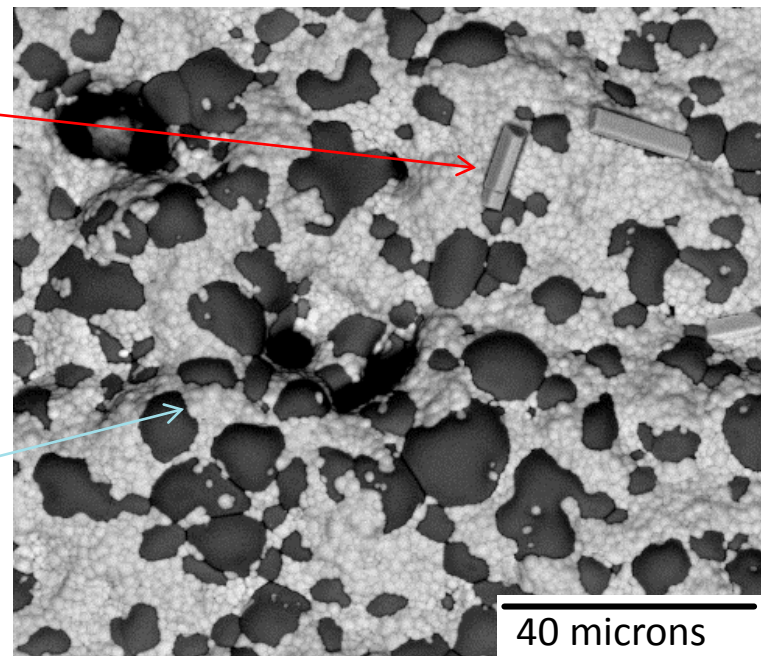


# BZY10 // BZY10-NiO using $\text{BaCO}_3$ based precursor mixture

1610°C - 6h: surface view of electrolyte

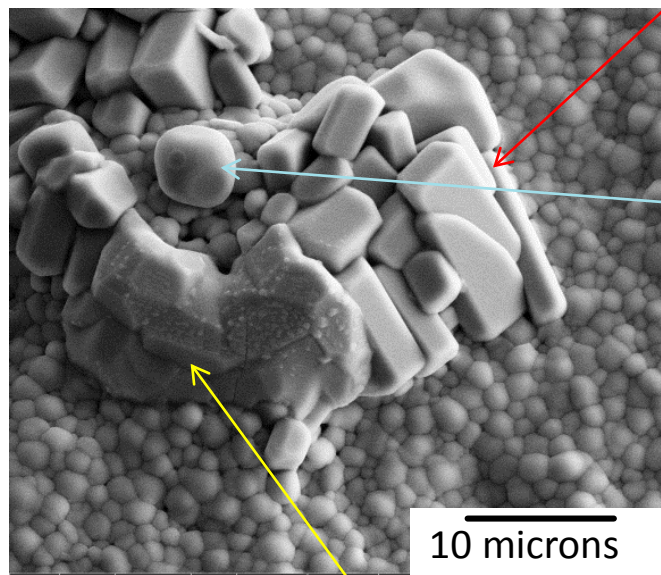


1610°C - 6h: surface view of uncoated electrode



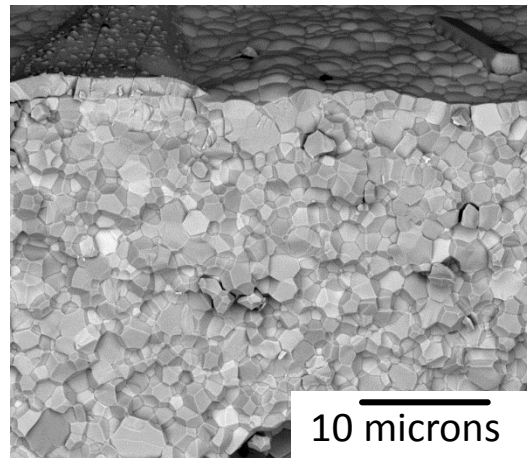
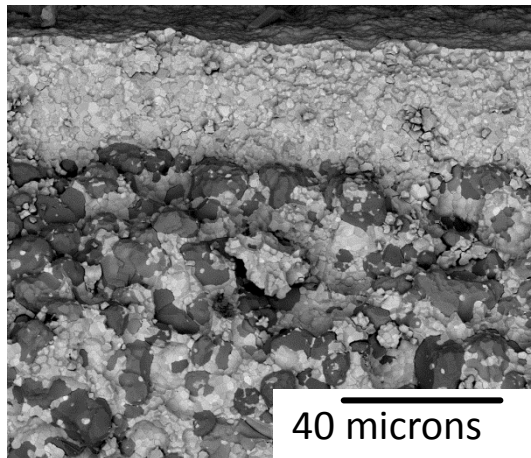
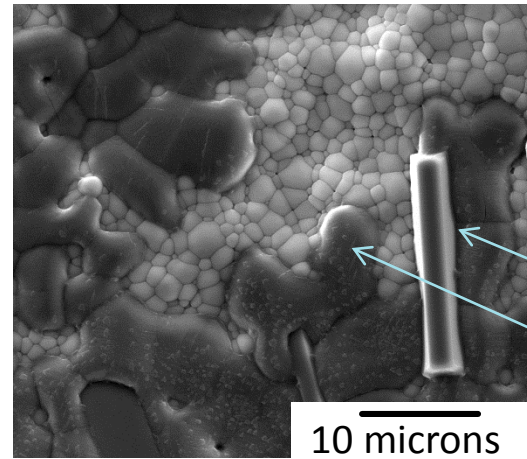
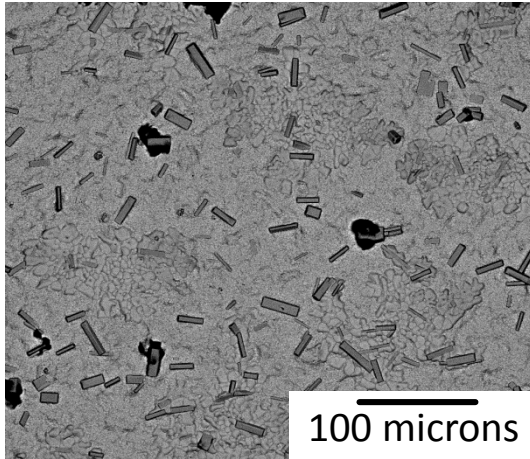
$\text{BaNiY}_2\text{O}_5$

$\text{NiO}$



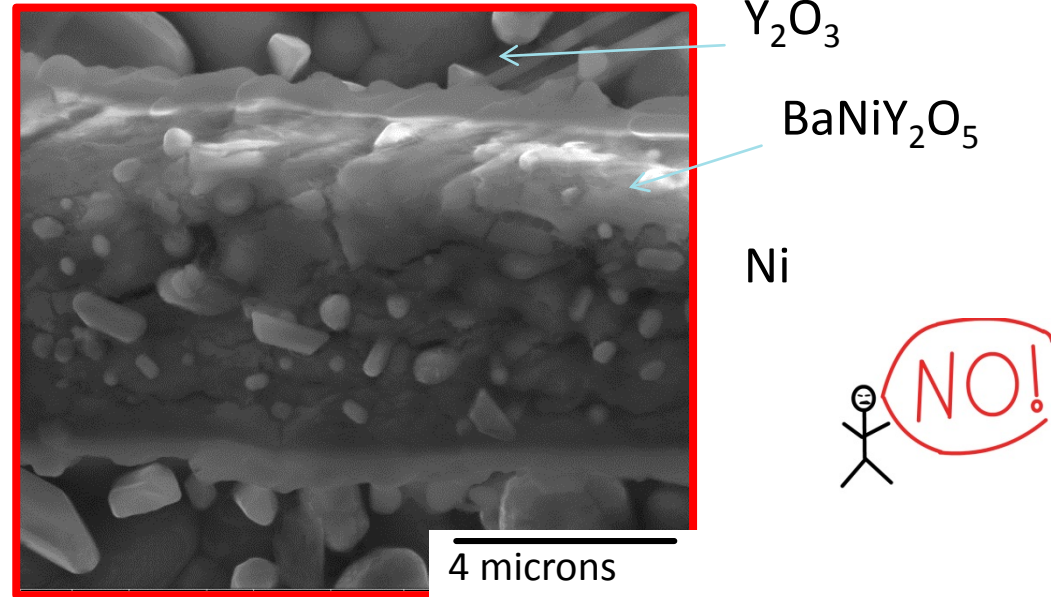
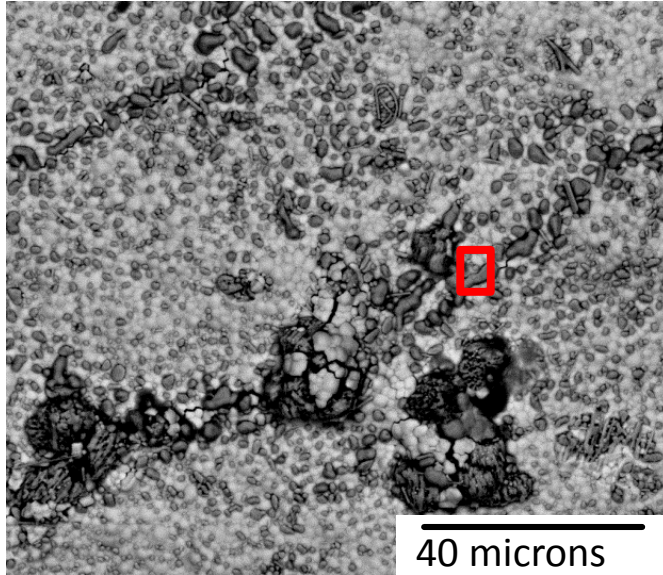
# BZY10 // BZY10-NiO using $\text{BaCO}_3$ based precursor mixture

1550°C - 24h

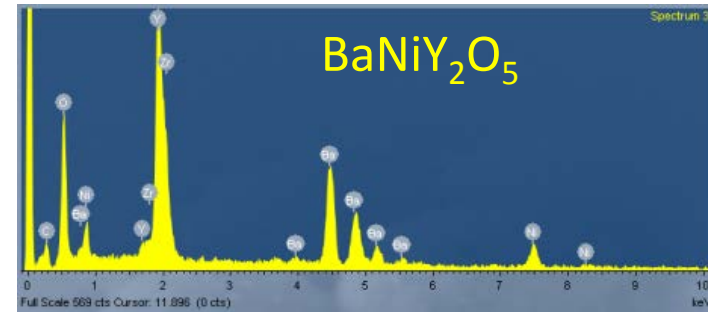
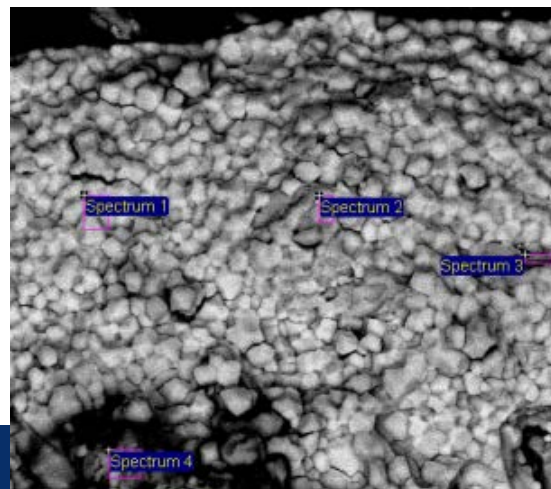


# BZY10 // BZY10-NiO using BaCO<sub>3</sub> based precursor mixture

Wet 4%H<sub>2</sub>/Ar @ 900°C

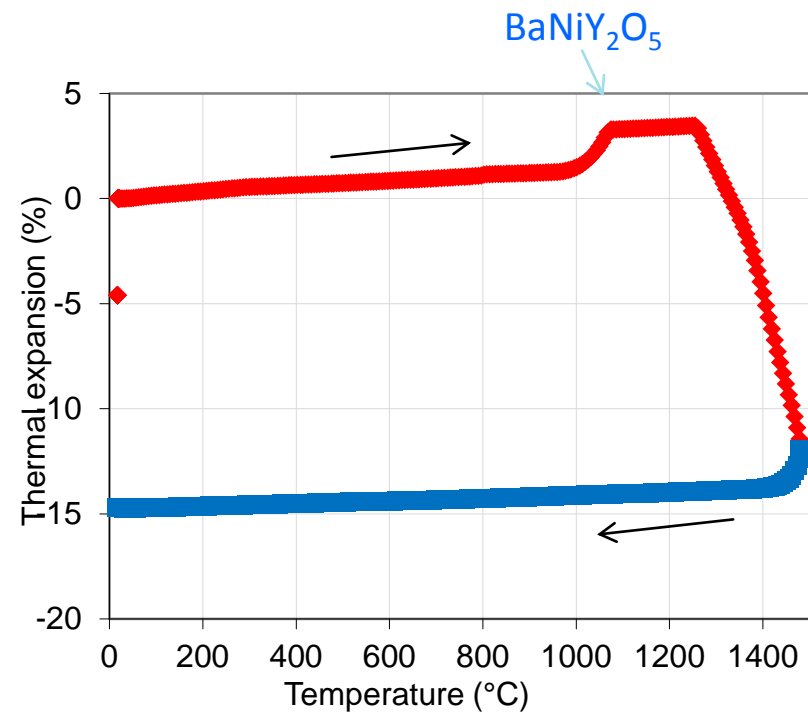


Cracks in electrolyte



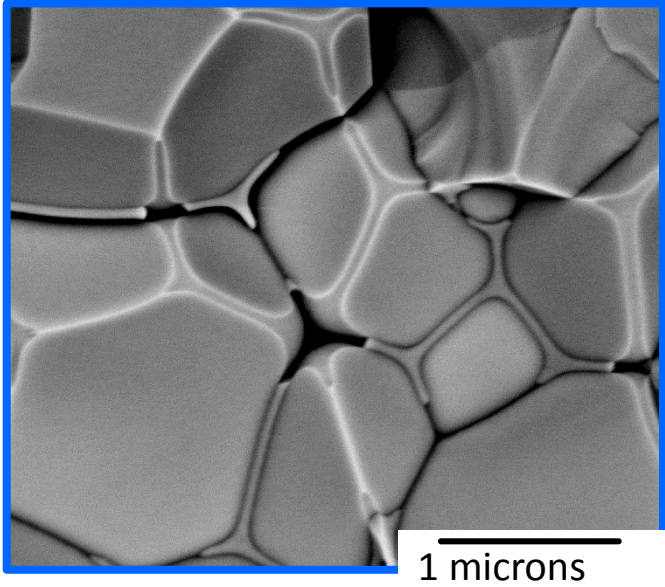
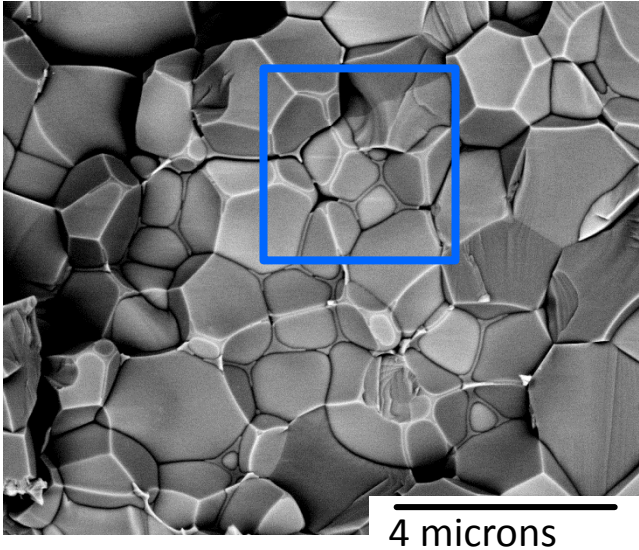
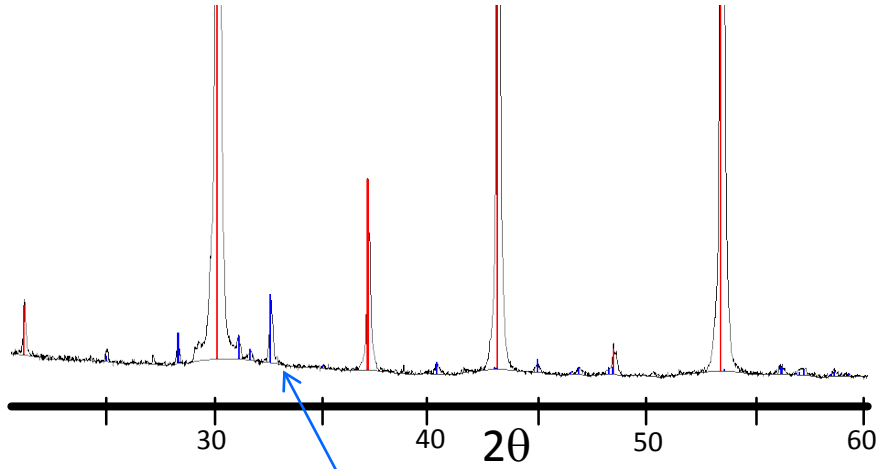
# SSRS BZY pellet with 2wt% NiO

Dilatometry in air  
HT XRD



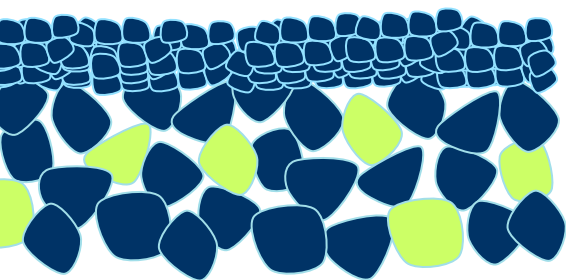
*J. Tong, Ryan O'Hayre et al., J. Mater. Chem., 2010, 20*

# SSRS BZY pellet with 2wt% NiO



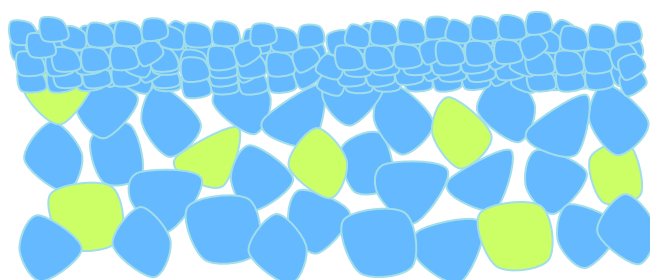
# Investigated half-cells with $\text{BaSO}_4$ precursor

BZCY72



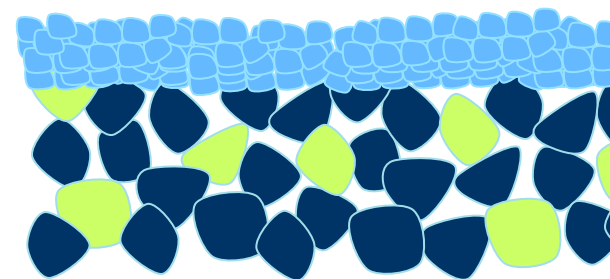
BZCY72 - NiO

BZY10

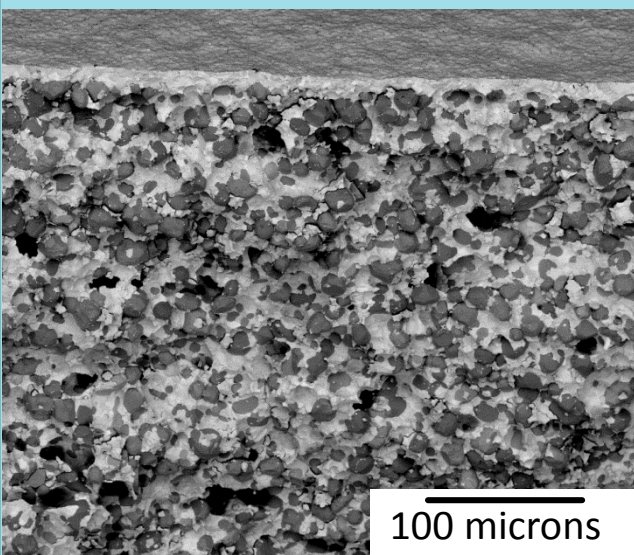


BZY10 - NiO

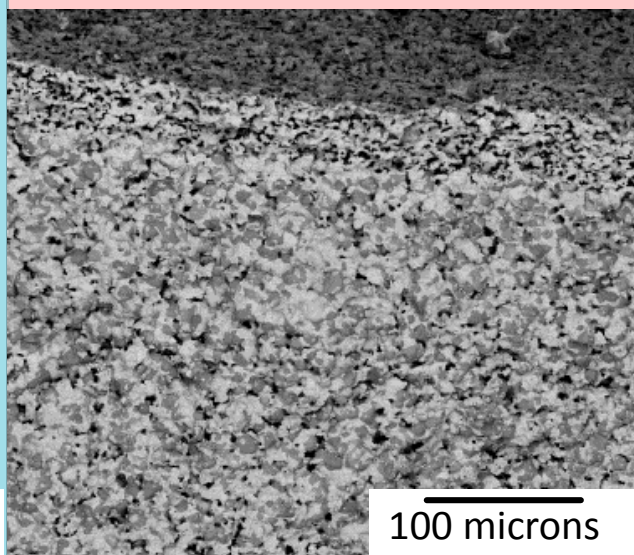
BZY10



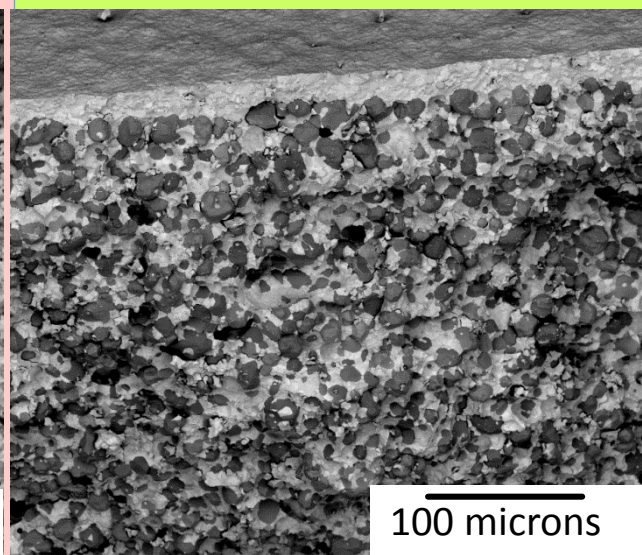
BZCY72 - NiO



100 microns



100 microns

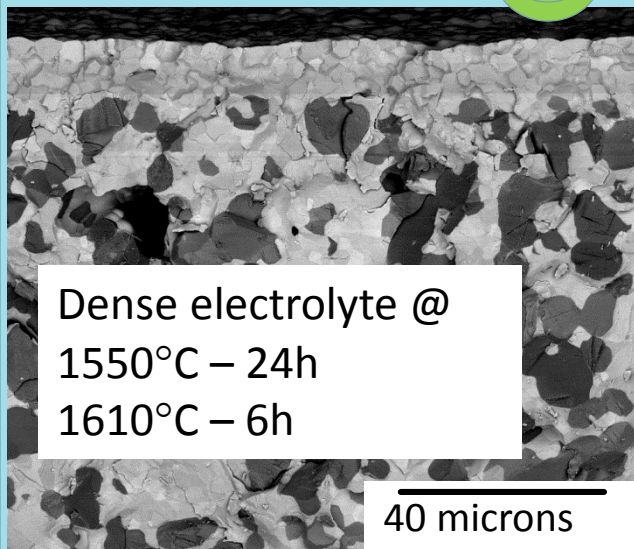


100 microns

BZCY72 // BZCY72-NiO 😊

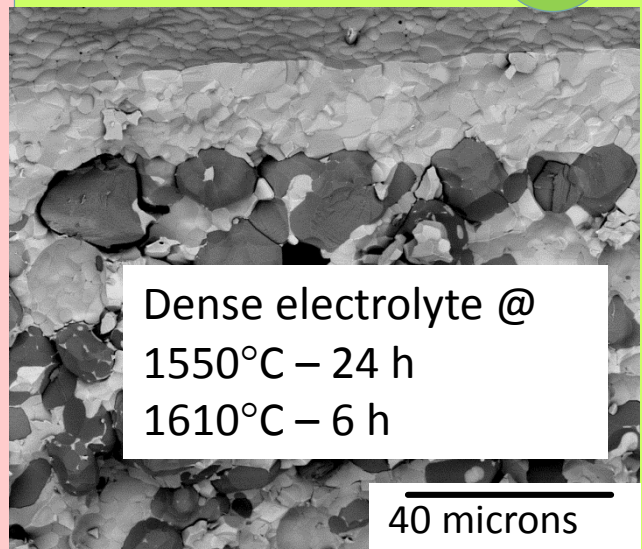
BZY10 // BZY10-NiO

BZY10 // BZCY72-NiO 😊



Dense electrolyte @  
1550°C – 24h  
1610°C – 6h

40 microns



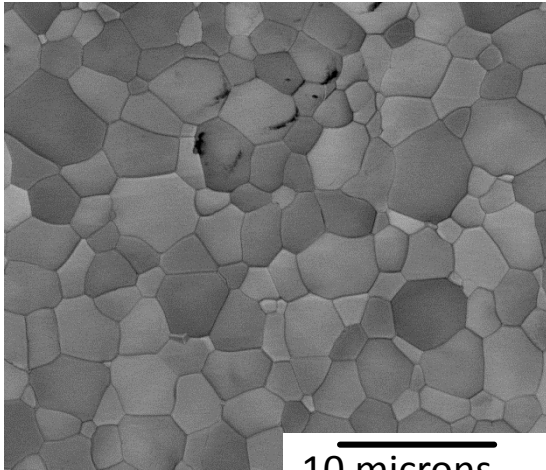
Dense electrolyte @  
1550°C – 24 h  
1610°C – 6 h

40 microns

# BZCY72 // BZCY72-NiO

Grain size:  
5-10 microns

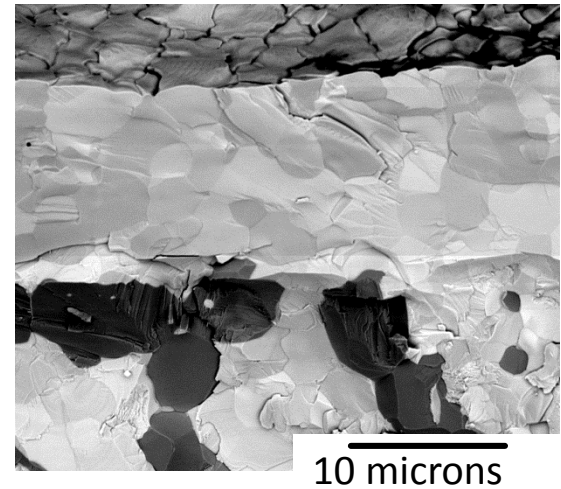
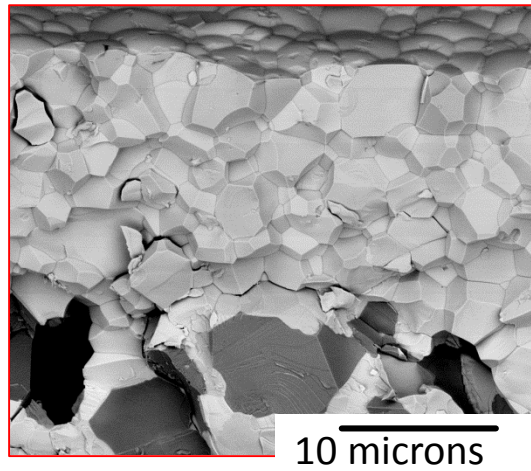
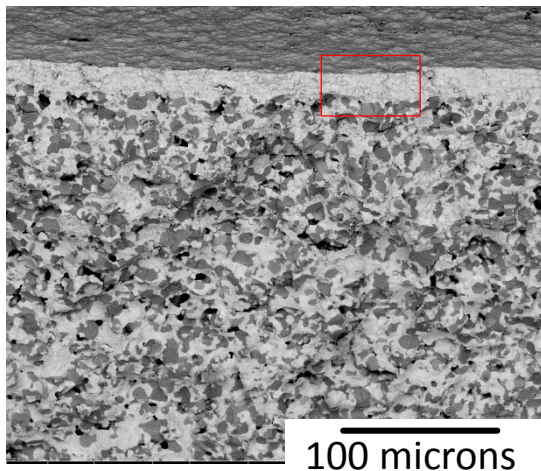
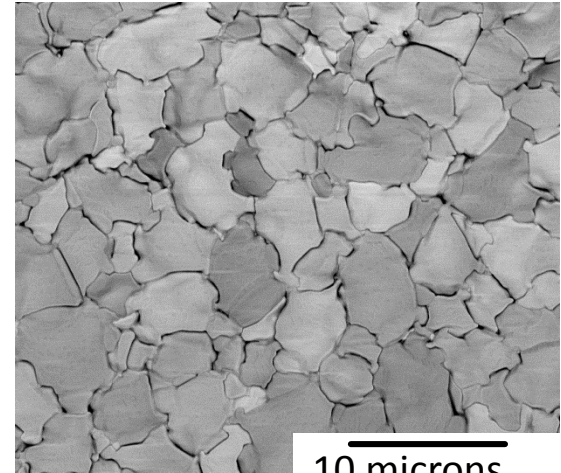
1550°C – 24h



Grain size:  
Large: 5 microns  
Small: 2 microns

Grain growth

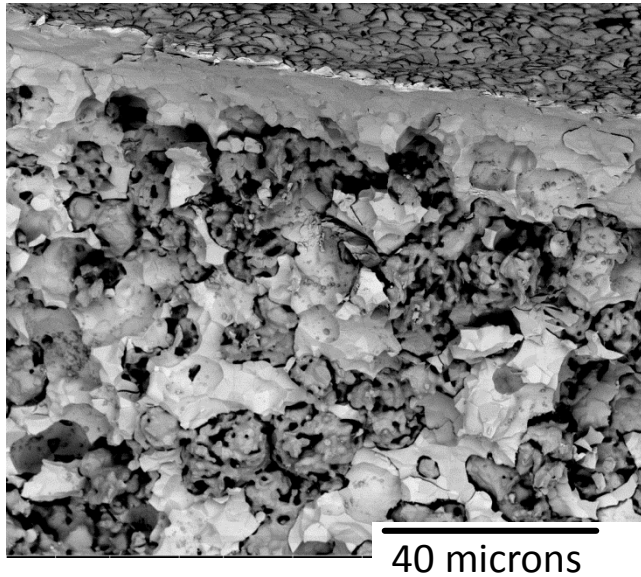
1610°C – 6h



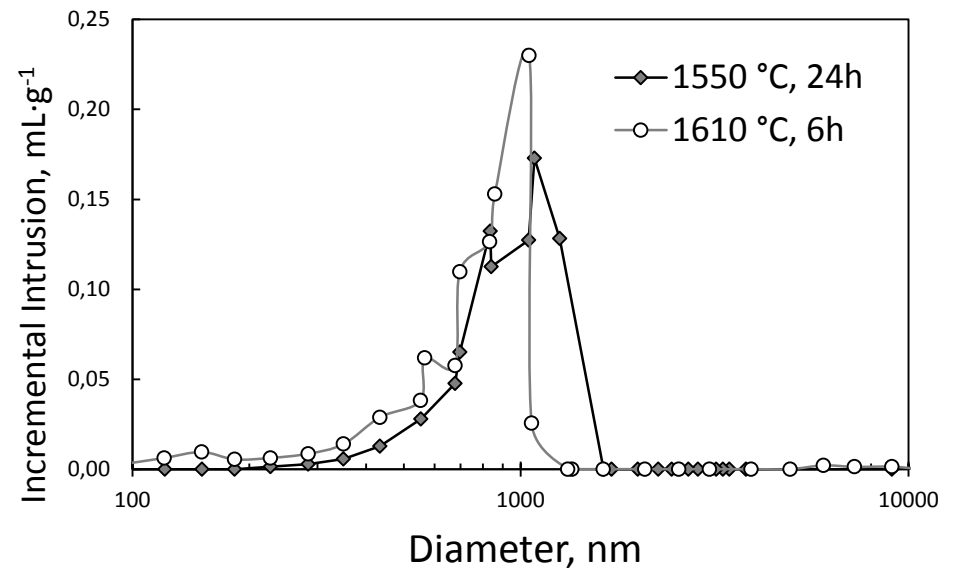


# Reduction of half-cells

- Wet Harmix at 900°C



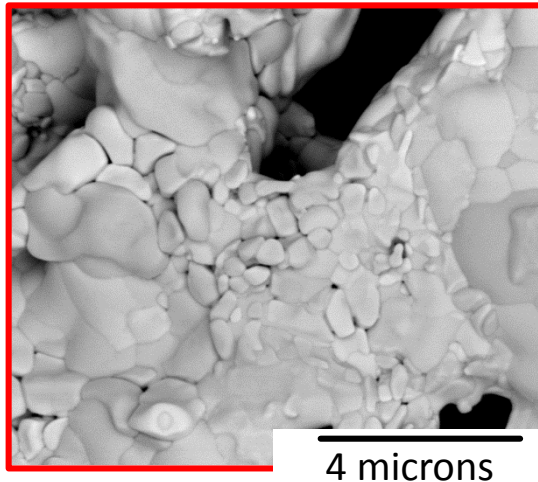
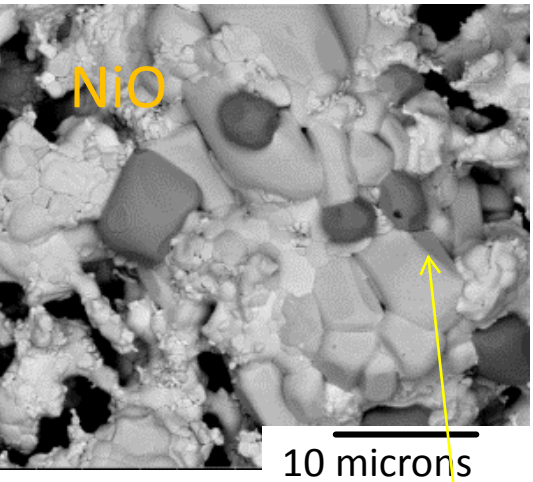
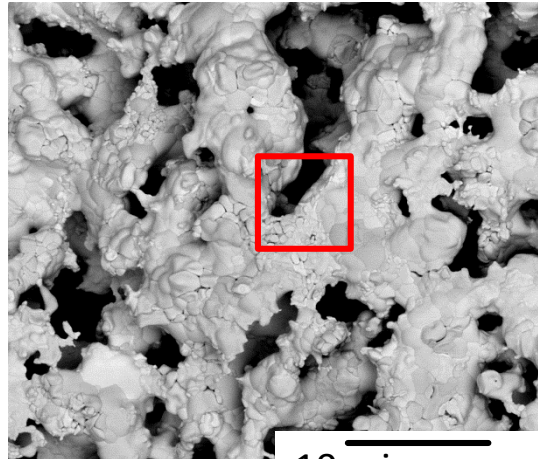
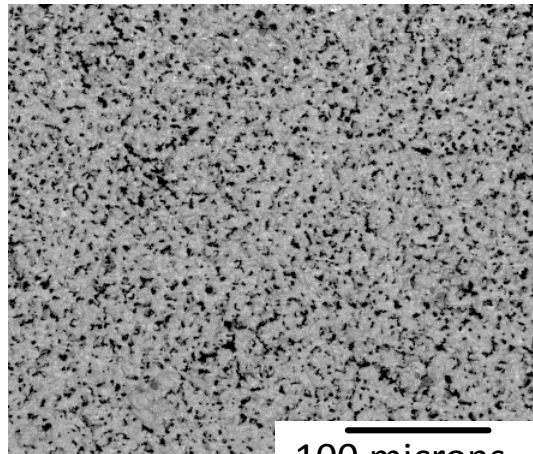
## Hg-porosimetry



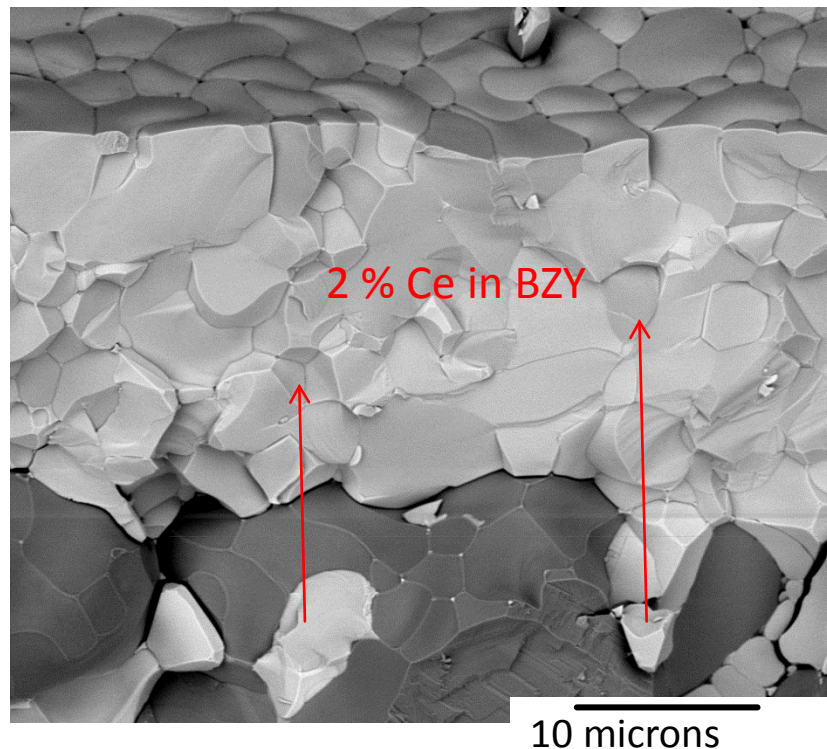
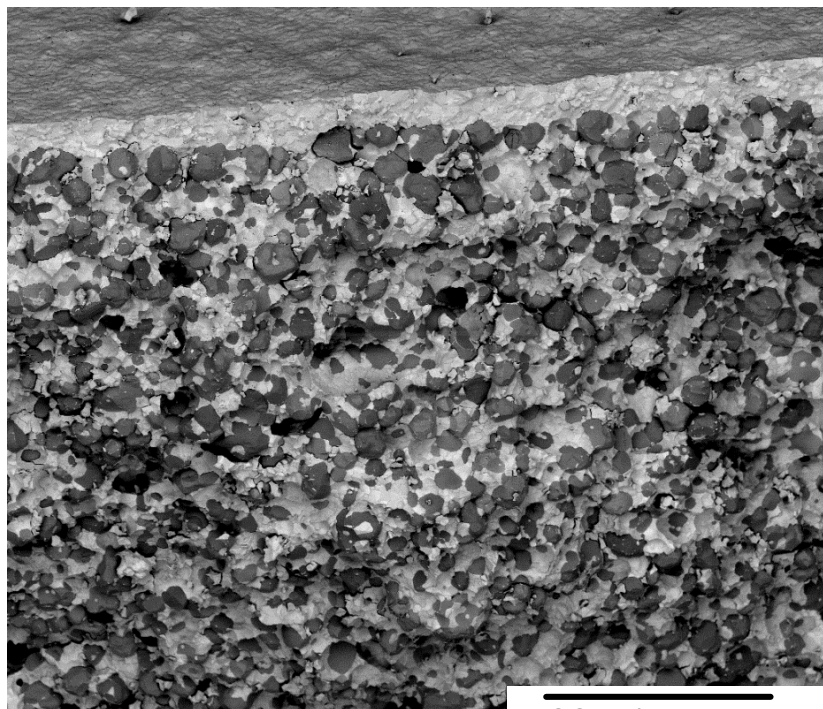
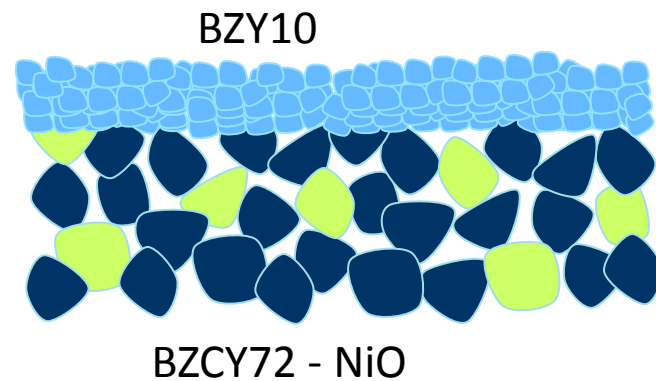
Between 27-32 vol% porosity (with 60 vol% Ni)

# BZY10 // BZY10-NiO

1610°C - 6h



"BZY10"//BZCY72-NiO



# Characterization

Phases evolution

HT-XRD up to 1200°C  
TGA / DSC up to 1400°C

- BaSO<sub>4</sub>
- BaSO<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> or without CeO<sub>2</sub>
- NiO - BaSO<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> or without CeO<sub>2</sub>

Microstructural evolution

HT-ESEM up to 1400°C  
Ex-situ SEM-EDS analyses

- Green half-cells
- Green coated half-cells
- Half-cells annealed from 1550°C – 1670°C

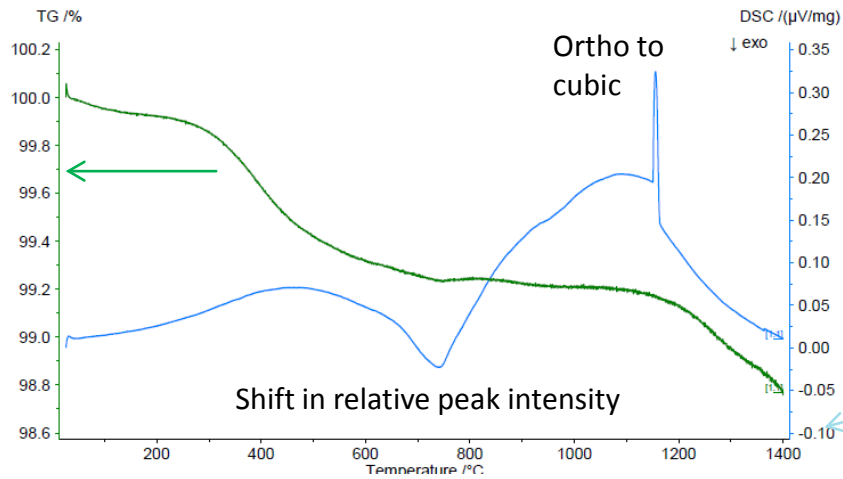
Sintering behaviour

Dilatometry (push rod) up to 1500°C  
Fast sintering up to 1600°C

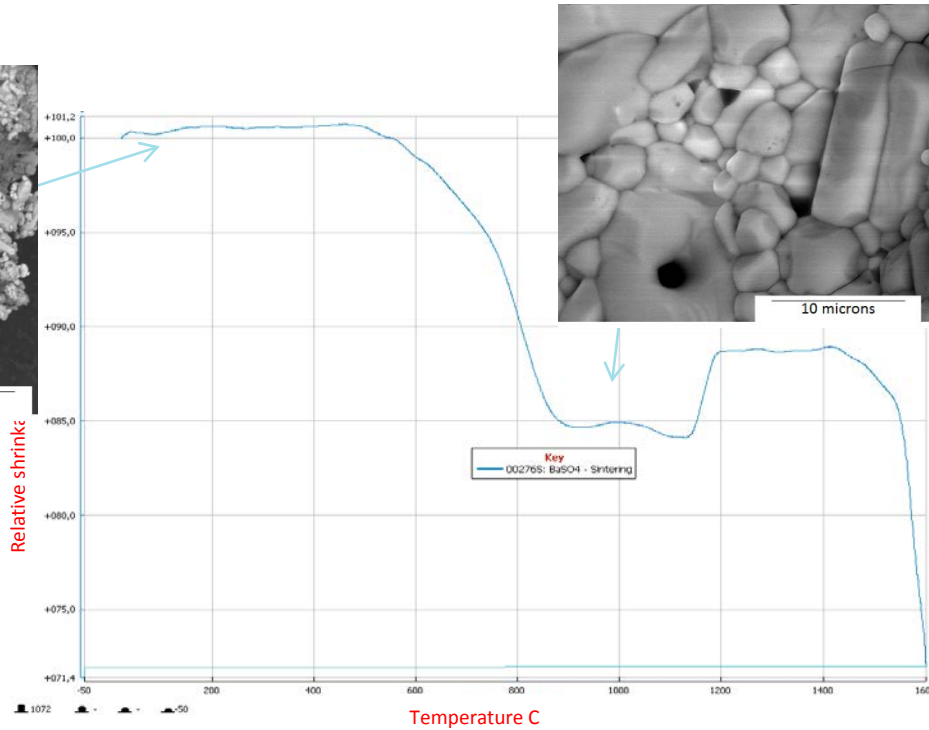
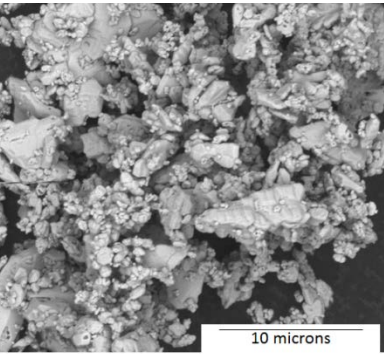
- BaSO<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> or without CeO<sub>2</sub>
- NiO - BaSO<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> or without CeO<sub>2</sub>
- Green half-cells



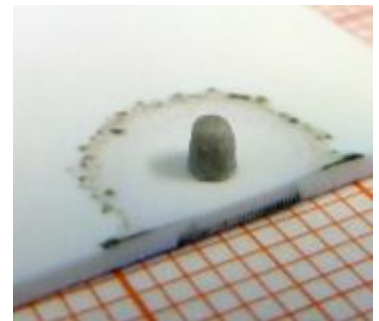
TGA/DSC in air & HT-XRD



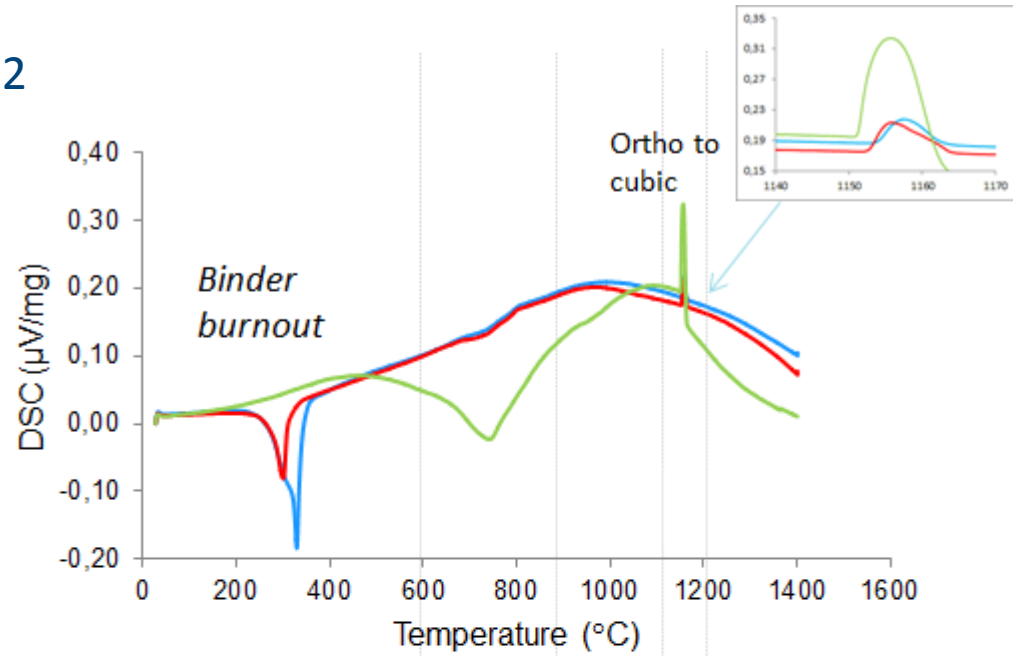
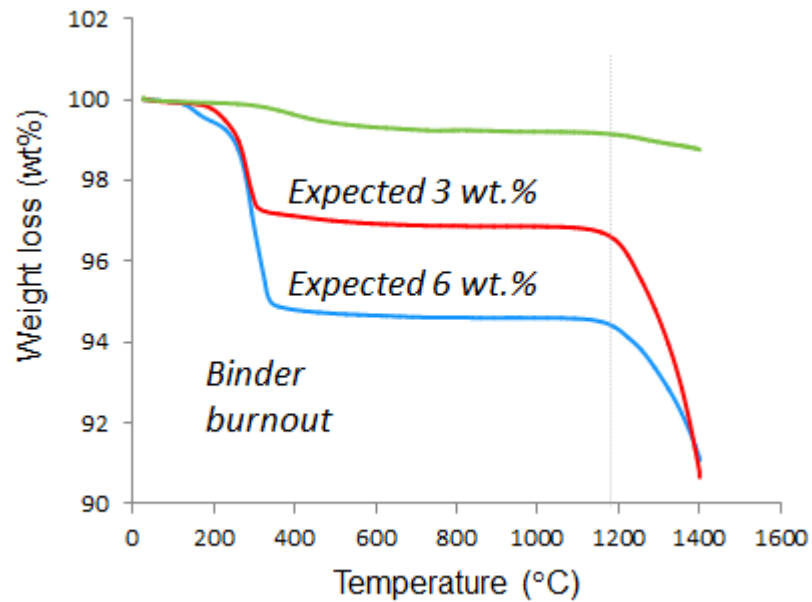
XRD: BaSO<sub>4</sub>  
Pbnm



Optical dilatometry



# NiO - BaSO<sub>4</sub>, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>

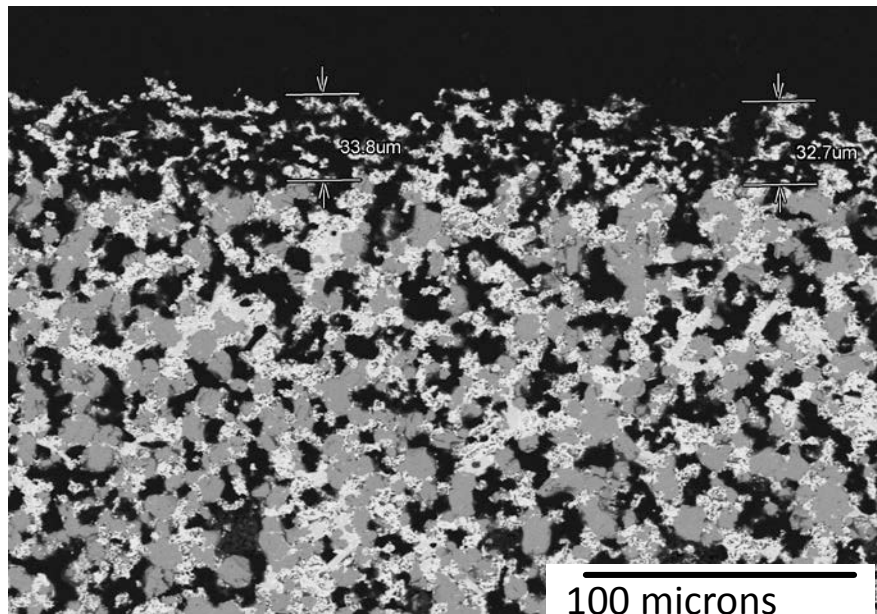


SSRS mixture BZY10-NiO

SSRS mixture BZCY72-NiO

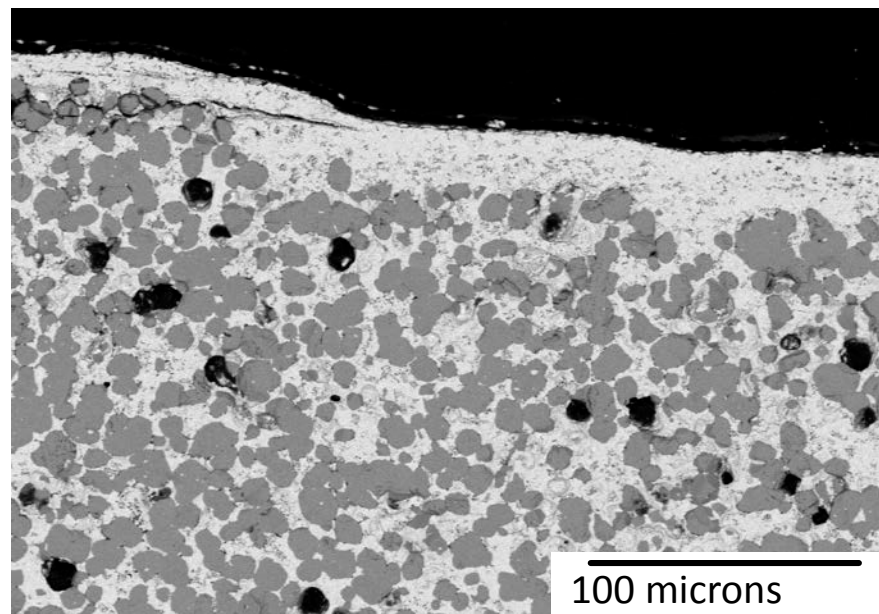
BaSO<sub>4</sub> powder

Heating to 1600°C @ 2°C/min - 10 min dwell



BZY10 // BZY10-NiO

*NiO ensures mechanical strength*



BZCY72 // BZCY72-NiO

*BZCY72+NiO ensure mechanical strength*

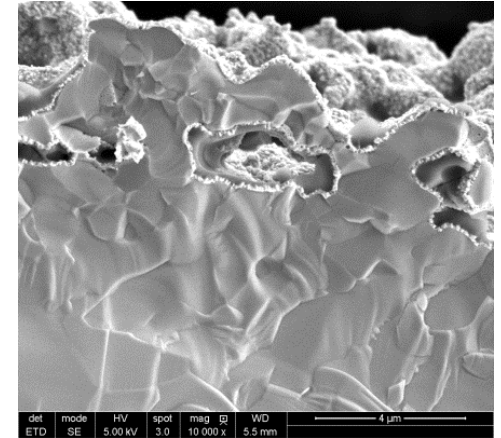
# Summary

- Sintering of BZY10 electrolyte not yet achieved
  - Further experiments in progress to understand limiting factors
- Successful fabrication of tubular half-cells with BCZY based electrolytes (20%Ce; 2%Ce)
  - Samples are given for air electrode development



*Presentation Einar Vøllestad A8.03*

*Cross-section view of air electrode*





# Acknowledgements



The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621244.

Research Council of Norway for the BIOPCFC project (number 219731/O70)



The Research Council of Norway

## My colleagues at ELECTRA:

Dr. Dustin Beeff (CoorsTek Membrane Sciences)

Prof. Truls Norby (UiO)

Ragnar Strandbakke (UiO)

Dr. Anna Magraso (UiO, CSIC)

