N-INNER meeting, 5 February 2013

Next generation fuel cell materials (nextgenFCmat)

Per Martin Rørvik

SINTEF Materials and Chemistry, Oslo, Norway

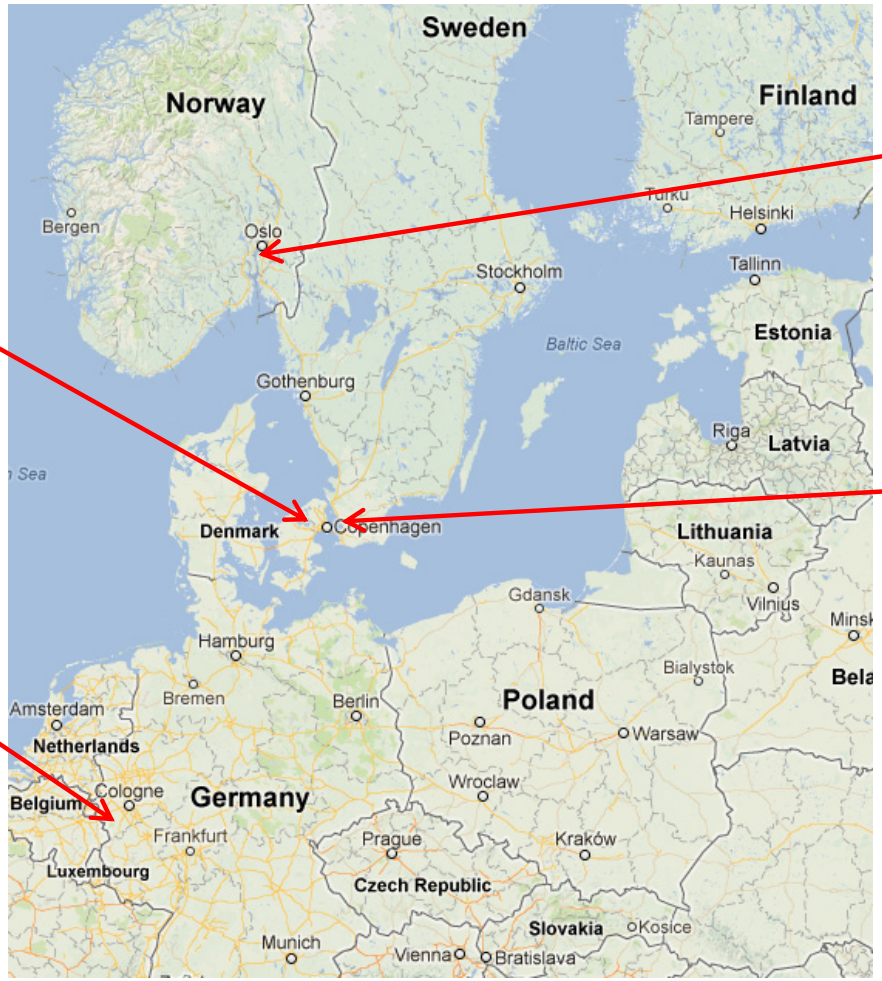
1. Overview of project participants

DTU National Laboratory for Sustainable Energy

Dr. Nikolaos Bonanos
Dr. Sandrine Ricote

RWTH AACHEN UNIVERSITY

Dr. Theodor Schneller
PhD stud. David Griesche



SINTEF

Dr. Camilla Haavik
Dr. Per Martin Rørvik

LUND UNIVERSITY

Prof. Reine Wallenberg
PhD stud. Filip Lenrick

2. Project budget

- Total and with an overview of external funding from other sources

Partner	N-INNER funding	External funding	Total
SINTEF	370 380	0	370 380
DTU	246 000	0	246 000
Lund	242 960	59 040	302 000
RWTH	219 196	0	219 196
Total	**1 078 536**	**59 040**	**1 137 576**

3. Project organisation

- Project coordinator: Camilla Haavik (from September 2011 Per Martin Rørvik)
- 4 work packages
  - WP1: Thin film fabrication (RWTH, SINTEF, DTU)
  - WP2: Structural/microstructural characterization (advanced: LU, basic: all)
  - WP3: Electrochemical characterization and modelling (DTU, SINTEF, RWTH)
  - WP4: Project co-ordination (SINTEF) and dissemination (all)
- 5 face-to-face meetings held so far (Oslo, Risø, Lund, Grenoble, Aachen)
- Final meeting in June
- Telephone/Skype meetings in between

4. Project progress and possible deviations

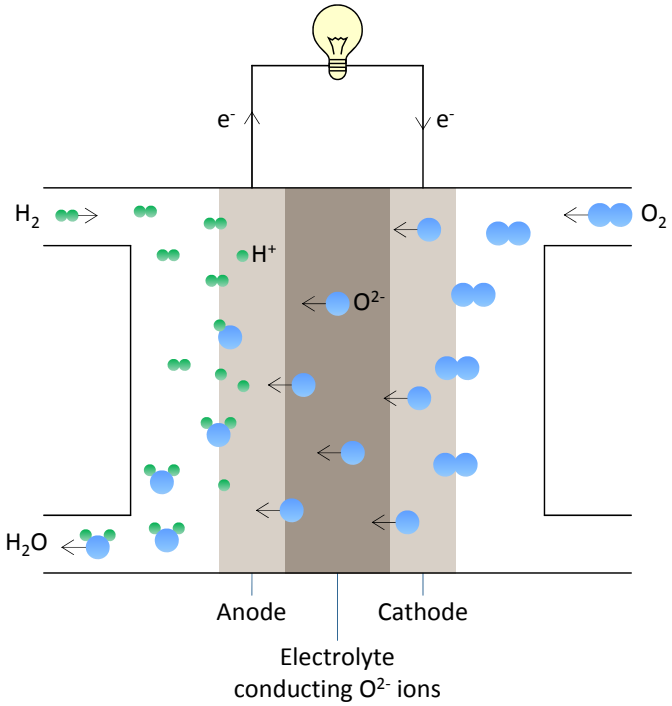
- The project started July 1st, 2010
  - Later start than planned due to funding issues
- The project ends June 31st, 2013
  - RWTH: 31st April (has applied for extension until June 31st)
  - Lund: has applied for extension due to PhD student start-up in 2011

- Two post docs started in 2010
- Two PhD students started in early 2011
  - Will finish in 2016

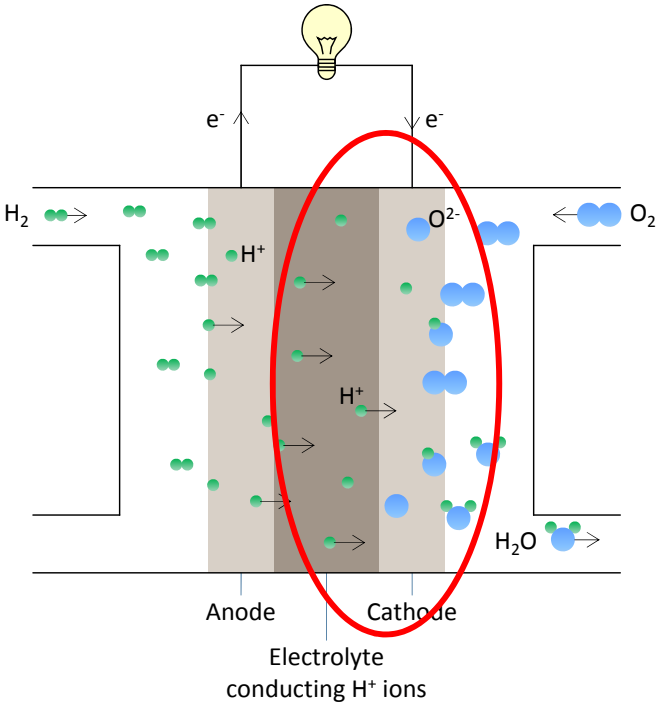
5. Scientific findings and uniqueness of the project

- Fuel cells are technology for efficient and clean conversion of chemical energy into electricity and heat

Solid Oxide Fuel Cell (SOFC)



Protonic Ceramic Fuel Cell (PCFC)



- The main innovative elements of nextgenFCmat are:
  1. The use of proton conducting ceramic electrolytes instead of the conventional oxygen ion-conducting ones
  2. Fabrication of genuine thin films instead of thick films
  3. The use of “gentle” fabrication methods for ceramic fuel cell materials

- This will facilitate the development of fuel cells with **low weight**, **compact design** and **low cost** that can operate at **low temperature**

Cathode microstructure and performance

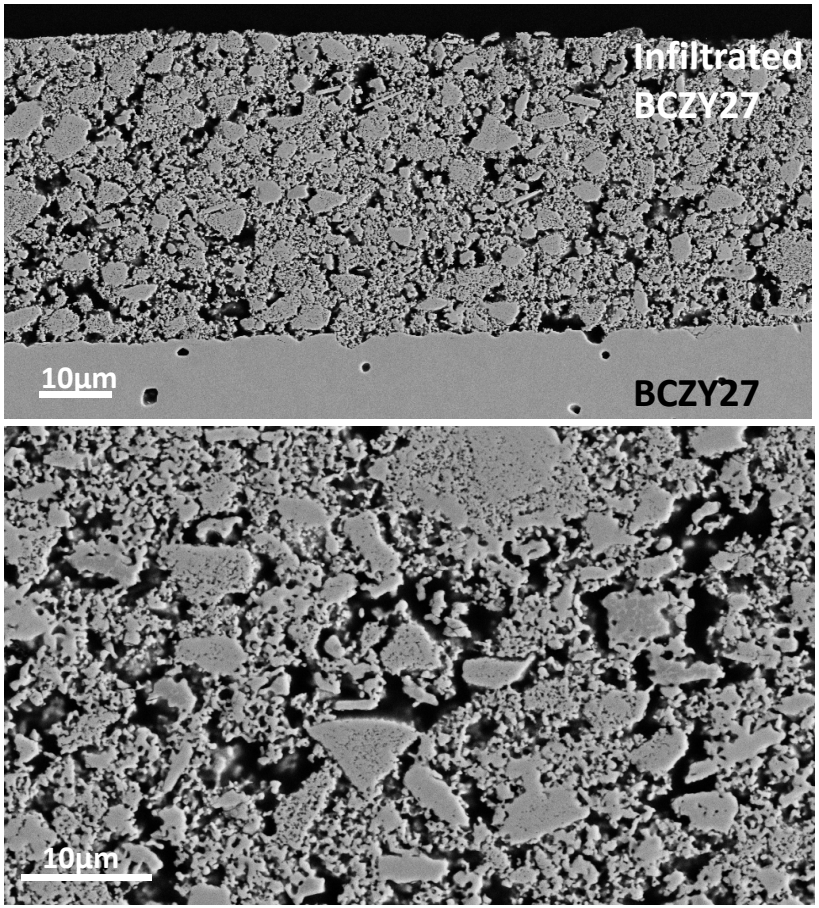
- Study of how the cathode microstructure and interface towards the electrolyte phase affects the performance
  - Spray pyrolysis of cathode
  - Infiltration of cathode
- Choice of materials
  - $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_3$ (BCZY27) is a good and stable proton conductor
  - $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) is a good oxide ion and electron conductor

- Published in *Journal of Power Sources* (S. Ricote *et al.*, 2012, vol. 209, p. 172-179)

LSCF cathode: microstructure

Infiltration:

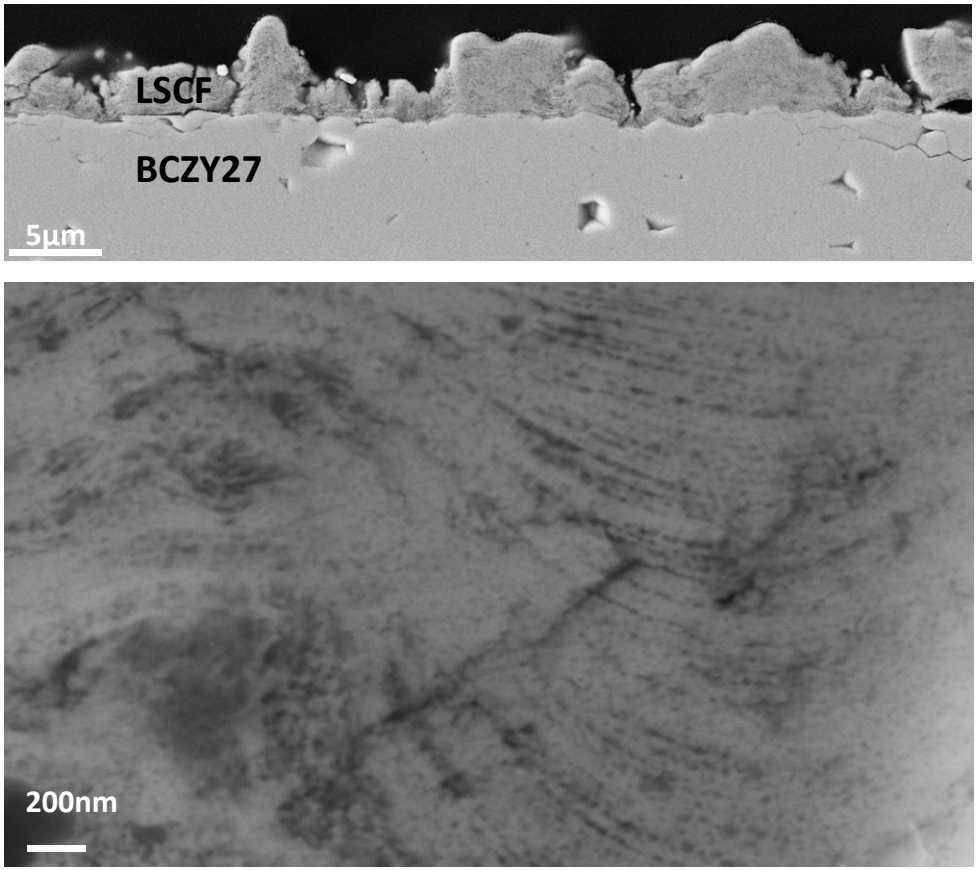
-Thickness cathode: 30-40 microns



- Porosity: 35 ± 2%
- **Micro-scale pores**

Spray pyrolysis:

- Thickness cathode: 2-5 microns

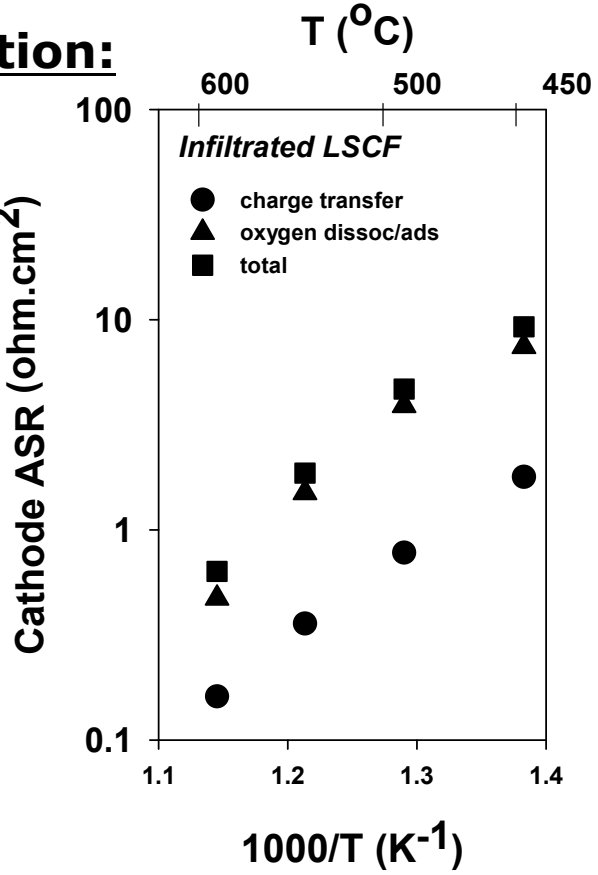


-Porosity: 37 ± 5%

- **Nano-scale pores**

LSCF cathode: AC spectroscopy

Infiltration:

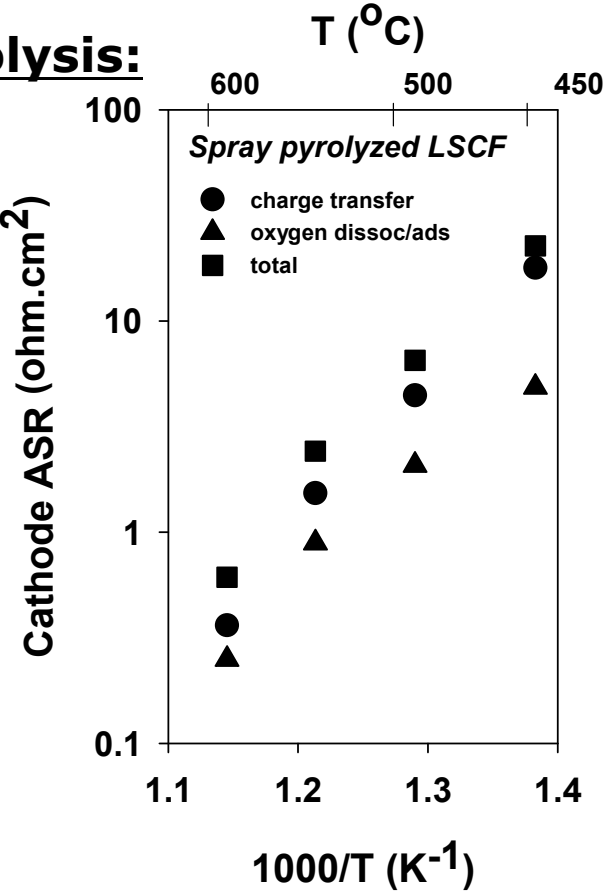


- Limited by oxygen ads./dissoc.

ASR 600ºC air, pH_2O=0.001atm:

Rp = 0.63 Ω·cm²

Spray pyrolysis:



- Limited by charge transfer

ASR 600ºC air, pH_2O=0.001atm:

Rp = 0.61 Ω·cm²

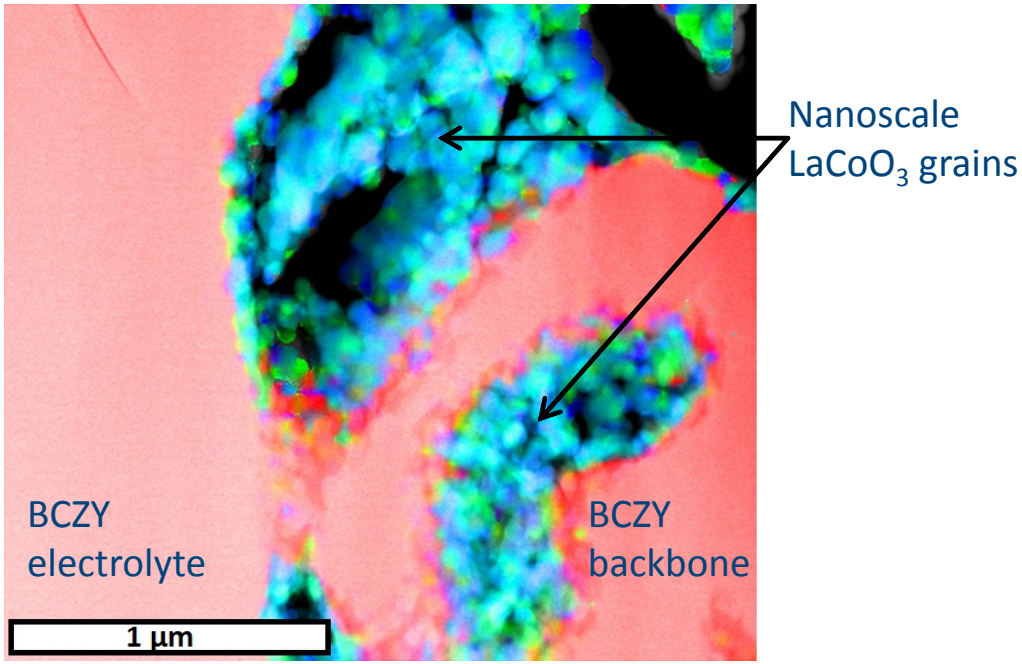
Performance of the cathode: highly dependent on the microstructure

Lowest values reported for LSCF

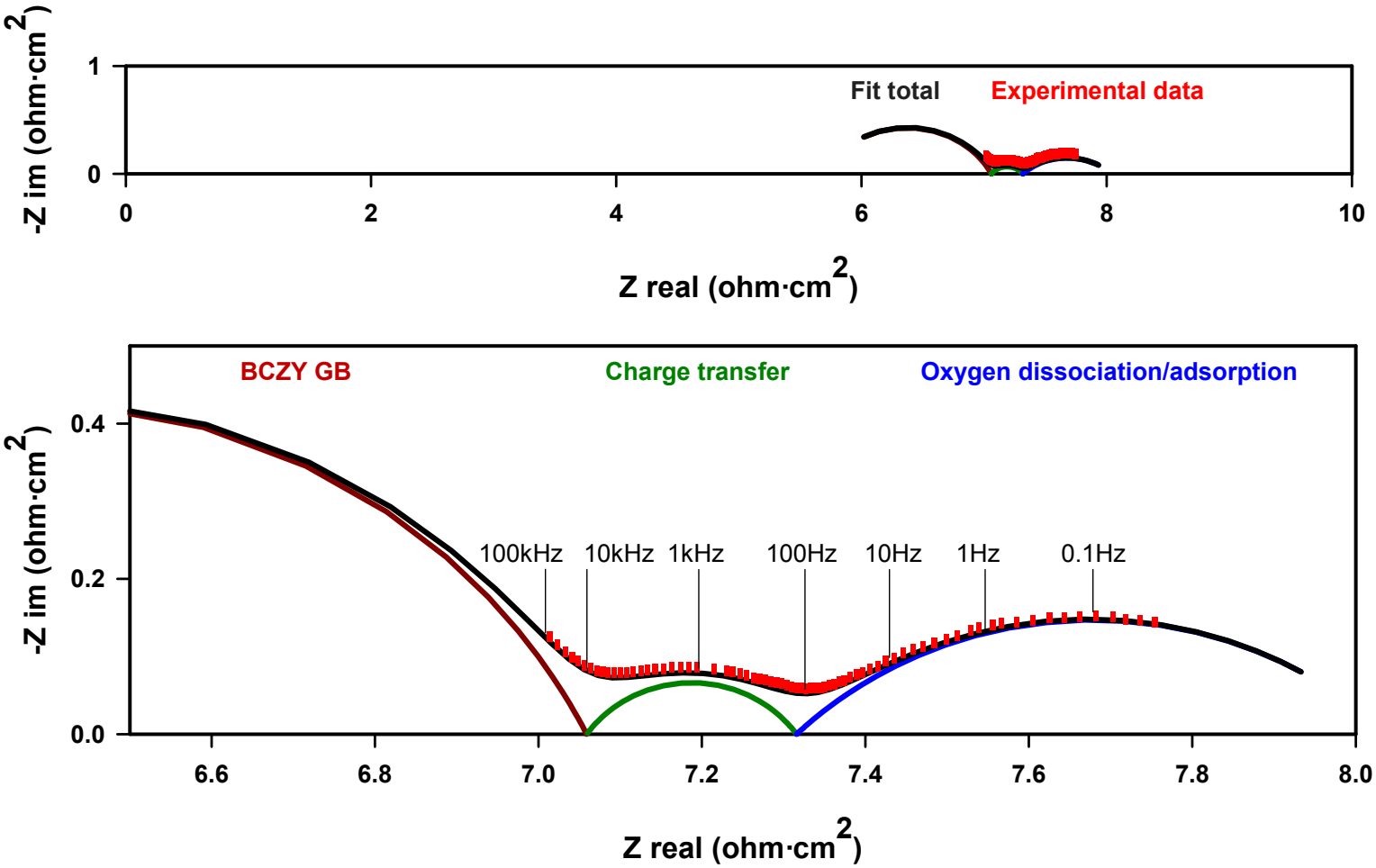
Improvement of cathode performance

- Infiltration of $LaCoO_3$ into $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_3$ backbone
- Results show that oxygen conduction is not necessary for the cathode process in a PCFC when infiltrating the cathode material
- Published in *Journal of Power Sources* (S. Ricote *et al.*, 2012, vol. 218, p. 313-319)

STEM-HAADF image combined with XEDS map



$LaCoO_3$ cathode: AC spectra



Spectrum in air, pH_2O=0.010 atm at 500ºC

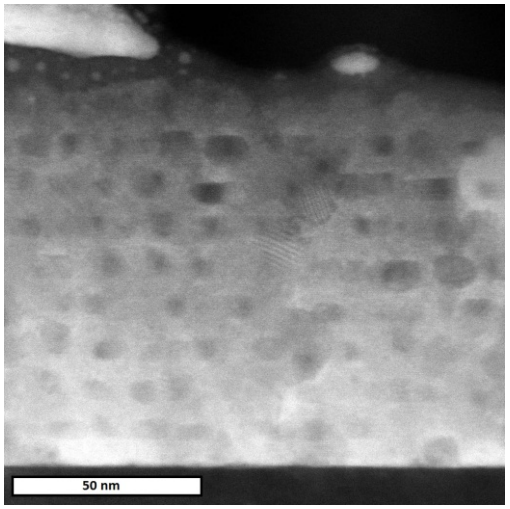
Rp=0.11 and 0.39 Ω·cm² at 600 and 500ºC in air, pH_2O=0.01 atm

Lowest values reported so far

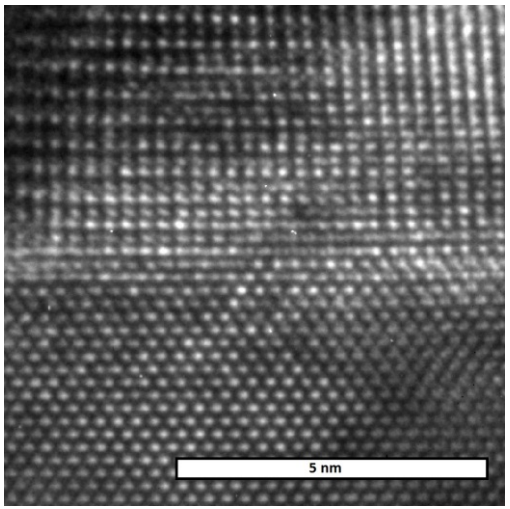
Electrolyte thin film – microstructure and interface

- By adjusting the deposition parameters thin electrolyte films with controlled thickness (100-600 nm) and microstructure were obtained
- The figures show a BZY film with epitaxial interface to the MgO substrate
- The film was monolithic and without grain boundaries

- Published in *ECS Transactions* (F. Lenrick *et al.*, 2012, vol. 45, p. 121-127)



$BaZr_{0.9}Y_{0.1}O_3$ electrolyte



$BaZr_{0.9}Y_{0.1}O_3$ electrolyte

Epitaxial interface

MgO substrate

6. Networks, co-operations, seminars and mobility

- Cooperation with other projects: only internally at the partner institutions
- No summer schools or international conferences have been arranged

- Mobility
  - Exchange of PhD students are planned (Lund ↔ Aachen)

7. Results

- PhD degrees
  - Two PhD students in progress, they will finish in 2016
- MSc degrees
  - 1 at Lund University
  - 2 at RWTH Aachen
- BSc degrees
  - 3 at RWTH Aachen
- Academic publications
  - 13 conference contributions (7 lectures, 6 posters)
  - 4 papers published
  - ~7 papers planned/in progress

8. Other publications / information activities (web, social media, television, daily press et cetera)

- A web site for the project has been established: http://www.sintef.no/Projectweb/nextgenFCmat/

- Lund: interview in local University paper to appear
- SINTEF: in contact with *International Innovation*

9. Patents

- None submitted

10. What did the N-INNER call do for the initiation of collaboration, research area and network, how will it move forward?

- The N-INNER call has been very useful in establishing collaboration between the North European partners and allowed us to do work we could not have done in FP7
- N-INNER is small but significant
- The project has been very fruitful in bringing together specialists in various fields working towards a common goal
- The consortium would like to continue the collaboration after the official project end
- The two PhD students are planned to finish in 2016 (three more years)
- New joint proposals will be prepared in appropriate calls
  - Structuring of cathode
  - Fabrication of full cell
  - Up-scaling to cm-scale (5×5 cm^2)

Acknowledgements

- Partners

DTU National Laboratory for Sustainable Energy

RWTH AACHEN UNIVERSITY

LUND UNIVERSITY

SINTEF

- Funding

INNER ERA-NET Innovative Energy Research

Danish Agency for Science, Technology and Innovation

norden Nordic Energy Research

The Research Council of Norway

Swedish Energy Agency

ptj Projektträger Jülich Forschungszentrum Jülich

Papers

- S. Ricote, N. Bonanos, A. Manerbino, W.G. Coors, *Conductivity study of dense $BaCe_xZr_{(0.9-x)}Y_{0.1}O_{(3-d)}$ prepared by solid state reactive sintering at 1500 °C*, International Journal of Hydrogen Energy, 2012, 37, 7954-7961
- S. Ricote, N. Bonanos, P.M. Rørvik, C. Haavik, *Microstructure and performance of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathodes deposited on $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ by infiltration and spray pyrolysis*, Journal of Power Sources, 2012, 209, 172-179
- S. Ricote, N. Bonanos, F. Lenrick, L.R. Wallenberg, *$LaCoO_3$: promising cathode material for protonic ceramic fuel cells based on a $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$ electrolyte*, Journal of Power Sources, 2012, 218, 313-319.
- F. Lenrick, D. Griesche, J.-W. Kim, T. Schneller, L.R. Wallenberg, *Electron microscopy study of single crystal $BaZr_{0.9}Y_{0.1}O_{3-x}$ films prepared by chemical solution deposition*, ECS Transactions, 2012, 45, 121-127.

Presentations

- P.M. Rørvik and C. Haavik, *Low-temperature deposition of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-d}$ thin film cathodes* [Poster], 7th Petite Workshop on the Defect Chemical Nature of Energy Materials, Storaas, Norway, March 14-17, 2011
- S. Ricote, N. Bonanos, R. Haugsrud, *Conductivity measurements on $BaCe_{(0.9-x)}Zr_xY_{0.1}O_{(3-d)}$ prepared using NiO as sintering aid* [Poster], 7th Petite Workshop on the Defect Chemical Nature of Energy Materials, Storaas, Norway, March 14-17, 2011
- P.M. Rørvik, Y. Larring, C. Haavik, *Cathode performance of spray pyrolysis-deposited $La_{1-x}Sr_xFe_{1-y-z}Co_yNi_zO_{3-d}$ thin films for micro-solid oxide fuel cells* [Lecture], 18th International Conference on Solid State Ionics, Warsaw, Poland, July 3-8, 2011
- J.-W. Kim, D. Griesche, T. Schneller, *Chemical solution deposition of proton conducting Y-doped $BaZrO_3$ thin films for low temperature operating solid oxide fuel cells* [Lecture], E-MRS 2011 Fall Meeting, Warsaw, Poland, September 19-23, 2011
- S. Ricote, N. Bonanos, P.M. Rørvik, C. Haavik, *Study of spray-pyrolyzed LSCF and BCZY27 porous backbone infiltrated with LSCF as cathode materials for Proton Ceramic Fuel Cells* [Poster], Prospects protonic ceramic cells 2011 – International Workshop on Protonic Ceramic Fuel Cell and Steam Electrolysis: Status and Prospects, Montpellier, France, November 3-4, 2011

Presentations continued

- T. Schneller, *Advanced chemical solution deposition methods of complex electronic oxide films* [Invited lecture], Electronic Materials and Applications 2012, Florida, USA, January 18-20, 2012
- F. Lenrick, D. Griesche, J.-W. Kim, T. Schneller, L.R. Wallenberg, *Electron microscopy study of single crystal $BaZr_{0.9}Y_{0.1}O_{3-x}$ films prepared by chemical solution deposition* [Lecture], The 8th International Symposium on Ionic and Mixed Conducting Ceramics, 221st Electrochemical Society Meeting, Seattle, USA, May 6-11, 2012
- S. Ricote, N. Bonanos, P.M. Rørvik, C. Haavik, *Performance of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ and $LaCoO_3$ cathodes deposited on $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$ by infiltration and spray pyrolysis* [Lecture], E-MRS Spring meeting, Strasbourg, France, May 14-18, 2012
- D. Griesche, T. Schneller, R. Waser, *Tailor-made complex oxide thin films as proton-conducting electrolytes for low temperature operating solid oxide fuel cells* [Poster], Frontiers in Electronic Materials: Correlation Effects and Memristive Phenomena, Aachen, Germany, June 17-20, 2012
- P. M. Rørvik, F. Lenrick, Y. Larring, L. R. Wallenberg, C. Haavik, *Cathode performance of spray pyrolysis-deposited $La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-d}$ and $La_{0.58}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3\,d}$* [Lecture], Electroceramics XIII, Enschede, Netherlands, June 24-27, 2012

Presentations continued

- S. Ricote, N. Bonanos, F. Lenrick, L. R. Wallenberg, A. Manerbino, G. Coors, *$LaCoO_3$: promising cathode material for protonic ceramic fuel cells based on a $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$ electrolyte* [Poster], Solid State Protonic Conductors 16, Grenoble, France, September 10-14, 2012
- P. M. Rørvik, F. Lenrick, L. R. Wallenberg, C. Haavik, *Chemical solution deposition of $La_{28-x}W_{4+x}O_{54+d}$ thin films* [Poster], Solid State Protonic Conductors 16, Grenoble, France, September 10-14, 2012
- S. Ricote, N. Bonanos, P. M. Rørvik, C. Haavik, F. Lenrick, L. R. Wallenberg, *Performance of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ and $LaCoO_3$ cathodes deposited by infiltration and spray pyrolysis on $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$* [Lecture], Solid State Protonic Conductors 16, Grenoble, France, September 10-14, 2012