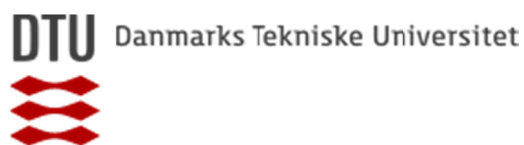Final report for N-INNER II

Next generation fuel cell materials (nextgenFCmat)

August 2013

Per Martin Rørvik, Filip Lenrick, L. Reine Wallenberg, David Griesche, Theodor Schneller, Nikolaos Bonanos

Participants:

SINTEF Materials and Chemistry, Oslo, Norway (coordinator)
Principal investigator: Dr. Camilla Haavik
Employed as temporary Research Scientist: Dr. Per Martin Rørvik

Lund University, Centre for analysis and synthesis / nCHREM, Lund, Sweden
Principal investigator: Prof. L. Reine Wallenberg
Employed as PhD student: Filip Lenrick

Technical University of Denmark, Department of Energy Conversion and Storage, Roskilde, Denmark
Principal investigator: Dr. Nikolaos Bonanos
Employed as temporary Research Scientist: Dr. Sandrine Ricote

RWTH Aachen, Institut für Werkstoffe der Elektrotechnik II, Aachen, Germany
Principal investigator: Dr. Theodor Schneller
Employed as PhD student: David Griesche

Steering committee: Rune Bredesen (SINTEF), Reine Wallenberg (Lund), Nikolaos Bonanos (DTU), and Theodor Schneller (RWTH)

Next generation fuel cell materials (nextgenFCmat)

Per Martin Rørvik [a], Camilla Haavik [a], David Griesche [b], Theodor Schneller [b], Filip Lenrick [c], L. Reine Wallenberg [c], Sandrine Ricote [d], and Nikolaos Bonanos [d]

[a] SINTEF Materials and Chemistry, Box 124 Blindern, 0314 Oslo, Norway
[b] Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen University, D52056 Aachen, Germany
[c] Centre for analysis and synthesis / nCHREM, Lund University, Box 124, S-221 00 Lund, Sweden
[d] Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Abstract

The main objective of this project has been to develop high-performance ceramic electrolytes and cathodes for low temperature (400-600 °C) fuel cell operation. To go beyond the state-of-the-art solid oxide fuel cells (SOFC) and to lower the operation temperature we have exchanged the oxide ion-conducting electrolyte of the SOFC with a proton-conducting electrolyte to make a protonic ceramic fuel cell (PCFC). To increase the performance it is also necessary to reduce the electrolyte thickness and develop novel cathodes; in this project chemical solution deposition has been used to make genuine thin films with nanoscale features. Advanced electron microscopy techniques have been used to study the crystallinity, morphology, interfaces and nanoscale features of the thin films. Electrochemical impedance spectroscopy was used for components' performance characterization.

As electrolytes $BaZr_{1-x}Y_xO_{3-\delta}$ (BZY) and $La_{28-x}W_{4+x}O_{54+\delta}$ (LWO) were deposited onto various substrates (single-crystalline MgO, platinized Si, and cermet anode) to study the effect of epitaxy and to measure in-plane and through-plane conductivity. For the cathode part several routes were pursued; air-blast spray pyrolysis, infiltration into porous backbone, ink-jet printing and spin coating. The best performance was obtained with $LaCoO_3$ infiltrated into a porous $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY) backbone – the obtained area specific resistance of 0.11 Ω cm^2 at 600 °C in air (p_{H2O} = 0.01 atm) is the lowest reported ASR for any PCFC cathode.

All in all, the project has shown the promise of using chemical solution deposition methods for deposition of high-performance materials for the next generation of protonic ceramic fuel cells.

Executive summary

Small fuel cell systems in the 1–100 kW power range have become the focus of intense research and development. Among the potential applications for fuel cells in this power range are propulsion for passenger and light-duty vehicles (50–100 kW), auxiliary power (APU) for trucks, automobiles and recreational vehicles (2–10 kW), and portable power generation for residential and recreational needs (3–5 kW). The operating mode of these systems differs significantly from that of larger fuel cell systems. The requirements on these fuel cells include low weight, compact design and low cost. Due to its very high energy density, the SOFC may fulfil these requirements. Compared to other types of fuel cells, they also offer high fuel flexibility: they can run on hydrogen, but also on reformed natural gas and liquid fuels, including diesel. There is one major disadvantage with such systems: the operating temperature is usually 750 °C or above. To make small and compact fuel cells and to lower the cost, this temperature must be reduced. To achieve lower operation temperatures significant improvements of the electrolyte, the electrodes and interfaces are necessary.

In the present project, "Next generation fuel cell materials" (nextgenFCmat), four partners with complementary expertise have come together to develop new fabrication methods for fuel cells: SINTEF Materials and Chemistry (Norway, coordinator), Lund University (Sweden), Technical University of Denmark (DTU, Denmark), and RWTH Aachen (Germany). The project was granted through the second call of the Northern European Innovative Energy Research Programme (N-INNER II).

The main objective of nextgenFCmat has been to facilitate the development of fuel cells with low weight, compact design and low cost. The focus has been on developing high-performance ceramic electrolytes and cathodes for low temperature (400-600 °C) fuel cell operation. To go beyond the state-of-the-art solid oxide fuel cells (SOFC) and to lower the operation temperature we have exchanged the oxide ion-conducting electrolyte of the SOFC with a proton-conducting electrolyte to make a protonic ceramic fuel cell (PCFC). To increase the performance it is also necessary to reduce the electrolyte thickness and develop novel cathodes; in this project chemical solution deposition has been used to make genuine thin films with nanoscale features.

Basic characterization such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) has been done by all partners, while Lund has had responsibility for the advanced characterization by transmission electron microscopy (TEM) and related techniques to study interfaces and nanoscale features. SINTEF, DTU, and RWTH have used electrochemical impedance spectroscopy (EIS) for characterization of the conductivity of the electrolytes and the resistance of the cathodes.

As electrolytes $BaZr_{1-x}Y_xO_{3-\delta}$ (BZY) and $La_{28-x}W_{4+x}O_{54+\delta}$ (LWO) have been deposited onto various dense substrates (single-crystalline MgO, platinized Si, and composite anode ($BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY27) 35 wt% - NiO 65 wt%)) to study the effect of epitaxy and to be able to measure in-plane and through-plane conductivity. BZY films with controllable thickness in the 20-800 nm range was successfully deposited on all substrates from a propionic acid-based solution. On MgO, the films were single-crystalline with epitaxial relation to MgO while on platinized Si and cermet columnar grain growth could be obtained. The BZY films contain some porosity between the deposited layers. At MgO these pores were highly oriented, while on the composite anode a more gradual porosity was observed. Besides spin coating BZY films have also been made by ink-jet printing which allows better deposition

control and less solution consumption. For the LWO films it was challenging to obtain dense films without excessive grain growth and pore formation.

Through-plane conductivity measurements of the electrolyte thin films deposited on platinized Si were hampered by pin hole formation in all of the films studied. In-plane conductivity measurements of BZY films deposited on insulating MgO have been successful and show clear difference between dry and wet atmosphere, demonstrating protonic conductivity.

For the cathode part several routes were pursued. $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode films with nanoscale grains and porosity were deposited by air-blast spray pyrolysis and an area-specific resistance (ASR) of 0.61 Ω cm^2 was obtained at 600 °C in dry air measured in a symmetrical cell with $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY) as electrolyte. LSCF was also infiltrated into a porous BCZY backbone to achieve a composite cathode; the resulting ASR was similar to the spray-pyrolyzed cathode. Interestingly, when LSCF was exchanged with $LaCoO_3$ the ASR of the infiltrated cathode was lowered to 0.11 Ω cm^2 at 600 °C in air (p_{H2O} = 0.01 atm) which is the lowest reported ASR for any PCFC cathode and indicates that oxide ion conductivity is less necessary in a nanoscaled PCFC cathode with a high number of triple phase boundaries. Finally, LSCF and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) thin film cathodes have been deposited by spin coating.

All in all, the project has shown the promise of using chemical solution deposition methods for deposition of high-performance materials for the next generation of protonic ceramic fuel cells. These methods allow thinner films to be made compared to, for example, screen printing techniques. In addition, the processing temperature is significantly lowered compared to traditional powder-based methods. By this, nanoscale structuring of the cathode and the use of cheaper support materials such as steel can be utilized to make better and cheaper fuel cells for the future. The next step will be to fabricate a model full fuel cell for testing the thin films' performance and stability under operational fuel cell conditions.

The collaboration between the four partners has been fruitful and there is a desire to continue the work that has started. During the last part of the project no suitable call with all four countries and within a relevant topic has been announced to our awareness. At the current stage the most likely outcome is for the partners to acquire financing from national sources and continue in a more informal collaboration. Possibilities within EU calls, M.Era-Net calls, and similar will be investigated, as well as industry collaboration.

The present project has educated three Bachelors, three Masters and two PhDs, while two post docs/ research scientists have been given the opportunity to develop their skills. Both PhDs are planned to be defended in 2016 due to late start (2011) and 5 years PhD period in Sweden and Germany. Results from the project have been, and will be, actively presented to the international scientific community. So far this has resulted in and will result in (based on working titles) 17 presentations at international conferences and 12 publications in peer-reviewed international journals, books, etc.

These types of Nordic collaborative projects are very good in order to create synergies of the cooperation of Nordic research institutions (and industry) with various unique competences. Such projects also facilitate the spread of leading international knowledge between the Nordic partners

and to the next generation of Nordic scientists within the field. All authors of this report believe that these types of projects should continue to be funded.

Table of contents

1.   Introduction

1.1   Background

Small fuel cell systems in the 1–100 kW power range have become the focus of intense research and development. Among the potential applications for fuel cells in this power range are propulsion for passenger and light-duty vehicles (50–100 kW), auxiliary power (APU) for trucks, automobiles and recreational vehicles (2–10 kW), and portable power generation for residential and recreational needs (3–5 kW). The operating mode of these systems differs significantly from that of larger fuel cell systems. The requirements on these fuel cells include low weight, compact design and low cost. Due to its very high energy density, the solid oxide fuel cell (SOFC) may fulfill these requirements. Compared to other types of fuel cells, they also offer high fuel flexibility: they can run on hydrogen, but also on reformed natural gas and liquid fuels, including diesel. There is one major disadvantage with such systems: the operating temperature is usually 750 °C or above. To make small and compact fuel cells and to lower the cost, this temperature must be reduced.

The SOFC consists of electrodes (cathode and anode) and an electrolyte. The performance of the SOFC depends on:

1)   The electrodes' ability to "react" with the gaseous species (catalytic activity)
2)   The electrodes', electrolyte's and interface layers' ability to transport ions and electrons

The transport of ions through the electrolyte is a temperature-activated process. It normally drops to an unacceptable level at low operation temperature. The same is true for the catalytic activity of the electrodes. The interfaces between the electrolyte and electrodes often suffer from detrimental inter-diffusion caused by high fabrication temperature. Significant improvements of the electrolyte, the electrodes and the interfaces are necessary to reduce the operating temperature of the fuel cell.

1.2   Prospects and objectives of the nextgenFCmat project

The main objective of the "Next generation fuel cell materials" (nextgenFCmat) project has been to facilitate the development of fuel cells with low weight, compact design and low cost. This can be accomplished by:

1)   Developing high performance ceramic electrolytes for low temperature (400-600 °C) operation
2)   Developing high performance cathodes for low temperature (400-600 °C) operation
3)   Increasing our knowledge and understanding of the processing and electrochemical behaviour of true thin film electrolytes, cathodes and interfaces in SOFC/PCFCs

To obtain high performance electrolytes at low temperature it is necessary to develop materials with much higher ionic conductivity, or to make the electrolyte even thinner than today, or preferably a combination of the two. In nextgenFCmat we have exchanged the state-of-the-art SOFC electrolyte with a *proton-conducting* one to make a *protonic ceramic fuel cell (PCFC)* to increase the conductivity at intermediate temperatures, *and* we have reduced the thickness of the electrolyte layer. State-of-the-art SOFC electrolytes are 10-20 μm thick. They are produced by powder processing or by thick film techniques, such as tape-casting. To reduce the ohmic loss the thickness of the electrolyte has to be reduced, and in nextgenFCmat we have used genuine thin film techniques. Such techniques are

well known from the semi-conductor industry and are used to process high quality metal-oxide thin films for a range of applications.

For the cathodes, the idea of nextgenFCmat has been to develop cathode materials with high chemical diffusion and oxygen exchange coefficients to achieve efficient low temperature fuel cells. PCFC electrolytes are currently at a less advanced state than the SOFC electrolytes. The same is true for the PCFC electrodes. In nextgenFCmat we have focused on the cathode in addition to the electrolyte. High performance PCFC cathodes are lacking completely as there are no (or very few) materials that exhibit good protonic conductivity, good electronic conductivity and high activity for oxygen dissociation. In nextgenFCmat, we have worked on developing high performance (high chemical diffusion and oxygen exchange coefficient) thin film cathodes based on promising perovskite type materials (BSCF/LSCF/LaCoO$_3$). A full fuel cell has been beyond the ambitions of nextgenFCmat, we have focused on the electrolyte, the cathode and the interfaces between them.

The use of genuine thin film technology will reduce the thickness of the individual layers and in turn reduce the ohmic loss. In addition, the thin film techniques also lower the sintering temperatures during processing and might, in the extreme case, remove the need of sintering entirely. This could lead to electrolyte-electrode assemblies with substantially higher performance, as the interfaces between electrolyte and electrodes suffer much less damage due to reaction and thermal expansion differences during processing. The use of thin film techniques also opens up a totally new range of possibilities for "nano-engineering" of the materials including possibilities for introducing fast ion-conducting interfaces. In nextgenFCmat extensive structural/microstructural and electrochemical characterization have been used to increase our possibility to understand and thereby control the crucial processes at the "nano"-level.

1.3   Relevance and value added to stakeholders in the energy sector

Due to their high energy efficiency, a wide implementation of fuel cells will contribute to low CO$_2$ emissions. Use of fuel cells in urban areas will improve air quality and the health of the world's growing urban population. Relative to other fuel cell technologies, SOFCs and PCFCs offer high energy density due to the possible use of hydrocarbon fuels. They can use fuels that are widely available and easy to transport. This fuel flexibility will offer an important contribution to the stability of the energy sector worldwide. The technology will also offer essential components for any future hydrogen economy.

For many of the promising applications of SOFC/PCFCs there are still research and development issues that need to be solved, many of them related to the cost of materials caused by the high operating temperature. The contribution of nextgenFCmat; to provide materials that will ease development of low temperature operation will open up possibilities for introducing SOFC/PCFCs to new markets.

One promising market is APUs for parked long-haul trucks. Other – and even larger – markets with similar requirements are fuel cells for car propulsion and portable power generation units.

nextgenFCmat is focused on materials for compact fuel cells and is relevant also to is small combined heat and power units for buildings, industries, off-shore installations, and small communities. PCFCs, in particular, offer unique energy efficiency (no fuel dilution) and a simple balance of plant. PCFC modules are also well suited for small- and medium-sized power plants running on highly reformed

fossil fuels, like natural gas, coal gas, propane etc., and reformed biofuels. If the full potential for PCFCs is obtained for this latter application it would mean enormous savings on fuel usage and CO_2 reduction compared to other fuel cell technologies (PEMFC and conventional SOFC).

1.4   Choice of materials

1.4.1   Electrolytes

Yttrium-doped barium zirconate, $BaZr_{1-x}Y_xO_{3-\delta}$ (BZY) is a good proton conductor and is stable towards CO_2, and has become one of the most promising ceramic proton conductors for fuel cell and electrolyser use. In this project BZY has been used for thin electrolyte films made by chemical solution deposition. A challenge with BZY is the high grain boundary resistance. A previous study from RWTH was used as starting point.[1]

Cerium can be added to increase the conductivity of BZY while maintaining stability. For instance, $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-d}$ (BCZY27) is a good and stable proton conductor that combines the stability of BZY with the higher conductivity of the barium cerates. Here we have used BCZY27 as electrolyte in the symmetrical cell tests and as cathode backbone for infiltration.

As an alternative to the barium-containing conductors, $La_{28-x}W_{4+x}O_{54+\delta}$ (LWO) has also been studied. In LWO, the grain boundary resistance is much lower than for BZY.

1.4.2   Cathodes

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) is a good oxide ion and electron conductor and is one of the standard cathode materials for SOFCs. Therefore it was of interest to also study this material for PCFC. The lanthanum deficiency (0.58 instead of 0.60) has been used to increase the number of oxygen vacancies and to reduce the possibility of $SrCO_3$ formation.

$LaCoO_3$ was used as an alternative to LSCF to investigate whether oxide ion conductivity really is necessary in a nanoscaled PCFC cathode with a high number of triple phase boundaries. $LaCoO_3$ is a good electron conductor and has oxygen splitting catalytic properties due to the presence of cobalt.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) has also been investigated briefly as cathode. The material has high oxygen diffusion but is thermodynamically unstable at intermediate temperatures.

1.4.3   Substrates

Single-crystalline MgO was used for deposition of electrolyte thin films onto an insulating substrate, for in-plane conductivity measurements. Also, the crystal lattices of MgO and BZY match well, so epitaxial growth of BZY can be achieved on MgO.

Platinized silicon wafers ($Pt/TiO_x/SiO_2/Si$ or $Pt/AlO_x/SiO_2/Si$) were used for deposition of electrolyte thin films onto a conducting substrate, for through-plane conductivity measurements.

For deposition of electrolyte thin films onto a realistic anode, composite anodes composed of 35 wt% $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY27) and 65 wt% NiO were used. These anodes were sintered disks that were polished before deposition. The anodes are dense during deposition but subsequent heat treatment

---

[1] T. Schneller and T. Schober, *Chemical solution deposition prepared dense proton conducting Y-doped BaZrO₃ thin films for SOFC and sensor devices*, Solid State Ionics, 2003, 164, 131-136.

in H_2/Ar at elevated temperature induces porosity due to reduction of the NiO to metallic Ni. The anodes were supplied by CoorsTek.

BCZY27 sintered disks were used as substrate (and electrolyte) for the symmetrical cell test of LSCF and $LaCoO_3$ cathodes.

For the spray pyrolysis deposition of LSCF, single-crystalline yttria-doped zirconia (YSZ) substrates were also used as substrate, in addition to BCZY27.

2. Methodology and experimental procedure

Functional ceramic thin films can be prepared by a number of physical and chemical deposition methods. Among these methods, chemical solution deposition (CSD) has specific advantages such as the possibility to coat large area substrates, excellent stoichiometry control and flexibility with regard to composition variations as well as coating technique (spin-, dip-, and spray coating/pyrolysis). Since it is a non-vacuum method, the investment costs of the CSD technology are lower by one to two orders of magnitude, which makes it ideally suitable for the study of new materials in thin film form, small series production, and for small and medium-sized enterprises.

The chemistry of the precursors and their solutions has large impact on the quality of the resulting CSD-derived thin films. On the other hand, this influence together with the thermal processing (atmosphere, heating ramp etc.) enables the tailored modification of the final film properties (microstructure, orientation, density). Even highly textured and epitaxial film growth, respectively, could be achieved on lattice matched substrates.

In the following, the deposition methods and characterization methods that have been used are summarized.

2.1 Deposition methods

2.1.1 Spin coating

For $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY) electrolyte thin films a propionic acid-based solution was used. The preparation of the optimized precursor solution consists of two main steps, first stoichiometric amounts of $BaCO_3$ and $Y(OOCCH_3)_3 \cdot 4\,H_2O$ were dissolved at elevated temperature in a mixture of propionic acid and propionic acid anhydride. The propionic acid anhydride was added to remove the water of constitution of the $Y(OOCCH_3)_3 \cdot 4\,H_2O$. In the second step $Zr(OCH_2CH_2CH_2CH_3)_4 \cdot HOCH_2CH_2CH_2CH_3$ was diluted with anhydrous n-butanol and stabilized with an equimolar amount of acetylacetone. The two solutions were mixed and filled up to reach an A cation concentration of 0.3 mol/L in the final precursor stock solution.

The deposition was performed by spin coating onto single crystalline MgO(100), platinized Si substrates ($Pt/AlO_x/SiO_2/Si$), wet oxidized Si substrates (Si/SiO_2) or composite anodes ($BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY27) 35 wt% - NiO 65 wt%, supplied by CoorsTek) followed by a one-step thermal treatment in a diffusion furnace after each deposition cycle at temperatures of 800-1000 °C.

For $La_{28-x}W_{4+x}O_{54+\delta}$ electrolyte thin films, aqueous La and W solutions were made stabilized with citric acid (CA) or ethylenediaminetetraacetic acid (EDTA). $La(NO_3)_3$ was dissolved in water followed by EDTA (or CA) addition and NH_4OH to obtain a neutral pH. WO_3 was dissolved in NH_4OH followed by EDTA (or CA) addition. The La and W solutions were mixed to obtain the desired La/W atomic ratio, typically La/W = 5.5 ($La_{5.5}WO_{11.25}$, LWO). The cation:EDTA(CA) molar ratio was 1:1 and the total salt concentration of the final solution was typically 0.45 $mol \cdot L^{-1}$ for the EDTA solution and typically 0.66 $mol \cdot L^{-1}$ for the CA solution.

The LWO electrolyte thin films were deposited by spin coating onto single-crystalline MgO or platinized Si wafers ($Pt/TiO_x/SiO_2/Si$ or $Pt/AlO_x/SiO_2/Si$), followed by pyrolysis on a hot plate and crystallization annealing in a muffle furnace or a rapid thermal annealing (RTA) furnace.

LSCF layers were also deposited by spin coating on different substrates. The aim of this part of the project was to fabricate porous layers with an adequate crystalline quality by a further alternative coating technique. At first a propionic acid route was developed. The acetates of lanthanum, strontium, and cobalt and the corresponding iron acetylacetonate salt were mixed in propionic acid and propionic acid anhydride in the desired stoichiometry. After refluxing the mixture, a dark brown solution resulted which was stable for more than six months. The solution was spun on platinized silicon substrates and oxidized silicon wafers and subsequently heat treated to induce crystallization in a diffusion furnace or an RTA furnace.

2.1.2 Spray pyrolysis

Spray pyrolysis is a simple and cost-effective technique for film deposition onto a flat sample in reasonable time. A solution is fed to a nozzle where it is atomized by air pressure, ultrasonic waves, or a high electric field. The spray is directed towards a heated substrate where the film is deposited. Usually the film will be amorphous and subsequent annealing is necessary for crystallization. In our work an *air blast* spray pyrolysis setup was used (Figure 1).
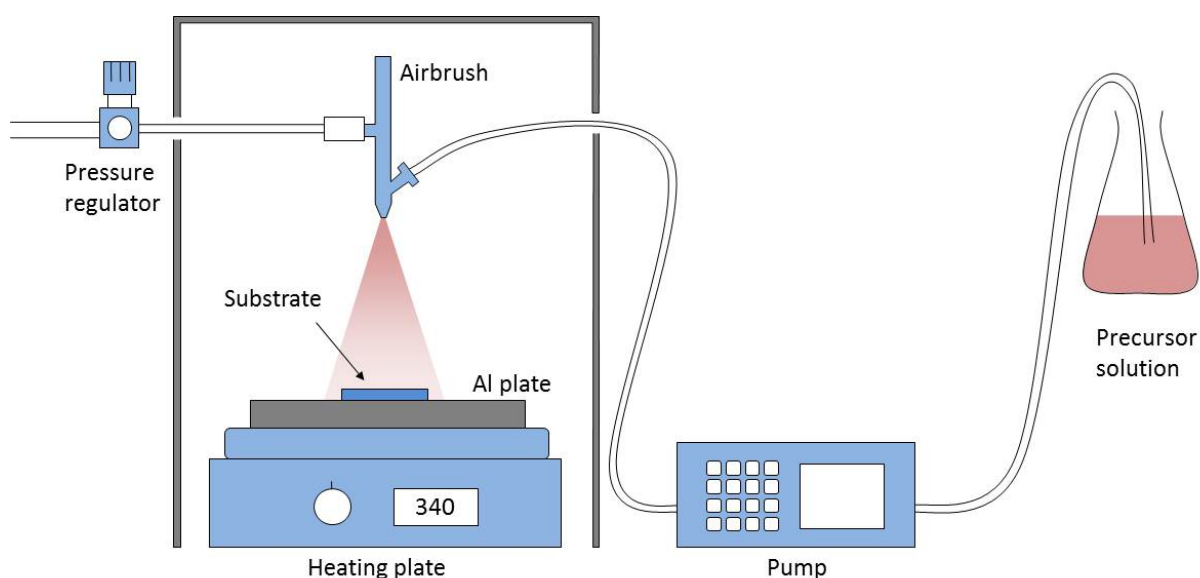

Figure 1. Schematic of the spray pyrolysis equipment used in the project.

The LSCF solution for spray pyrolysis (and infiltration) was made by dissolving $La(NO_3)_3 \cdot 6H_2O$ (Merck, p.a., >96%), $SrCl_2 \cdot 6H_2O$ (Fluka, >99%), $Co(NO_3)_2 \cdot 6H_2O$ (Fluka, >98%) and $Fe(NO_3)_3 \cdot 9H_2O$ (Merck, >99%) in molar ratio La:Sr:Co:Fe = 0.58:0.4:0.2:0.8 in a 1:1 volume mixture of absolute ethanol (Arcus) and diethylene glycol butyl ether (Aldrich, >99.2%) to give a 0.04 M total salt concentration.

LSCF thin films were deposited onto polished BCZY27 substrates or single-crystalline YSZ substrates by air blast spray pyrolysis. The solution was pumped (Merck Hitachi L-7110 isocratic pump, 0.5 mL min^{-1}) to an airbrush (Badger no. 150) where it was atomized by 1 bar air pressure and sprayed onto a heated substrate with surface temperature 240 $\pm$ 5 °C for 120 min. The distance between the airbrush nozzle and the substrate was 20.0 cm. For symmetric cells, the substrate was turned and the deposition was repeated after stabilization of the surface temperature. The samples were finally calcined at 700 °C for 2 h in air (100 °C h^{-1}) to crystallize and sinter the LSCF.

2.1.3 Infiltration

For many years, SOFC electrodes have been prepared using composites of electrode and electrolyte to increase the three phase boundary necessary for reaction. Until recently, composites were made by co-sintering, and these have performed relatively well. However, the advantages of infiltration as an alternative method are becoming increasingly apparent for both SOFC anodes, and cathodes.

The technique is simply to prepare a solution containing the required cations in the right ratio and to drop it into a porous backbone often, but not necessarily, of the same composition as the electrolyte. The sample is is then dried and calcined to decompose the soluble salt and form the active phase. The relatively low calcination temperatures minimize possible reactions and cation inter-diffusion. Furthermore, the nano-sized particles obtained frequently have better electrocatalytic properties than the bulk phase.

In this project, cathodes based on the lanthanum cobaltite system were prepared by infiltration and by spray pyrolysis. Specifically, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) was prepared by spray pyrolysis and infiltration of a LSCF solution similar to the one described for spray pyrolysis above into a backbone of BCZY,[2] while $LaCoO_3$ was prepared by infiltration only, from an aqueous solution.[3]

2.1.4 Ink-jet printing

For BZY layers prepared by ink-jet printing a Pixdro LP50 DOD (Drop-On-Demand) printer with a Spectra S-Class print head was used. The print head has 128 nozzles arranged in a distance of 508 μm between each other; it can be used with basic and acidic solvents. The head and the substrate holder can be aligned in five directions, so the x-,y- and z- directions in the Cartesian coordinate system can be defined as well as two angles.

Two different kinds of inks were studied. The first ink was made from the solution described in section 2.1.1, which had to be diluted with propionic acid to have a final A cation concentration of 0.15 mol/L. The second ink had an A cation concentration of 0.15 mol/L as well, but was a nanoparticle containing suspension prepared by reverse micelle polymerization known from the literature.[4] The optimal resolution of each printing process was found to be 500×500 dpi.

2.2 Characterization

2.2.1 Basic characterization

Basic microstructure characterization of the films was done by scanning electron microscopy (SEM, FEI Nova NanoSEM 650, FEI Quanta 200, Zeiss Supra 35, or FEI Nova NanoLab 600) by all partners.

---

[2] S. Ricote, N. Bonanos, P.M. Rørvik, and 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*, J. Power Sources, 2012, 209, 172-179.

[3] S. Ricote, N. Bonanos, F. Lenrick, and R. Wallenberg, *$LaCoO_3$: promising cathode material for protonic ceramic fuel cells based on a $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_3$ electrolyte*, J. Power Sources, 2012, 218, 313–319.

[4] T. Schneller, S. Halder, R. Waser, C. Pithan, J. Dornseiffer, Y. Shiratori, L. Houben, N. Vyshnavi, and S. B. Majumder, *Nanocomposite thin films for miniaturized multi-layer ceramic capacitors prepared from barium titanate nanoparticle based hybrid solutions*, J. Mater. Chem. 2011, 21, 7953-7965

Crystallographic phases were determined by X-ray diffraction (XRD) at room temperature, either in grazing incidence mode (GIXRD) or in $\theta/2\,\theta$ mode (Bragg-Brentano), using Bruker AXS D8 Discover and Stoe $\theta/2\,\theta$ diffractometers.

2.2.2 Advanced electron microscopy characterization

For advanced characterization a (scanning) transmission electron microscope ((S)TEM, JEOL 3000F) was used. X-ray energy-dispersive spectroscopy (XEDS, Oxford instruments) was used for elemental quantification and mapping. High (atomic) resolution TEM (HRTEM), High Angle Annular Dark Field (HAADF) STEM and electron diffraction was typically used for determining overall morphology, grain structure and crystallography. Energy-filtered TEM (EFTEM) and Electron Energy Loss Spectroscopy (EELS) with a Gatan Image Filter were also used. TEM specimens were prepared by focused ion beam (FIB) machining (FEI Nova NanoLab 600).

Structural/microstructural characterization of the films was done with particular emphasis on texture, grain boundaries, interfaces and pores, using HRTEM, XEDS, EELS, EFTEM, FIB and SEM.

FIB/SEM tomography 3D reconstruction was also used to visualize the 3D network of open porosity.

2.2.3 Electrochemical impedance spectroscopy

2.2.3.1 Symmetric cell for cathodes

Electrochemical impedance spectroscopy (EIS) of symmetric cells (cathode|electrolyte|cathode) was used for the determination of the cathode area-specific resistance (ASR). For instance, 800 μm thick BCZY27 pellets were used as electrolytes and cathodes were applied to both sides. The current collection was achieved with Pt or Au electrodes. The impedance spectra, recorded with a Solartron 1260, were fitted with the Zsimpwin software.

2.2.3.2 Thin film electrolytes

EIS measurements on the epitaxial BZY-layers on single crystalline MgO(100) substrates were carried using a modified Novocontrol high temperature setup. The whole setup consists of a potentiostat, diplexer and oven ($T_{max.}$ 1200 °C) from the Novocontrol GmbH, Germany, equipped with a gas mixer and a high temperature (HT) measuring cell from Norecs AS, Norway. In order to facilitate the measurement of the thin films a self-constructed two-point measuring head was implemented into the HT cell. Due to the insulating nature of the MgO substrate only in-plane measurement could be performed. For these in-plane measurements, two Pt pads with a thickness of 50 nm were sputtered onto the BZY layer. The distance between them was 1 mm and the feed size of the Pt electrodes was 5 mm. First measurement results on these samples revealed that the conductivity values were in a comparable range to the values of Pergolesi et al.[5] taking into account that the present samples had a thinner film thickness.

For the through-plane conductivity measurements it proved difficult to avoid pin holes, both for BZY and LWO thin films, thus no trustworthy results could be obtained.

---

[5] D. Pergolesi, E. Fabbri, A. D'Epifanio, E. Di Bartolomeo, A. Teban, S. Sanna, S. Licoccia, G. Balestrino, and E. Traversa, *High proton conduction in grain-boundary-free yttrium-doped barium zirconate films grown by pulsed laser deposition*, Nat. Mater., 2010, 9, 846-852.

3. Results and discussion

3.1 Electrolyte development

3.1.1 BZY thin films

A detailed study of the phase and microstructure evolution by DTA/TG, SEM and XRD allowed for an engineering of the microstructure of BZY films on platinized Si substrates (from grainy to columnar microstructure). By using MgO substrates and an ultrathin seed layer in the very first coating step even epitaxial BZY films could be prepared by CSD.

An electron microscopy study of thin single-crystal $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) films epitaxially grown on MgO (100) substrates was reported in a recent paper.[6] Two samples were investigated; one crystallized at 800 °C and the other at 1000 °C. Both samples were prepared by FIB machining and TEM analysis confirmed that the films were both epitaxial and single-crystalline. Surprisingly, contrast features with the spacing of the original spin coated layers (Fig. 2) were also visible in the HRTEM and STEM-HAADF images. These features were not related to variations in chemical composition (measured using XEDS) of the main components, and using multiple complementary techniques (HRTEM, STEM-HAADF/BF, EFTEM, and SEM) we could show that the film crystallized at 1000 °C consisted of alternating layers of solid and porous material, where the porous material included facetted voids (negative crystals). The porous layers had a volume fraction of 20-25% voids, and the overall film 10-13%. The voids possibly originates from incomplete removal of carbonate species during the initial crystallization of that layer followed by removal at later crystallization steps.
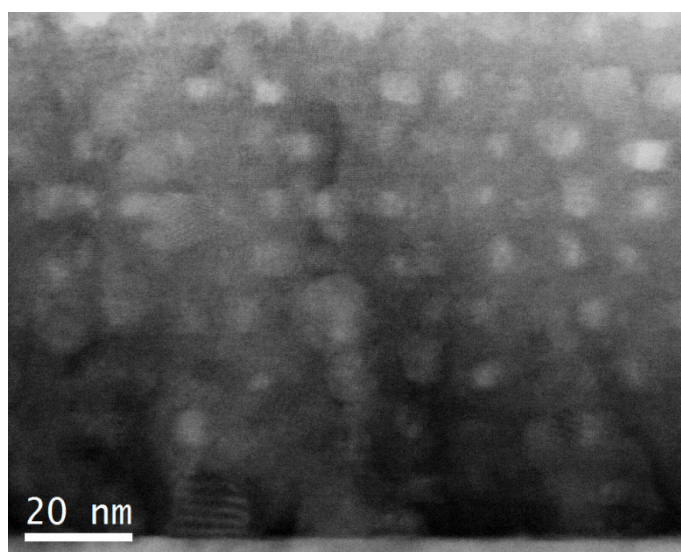

Figure 2. STEM bright field image of an epitaxial BZY film on MgO annealed at 1000 °C. The regular brighter spots are volumes of lower density (voids), in an otherwise monolithic (single crystal) matrix.

In a real fuel cell the electrodes naturally have to be porous to allow gas transport towards the electrolyte. It is challenging to deposit a thin, even and dense film onto a porous support, especially if

---

[6] F. Lenrick, D. Griesche, J.-W. Kim, T. Schneller, and 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.

the pores are large. Solutions to this challenge can be to minimize the pores in the electrode closest to the electrolyte by reducing electrode grain size, to clog the pores with electrolyte phase grains, to deposit thicker films that more easily cover the pores, or to introduce the pores after electrolyte deposition. The last option is probably the easiest when using a NiO-electrolyte material cermet as anode; the NiO of the cermet is reduced to Ni in reducing atmosphere at the operating conditions, which induces porosity for gas diffusion. The film can therefore be deposited onto a dense support. Fig. 3 shows an example of such a BZY film deposited onto a BCZY27-NiO anode and annealed at 1000 °C. The anode was not reduced before the TEM study so the anode is still dense. The film was shown to consist of columnar grains, around 50 nm in diameter and full film thickness long (about 800 nm). The parts of the film in contact with BCZY27 had an epitaxial relationship with the substrate. Visual traces of each layer spin-deposited by the chemical solution deposition were detected using both SEM and STEM. Regions with lower density was also discovered (using STEM HAADF) at the junctions between grain boundaries and spin layer boundaries. The columnar growth is a result of the crystallization between each layer to promote heterogeneous nucleation on the grains of the previous layer, instead of homogeneous nucleation in the deposited layer that would have given a random crystalline structure.
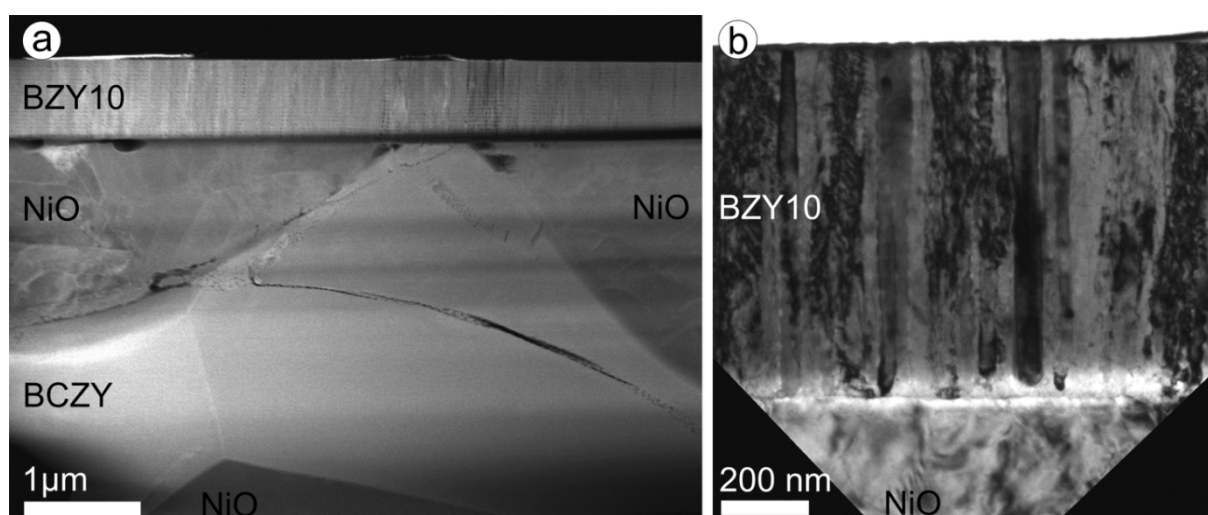

Figure 3. (S)TEM images of BZY film deposited by CSD (20 layers) on a dense BCZY27-NiO anode and annealed at 1000 °C. (a) Overview STEM HAADF image. (b) Higher magnification TEM image of the columnar BZY growth on a NiO part of the anode.

The columnar film structure should in principle avoid the problem of low proton conduction along the grain boundaries of BZY, as each grain stretches through the whole electrolyte thickness so that a proton traveling through the electrolyte do not have to pass any grain boundaries from the anode to the cathode side. The in-plane conductivity is however expected to be low due to the high number of grain boundaries in that direction. For a practical fuel cell, columnar grain growth with partial epitaxial relation to the electrodes is more realistic than single-crystalline electrolyte films, as the latter are difficult to deposit onto functional anodes.

3.1.2   LWO thin films

LWO electrolyte thin films were deposited on $Pt/TiO_x/SiO_2/Si$ or $Pt/AlO_x/SiO_2/Si$. For the films deposited from citric acid (CA) solution craters were observed in the films (Fig. 4) and there was significant porosity in the film as seen in Fig. 5, where the individual layers can be seen. The crater

formation was more pronounced for increased temperatures. The origin is probably incomplete burnout of organic residue in the intermediate heat treatment on hot plate between each layer; also, citrate compounds can be more explosive than other stabilizing agents. The films became crystalline after heat treatment at 800 °C for 30 min in a rapid thermal processing (RTP) furnace (Fig. 6).
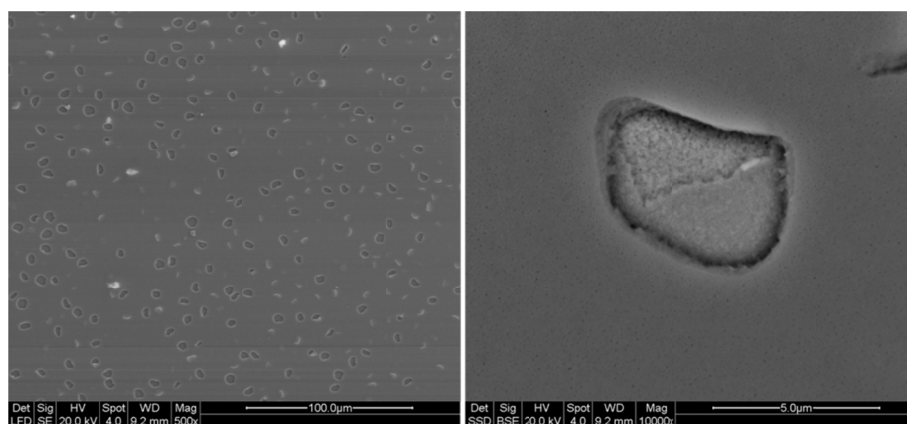

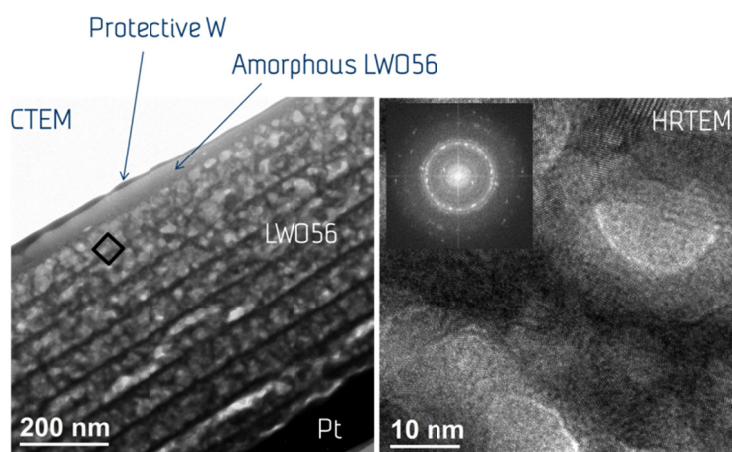**Figure 4**. SEM images of LWO thin films deposited from CA solution, heat-treated at 800 °C for 30 min by RTP.

Figure 5. (Left) CTEM image and (right) HRTEM image of LWO film deposited from CA solution, heat-treated at 800 °C for 30 min by RTP. A fast Fourier transform of the HRTEM image is displayed in inset showing a polycrystalline pattern.
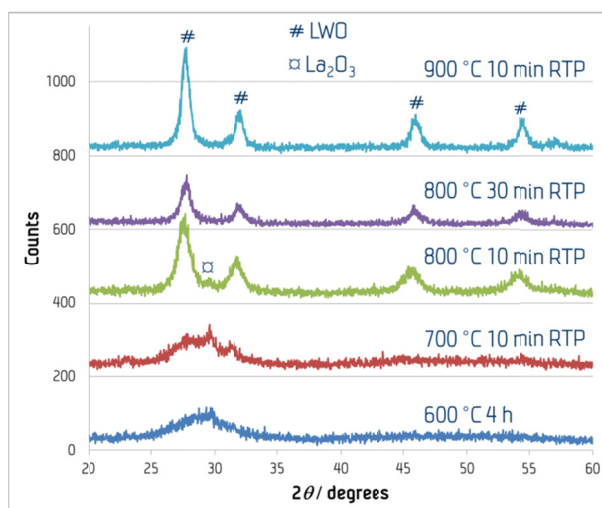
Figure 6. Grazing incidence X-ray diffractograms of heat-treated LWO films from CA solution.

For the EDTA films, crater formation was not observed as for the CA films. A thickness of about 350 nm was achieved after 10 successive depositions (Fig. 7a). Annealing at 800 °C for 4 h led to a polycrystalline film with nanoscaled grains (20-60 nm). The film had some porosity especially in the in-plane direction reflecting the multi-layer deposition. Final annealing at higher temperatures generally led to substantial grain growth and formation of larger pores. The diffractogram in Fig. 7b corresponds well to the PDF pattern of La_6WO_{12} (30-686) and to the diffractograms for lanthanum tungstate with La/W atomic ratio 5.5 reported by Magraso *et al*.[7] Heat treatment at higher temperatures (900 °C to 1000 °C) resulted in formation of larger LWO grains, these grains were oriented in different crystallographic directions (Fig. 8). The large grains were accompanied by large pores.

[7] A. Magrasó, C. Frontera, D. Marrero-López, and P. Núñez, *New crystal structure and characterization of lanthanum tungstate "La₆WO₁₂" prepared by freeze-drying synthesis*, Dalton Trans., 2009, 10273-10283.
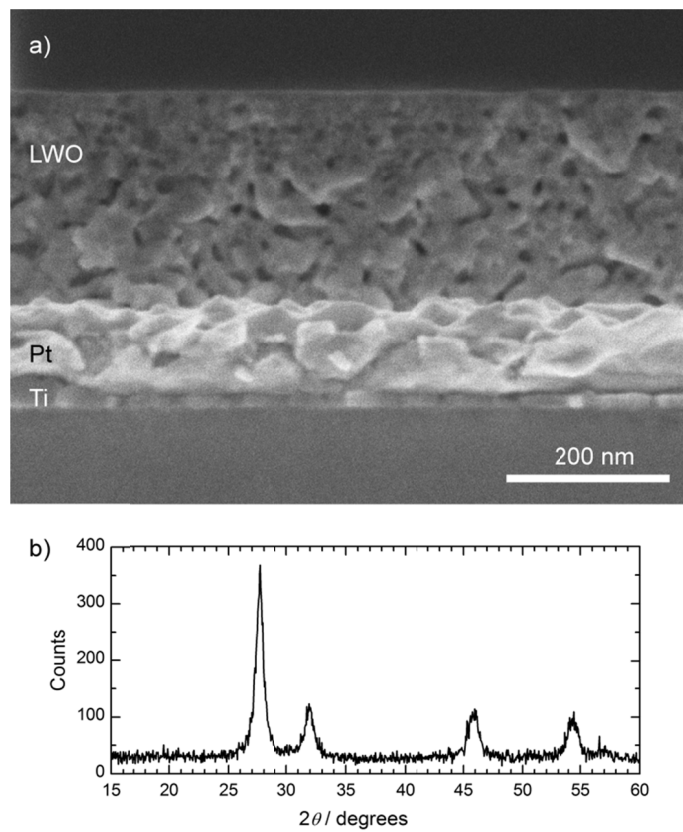
Figure 7. (a) SEM image of LWO thin film deposited from an EDTA-stabilized aqueous solution on platinized Si. 10 layers were deposited with pyrolysis at 500 °C on a hot plate between each layer. The film was finally crystallized at 800 °C for 4 h in air. (b) X-ray diffractogram with grazing incidence θ = 1° of the LWO thin film imaged in (a).
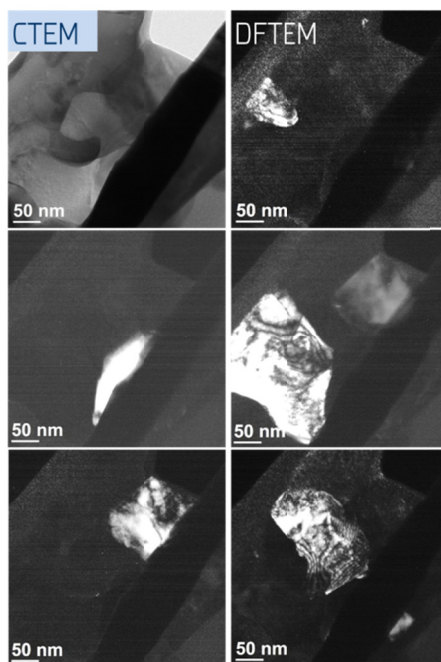
Figure 8. CTEM image (upper left) and DFTEM images of LWO film deposited from EDTA solution, heat-treated at 1000 °C. The grains are oriented in different crystallographic orientations. The grains are much larger than the grains in the 800 °C heat-treated films.

For use as a gas-tight electrolyte the density has to be improved, but this LWO example anyway shows the promise of CSD to be able to fabricate very thin films at much lower temperatures than powder methods.

3.1.3   Tape casting and warm pressing of BCZY

As reported later, PCFC cathodes of satisfactory performance have been developed using suitably impregnated BCZY backbones. Symmetrical cells for these studies were prepared by cutting pellets which was time consuming and produced only small samples. Further the testing of a BCZY fuel cell would give valuable data on its performance under load, i.e. when water is being produced. Such a test cannot be made using BCZY pellets. For these reasons, we have worked on tape casting of BCZY, and in particular the composition BCZY27.

A slurry was prepared using ethanol, PVP, and BCZY with small amount of NiO sintering aid and was tape casted, producing a green tape of 30 µm thickness after drying, which could be laminated (x16) to produce thicker tapes. Fig 9 shows a green BCZY tape of diameter 16 mm.

Figure 9: Image of a green BCZY tape of diameter 16 mm.

22

While the tape casting was achieved without major difficulties, sintering of the green tapes proved to be difficult, due to loss of the NiO sintering aid. The samples had with varying degrees of deformation and cracking and, after several unsuccessful attempts to cure the problem, the alternative method of warm pressing was adopted.

Powders were homogenized by mixing in warm toluene at 200 °C and were warm-pressed at 120 °C for 15 s, at 500 MPa, into a membrane having a thickness of 600 μm. This could be handled and cut into the desired shape (see Fig. 10). It proved possible to sinter small pieces of this membrane, but not to the same quality as that of the pellets and therefore these were not used to make symmetrical cells for cathode tests. In our opinion, the problems encountered would be much smaller if we switched to anode-supported electrolyte and this option is now being pursued outside of the project.
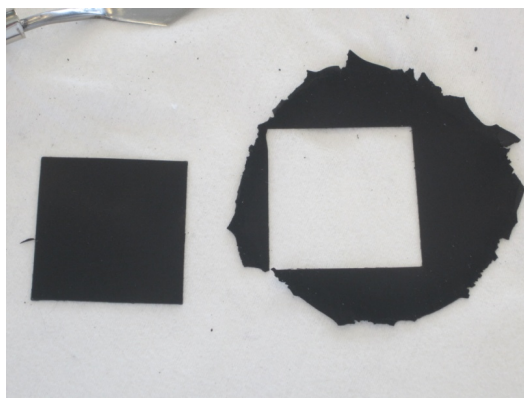

Figure 10: Image of BCZY based membrane as it appears after several warm press loads, cut in a 40x40 mm^2 piece.

In the course of preparing the tape casting slurries, the possibility of making these water-based instead of organic-based was considered. In this connection, the compatibility of BCZY with water was studied by XRD, TEM and chemical analysis of leaching. The results are summarized in a paper soon to be submitted.[8]

3.1.4   Electrolyte summary

The aim of the project for the electrolyte component was to be able to deposit the electrolyte on dense and porous substrates and achieve an ASR at 500 °C below 0.2 Ω cm^2. We have successfully deposited proton-conducting electrolyte films on dense substrates using genuine thin film techniques. For the porous substrates we chose a strategy to deposit on dense anode substrate which subsequently can become porous during reduction as it simplifies the deposition procedure significantly.

Due to challenges with the conductivity measurements of the electrolyte thin films, especially pin holes for the through-plane measurements, any ASR values have not been obtained at the time of writing. However, in-plane measurements are being done and will be continued at RWTH. It is believed that the high quality of the thin films will result in the ASR target being met.

---

[8] M. Della Negra, W. Zhang, N. Bonanos, and S. Ricote, *Leaching of BaCe$_{0.9-x}$Zr$_x$Y$_{0.1}$O$_{3-\delta}$ in aqueous slurries and investigation of the degradation products*, to be submitted to J. Mat. Sci. August 2013.

3.2   Cathode development

3.2.1   Spray pyrolysis

Air blast spray pyrolysis was used to fabricate LSCF films on BCZY27 electrolytes (Fig. 11). These cathodes were crystallized at 700 °C after deposition. As seen in Fig. 11a and b, ridges form especially when long deposition time and low air pressure are used on uneven substrates. The lines seen in Fig. 11a originate from polishing stripes of the BZCY pellet. This ridge formation mechanism opens up possibilities of structuring of the cathode.
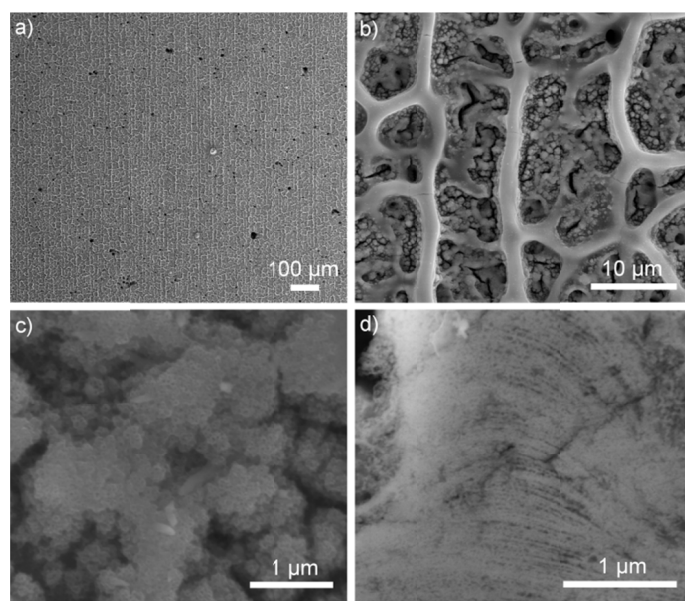

Figure 11. SEM images of LSCF cathode spray-pyrolyzed onto BCZY27 and annealed at 700 °C. (a)-(c) Surface of the LSCF film. (d) Polished cross-section of the LSCF film.

The low processing temperature results in small grain sizes and a high cathode surface area which represented itself in relatively low area specific resistances (ASR) of 0.61 $\Omega \cdot cm^2$ in dry air and 0.89 $\Omega \cdot cm^2$ in wet air at 600 °C (Fig. 12). The impedance spectra were fitted with equivalent circuit as shown in Fig. 12b and the cathode contribution was split into charge transfer and oxygen adsorption/dissociation based on capacitance values. The charge transfer resistance was higher than the oxygen adsorption/dissociation resistance, which was attributed to a limited interface area between LSCF and BCZ27 (giving high charge transfer resistance) and high surface area (giving low oxygen adsorption/dissociation resistance).
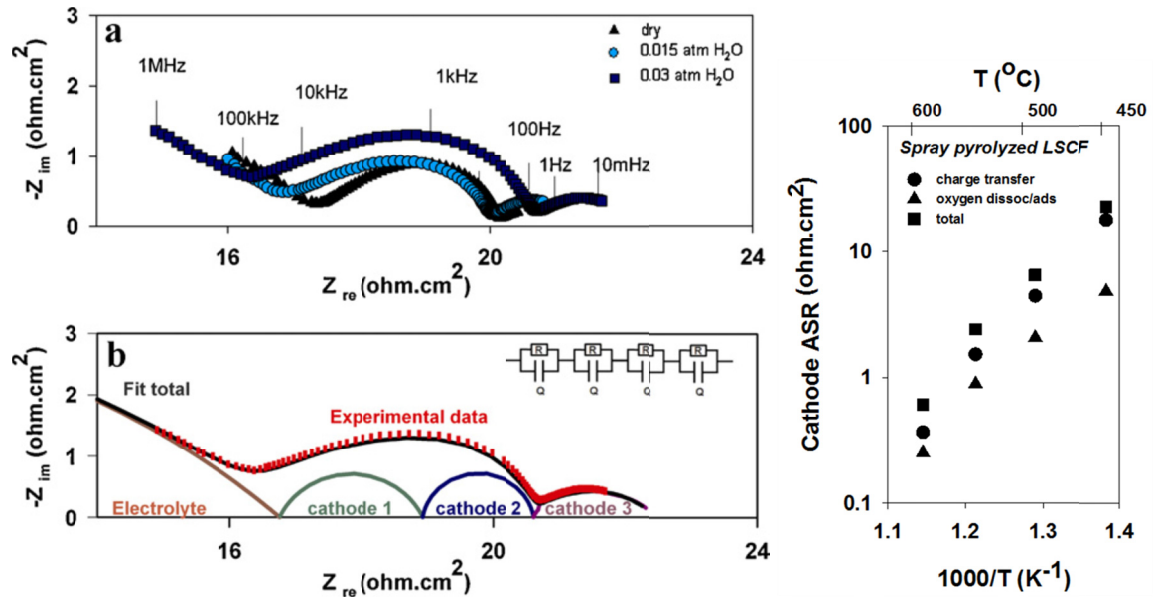
Figure 12. Electrochemical impedance spectroscopy of spray-pyrolyzed LSCF on BCZY27. (a) AC spectra at 550 °C in air with different water vapor pressures. (b) Fit of the AC spectrum recorded at 550 °C in air with $p(H_2O)$ = 0.03 atm. The solid lines correspond to the fit and the dots to the experimental data. The equivalent circuit used for fitting is shown in (b). (Right) Area specific resistances (ASR) corresponding to the cathode processes (charge transfer and oxygen dissociation/adsorption) for the spray-pyrolyzed LSCF cell in air with $p(H_2O)$ = 0.03 atm.

LSCF was also spray-pyrolyzed onto single-crystalline YSZ substrates for optimization of the spray pyrolysis procedure and comparison with SOFC performance. A Gd-doped CeO_2 (CGO) layer was deposited between the YSZ substrate and LSCF film as barrier layer to avoid any harmful reaction between the two phases. In Fig. 13 the diffractograms show that the CGO layer was partly crystalline as-deposited, while the LSCF film layer was amorphous after deposition, but became crystalline without any secondary phases after heat treatment at 650 °C. The cathode performance was studied using symmetrical cells and is summarized and compared with literature values in Fig. 14. The best performance was obtained using nanosized carbon black (Special Black 6 fra Evonik Degussa) as pore former; at 600 °C the ASR was 0.59 $\Omega \cdot cm^2$ in wet O_2/Ar mixture ($p(O_2)$ = 0.20 bar). The obtained ASR values were similar or better than ASR values previously obtained by spray pyrolysis of LSCF, but as can be seen in Fig. 14 the ASR was higher than for double layered cathodes with a thicker LSCF current collector layer reported in the literature. Efforts to fabricate similar double-layered cathodes in this project were not successful in lowering the ASR below the value obtained without LSCF current collector layer.
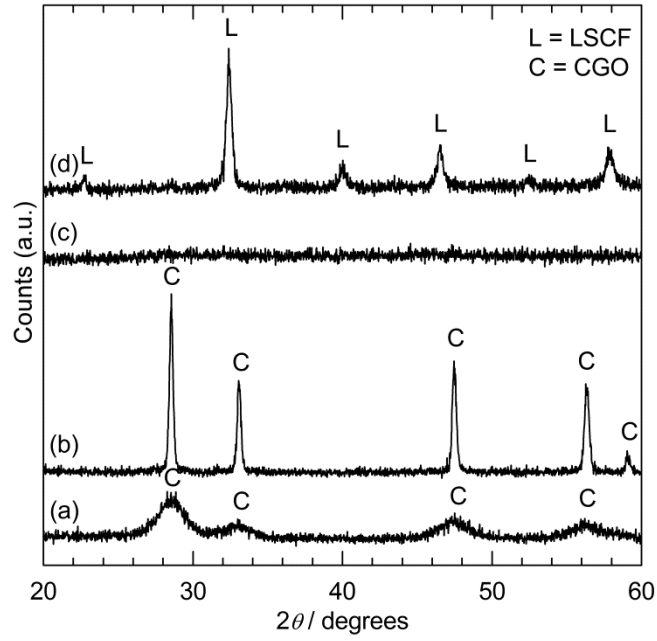
Figure 13. Grazing incidence X-ray diffractograms of (a) as-deposited CGO barrier layer on YSZ single-crystalline substrate, (b) CGO layer annealed at 1000 °C for 1 h, (c) as-deposited LSCF film on top of CGO barrier layer, and (d) LSCF film annealed at 650 °C for 4 h.
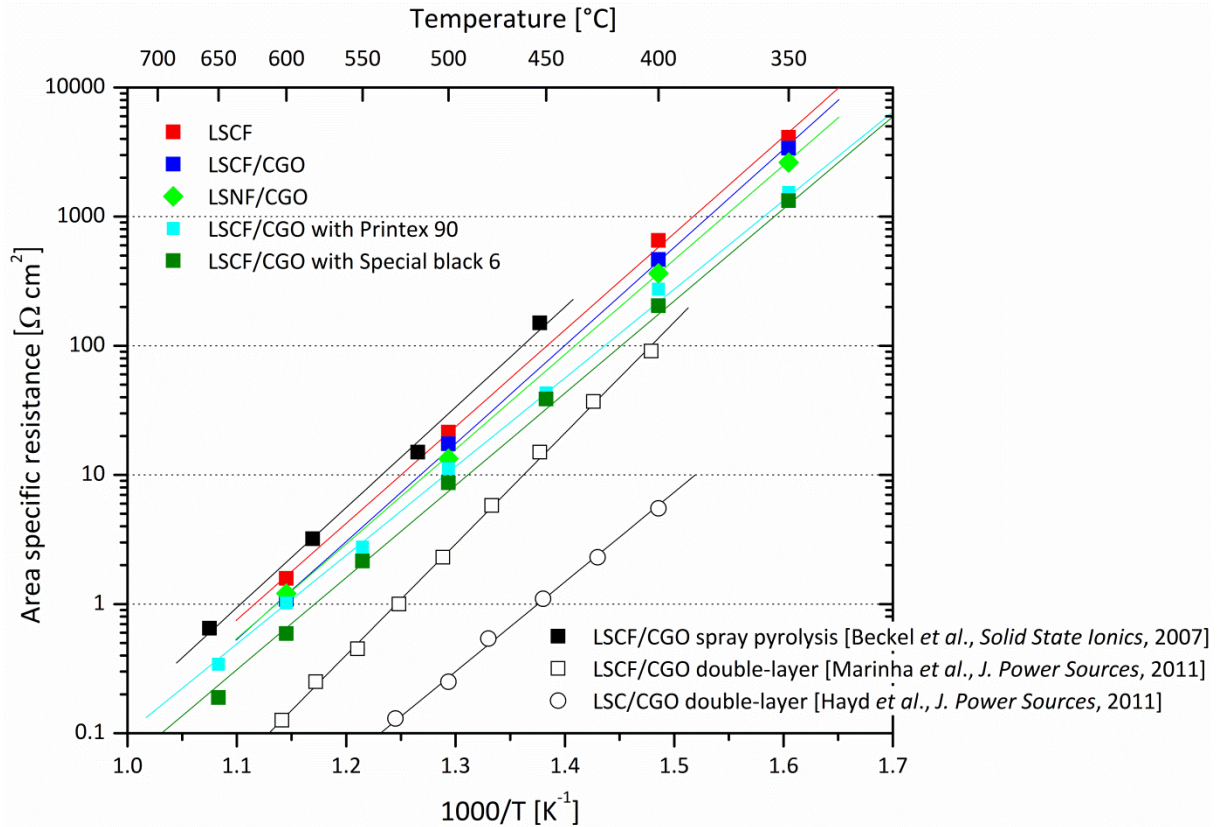

Figure 14. Temperature dependence of ASR of various LSCF/LSNF cathodes deposited on YSZ. In LSNF Co was replaced by Ni. Results obtained in this project (coloured points) are compared with literature values (black/open).

3.2.2 Infiltration

In this project we have infiltrated LSCF from an organic solution and LaCoO$_3$ from an aqueous solution into BCZY27 backbones. Fig. 15 shows the microstructure of the fabricated LSCF-BCZY27 cathode. LSCF was infiltrated either 4 or 12 times and the best ASR was obtained for the 12 times infiltrated cathode (Fig. 16); at 600 °C the ASRs were 0.63 $\Omega \cdot cm^2$ in dry air and 0.98 $\Omega \cdot cm^2$ in humidified air. The charge transfer part of the total ASR was significantly lower than the oxygen dissociation/adsorption part and this was attributed to the high number of triple phase boundaries due to the backbone-infiltrated structure.
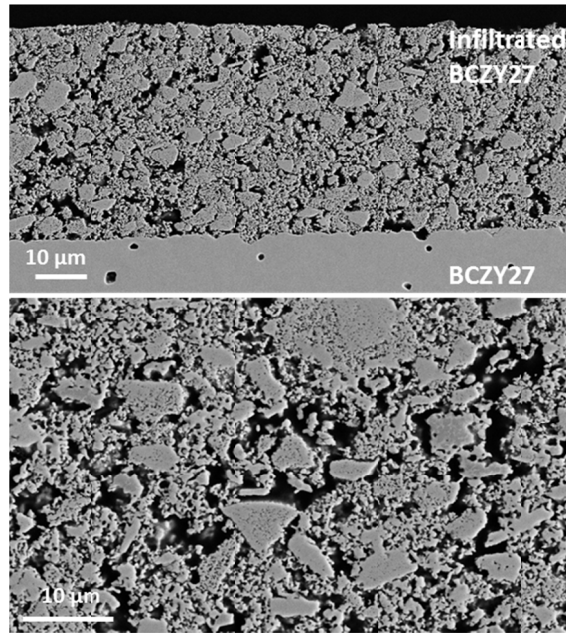

Figure 15. SEM images of a polished section of BCZY27 electrolyte and 12 times LSCF-infiltrated BCZY27 backbone.
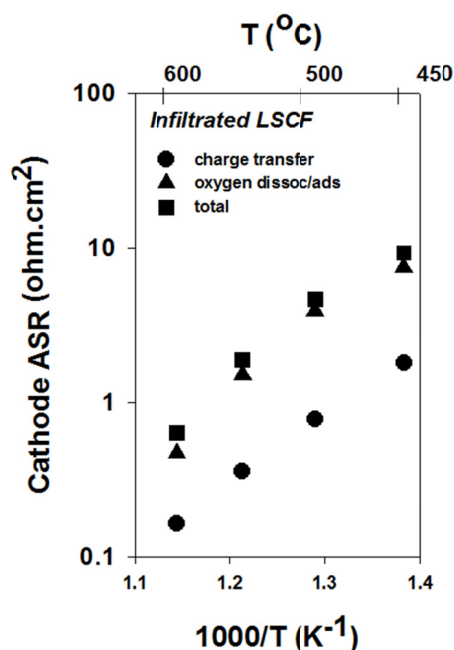
Figure 16. Area specific resistances for the cathode made by 12 times LSCF infiltration into BCZY27. The atmosphere was dry during these measurements.

To possibly increase the cathode performance and lower the ASR further, $LaCoO_3$ was infiltrated into BCZY27 porous backbone from an aqueous solution. The use of water as solvent allowed a higher concentration to be used and is a more environmentally friendly route. HRTEM and STEM were used to measure the particle sizes of the infiltrate with high accuracy, which varied in the range 50-95 nm. STEM XEDS provided a detailed element map of the interface between electrolyte and cathode were is was also possible to show that La and Co does not diffuse into the BZCY27 material (which was measured with a resolution of a few nanometers) (Fig. 17).
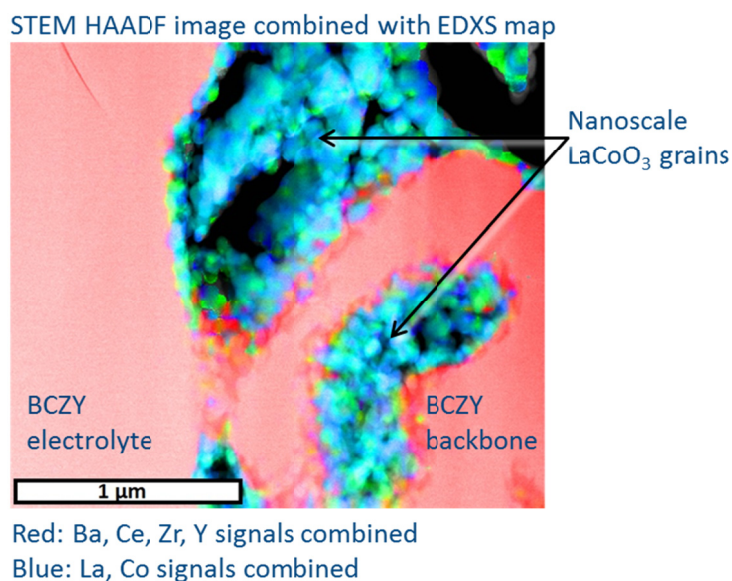
Figure 17. STEM HAADF image combined with EDXS map of a cross-sectional area at the border between the BCZY27 electrolyte and the BCZY27 backbone infiltrated with $LaCoO_3$ from an aqueous solution.

Evaluation of impedance spectra obtained on symmetrical cells with $LaCoO_3$-infiltrated cathode (see an example in Fig. 18) gave an ASR of 0.11 $\Omega \cdot cm^2$ at 600 °C (pH_2O = 0.01 atm), which is the lowest reported ASR for PCFC cathodes to our knowledge. The low ASR is a result of the cathode material's properties combined with its microstructure. $LaCoO_3$ is a pure electronic conductor at 600 °C and below and the cobalt ensures good catalytic activity for oxygen dissociation. The small size of the infiltrated and annealed $LaCoO_3$ and the large interface area of the composite cathode ensure a large amount of triple phase boundaries where the water can form. A pure electronic conductor may actually be favourable as the water cannot be formed at the interface between electrolyte and electrode leading to possible breaking up of the interface, rather it has to be formed at the triple phase boundary. Of course, using $LaCoO_3$ instead of LSCF or other multi-cation oxides also reduces the complexity of the chemical solution and the possibility of secondary phase formation.
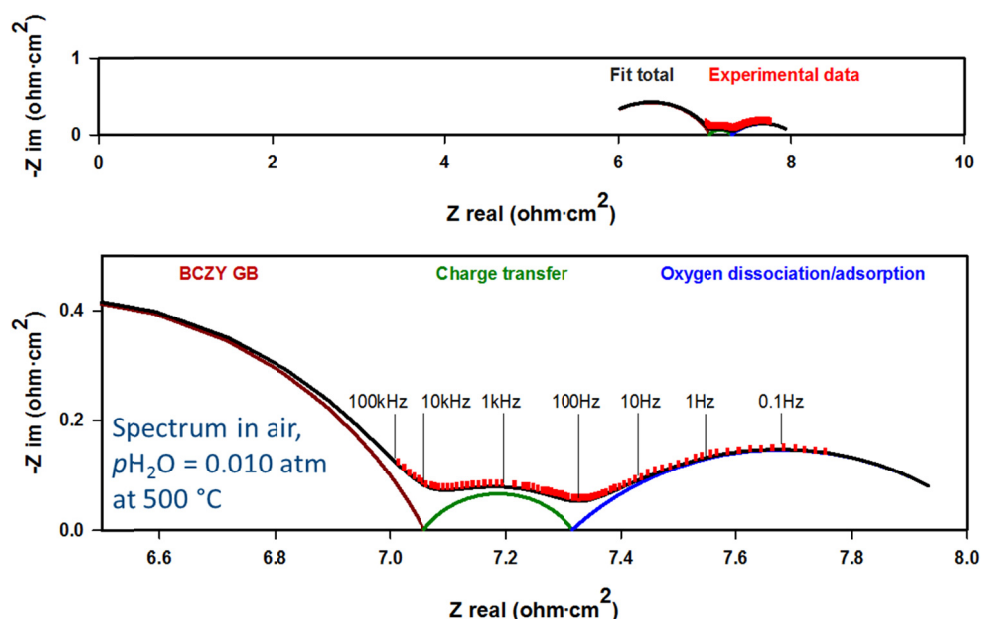
Figure 18. Impedance spectrum at 500 °C in air , $p(H_2O)$ = 0.01 atm of a symmetrical cell with BCZY27 electrolyte and $LaCoO_3$ infiltrated into a BCZY27 porous backbone as cathode. Dots are the experimental data and solid lines the fit using an R(RQ)(RQ)(RQ) circuit.

Although the infiltration itself requires only a modest annealing temperature well below 1000 °C, the formation of the backbone requires a much higher processing temperature (here 1300 °C) to develop good grain connectivity and mechanical strength through the whole backbone, so for use with metal supports for instance the backbone annealing will have to be lowered. In addition, the relatively thick BCZY backbone will necessarily have a high number of blocking grain boundaries for the protons to pass so ideally the backbone could be thinner, with a current collector layer on top for electronic conduction.

3.2.3   Spin coating

LSCF layers were also deposited by spin coating on different substrates. The aim of this part of the project was to fabricate porous layers with an adequate crystalline quality by a further alternative coating technique. At first a propionic acid route was developed. The acetates of lanthanum, strontium, and cobalt and the corresponding iron acetylacetonate salt were mixed in propionic acid and propionic acid anhydride in the desired stoichiometry. After refluxing the mixture, a dark brown solution resulted which was stable for more than six months. The solution was spun on platinized silicon substrates and oxidized silicon wafers and subsequently heat treated to induce crystallization. On platinized silicon and silicon oxide it was found that the crystallization was complete at temperatures of 700 °C to 800 °C (see the X-ray diffractogram in Fig. 19).
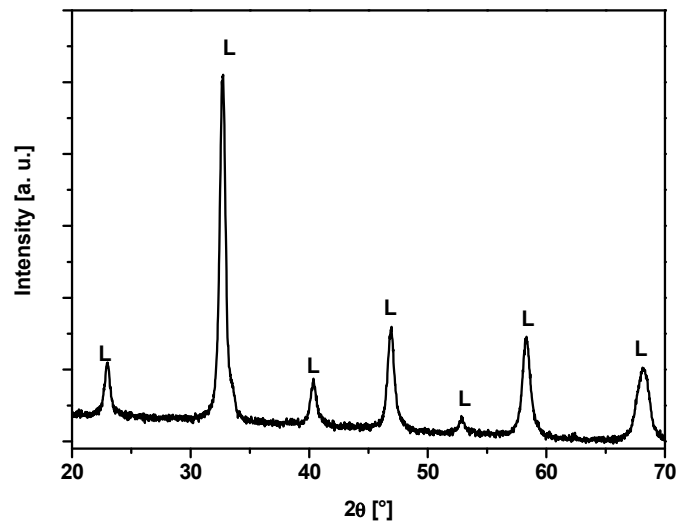
Figure 19: X-ray diffractogram (glancing incidence) of a LSCF layer crystallized at 800 °C in the RTA furnace. No secondary phases are visible, all LSCF reflexes are marked with an L.

The layer morphology was found to be strongly dependent on the nature of the temperature treatment. Comparably slow heating rates lead to rather dense LSCF layers (Fig. 20), whereas quick heating rates (RTA) were found to be essential for generating pores in the material. This behavior may be explained by an ultrafast crystallization occurring during RTA annealing leading to entrapment of the generated gases from the organic decomposition and hence pores are formed in the crystalline LSCF layer (Fig. 21).
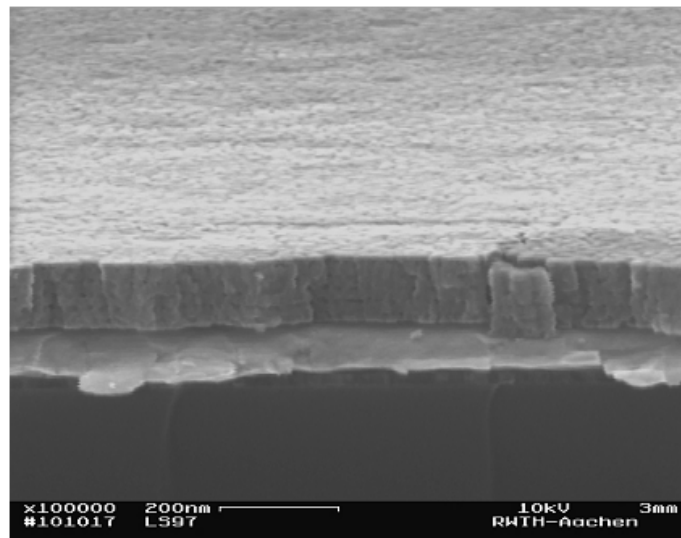

Figure 20: SEM image of a LSCF layer crystallized in the diffusion furnace at 700 °C. One can see the comparably dense layer formation.
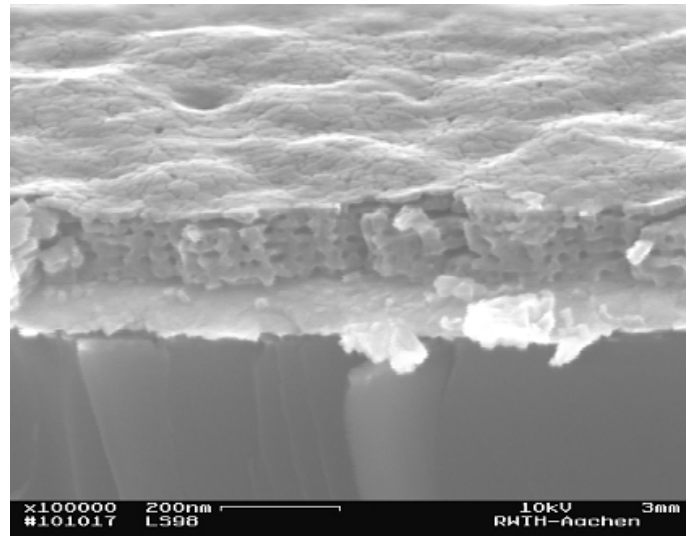
Figure 21: SEM image of a LSCF layer on platinized silicon crystallized at 800 °C in the RTA. Notice the pore formation with this kind of thermal treatment.

To enforce this effect, some large organic molecules were added to the precursor solution. The addition of PVP (Polyvinylpyrrolidone) and an intermediate pyrolysis at 400 °C on a hotplate resulted in the formation of large cavities in the material (Fig. 22).
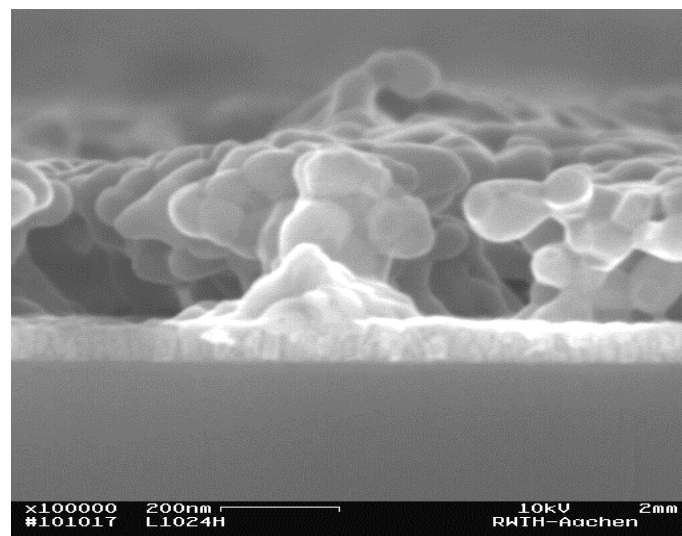

Figure 22: SEM image of a structurized LSCF layer on silicon dioxide. The addition of polyvinylpyrrolidone (PVP) as porogene lead to the formation of large cavities when a pyrolysis step at 400 °C on a hotplate was done before the crystallization at 700 °C in the diffusion furnace.

No phase separation could be detected via XRD. This kind of microstructure formation is naturally a random process, which means that the formation of the pores related to their size and number is statistic and can only be influenced to a minor extent. In order to get a more controlled arrangement of the pores, a second method was developed, which is based on the application of polystyrene (PS) nanospheres in the diameter range of 100 nm to 1000 nm. A kind of hexagonal self-assembly of PS monolayers occurred when the sphere suspension was drop-coated onto silicon oxide substrates.

When the interstices of these layers were infiltrated with the LSCF precursor solution and the organic material was carefully heat treated, negative crystalline LSCF honeycomb structures remained.

3.2.4 Cathode summary

The aim of the project was to develop cathode material with high chemical diffusion and oxygen exchange coefficients to achieve efficient low temperature fuel cells. The ASR target for the cathode at project end was 0.5 Ω cm^2 at 500 °C. Several low-temperature methods for cathode fabrication have been investigated. The lowest ASR was obtained for the composite cathodes with $LaCoO_3$ infiltrated into a porous BCZY27 backbone: 0.39 Ω cm^2 at 500 °C in air with $p(H_2O = 0.01$ atm), which is the lowest ASR value ever reported for a PCFC cathode to our knowledge. It is very interesting that the low ASR was obtained with $LaCoO_3$, a good electronic conductor but poor oxide ion conductor; this indicates that oxide ion conductivity is less important for a PCFC cathode as long as the cathode has catalytic activity for oxygen adsorption/dissociation and there are long triple phase boundaries between the proton-conducting phase and the electron-conducting phase. The cathode results obtained in this project shows the promise of low-temperature processes for achieving high-performance nanoscale electrodes for SOFC and PCFC.

4.   Outlook and further collaboration

In the nextgenFCmat project we have shown that compared to traditional powder-based methods, chemical solution deposition (CSD) offers the opportunity to fabricate very thin electrolyte films (< 1 µm) and cathodes with nanoscale grain size (20-50 nm), at much lower temperatures ($\leq$ 1000 °C). The investment costs of CSD are lower than for physical and chemical vapour deposition techniques and the cation composition can more easily be modified. As such, CSD offers the opportunity to rapidly develop routes for making films for evaluation of new material systems and is an alternative to powder-based methods for up-scaling of SOFCs and PCFCs to industrial scale.

In this project the aim was to study the electrolyte and cathode and the interface between them. A natural next step is to fabricate full fuel cells (with anode) using the developed methods and to test the fuel cells under relevant conditions. Based on findings in the project there are also several more fundamental issues that are of interest to study: the void pattern formation in BZY thin films; tomography studies of porous cathodes; spray pyrolysis of composite cathodes; PCFC cathode mechanisms, etc.

All partners have expressed interest in continuing the collaboration after project end. For Lund and RWTH the PhD students are now in the middle of their study (2011-2016) and both are interested in continuing work within this field. During the last year we have investigated possibilities for joint funding of further activities, but no suitable calls have been found yet that incorporated all four countries *and* were within relevant fields. As the research in the project still is at a relatively fundamental level, direct financing from industry is believed to be less relevant at this stage. The option that seems most likely at the moment of writing is to acquire funding from national sources and continue collaboration on a more informal level. Future EU and M-Era.Net calls will also be considered.

5.   Education

The project has educated two PhDs that will be defended in 2016 due to late start (2011) and 5 years PhD period in Sweden and Germany:

- Filip Lenrick, Lund University, February 2011 – February 2016
- David Griesche, RWTH Aachen, January 2011 – January 2016

The project has trained two post docs/research scientists:

- Sandrine Ricote, DTU, September 2010 – August 2012
- Per Martin Rørvik, SINTEF, September 2010 – June 2013

In addition, the project has educated three bachelors and three masters. Below is a list of the master and bachelor theses that has been part of the project.

5.1   Theses

Filip Lenrick
Characterization of Proton Conducting Thin Film Solid Oxide Fuel Cells using Focused Ion Beam and Transmission Electron Microscopy
M. Sc. Thesis, Center for Analysis and Synthesis, Department of Chemistry, Lund University. Media-tryck, Lund, 2011

Jae-Wuk Kim
Chemical solution deposition and characterisation of proton conducting perovskite thin film electrolytes for solid oxide fuel cells [in German]
MSc thesis, Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen, 2011

Michael Lübben
Studies to the wet-chemical fabrication of mixed conducting cathode thin films for solid oxide fuel cells [in German]
BSc thesis, Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen, 2011

Martin Knoppe
Comparative study on B-site substituted Y-doped $BaZrO_3$ as proton conducting thin films for solid oxide fuel cells [in German]
BSc thesis, Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen, 2011

Philip Wunderlich
Synthesis and characterization of 2D-pored and ordered cathode thin films through nanosphere templates [in German]
BSc thesis, Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen, 2012

Nghia Trung-Nguyen
Inkjet printed thin film electrolytes for micro solid oxide fuel cells [in German]
MSc thesis, Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen, 2013

6. Dissemination

6.1 Publications

S. Ricote, N. Bonanos, A. Manerbino, W.G. Coors
Conductivity study of dense $BaCe_xZr_{(0.9-x)}Y_{0.1}O_{(3-\delta)}$ 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

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

S. Ricote, N. Bonanos, F. Lenrick, L.R. Wallenberg
$LaCoO_3$: promising cathode material for protonic ceramic fuel cells based on a $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ electrolyte
Journal of Power Sources, 2012, 218, 313-319

J.S. Fish, S. Ricote, F. Lenrick, L.R. Wallenberg, T.C. Holgate, R. O'Hayre, N. Bonanos
Synthesis by spark plasma sintering of a novel protonic/electronic conductor composite: $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}/Sr_{0.95}Ti_{0.9}Nb_{0.1}O_{3-\delta}$ (BCZY27/STN95)
Journal of Materials Science, 2013, published online, DOI: 10.1007/s10853-013-7414-6

C. Haavik, P.M. Rørvik
Conducting oxide thin films
In *Chemical Solution Deposition of Functional Oxide Thin Films*, eds. T. Schneller, R. Waser, M. Kosec, and D. Payne, 2013, Springer, ISBN 978-3-211-99310-1, 35 pages, to be published October 2013

P. M. Rørvik, C. Haavik, D. Griesche, T. Schneller, F. Lenrick, L. R. Wallenberg, S. Ricote
Chemical solution deposition of thin films for protonic ceramic fuel cells
Submitted to Solid State Ionics

F. Lenrick, M. Ek, D. Jacobsson, M.T. Borgström, L.R. Wallenberg
FIB plan and side view cross-sectional TEM specimen preparation of nanostructures
Submitted to Microscopy and Microanalysis

M. Della Negra, W. Zhang, N. Bonanos, S. Ricote
Leaching of $BaCe_{0.9-x}Zr_xY_{0.1}O_{3-\delta}$ in aqueous slurries and investigation of the degradation products
To be submitted to Journal of Materials Science, August 2013

P. M. Rørvik, F. Lenrick, C. Haavik, Y. Larring, L. R. Wallenberg
Cathode performance of spray pyrolysis-deposited $La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ thin films for intermediate temperature solid oxide fuel cells
Manuscript in preparation

D. Griesche, F. Lenrick, L.R. Wallenberg, T. Schneller

Influence of different microstructures on the electrochemical properties of chemical solution deposition derived BaZr$_{0.9}$Y$_{0.1}$O$_{3-x}$ thin films

Manuscript in preparation

D. Griesche, M. Lübben, P. Wunderlich, T. Schneller

Control of porosity in La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ thin film cathodes fabricated by chemical solution deposition

Manuscript in preparation

6.2   Conference presentations

P.M. Rørvik and C. Haavik

Low-temperature deposition of La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ 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$_x$Y$_{0.1}$O$_{(3-\delta)}$ 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$_x$Fe$_{1-y-z}$Co$_y$Ni$_z$O$_{3-\delta}$ 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

T. Schneller

Functional Oxide Thin Films for Energy Efficient Devices by Chemical Solution Deposition [Invited lecture]

Materials Science & Technology 2011, Columbus (OH), USA, October 16-22, 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

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 $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $LaCoO_3$ cathodes deposited on $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ 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 $La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3\,\delta}$ [Lecture]
Electroceramics XIII, Enschede, Netherlands, June 24-27, 2012

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 $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ 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 $La_{28\,x}W_{4+x}O_{54+\delta}$ 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 $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $LaCoO_3$ cathodes deposited by infiltration and spray pyrolysis on $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ [Lecture]
Solid State Protonic Conductors 16, Grenoble, France, September 10-14, 2012

P. M. Rørvik, C. Haavik, D. Griesche, T. Schneller, F. Lenrick, L. R. Wallenberg, S. Ricote, N. Bonanos
Chemical solution deposition of thin films for protonic ceramic fuel cells [Lecture]
19th International Conference on Solid State Ionics, Kyoto, Japan, June 2-7, 2013

F. Lenrick, D. Griesche, P.M. Rørvik, N. Bonanos, T. Schneller, L.R. Wallenberg
Transmission Electron Microscopy characterisation of thin film materials for protonic ceramic fuel cells prepared by Focused Ion Beam [Lecture]
Prospects Protonic Ceramic Cells 2013 - International Workshop on Protonic Ceramic Fuel Cells Status & Prospects, Montpellier, France, July 10-12, 2013

N. Bonanos, J.S. Fish, S. Ricote, T.C. Holgate, R. O'Hayre
Impedance response of BaCe$_{0.2}$Zr$_{0.7}$Y$_{0.1}$O$_{3-\delta}$/Sr$_{0.95}$Ti$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$ (BCZY27/STN95) composite at near-ambient temperatures [Poster]
Prospects Protonic Ceramic Cells 2013 - International Workshop on Protonic Ceramic Fuel Cells
Status & Prospects, Montpellier, France, July 10-12, 2013

6.3   Website

A website for the project was established in 2010 and has been regularly updated:
http://www.sintef.no/Projectweb/nextgenFCmat/