



# **PROJECT PUBLISHABLE FINAL REPORT**

**Grant Agreement number: 227560**

**Project acronym: EFFIPRO**

**Project title: Efficient and robust fuel cell with novel ceramic proton conducting electrolyte**

**Funding Scheme: FP7-Energy-NMP-2008-1 Novel materials for energy applications**

**Period covered: From 2009-05-01 to 2012-04-30**

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## 1. Final publishable summary report

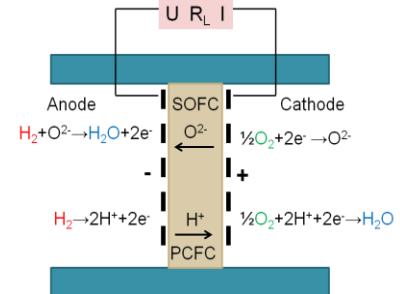
The next pages contain a 1-page executive summary, a section on context and objectives, a report of the main scientific and technological results, and a section on potential impact.

Thereafter follows general information about partners and contacts, Logo and highlights material, and finally the list of publications.

## 1.1. EFFIPRO Executive Summary

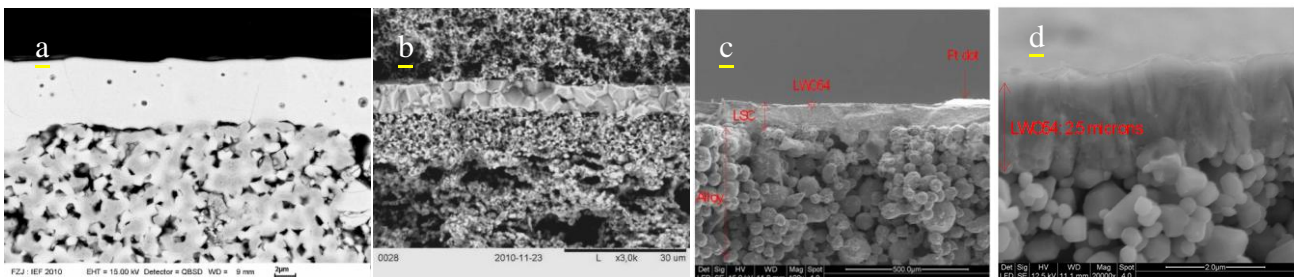
**Proton ceramic fuel cells (PCFCs)** can operate at temperatures lower than traditional SOFCs due to lower activation energy of migration of protons than of oxide ions. In PCFCs, H<sub>2</sub>O forms on the air side and does not dilute the fuel or constitute danger of oxidising the anode. This results in a unique 100% fuel utilisation, simpler BoP, and overall efficiency at least 10% higher than for SOFCs, other characteristics assumed equal.

**Proton conducting oxides** have traditionally been Sr- or Ba-based perovskites like Y-doped BaCeO<sub>3</sub> or BaZrO<sub>3</sub> which have suffered from poor stability towards CO<sub>2</sub> due to Sr/Ba basicity, or high sintering temperatures and grain boundary resistance. **EFFIPRO** explored Sr/Ba-free oxides, notably **Ca-doped LaNbO<sub>4</sub> (LCN)** among a new class of stable but modest proton conductors, requiring thin electrolytes and efficient electrodes. The aim was not to assemble a complete cell, but reach quantifiable goals of electrolyte thickness, conductivity, and electrode polarisation of support-anode-electrolyte and electrolyte-cathode assemblies. Midterm, final and long term goals have been, respectively, 0.5, 0.2, and 0.1 Ωcm<sup>2</sup> ASR at 800, 700, and 600°C for each of the anode, electrolyte, and cathode. Additional goals comprised electrode mechanistics, stability towards thermal cycling and CO<sub>2</sub>, and cost reduction. Initial phase purity problems of LCN were solved in collaboration with national projects, and thin electrolytes were made by e.g. electrophoretic deposition (EPD) on porous Ni-LCN cermet. The anode met target performance, but LCN remained with a too low proton conductivity and could not sustain a satisfactory cathode.



At midterm, the electrolyte was thus changed to the emerging “La<sub>6-x</sub>WO<sub>12-3x/2</sub>” (LWO) class of materials. **La<sub>54</sub>W<sub>10</sub>O<sub>111</sub>v (LWO54)** was found to be most stable, also in CO<sub>2</sub>, with a proton conductivity of 0.0015 S/cm satisfying final target. Cost effective spray pyrolysis synthesis was developed. LWO reacts with NiO, and EFFIPRO has investigated **Sr-doped LaCrO<sub>3</sub> (LSC)** as barrier and functional anode. It made a 2.5 μm LWO electrolyte by PLD on a porous LSC layer spray-deposited on an alloy support, the **first so-called 3<sup>rd</sup> generation PCFC structure** reported. Other developments included Ni post-sintering infiltration and reductive precipitation of catalytic Ni nanoparticles from Ni-substituted LSC. As cathode for LWO we investigated substituted, infiltrated, and nanostructured **LaMnO<sub>3</sub>** and **La<sub>2</sub>NiO<sub>4</sub>** as well as the fundamentals of **La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>** as mixed conducting electrode component. EFFIPRO has contributed understanding of ohmic, charge transfer, catalytic, and mass transport limitations of PCFC electrodes, helping to reach polarisation resistances of 0.4-0.6 Ωcm<sup>2</sup> in wet atmospheres at 700°C, only factors 2-3 off project targets.

EFFIPRO counts 7 partners in 5 countries, coordinated by Univ. Oslo. It has met a majority of its milestone targets and at closure lists one patent, 11 articles, and 26 presentations. It has led to several follow-up projects to make PCFCs an effective alternative for the emerging hydrogen economy.



a) 7 μm LCN on Ni-LCN cermet. b) LCN between supported functional anode and cathode. c) 3<sup>rd</sup> generation PCFC; coarse alloy support, fine LSC anode and thin dense LWO (hardly visible). d) Close-up of the same LWO on LSC.

## 1.2. Summary of EFFIPRO context and objectives

**Proton ceramic fuel cells (PCFCs)** with proton conducting oxides can operate at intermediate temperatures (e.g. around 4-600°C), in principle lower than oxide ion conductors due to lower activation energy of migration of the dissolved protons than of oxide ion defects. Most importantly, H<sub>2</sub>O – the major product – appears on the cathode side, and does not dilute the fuel or constitute a danger of oxidising the anode, as in a regular solid oxide fuel cell (SOFC), see **Figure 1**. Thus, the fuel utilisation can be a unique 100%, the balance-of-plant (BoP) simpler, and the overall efficiency in principle at least 10% higher than for SOFCs, all other characteristics assumed equal.

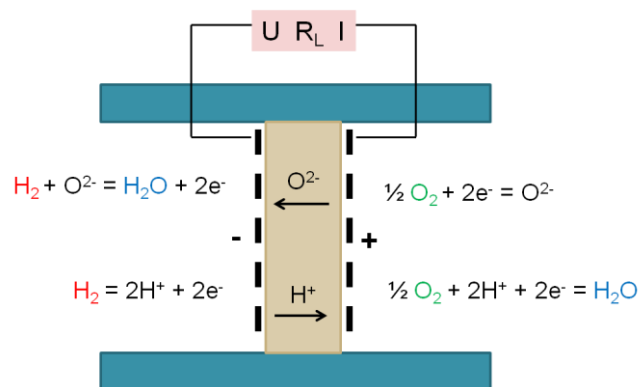


Figure 1. Comparison of O<sup>2-</sup> conducting SOFC and H<sup>+</sup> conducting PCFC, both with H<sub>2</sub> as fuel, showing how H<sub>2</sub>O in the PCFC is produced at the cathode (right hand side electrode), thus not diluting the H<sub>2</sub> fuel.

**Proton conducting oxides** have traditionally been Sr- or Ba-containing perovskites like acceptor-doped SrCeO<sub>3</sub> or BaCeO<sub>3</sub> which suffer from chemical instability towards reaction with acidic gases such as CO<sub>2</sub> due to the basicity of the alkaline earth cation. BaZrO<sub>3</sub> has better stability and high bulk conductivity, but has suffered from high sintering temperatures and grain boundary resistance.

**EFFIPRO** explores the use of novel Sr- and Ba-free stable oxides that may make an efficient PCFC also robust. It took as a starting point the discovery at UiO in 2004 of Ca-doped LaNbO<sub>4</sub> (LCN)<sup>1</sup> as the best among a new class of stable but modest proton conductors,<sup>2,3</sup> which require novel electrodes and fabrication of thin film electrolytes. During the course of the project, however, it became clear that LCN or other LaNbO<sub>4</sub> class formulations could not be brought to the targeted conductivity, and they were replaced with the emerging “La<sub>6-x</sub>WO<sub>12-3x/2</sub>” (LWO) class of proton conducting oxides. The project aims at improvement of proton conductivity of the stable oxides, developing support–anode–electrolyte film assemblies, efficient and compatible cathodes, understanding surface and electrode kinetics of PCFC electrodes, and pilot scale powder production for the project. The latter

<sup>1</sup> R. Haugsrud, T. Norby *Solid State Ionics*, **177** [13-14] (2006) 1129-35.

<sup>2</sup> R. Haugsrud, T. Norby, *Nature Materials*, **5** (2006) 193.

<sup>3</sup> T. Norby, R. Haugsrud, S. Marion, K. Wiik, M.-A. Einarsrud, Ø. Andersen, R.A. Strømme, T. Grande, International patent application PCT/EP2005/013873, 22 December 2005, priority 23 December 2004; “Proton Conductors”. Granted.



includes general cost-reduction strategies and use of mischmetal rare earth mixtures that alleviate the expensive separation steps).

Before we move on to the selected scope, aims and targets in more detail, it is worth looking at how these and the context of PCFC developments have changed during the five years of application, acceptance, contracting, and execution of EFFIPRO. We choose to restrain this to four main issues:

During the 2000's there has been progress in PCFCs using solid solutions of  $\text{BaCeO}_3$  and  $\text{BaZrO}_3$  compromising between the lower grain boundary resistance and easier sintering of the former and the higher grain interior conductivity and chemical stability of the latter. Y-doped  $\text{Ba}(\text{Ce},\text{Zr})\text{O}_3$  compositions have thus yielded good performance of PCFCs (and proton ceramic electrolyzer cells, PCECs) running  $\text{H}_2$  or  $\text{NH}_3$  as fuels, with claimed acceptable stability.<sup>4</sup> It has also been claimed that they can be used for reformed natural gas or biogas, especially if utilising their mixed proton and oxide ion conductivity at higher temperatures (co-ionic mode).  $\text{BaZrO}_3$  itself and related perovskites have recently seen advances in that sintering aids ZnO and NiO have been developed that reduce sintering temperatures and cost of production, and increase grain size to reduce the effect of grain boundary resistance.<sup>5 6</sup> One must thus at the end of EFFIPRO and in onward developments evaluate its non-Ba-based electrolytes against the modified  $\text{BaZrO}_3$ -based systems.

Over the last few years it has become clear that hydrogen-fuelled polymer electrolyte fuel cell (PEMFC) cars are ready for mass-production. The demonstration fleets of full-scale cars like Mercedes B-class and Hyundai ix35 hydrogen fuel cell vehicles are now running and filling hydrogen routinely at selected hubs in Germany, Norway, and elsewhere throughout Europe. The factories for large series production are being planned and erected, with expected first commercial sales in 2015. This has many important consequences (apart for the good news for emission cut and the climate), of which some are especially noteworthy here: Hydrogen purity is critical for the PEMFC. While PEMFC development has been a great success, an important part of the cost of the fuel will be purification and monitoring the purity at all stages of fuelling. An increased temperature of the operation of the electrolyte will make the fuel cell less susceptible to poisoning with less need of Pt catalysts. This will inevitably lead to development of new materials sooner or later hybridised or mixed with materials or concepts from proton conducting ceramics.

The third issue is the need to make hydrogen for transport from renewable sources of electricity. In many cases this is best done on-site. A related market is the need to store peaks of renewable electricity, and hydrogen is named as one attractive possibility in many locations. Such production can utilise solar or waste heat to generate steam to increase the efficiency of the electrolysis, and in all these instances high temperature solid oxide electrolyser cells (SOECs) are being considered suitable for thermal integration and potentially superior to PEM or alkaline electrolyzers. Needless to say, a proton ceramic electrolyser cell (PCECs) will produce dry hydrogen directly while the SOEC produces wet hydrogen, in correspondence with the PCFC producing water at the air side, while the SOFC produces water on the fuel side. Since the fuel cell and electrolyser cells are reciprocal but otherwise similar – and perhaps can be used for both purposes depending on the need for energy or storage – the development of PCFC technology is clearly very worthwhile.

Finally, the use of biomass and derived biogas is becoming more important, as a carbon-neutral fuel. In certain uses, for instance in combination with membranes or fuel cells, carbon or  $\text{CO}_2$  can be

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<sup>4</sup> e.g. Y. Lin, R. Ran, Y. Guo, W. Zhou, R. Cai, J. Wang, Z. Shao., *Int. J. Hydrogen Energy*, **35** (2010) 2637.

<sup>5</sup> J. Irvine *et al.*, *US Pat Appl* 7,906,006 (2005). E. Ruiz-Trejo, J.T.S. Irvine, *Solid State Ionics*, **216** (2012) 36.

<sup>6</sup> S. Ricote, N. Bonanos, A. Manerbino, W.G. Coors, *Int. J. Hydrog. Energy*, **37** (2012) 7954.



captured and sequestered, making the technology even carbon-negative. Also here, PCFCs and related hydrogen permeable membrane technologies are of potential benefit, and projects following EFFIPRO have been granted on biogas-fuelled PCFCs in Norway in 2012. Very important in this context is that biogas normally holds very high contents of sulphur. Fuel cells where the Ni in the anode is replaced (as we shall see we do in the final 3<sup>rd</sup> generation PCFC of EFFIPRO) and where the electrolyte tolerates high contents of sulphur are thus essential. It is not certain that BaZrO<sub>3</sub>-based systems can do this, due to the high stability of BaSO<sub>4</sub>. Thus, although one must not underestimate the stability also of for instance La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, the EFFIPRO strategy of non-Ba-containing PCFCs has become more relevant than ever.

**EFFIPRO** leaves out of its scope the assembly of a complete cell, and defines instead quantifiable goals for individual materials and interfaces. These comprise on the one hand side area specific resistances (ASR) of the electrolyte film and the anode polarisation of the supported anode-electrolyte thin film assembly. On the other side it comprises the electrode polarisation of the electrolyte-cathode assembly. In the long term the three are each required to be less than 0.1 ohm cm<sup>2</sup> at operating temperature assumed to be 600°C under realistic atmospheres and withstanding presence of acidic gases and thermal cycles. The target values for EFFIPRO components are correspondingly 0.5 ohm cm<sup>2</sup> at 800°C at midterm and 0.2 ohm cm<sup>2</sup> at 700°C at end of project for each of the three contributions. To reach these objectives, it is required to make supported electrolyte films of 5 and 3 µm, and have an electrolyte conductivity of 0.001 and 0.0015 S/cm, at project midterm and end, respectively.

It may be noted that a complete fuel cell also has losses and resistance from current collectors, also preferably not higher than each of the contributions above. This has not been specifically included in EFFIPRO targets, but in order to have sufficient local in-plane current collection, there are midterm and final targets set also for the electronic conductivities of the electrode materials of 50 and 75 S/cm for the cathode and 100 and 200 S/cm for the anode. Long term developments should preferentially reach still higher values.

EFFIPRO aims at developing anode supported electrolytes on ceramic-metal or alloy supports (2<sup>nd</sup> or 3<sup>rd</sup> generation of fuel cells). The alloy-supported design has not been realised for PCFCs elsewhere up to date, and further amplifies the range of innovation in the project.

Additional objectives are cost reduction of manufacturing by process efficiency and if viable the use of mischmetal precursors, stability of materials, interfaces, and components towards thermal cycling and exposure to CO<sub>2</sub> and other acidic gases (e.g. H<sub>2</sub>S and SO<sub>2</sub>), and establishment of novel instrumentation and approaches in studies of kinetics of PCFC electrodes.

The overall objectives for EFFIPRO were described as follows in Annex I: “EFFIPRO shall establish the first set of chemically and mechanically robust PCFC electrolyte and electrodes that demonstrates acceptable single cell performance, and in this manner lead towards a future superior fuel cell technology for power production from reformed fossil as well as hydrogen-based renewable energy. On long term a PCFC shall run at 0.1 Ωcm<sup>2</sup> per each of the four essential loss processes (electrolyte, anode, cathode, interconnect contacts) at > 95 % fuel utilisation and 600 °C. The project goals are 0.2 Ωcm<sup>2</sup>, 90 %, and 700 °C. The project runs in parallel with complementary national and Nordic projects. The objective of EFFIPRO is thus to contribute to the overall realisation of a successful and progressing European PCFC development, to solve particular issues not addressed in the national projects, and to bring essential EU expertise and resources into play. Europe invests more in fuel cell

research than USA or Japan<sup>7</sup> and is a stronghold for ceramic proton conductors<sup>8</sup> and is thus well suited to establish long term development towards leadership in commercial PCFCs. It is also a moral obligation of a gas-exporting nation like Norway and of EU to contribute to the development of such technologies for combating CO<sub>2</sub> emissions worldwide.”

The following table – from Annex I – details the **goals/targets** of the project after work in Period 1, i.e. at midterm, after work in Period 2, i.e. at end of project, and long term (after following projects/commercialisation). The goals for the Period 2 – this report – are therefore highlighted:

Table 1. Overall goals of development of materials and interfaces in and after EFFIPRO separated into 1<sup>st</sup> period (project midterm), 2<sup>nd</sup> period (project final) and long term future developments.

Property or conditions	Period 1 Project midterm	Period 2 Project final	Long term future developments
Temp. of operation	800 °C	700 °C	5-600 °C
Atmospheres	Moist H <sub>2</sub> /air	Moist H <sub>2</sub> /moist air	Dry H <sub>2</sub> /air
Fuel utilization	Small	> 90 %	> 95 %
Electrolyte $\sigma_{H^+,DC}$ , S/cm	0.001	0.0015	0.002
Electrolyte thickness; ASR	5 $\mu\text{m}$ ; 0.5 $\Omega\text{cm}^2$	3 $\mu\text{m}$ ; 0.2 $\Omega\text{cm}^2$	2 $\mu\text{m}$ 0.1 $\Omega\text{cm}^2$
$\sigma_{\text{anode}}$ , $\sigma_{\text{cathode}}$ , min., S/cm,	100; 50	200; 75	300; 100
Electrode kinetics, each	0.5 $\Omega\text{cm}^2$	0.2 $\Omega\text{cm}^2$	0.1 $\Omega\text{cm}^2$ (0.1 V overp.)
Thermochemical and – mechanical stability	No reactions between electrolyte, electrodes, CO <sub>2</sub> . Structures thermally cycleable without electrolyte cracks.		

At midterm, it was acknowledged that the conductivity of the chosen Ca-doped LaNbO<sub>4</sub> (LCN) electrolyte class could not be increased to meet the midterm target of 0.001 S/cm at 700°C, much less the end target (0.0015 S/cm at 600°C), and that it could not sustain cathodes anywhere near their target. The electrolyte was thus changed to the emerging “La<sub>6-x</sub>WO<sub>12-3x/2</sub>” (LWO) class of materials. La<sub>54</sub>W<sub>10</sub>O<sub>111v</sub> (LWO54) was found to be most stable, also in CO<sub>2</sub>, with a proton conductivity of 0.0015 S/cm satisfying final target. A new support, anode, and cathode had therefore to be developed from scratch. This led to decisions for Period 2 to reallocate resources from electrolyte work to work on anode support, thin film, and electrode developments, as described in the amended Annex I. The targets for the project at closure after the 2<sup>nd</sup> period were still kept as in Table 1.

<sup>7</sup> G. Crawley, Fuel Cell Today – Jan. 2007

<sup>8</sup> For instance, of the 16 international conferences in solid state proton conductors (SSPC 1-16) all but two have been held in Europe.



### 1.3. Main science and technology results

We here describe EFFIPRO achievements covering mainly proton conducting electrolytes, cost-effective synthesis of materials for the project and beyond, substrate-anode-electrolyte film half-cells, and electrode studies and developments. This follows partly the work packages of the project, and partly themes *across* work packages. Moreover, developments with integrated parallel projects are drawn upon where appropriate. Each section moves along ideas, results and actions spanning from EFFIPRO design till its conclusion, but restricted to those with essential learning and outcome.

#### Novel ceramic proton conductors

An objective of EFFIPRO has been to develop stable ceramic materials with sufficient DC proton conductivity for use as electrolyte in high drain electrochemical energy conversion processes. Specific goals comprise proton conductivities in wet atmospheres of 0.001 S/cm at 800°C at midterm and 0.0015 S/cm at 700°C at project end. Stability and performance in the presence of CO<sub>2</sub> is a prerequisite. EFFIPRO has investigated candidates which therefore do not contain Sr or Ba as main constituents, divided into oxyacid salts and rare-earth based ternary oxides.

#### Oxyacid salts

Oxyacid salts are stable due to their combination of the oxyacid with a basic oxide. Many rare-earth phosphates, borates and silicates among these dissolve water and become high temperature proton conductors. They were evaluated at the beginning of the project and mostly exhibit proton conductivities below 0.0005 S/cm and would accordingly require significant improvement to reach the targeted conductivity of 0.001 S/cm at midterm. Inherently deficient rare-earth borates, e.g. Ln<sub>26</sub>O<sub>27</sub>□(BO<sub>3</sub>)<sub>8</sub> which upon hydration form Ln<sub>26</sub>O<sub>26</sub>(OH)<sub>2</sub>(BO<sub>3</sub>)<sub>8</sub> were considered promising, with proton conductivities under wet conditions reaching 0.0003 S/cm already at 500°C. However the material dehydrates around this temperature, and thus this value represents the actual maximum in proton conductivity. Within EFFIPRO it was tried to stabilize protons in the structure by partial substitution of the La with other rare-earth cations, but without achieving any improvement.

#### Rare-earth based ternary oxides - overview

In our survey rare-earth based ternary oxides, we covered different structure types including pyrochlores (e.g. acceptor-doped La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>), fluorites (e.g. “La<sub>6-x</sub>WO<sub>12-3x/2</sub>” based materials, LWO), Scheelites (e.g. Ca-doped LaNbO<sub>4</sub>, LCN), Fergusonites (e.g. Ca-doped doped LaTaO<sub>4</sub>), in addition to one perovskite, acceptor-doped LaScO<sub>3</sub>. Except for the tungstate (LWO) the materials were all acceptor doped to enhance the concentration of oxygen vacancies and, in turn, protons under wet conditions. Figure 2 summarizes the conductivities of these materials under wet hydrogen. Notably, in the temperature range of interest to PCFC (T>800°), these materials are dominated by ionic charge carriers. Under oxidizing conditions (not shown), La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> is reported to exhibit considerable p-type electronic conductivity at temperatures above approximately 500°C.

Clearly, Ca-doped LaScO<sub>3</sub> shows the highest conductivity, but its stability is questionable, and with Sc as a main constituent cost reduction will be challenging. Next the significant mixed conductivity of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> excluded this material from the top candidates. This left us with “La<sub>6-x</sub>WO<sub>12-3x/2</sub>” (LWO)



and Ca-doped  $\text{LaNbO}_4$  (LCN) as the two prime electrolyte candidates, and LCN was selected, as the structure and phase stability of LWO at that time were debated. In the following sections we will describe work and achievements with LCN, thereafter return to LWO, and finally present results of the EFFIPRO PhD study on  $\text{La}_2\text{Ce}_2\text{O}_7$  and related oxides – a system of potential use both a electrolyte and as mixed conducting electrode component.

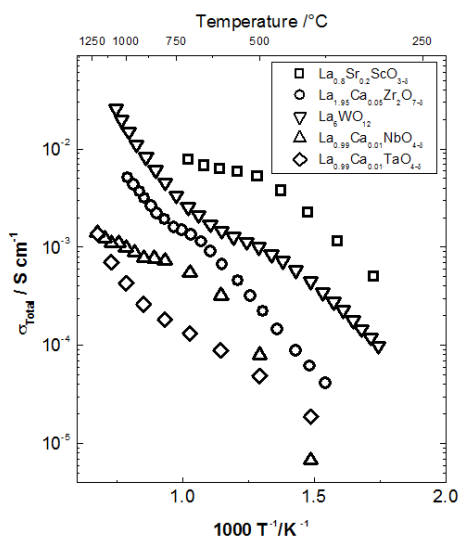


Figure 2. Conductivities in wet hydrogen of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{ScO}_{3-\delta}$ ,  $\text{La}_{1.95}\text{Ca}_{0.05}\text{Zr}_2\text{O}_{7-\delta}$ ,  $\text{La}_6\text{WO}_{12}$ ,  $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-\delta}$ , and  $\text{La}_{0.99}\text{Ca}_{0.01}\text{TaO}_{4-\delta}$ .

### Ca-doped $\text{LaNbO}_4$ (LCN)

The superior stability of LCN versus  $\text{CO}_2$  was confirmed in EFFIPRO by thermogravimetry: No weight increase was observed in wet 1 atm  $\text{CO}_2$  at any temperature. It was also confirmed that the material is stable at high water pressure (in autoclave) at low temperatures such as  $200^\circ\text{C}$ .

The conductivity of  $\text{LaNbO}_4$  based materials was investigated in more detail in many partner laboratories in order to increase it to the required  $0.001 \text{ S/cm}$ . This was attempted by using B-site instead of A-site doping, and by using co-doping strategies of both sites simultaneously. However, it was found that protons are trapped more strongly to B-site dopants, and co-doping leads to greater tendency of precipitation of secondary phases. These lessons learned apply apparently not only to LCN, but to ternary oxide electrolytes in general.

In the course of EFFIPRO, it also became clear by studies in partner laboratories and elsewhere that grain boundaries in proton conducting ceramics such as Y-doped  $\text{BaZrO}_3$ <sup>9</sup> and Ca-doped  $\text{LaNbO}_4$ <sup>10</sup> are not resistive due to impurities and foreign phases. Instead, this is an inherent property caused by oxygen vacancy accumulation in the boundary core. This is accompanied by depletion of protons and other positive carriers in adjacent space charge layers, where the resistance hence resides. This is analogous to the same phenomenon in oxygen vacancy conductors like YSZ or GDC. One can thus not reduce the resistance by making purer materials, and a strategy to counter-act the core charge by engineering the grain boundaries otherwise have so far not emerged.

<sup>9</sup> C. Kjølseth, H. Fjeld, P.I. Dahl, C. Estournés, R. Haugrud, T. Norby, *Solid State Ionics*, **181** (2010) 268.

<sup>10</sup> H. Fjeld, D.M. Kepaptsoglou, R. Haugrud, T. Norby, *Solid State Ionics*, **181** (2010) 104.

LCN was a challenge to manufacture. Batches from spray-pyrolysis synthesis of kg-batches in EFFIPRO were highly variable in terms of conductivity. The way to understanding and mitigation came through focused collaboration between EFFIPRO and national projects.  $\text{LaNbO}_4$  is a so-called line compound; it tolerates no cation non-stoichiometry, which thus instead leads to secondary phases, and the  $\text{La}_2\text{O}_3$ - $\text{Nb}_2\text{O}_5$ - $\text{CaO}$  turns out to be rich of possibilities, see Figure 3 (right). The spray-pyrolysis tended to produce Nb-rich products, with  $\text{LaNb}_3\text{O}_9$  as secondary phase. This phase moreover has a higher solubility of Ca than the  $\text{LaNbO}_4$  phase, effectively emptying  $\text{LaNbO}_4$  of acceptor doping and leaving a poorly conducting nominal LCN. Finally,  $\text{LaNb}_3\text{O}_9$  reacts with Ni in the anode cermets, quickly destroying any sample, see Figure 3 (left).

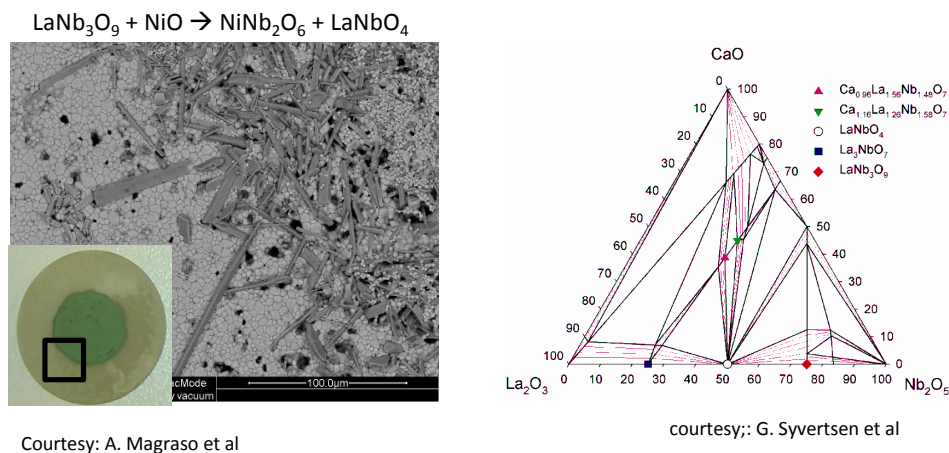


Figure 3. Left: SEM image showing the formation on secondary phases at the rim of an electrode due to reaction with secondary phase  $\text{LaNb}_3\text{O}_9$  in the LCN-NiO cermet for PCFC anode. Right: Ternary  $\text{La}_2\text{O}_3$ - $\text{Nb}_2\text{O}_5$ - $\text{CaO}$  phase diagram.<sup>11</sup>

It was thus necessary for the development of cost-effective synthesis to find a simple remedy to overcome the destructive phase purity problem, and it came as deliberate use of excesses of La and Ca to counteract variations in precursors or processing conditions, ensuring that no  $\text{LaNb}_3\text{O}_9$  was formed and that the  $\text{LaNbO}_4$  remained saturated with Ca. By this, any secondary phase would mostly be Ca-doped  $\text{La}_3\text{NbO}_7$  which is itself a proton conductor and does not react with Ni in the anode.

From what was learned, support-anode-electrolyte and electrolyte-cathode structures were made using LCN as described later, reaching the target electrolyte thickness and anode performance. The work and advances in EFFIPRO inspired and was accompanied by many complementary student and fellowship projects in the partner laboratories, e.g. regarding doping as mentioned above, electrode development as we will come back to later, and details of hydration and proton transport in the two polymorphs of  $\text{LaNbO}_4$ .<sup>12 13</sup> However, the conductivity of  $\text{LaNbO}_4$  based electrolytes remained too low, and cathodes for and with LCN did not perform well.

## Lanthanum tungstates - LWO

It was thus decided at midterm to change electrolyte to “ $\text{La}_{6-x}\text{WO}_{12-3x/2}$ ” (LWO). This had in the meantime been shown to be more stable towards reactivity with  $\text{CO}_2$  and evaporation of W than

<sup>11</sup> G. E. Syvertsen, A. Magrasó, R. Haugrud, M.-A. Einarsrud, T. Grande, *Int. J. Hydrogen Energy*, **37** (2012) 8017.

<sup>12</sup> H. Fjeld, K. Toyoura, R. Haugrud, T. Norby, *Phys. Chem. Chem. Phys.*, **12** (2010) 10313.

<sup>13</sup> M. Huse, A.W.B. Skilbred, M. Karlsson, ... T. Norby, R. Haugrud, C. Knee, *J. Solid State Chem.*, **187** (2012) 27.

suspected. The composition selected for EFFIPRO at midterm was  $\text{La}_{5.6}\text{WO}_{11.4}$  (LWO56) based on stability reported in literature and parallel projects. Figure 4 – displaying the transport numbers of protons, oxide ions, and electrons vs temperature in LCN (left) and LWO56 (right) – shows that LWO is a better, but less pure proton conductor at PCFC operating temperatures, e.g. 600°C.

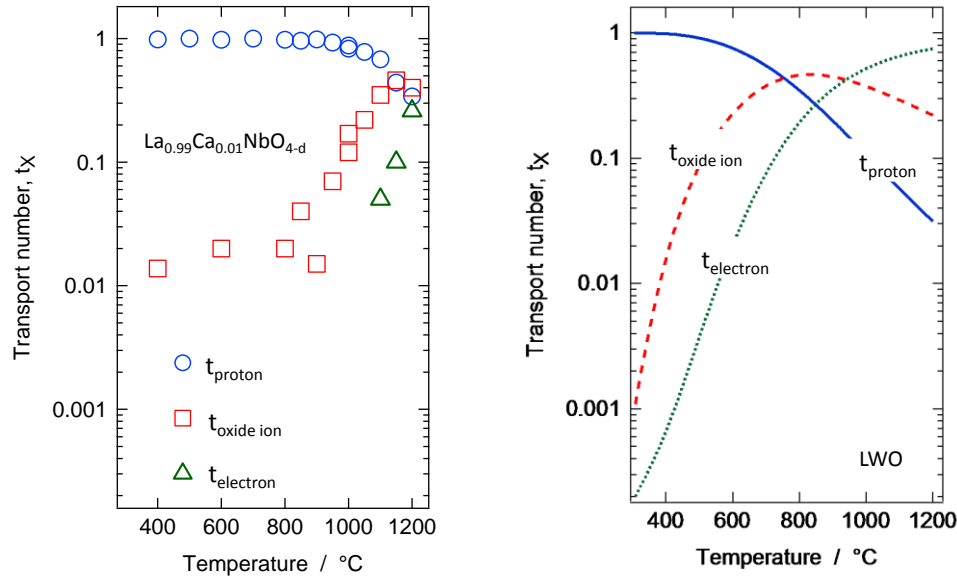


Figure 4. Transport numbers as a function of temperature under reducing conditions; based on experimental data for  $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$  and estimated from curve fitting the conductivity data for the LWO56 to a defect chemical model.

During the work in EFFIPRO and other projects, it became clear, however, that LWO56 is too La-rich and only metastable at operating temperatures, and slowly precipitates  $\text{La}_2\text{O}_3$  which decreases the conductivity, see Figure 5 (left and middle), and deteriorates the material during thermal cycling.

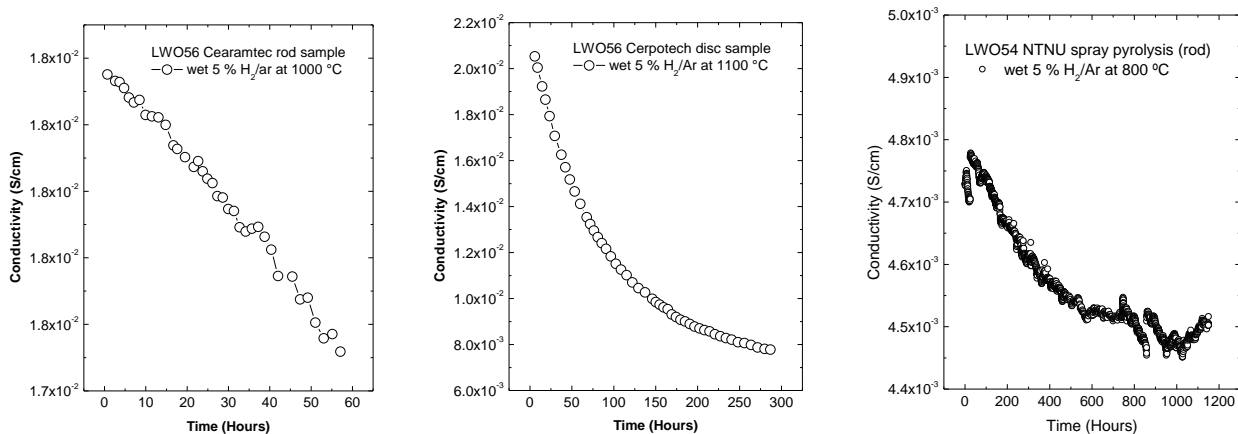


Figure 5. Left: Degradation of the conductivity of LWO56 as a function of time in wet 5 %  $\text{H}_2$  at 1000 °C. Middle: Same at 1100 °C. Right: LWO54 at 800°C.

In contrast, the composition LWO54 is thermodynamically stable. Figure 5 (right) presents the conductivity of LWO54 as a function of time at 800°C under wet reducing conditions. It encounters in comparison only a small and decaying decrease in the conductivity over a total of 1000 h. To the extent possible the project thus changed to LWO54 in its final stage.

It has in fact been shown that the stable series of LWO compositions belong to compounds in the series  $\text{La}_{28-x}\text{W}_{4+x}\text{O}_{54+3x/2}\text{V}_{2-3x/2}$ .<sup>14</sup> This has many unique features: the structure itself can be assigned to  $\text{La}_{28}\text{W}_4\text{O}_{54}\text{V}_2$ , i.e., a fluorite-related structure with a La/W-ratio of 7.0 (LWO70) and 2 out of 56 oxygen sites randomly vacant. It is however not stable as such, as it prefers to lower the number of vacancies. It does this by donor-doping itself by substituting some  $\text{La}^{3+}$  with  $\text{W}^{6+}$  to form the  $\text{La}_{28-x}\text{W}_{4+x}\text{O}_{54+3x/2}\text{V}_{2-3x/2}$  series. The required  $x$  increases with decreasing temperature. The preferred composition LWO54 corresponds in fact to  $x=1$ , giving the composition  $\text{La}_{27}\text{W}_5\text{O}_{55.5}\text{V}_{0.5}$  or  $\text{La}_{54}\text{W}_{10}\text{O}_{111}\text{V}$ . It thus has 1 out of 112 vacancies available for hydration to make the material a proton conductor. This amount has been confirmed by thermogravimetry.<sup>15</sup> The defect chemistry of the material has been clarified and a nomenclature for it devised.<sup>16</sup> Altogether, these detailed studies carried out in independent national researcher and PhD projects have greatly facilitated the implementation of LWO as electrolyte in EFFIPRO. LWO54 is stable and exhibits a proton conductivity surpassing 0.0015 S/cm in wet atmospheres at 700°C, and thus satisfies the final target electrolyte conductivity for EFFIPRO.

**Figure 6** compares the thermal expansion of LNO and LWO. In the LNO system we recognize the phase transition from the low temperature monoclinic to the high temperature tetragonal structure at approximately 520 °C. In the LWO system the thermal expansion is essentially linear and with a thermal expansion coefficient of  $11.3 \cdot 10^{-6}/\text{K}$ . The small difference between wet and dry conditions most probably reflects chemical expansion upon hydration. The difference in thermal expansion below and above the phase transition in the ortho-niobate system may create challenges to fabrication and operation upon thermal cycling. This is not the case in the LWO system and, moreover, the thermal behavior of LWO matches closely ferritic stainless steels which are developed as interconnect for solid oxide fuel cells.

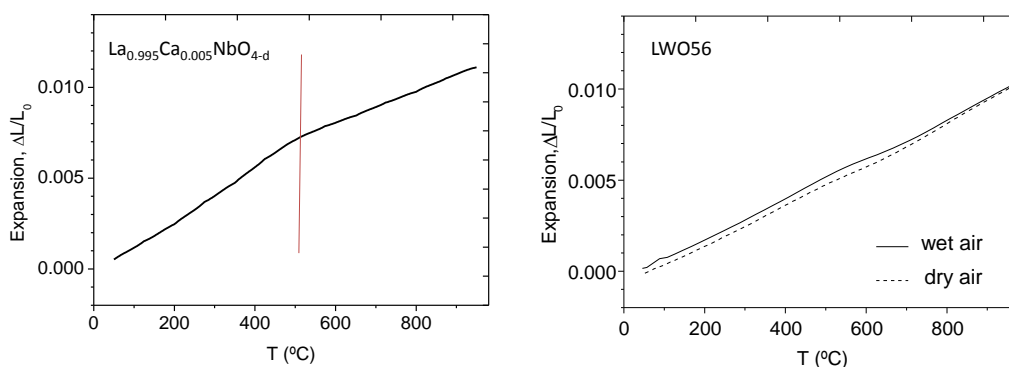


Figure 6. Linear thermal expansion of 0.5%Ca doped  $\text{LaNbO}_4$  and LWO56.<sup>17</sup>

<sup>14</sup> A. Magrasó, J. Polfus, ... S. Erdal, R. Hancke, S. Islam, T. Norby, R. Haugsrud, *J. Mater. Chem.*, **22** (2012) 1762.

<sup>15</sup> R. Hancke, A. Magrasó, T. Norby, R. Haugsrud, *Solid State Ionics*, submitted.

<sup>16</sup> S. Erdal, L.-E. Kalland, R. Hancke, *et al.*, *Int. J. Hydrogen Energy*, **37** (2012) 8051.

<sup>17</sup> EFFIPRO Deliverable D1.6 and A.W.B. Skilbred, Univ. Oslo, Personal communication/unpublished results.

## La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>-based materials

The PhD student at UiO has as one task studied La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> and related pyrochlore oxides, known to exhibit interesting properties as electrode components for PCFCs based on a report in the literature.<sup>18</sup> The developments have led him to focus on the solid-solution series La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>-La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> (LZO-LCO): LZO is an ordered pyrochlore which is a mixed proton-oxide ion conductor depending on acceptor doping, temperature and  $p\text{H}_2\text{O}$  in the normal manner. LCO, on the other hand is – based on the work in EFFIPRO - an inherently disordered material, thus acting effectively as 50% La-doped CeO<sub>2</sub>. It is therefore almost unaffected by doping and exhibits high oxide ion conductivity and modest hydration and proton conductivity. By help of experiments and *ab initio* DFT simulations in collaboration with an independent PhD student, the details of the development of hydration and proton mobility along the LZO-LCO series has been studied in detail and under publication.<sup>19 20 21</sup>

As examples of the results and new learning, we show below the hydration of La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> from thermogravimetry (TG). The material follows a model in which it remarkably fills all its oxygen vacancies (1 out of 8 sites) with water, replacing the positive charge by protons. The material remains an oxide ion conductor down to around 450°C, but the hydration and consequent minor proton conductivity rationalises the material's good properties as electrode component at the operating temperature ranges of PCFCs, typically 600°C. This kind of function – mainly at the cathode – can be useful in order to facilitate the reaction between protons from the electrolyte and oxygen gas, but the electronic component should be optimised first.

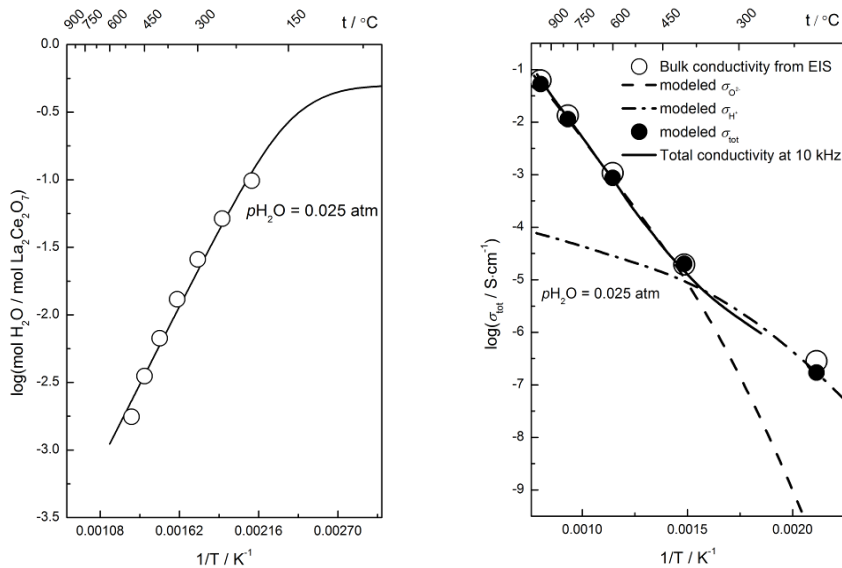


Figure 7. Left: Hydration of La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>. Points are as measured by TG, while the solid line shows a model by which all oxygen vacancies are filled. Right: Total and partial ionic conductivities from oxide ions and protons based on obtained thermodynamics of hydration and mobility parameters, and the sum compared with measured total conductivity.<sup>20</sup>

<sup>18</sup> B. Lin, S. Wang, X. Liu, G. Meng, *J. Alloy Compd.*, 478 (2009) 355.

<sup>19</sup> V. Besikiotis, S. Ricote, M. Hjorth Jensen, T. Norby, R. Haugrud, *submitted*.

<sup>20</sup> V. Besikiotis, C.S. Knee, I. Ahmed, R. Haugrud, T. Norby, *in prep*.

<sup>21</sup> T.S. Bjørheim, V. Besikiotis, R. Haugrud, , *in prep*.



## A potentially important finding regarding grain boundary and electrode resistances

As we have seen, Ca-doped  $\text{LaNbO}_4$ , like Y-doped  $\text{BaZrO}_3$ , and many other acceptor-doped proton (and oxygen ion) conductors exhibit high grain boundary resistances, attributed to accumulation of positive oxygen vacancies in the grain boundary core in order to release lattice misfit stresses, leading in turn to proton depleted space charge layers on each side. The grain boundary resistances seem however much smaller for LWO,  $\text{La}_2\text{Ce}_2\text{O}_7$ , and in our experience also other *inherently* oxygen deficient materials and their hydrated proton conducting variants. We raise the hypothesis that this is related to an effective *neutrality* of the “structurally disordered” occupied and vacant oxygen sites as opposed to the effectively positive ones in the ordered doped materials: A grain boundary core may use the inherently empty sites to release its stresses with less charge buildup, giving a smaller or zero charge and consequently weak space charge layer and little depletion of charged oxygen vacancies and protons. This is important in future evaluation of the DC conductivity of new ionic conductors.

An electrolyte-electrode interface may suffer from a depleted space charge layer for the same reason – accumulation of oxygen vacancies. If the hypothesis holds, inherently oxygen deficient and disordered oxides may have exhibit correspondingly smaller charge transfer polarization resistances. We will come back to this suggestion, and an observation supporting it, under cathode development.

## Powder synthesis and reduction of production costs

SME partner CERPOTECH produced kg quantities of powders of electrolytes and electrodes by spray pyrolysis for the project. Capability of prototype and pilot-scale quantities of specialty functional ceramic powders is important for European scientific and industrial leadership. An important part of the work, to increase competitiveness of the SME and PCFC technologies alike, was thus reduction of cost by use of time-saving procedures and less expensive precursors.

For LCN synthesis, this was done by using fewer and more efficient washing and separation steps. Moreover, early compaction of the fluffy product added to handling simplicity and reduced risk of contamination. All in all, labour was reduced by 43% and final powder cost correspondingly by 30%.

In the further developments during synthesis of LWO and perovskite related cathodes for it, the largest potential for improvement and cost saving was in the post treatment of the as-spray-pyrolysed powder. The ball milling compaction and homogenisation process is time consuming. After ball milling a slurry of powder and ethanol, the ethanol needs to be evaporated and the dry powder “cake” has to be sieved and heat treated before the powder is ready. In collaboration with JetPharma and Dec group, jet milling has been identified as a far more efficient milling method, more suitable for industrial scale powder production. By replacing the ball milling and the processing steps following, a major reduction in time consumed can be realised, as shown in Figure 8. In addition, by avoiding the use of ethanol in the milling process the material cost is reduced further. A jet mill will also allow better control on particle size, reduce risk of contamination, and increase yield. Testing on JetPharma’s test plant is scheduled for medio 2012.

A next level of cost saving involved the planned attempts to use less pure raw materials, i.e. mischmetal strategies: Minerals generally never exist with high levels of purity in nature, but rather consist as a blend of elements. Consequently, costly steps may be required during production to purify raw materials. Often, these blends contain elements of very similar physicochemical characteristics, so that one may tolerate a reasonably low purity level, at least in the more structural parts of the assembly, e.g. in a substrate. The rare-earth elements exist in such blended minerals and alloys formed upon reduction of these oxide minerals are termed mischmetal.

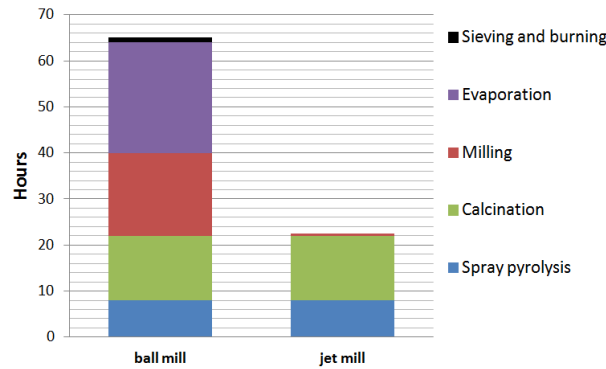


Figure 8. Time consumption for production of one powder batch (2-5 kg depending on composition)

Two test batches of LCN with 0.5 % Ca doping and 1.5 % excess Ca, respectively, were prepared from nitrates based on La rich mischmetal of the following composition: 80% La, 10% Ce, 10% Pr and 1% Fe (Shanghai Jiangxi Metals Co., Ltd). The same strategy was applied for niobium by replacing 1% of the niobium with Ta to imitate the natural coexistence of Nb with Ta. The same supply of rare earth mischmetal solution was used to make LWO56, and here only 1% Fe was used to substitute W. The phase-purity, the microstructure and the conductivity of highly substituted batches were characterized. **Figure 9** illustrates, by way of example, how the total conductivity of these blends differs from the nominally pure LCN and LWO56 under reducing conditions.

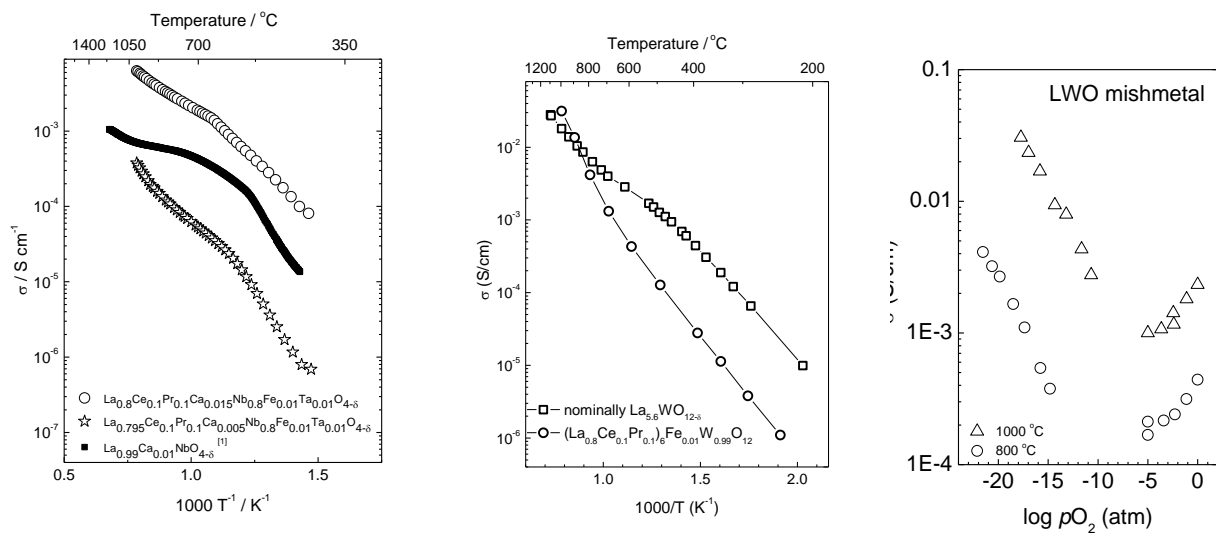


Figure 9. Total conductivity in wet 5%  $H_2$  vs  $1/T$  for LCN (left) and LWO (middle) mischmetal compositions. Right: Total conductivity of mischmetal LWO56 vs  $\log pO_2$  in wet atmospheres, showing high n-type and p-type electronic conductivity at low and high  $pO_2$ , respectively.

Variations in the conductivity behavior reflects changes in the major conductivity mechanism, e.g. as due to doping effects or as a consequence of segregation of secondary phases. In the LCN system, increased conductivity apparently reflects formation of  $LaNb_3O_9$  as a secondary phase, which is known as an n-type conductor. The conductivity of the mischmetal LWO56 is lower than in the pure material below  $\sim 800^\circ C$ , but higher above, also here reflecting electronic contributions, see **Figure 9**

(right). All in all, mischmetal compositions did not show properties as good as the nominally pure materials, and were thus not part of the final reduced cost components tested in EFFIPRO.

## Substrate - anode - electrolyte

An objective of EFFIPRO is to develop a stable, thin, anode-supported proton conducting electrolyte. The goals at midterm were 5  $\mu\text{m}$  electrolyte with area specific resistance (ASR) of 0.5  $\Omega\text{cm}^2$  and an anode polarisation ASR of 0.5  $\Omega\text{cm}^2$ , both in wet  $\text{H}_2$  at 800  $^\circ\text{C}$ . Target at project end was to have a 3  $\mu\text{m}$  electrolyte with ASR of 0.2  $\Omega\text{cm}^2$  and an electrochemical anode ASR of 0.2  $\Omega\text{cm}^2$  at 700  $^\circ\text{C}$ . The electronic conductivity of the anode material should surpass 100 S/cm at midterm and 200 S/cm at project end. The work has been done between three partners that offer partly complementary and partly overlapping technologies and were assigned three different routes – partly complementary and partly overlapping but most of all focussing on the different layers that make up the half-cell.

## Substrate – anode – LCN electrolyte

In the work with LCN, JÜLICH made half-cells with LCN-Ni cermet substrates (2<sup>nd</sup> generation SOFC technology) made by their warm-coating method and other methods. SINTEF used instead metallic alloy substrates (used in 3<sup>rd</sup> generation SOFCs). RISØ-DTU concentrated on the thin electrolyte as such and its characterisation. All three have had in common the concern for the so-called functional layer between substrate and electrolyte: This is the layer that enables the deposition of a thin dense electrolyte and ensures the role of the electrochemically active anode.

The collaborative work led to significant progress in manufacturing of half cells integrating thin and dense LCN electrolytes. This was produced by several processes, all of which have the potential for scaling up for this electrolyte and other solid-state electrolytes. The targeted thickness of 5  $\mu\text{m}$  was reached by two of the routes. Testing of produced samples indicates good agreement between the electrolyte thickness and the impedance of LCN materials, considering the conductivity of the various batches of LCN powder used.

JÜLICH developed assemblies of warm pressed LCN–Ni cermet supports with vacuum slip cast LCN electrolyte less than about 10  $\mu\text{m}$  on top, as well as tape casting of the cermet, screen-printing of the electrolyte film on the pre-sintered substrate, and final co-sintering, see Figure 10. A third approach involved sequential tape casting of support and electrolyte with subsequent co-sintering.

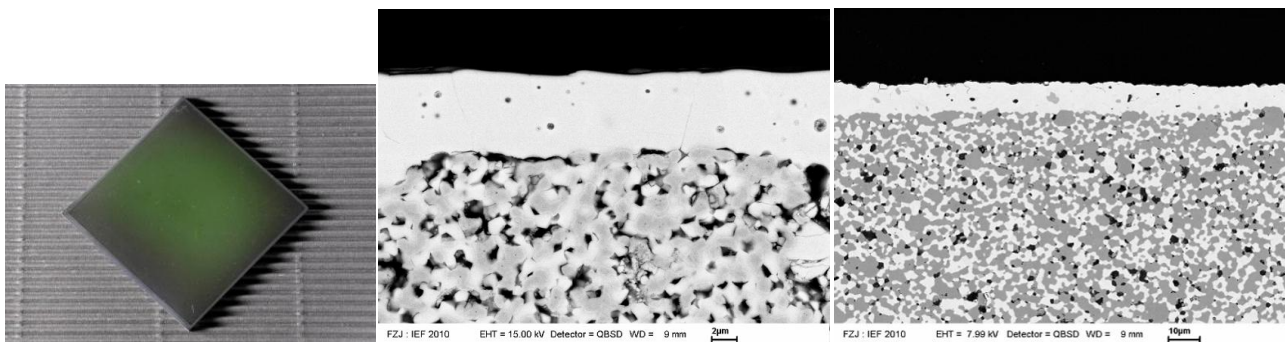


Figure 10. *Left: Warm-pressed LCN-Ni cermet substrate (before full reduction – hence the green colour of NiO) with a thin transparent film of vacuum slip cast LCN. Middle: Cross section of electrolyte after reduction. Right: Cross-section of tape-cast substrate pre-sintered at 1100 $^\circ\text{C}$  with electrolyte screen printed and co-sintered at 1300 $^\circ\text{C}$*



SINTEF developed assemblies based on metallic substrates. Two routes were successfully developed to produce flat porous ferritic alloy substrates (22 wt.% Cr) coated with LCN-Ni cermet anodes, see Figure 11. The first is based on water-based tape-casting of alloy and anode tapes. The tapes are then co-laminated and co-sintered in reducing atmosphere to avoid oxidation of the alloy substrates. The second route is based on tape-casting of the alloy substrate and spray-coating of the functional anode layer, enabling deposition of thinner anode layers. Results of the two routes are shown in Figure 12.

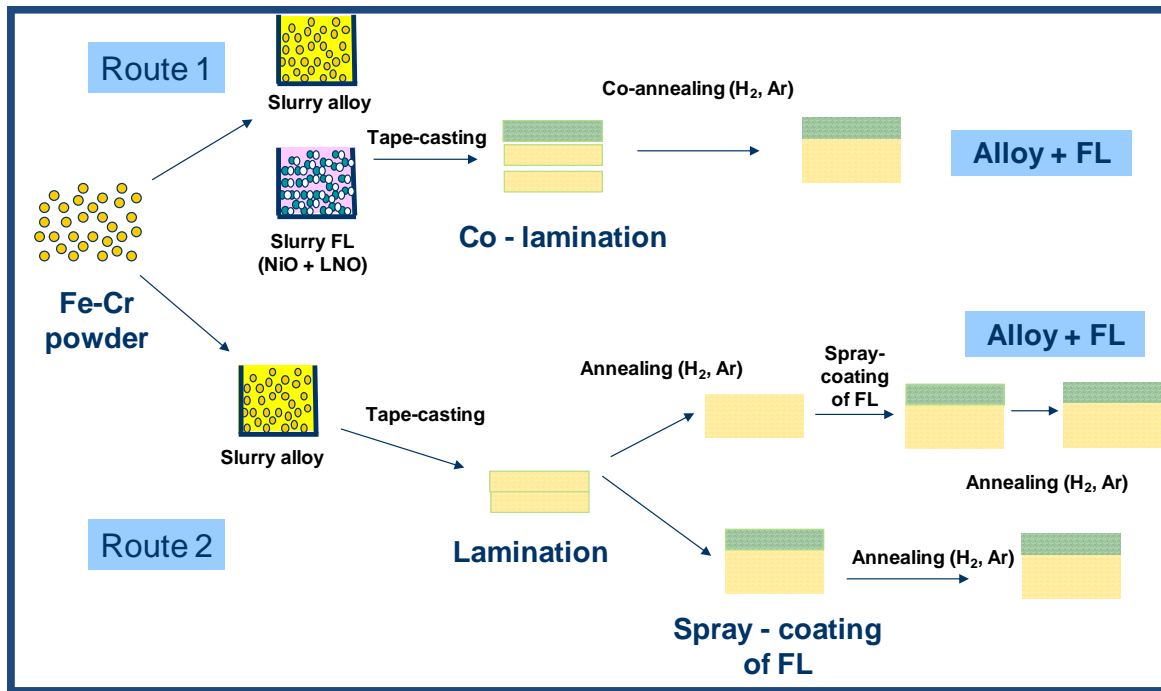


Figure 11. *Fabrication routes investigated for alloy substrates with anode functional layers (FL).*

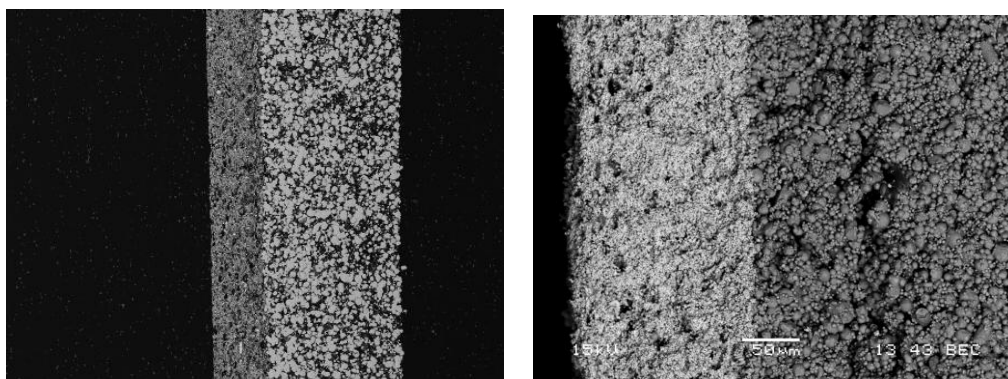


Figure 12. *Left: Cross-section of alloy substrate and functional anode by tape-casting and co-lamination after calcinations. Right: Alloy substrate with spray-coated anode after calcination.*

The production of dense thin electrolyte on the anode-alloy substrates proved challenging, however. The reason for this is the need for sintering the assembly in reducing atmosphere to avoid oxidation of the alloy substrate. Besides, the alloy substrate can not be used at the high temperature typically

used for sintering LCN electrolyte in air. Several procedures were investigated to circumvent these problems: In collaboration with RISØ-DTU, the electrolyte layer was deposited by electrophoretic deposition (EPD). Some experiments were started and it was found that the conductivity of the substrate needs to be increased for depositing the electrolyte by this technique. At SINTEF, wet ceramic coating deposition methods were investigated. Several sintering treatments, deposition procedures and compositions of slurries for coating were investigated. Thin electrolyte layers were obtained on flat anode-alloy substrates. However, the electrolyte layer contained micro-pores.

RISØ-DTU made electrolytes by electrophoretic deposition (EPD) on own and partner-supplied anode supports, reaching the 5  $\mu\text{m}$  midterm target thickness. The most interesting cell with an electrolyte of 7  $\mu\text{m}$ , and a functional fine grained functional anode layer yielded impedance spectra that could be delineated into contributions interpreted to reflect electrolyte and electrode ASRs of 1.3 and 0.25  $\text{ohm cm}^2$ , respectively, see Figure 13. The latter number thus meets the target value for the anode, and this was confirmed also in parallel studies of LCN-Ni cermet anodes on LCN.<sup>22 23</sup>

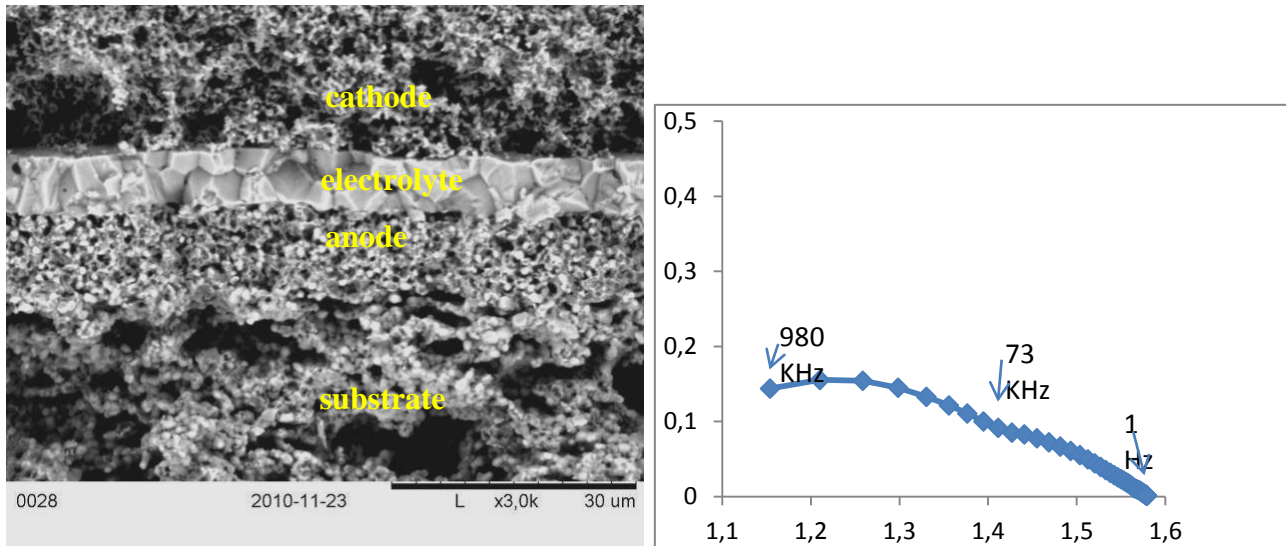


Figure 13. Left: Complete cell of LCN on LCN-Ni cermet anode. A green substrate was used for the deposition by EPD of anode and electrolyte layers. Right: Impedance spectrum of the cell at 800°C.

While sufficiently thin electrolytes could be made and measured, their ASRs were too high, in line with the sub-target proton conductivity. The anode polarisation of the LCN-Ni cermet electrodes was however well within midterm target. Modelling showed that this was still limited by the poor conductivity of the ceramic LCN phase of the cermet, and better performance would be expected with a better electrolyte. The electronic conductivity of the metallic LCN-Ni cermet supports and functional cermet layers were early on established to have surpassed the 100 S/cm goal for midterm.

### Substrate – anode – LWO electrolyte

At midterm, EFFIPRO changed electrolyte material from LCN to LWO, and the development of substrate, anode, and cathode started from scratch.  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  (LSC) was chosen as candidate

<sup>22</sup> A. Magrasó, ... M.F. Sunding, R. Strandbakke, R. Haugsrud, T. Norby, *J. Am. Ceram. Soc.*, **93** (2010) 1874.

<sup>23</sup> A. Magrasó, R. Haugsrud, T. Norby, *J. Am. Ceram. Soc.*, **93** (2010) 2650.

anode functional barrier layer between the Ni in the cermet and the LWO as they are known to react. The options were narrowed down from the work on LCN in order to succeed making LWO-based systems in the remaining time. JÜLICH would use standard Ni-YSZ SOFC substrates instead of developing new ones for LWO, since the LSC layer would in any case come in between. SINTEF would continue with their alloy-based substrate and start depositing LSC and LWO on that. RISØ-DTU contributed as before with LWO electrolyte film deposition on JÜLICH and SINTEF anodes, and with testing them. Finally, UiO assisted with its pulsed laser deposition (PLD) facility to make sufficiently thin functional electrolyte for the final tests. The work is described in more detail below.

The work at JÜLICH showed that it was difficult to sinter a dense electrolyte on top of LSC which was, in turn, on top of a Ni-YSZ cermet, without delamination or reaction between materials. This is caused by the high temperature needed for sintering and the consequent high cation inter-diffusion between and through the layers, possibly also over surfaces in the porous components. It was finally concluded that anodes based on Ni and LWO would have to be made by making dense LWO on a porous LWO substrate, and thereafter infiltrating the pores with a Ni-containing solution, which after reduction during operation as anode becomes metallic. This was tried by RISØ-DTU; after reduction to Ni and application of a gold counter electrode they measured an electrolyte resistance in correspondence with the conductivity of the 30 µm thick LWO electrolyte layer.

SINTEF focused on investigation of robust manufacturing routes for porous alloy substrates and compatible functional anodes with reduced production cost. These layers are integrated in the 3<sup>rd</sup> generation alloy supported fuel cells. Figure 14 shows an overview of the processes employed.

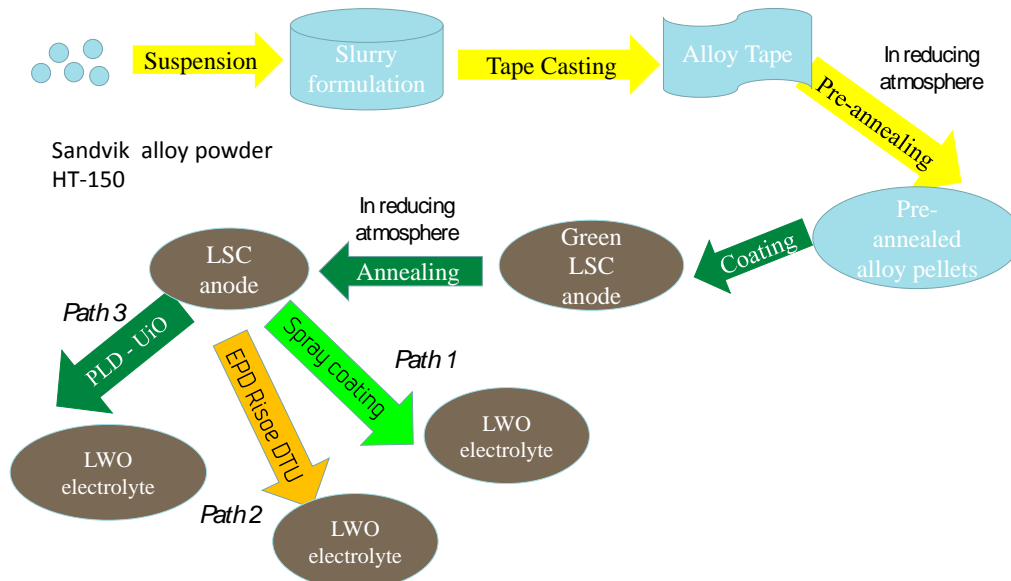


Figure 14. Flowchart of the fabrication processes investigated at SINTEF in collaboration with RISØ-DTU and UiO for the fabrication of alloy-supported PCFC in EFFIPRO.

Tape-casting was selected for producing porous substrates of ferritic alloys. A thorough investigation of slurry compositions, drying procedure, and annealing treatment, has been carried out to control the properties of the produced substrates. Flat alloy substrates 1 mm thick were successfully obtained with connected porous networks after a single casting and annealing step, see Figure 15.

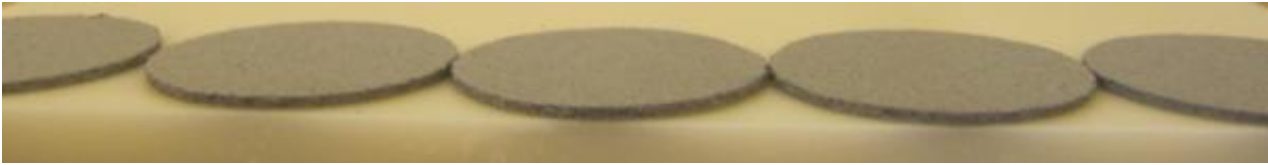


Figure 15. Flat pre-annealed porous metal substrates.

The anode functional layer (LSC or LSC/Ni) was then applied by spray-coating. Suspensions and parameters were optimised to avoid infiltration of LSC grains into the metallic substrates, to improve adhesion and to provide a suitable surface for the deposition of the electrolyte layer.

The application of the LWO54 layer was investigated through three main paths using: spray-coating, electrophoretic deposition in collaboration with RISØ-DTU and Pulsed Laser Deposition (PLD) in collaboration with UiO, see Figure 16.

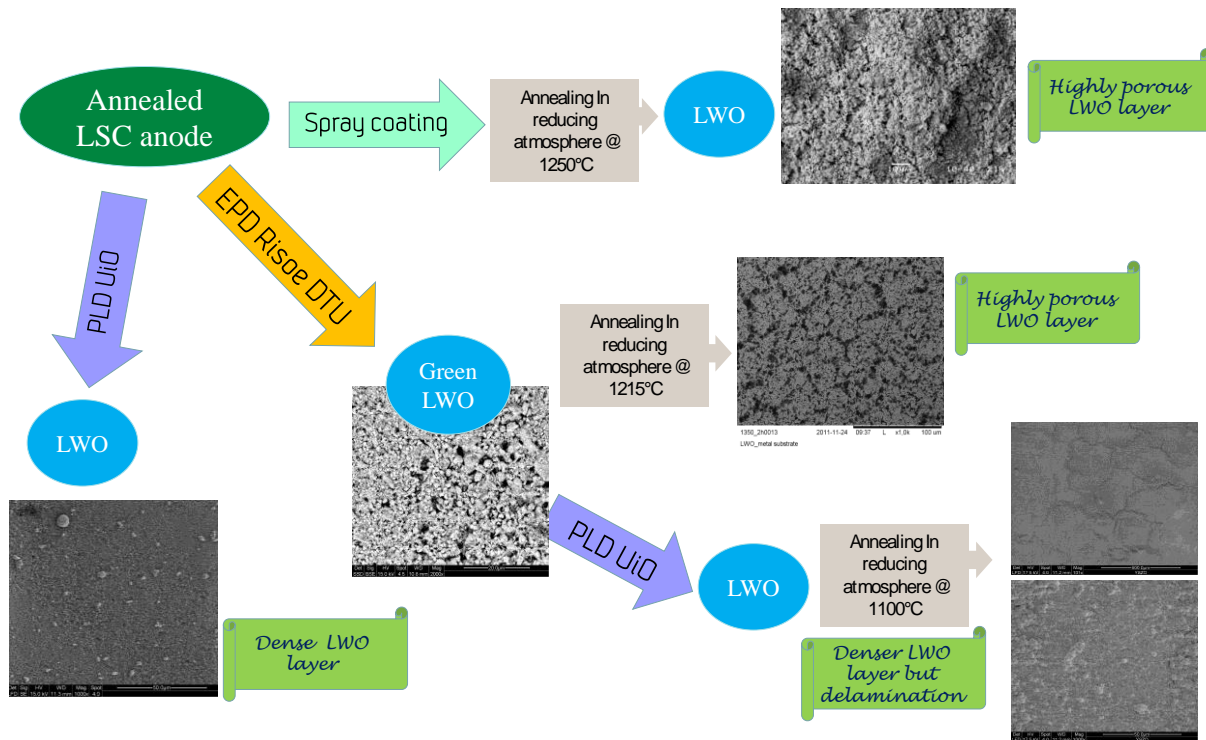


Figure 16. Flowchart of the fabrication processes investigated at SINTEF in collaboration with DTU, RISØ and UiO for the fabrication of LWO54 layer on alloy/LSC substrates.

Several samples were sent to RISØ-DTU for further deposition of LWO electrolyte by electrophoretic deposition. The produced LWO layers were homogeneous and well adhered to the anode/substrate assembly. However, the layers remained porous and it was not possible to sinter the cells at higher temperature due to melting of the alloy at temperature above 1350°C. Deposition of LWO layers by spray-coating at SINTEF resulted in similar outcomes.

The PLD enabled us to produce thin dense electrolyte layers of around 3 microns on the alloy/LSC substrates after adjustment of the substrate temperature and atmosphere in the PLD chamber, see Figure 17 and Figure 18. This electrolyte thickness reaches one of the final targets of the project. Post annealing did not cause microstructural changes, and the electrolyte remained crack-free.

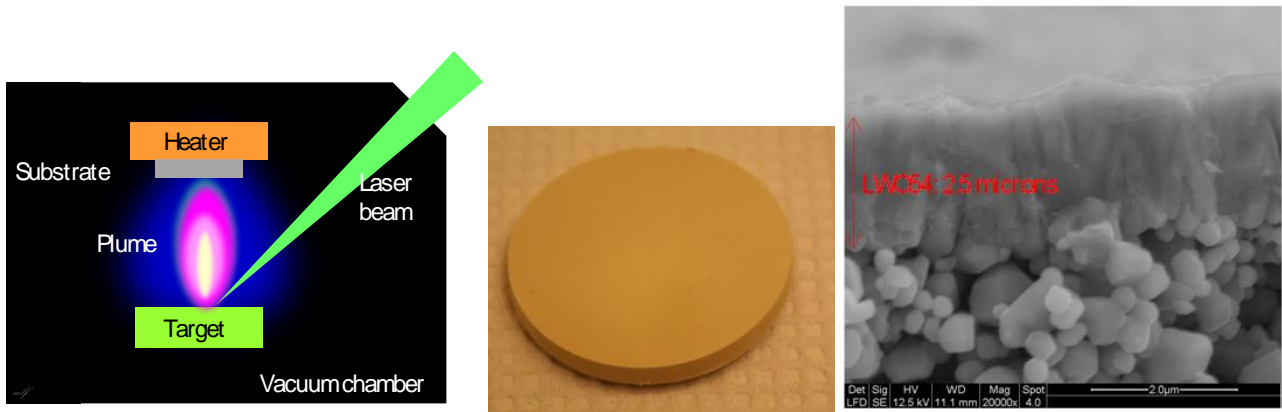


Figure 17. Left: Principle of PLD. Middle: LWO54 target pellet. Right: Dense 2.5 μm film of LWO deposited by PLD on a porous LSC layer on alloy substrate.

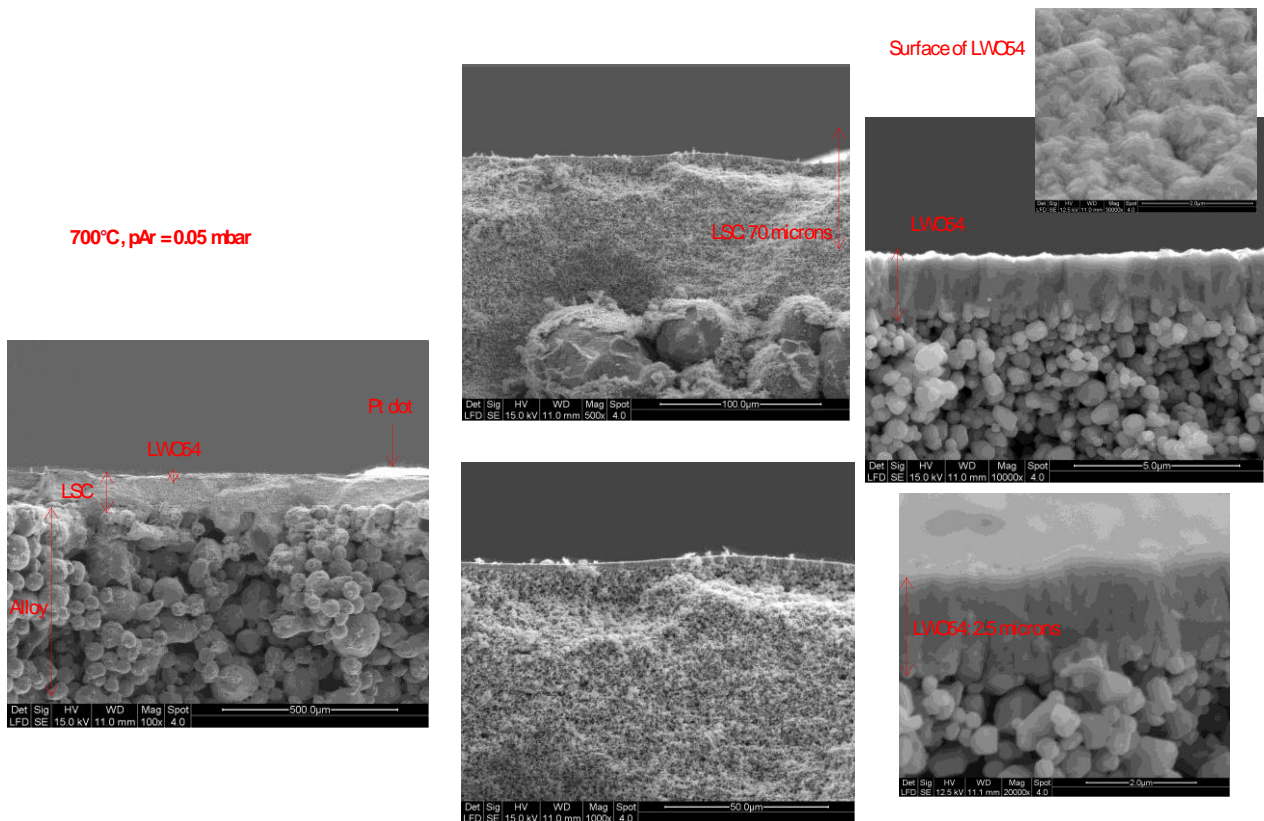


Figure 18. Left: SEM micrograph of the entire anode-supported structure, with coarse porous alloy, finer porous LSC, and dense thin (hardly visible) LWO. Middle: Close-ups of alloy-LSC interface (top) and LSC+LWO (bottom). Right: Further close-ups of the porous LSC and dense LWO.

Testing of cells was conducted at UiO on the PLD deposited LWO layers coated on LSC/alloy substrates, which were post annealed at 700°C and 800°C for 24 hours. For the testing, the counter electrode (see Figure 19) consisted of Pt dots deposited by e-beam. The electrodes were contacted using 0.5 mm gold wire pressed down in contact by spring loads.

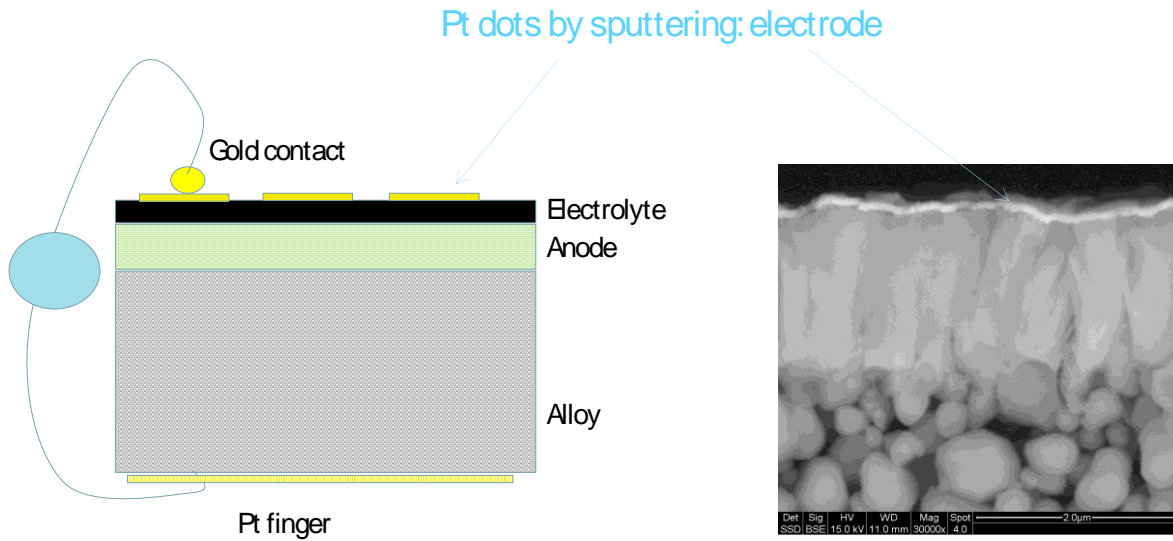


Figure 19. *Left: Scheme of cell with current collectors for electrical characterisation of the alloy-LSC-LWO. Right: LWO by PLD with thin Pt metal layer as counter-electrode.*

The cell was characterized by electrochemical impedance spectroscopy from 500 to 700°C in wet 5% H<sub>2</sub> in Ar, see **Figure 20**. The area specific resistance of the electrolyte is 1.2 ohm cm<sup>2</sup> at 700°C. The activation energy is approximately 50 kJ/mol, fairly similar to thicker electrolytes prepared at RISØ-DTU. The bulk resistance values are significantly higher than expected from the specific bulk conductivity. This is suspected to be due to an inaccuracy in defining the surface area of the contact electrode. Further measurements are still going on even at completion of the project to evaluate similar samples.

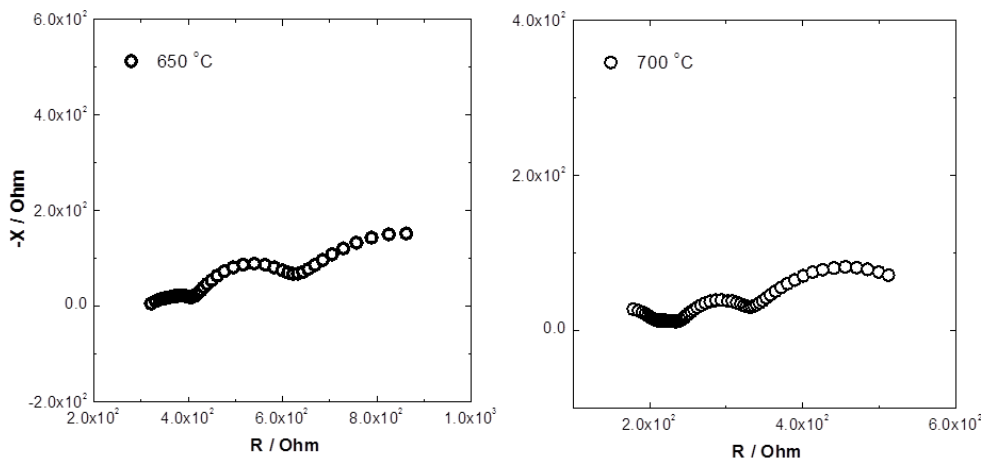


Figure 20. *Impedance spectra of an alloy-LSC-LWO (PLD) cell in wet 5% H<sub>2</sub> in Ar.*

As seen from the impedance spectra (as measured – not corrected for nominal electrode area) the electrode polarisations sum to values of the same order of magnitude as the bulk resistance, and the



spectra are of good quality and contain many features worth studying further. The performance of the cells does not degrade significantly by thermal cycling or exposure to CO<sub>2</sub>.

### **Reaction growth of thin electrolyte**

Partner JÜLICH has – prior to EFFIPRO - developed a novel general path named reaction growth to make thin electrolytes on electrode supports, and this was pursued in EFFIPRO as a high-risk “outsider strategy” to grow stable proton conductors on suitable electrodes. The technique consists of having an electrode structure with an excess of a component, or with a composition, that reacts with an applied thin layer of a reactant. The work has consisted of evaluation of possible reaction couples for various candidate proton conducting electrolytes. This did however not lead to new potential candidate couples, and the methodology was mainly used to test out some ways of doping and co-doping electrolytes by in-diffusion. In collaboration with UiO, a further development of the reaction growth concept was investigated, namely the in-situ growth of an electrolyte from anode and cathode layers placed in direct contact with each other. As one example, an idea from University of Oslo was to have electrodes or at least functional layers of TiNb<sub>2</sub>O<sub>7</sub> (anode) and Ca-doped LaMnO<sub>3</sub> (cathode) that would react to form Ca-doped LaNbO<sub>4</sub> as electrolyte in between. If successful this would give a self-assembling and – equally important – self-repairing thin electrolyte film.

The tests made in this direction were not successful. One reason may have been that it was chosen to test the reaction couple as deposited on an LCN-NiO green cermet body which is closer to a real system, but inflicts numerous possibilities for competing reactions, as confirmed by post-reaction analyses by SEM and XRD. The approach and work in this work task were deemed unsuccessful half-way in the project, and the task was decided stopped after accelerated final reporting, and the resources then reallocated. A few attempts to make the new LWO electrolyte by reaction growth were running as the work task stopped, but also these were unsuccessful.

### **Fundamental studies of novel electrode materials and structures**

We now describe the work on developing electrodes for PCFCs, notably LCN and LWO electrolytes. The fundamental studies of electrode and surface kinetics will be discussed along with the manufacture, performance, and optimisation. We start with anodes, since they are part of the substrate-anode-electrolyte structures discussed above. We thereafter discuss cathodes.

#### **Anode for LCN**

The active anode electrocatalyst for LCN was Ni – it is stable in contact with LCN both as NiO during manufacture and Ni during operation. Satisfactory performance was obtained for such anodes when prepared as cermet composites supporting the thin electrolyte or deposited on thick electrolytes. The project nevertheless investigated the kinetics of relevant species on Ni and LCN surfaces and on LCN-Ni electrodes, serving as a model system during setup of facilities for in-situ Raman and FTIR spectroscopy, isotope exchange studies, and impedance spectroscopy.

Firstly a literature and Raman spectroscopy study was done for H and OH species on Ni surfaces, employing also H/D isotope shifts. The detailed deliverable report serves as a useful reference. The Raman sample stage allowed in-situ spectra, but not employing electrochemical gradients, and this and the severity of operating conditions was acknowledged as limiting for the value of the data.

This was followed up by a dedicated study of H/D transients and hydration/dehydration of LCN and its surfaces using bulk and thin film samples. Methods comprised XRD, Raman spectroscopy, gas phase mass spectroscopy (MS), TG and conductivity in equilibrium and transients. The structural polymorphs and their hydration as well as physisorption of water as OH groups can be well monitored. Hydrogen dissociative adsorption is inactive on the LCN surface as compared to the Ni surface of an anode cermet, see **Figure 21**. Moreover, Ni-LSC is slower than a corresponding Ni-YSZ cermet, suggesting that LSC is not a very efficient promoter as support for the Ni catalyst. The work in EFFIPRO has been accompanied by DFT modelling of H on  $\text{LaNbO}_4$  surfaces,<sup>24</sup> confirming that LCN itself (without Ni) is inefficient for dissociative absorption of  $\text{H}_2$  for the anode function.

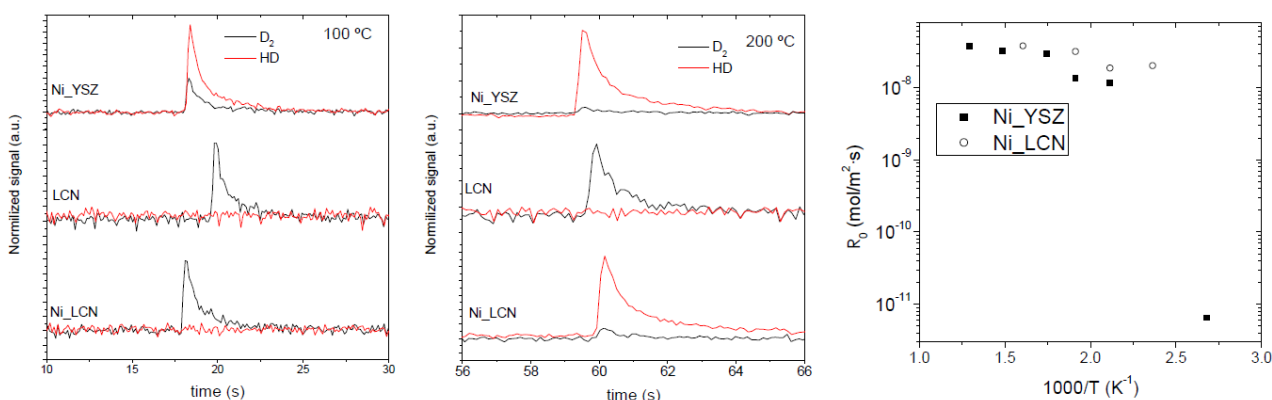


Figure 21. MS data for  $\text{H}_2/\text{D}_2$  pulse exchange at 100 and 200°C (left and middle) over 10 mg powder of Ni-YSZ, LSC, and Ni-LSC. Right: Temperature dependency of overall  $\text{H}_2$  exchange rate constant.

The anodes surpassed the targets at midterm, as we showed on page 18, but not by good margins. The main limitations are a limiting ionic conductivity of the LCN electrolyte of the anode cermet combined with an apparently modest promotion of Ni as electrocatalyst by LCN as support and electrolyte. A parallel study by high resolution TEM shows that the interface between Ni and LCN is atomically clean, while DFT modelling of the energetics of the Ni- $\text{LaNbO}_4$  interface suggests – as expected – that there are energy wells and activation energy losses for the  $\text{H}/\text{H}^+$  charge transfer.<sup>25 26</sup>

## Anodes for LWO

Anodes developed for LWO followed two main routes. In one,  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  (LSC) effectively became the anode, as a barrier between LWO and any transition metal source like NiO or substrate alloy that it would react with during sintering. In the other, Ni was introduced as anode by post-sintering infiltration. Combining the two, Ni was doped into LSC to substitute Cr up to 20% without reaction with the LWO. The Ni in these anodes was then precipitated under the reducing conditions of operation in wet hydrogen and became the active catalytic component.

<sup>24</sup> K. Hadidi, T. Norby, O.M. Løvrvik, A.E. Gunnæs, *Int. J. Hydrogen Energy*, **37** [9] (2012) 8033.

<sup>25</sup> T. Norby, H. Fjeld, A. Gunnæs, K. Hadidi, D.M. Kepaptsoglou, O.M. Løvrvik, M.F. Sunding, K. Toyoura, *Int. J. Adv. Microscopy and Theoretical Calculations (AMTC Letters, ISSN 1882-9465)*, **2** (2010) 206.

<sup>26</sup> D.-M. Kepaptsoglou, K. Hadidi, O.-M. Løvrvik, A. Magraso, T. Norby, A.E. Gunnæs, Q. M. Ramasse, in prep.



Anodes of LSC supported by alloy or cermet substrates and with thin LWO electrolyte layers deposited on top were described earlier. They exhibited relatively high polarisation resistances, probably due to the poor electrocatalytic activity of LSC resulting from a modest p-type electronic conductivity. The same result was obtained by  $\text{La}_{0.87}\text{Sr}_{0.13}\text{CrO}_3$  (LSC) anodes deposited on self-supported LWO electrolyte tablets. The Ni-doped  $\text{La}_{0.85}\text{Sr}_{0.15}\text{CrO}_3$  materials (LSCN) showed better performance. The precipitation of the catalytic Ni nanoparticles on the surface is shown in Figure 22.

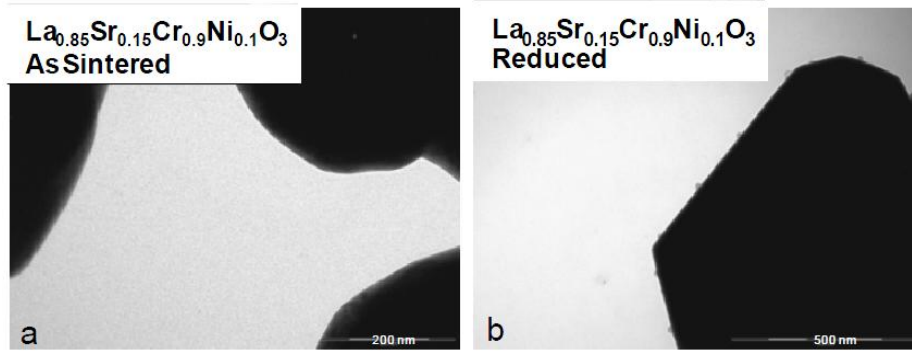


Figure 22. TEM images of LSCN10 before and after reduction. Note the appearance of the nanoparticles (of Ni) on the surface on the image to the right.

The role of the catalytic nanoparticles was clarified and EIS allowed the identification of the main rate limiting steps. Furthermore, EIS allows analysis and modelling of the anode polarisation with surface limiting processes, using Langmuir–Hinshelwood mechanism for describing their rate of dissociative adsorption of  $\text{H}_2$  (proportional to  $1/R_p$ ), see Figure 23 (left). Moreover, this model enables to calculate adsorption and rate constants and compare for different samples showing the importance of the catalytic active particles, see Figure 23 (right).

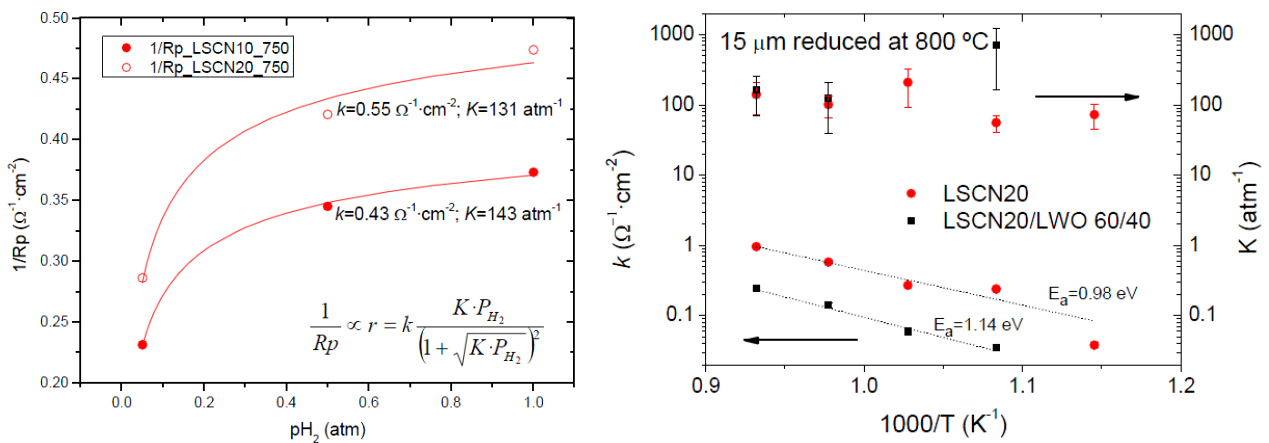


Figure 23. Left:  $1/R_p$  for LSCN10 and LSCN20 anodes sintered at  $1150^\circ\text{C}$  on LWO at  $750^\circ\text{C}$  vs  $p_{\text{H}_2}$ , with fitted model curve indicated. Right: Kinetic parameters  $k$  and  $K$  for the anode redox-reaction, proportional to rate and adsorption constants, respectively, vs  $1/T$ , for LSCN20 and LSCN20/LWO cermet electrodes on LWO electrolyte.

All in all, the insight provided recommendations for the improvement of the electrode. The best anode results reported in the project were observed with 20 mol-% Ni doped LSC which exhibits a polarisation ASR of  $3.5 \Omega \cdot \text{cm}^2$  at  $700^\circ\text{C}$  in wet  $\text{H}_2$ .

At the very end of the project – after finalization of partner periodic reports and deliverables – partner CSISC-ITQ prepared a new set of electrolyte and anode samples based on the latest understanding. This employed a Ni-free LSC sintered at  $1150^\circ\text{C}$  and then infiltrated four times with Ni nitrate. The obtained EIS results of the new anode are compared with our previous best anode, i.e.,  $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ni}_{0.2}\text{O}_{3-\delta}$  in Figure 24, Figure 25, and Figure 26. As seen, the polarization resistance at target conditions of  $700^\circ\text{C}$  in wet  $\text{H}_2$  is  $0.6 \text{ ohm cm}^2$  (as compared to the target value of  $0.2$ , i.e. a factor of 3.) This performance is ascribed to (1) the improved surface kinetics, and (2) probably the enhanced total (electronic) conductivity, all yielded by the Ni decorating the electrode pore walls. The Nyquist and Bode plots show that the new sample presents little resistance associated to low and medium frequency processes, i.e. surface reactions and surface/bulk ionic transport through the electrode, while the high frequency process are limiting the anode operation.

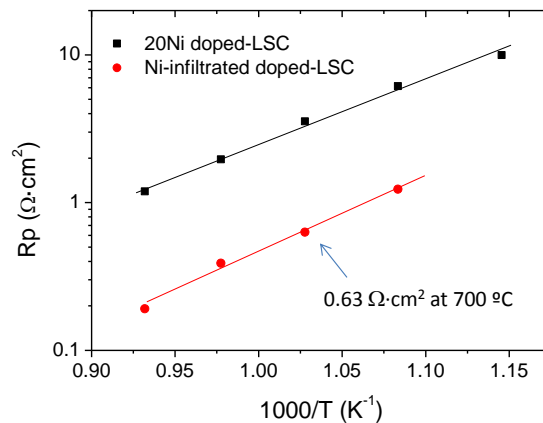


Figure 24. Arrhenius plot of the two best performing anodes on LWO in symmetrical cells.

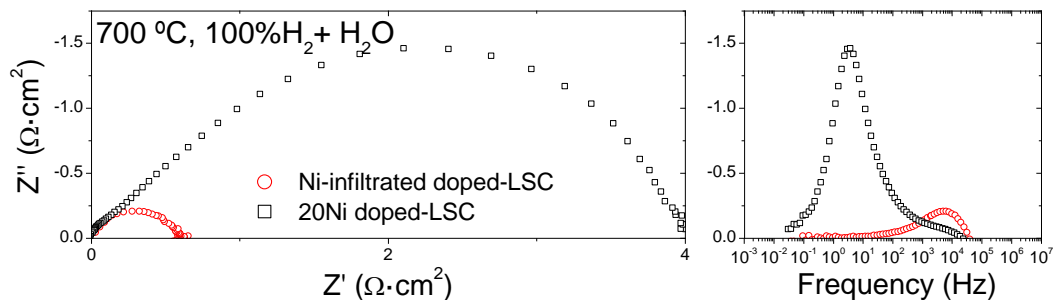


Figure 25. Impedance spectra (Nyquist and Bode plots) in wet  $\text{H}_2$  at  $700^\circ\text{C}$  of symmetrical LWO cells of  $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ni}_{0.2}\text{O}_{3-\delta}$  and the infiltrated doped-LSC anodes ( $15 \mu\text{m}$  of thickness) sintered at  $1150^\circ\text{C}$  and reduced at  $800^\circ\text{C}$ .

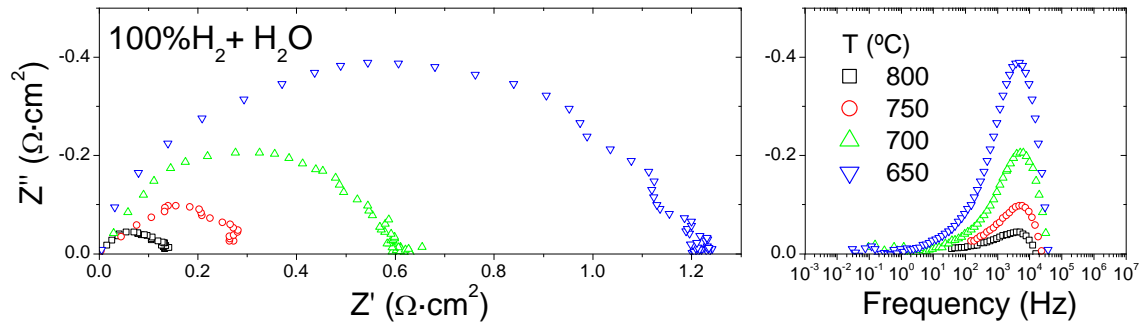


Figure 26. Impedance spectra (Nyquist and Bode plots) of the symmetric cell based on the infiltrated doped-LSC sintered at 1150°C and reduced at 800°C, measured in wet  $H_2$  at different temperatures.

### Cathodes for PCFC electrolytes

An objective of EFFIPRO has been to develop cathodes for the new proton conducting electrolytes. The goal is to identify functional materials stably incorporated into cercer composite cathodes that exhibit area specific electrochemical resistances (ASR) towards a stable proton conductor not higher than  $0.2 \Omega \text{ cm}^2$  at 700 °C in humid air, and that exhibits a conductivity of 75 S/cm. The midterm goals are, respectively,  $0.5 \text{ ohm cm}^2$  at 800°C and 50 S/cm. (Future long term goals will be  $0.1 \Omega \text{ cm}^2$  and  $> 100 \text{ S/cm}$  at 600°C.) While it was assumed that Ni would make a good anode for PCFCs in general, efficient cathode materials have been more difficult to identify, since high mixed protonic-electronic conduction at high  $pO_2$  (presumably p-type electronic conduction) was not known. This work was therefore given a high priority in EFFIPRO.

Experimental and calculational evaluation of a number of cathode material candidates was performed for the new Ca-doped  $\text{LaNbO}_4$  (LCN) electrolyte and for the best oxysalt electrolytes. A few which appeared stable in contact with electrolyte were applied as simple monophase electrodes and characterised with respect to interface microstructure (signs of reaction/interdiffusion) and polarisation resistance by impedance spectroscopy.

The midterm target of  $0.5 \Omega \text{ cm}^2$  at 800°C in wet air for cathode polarisation resistance was reached by a monophase electrode - a  $\text{La}_2\text{NiO}_4$  electrode on an oxoborate,  $\text{La}_{26}\text{O}_{27}(\text{BO}_3)_8$ , electrolyte.

For LCN, the resistances were however too high (order of magnitude  $100 \text{ ohm cm}^2$ ), though still promisingly low for being non-composite electrodes. The best results were obtained for Ca- or Sr-substituted  $\text{La}(\text{Mn},\text{Co})\text{O}_3$  perovskites (abbreviated LCM, LSM, and LSCM).

The good performance of the cathode on the oxoborate and the difference between the oxoborate and LCN are unexpected. Let us therefore return for a moment to the observation mentioned earlier that inherently oxygen deficient disordered electrolytes exhibit less grain boundary resistance – attributed to smaller core charge and space charge effects. We suggest that the same effect may decrease the space charge effect of electrodes and reduce the charge transfer polarisation resistance, in this case of the disordered oxoborate, a hypotheses and possibilities that should be explored in future work.

The work on cathodes for LCN proceeded to make composite electrodes consisting of the electron conducting phase identified as candidates and the LCN electrolyte. This was only partly successful, as the resistances decreased only about one order of magnitude, to the  $10 \text{ ohm cm}^2$  range, and were

thus still far from acceptable. This is attributed for a large part to the limited proton conductivity of the proton conducting phase of the cathode (similarly to the limitations of the composite anode), the lack of mixed proton conduction of the cathode material, and the inefficient charge transfer. Figure 27 shows the temperature dependencies of polarisation of LCN-LSM composite electrodes on LCN electrolyte. The activation energy is as large as 1.5 eV – emphasising not only the problem of too few reaction sites, but also that of the high activation needed for the electrochemical process.

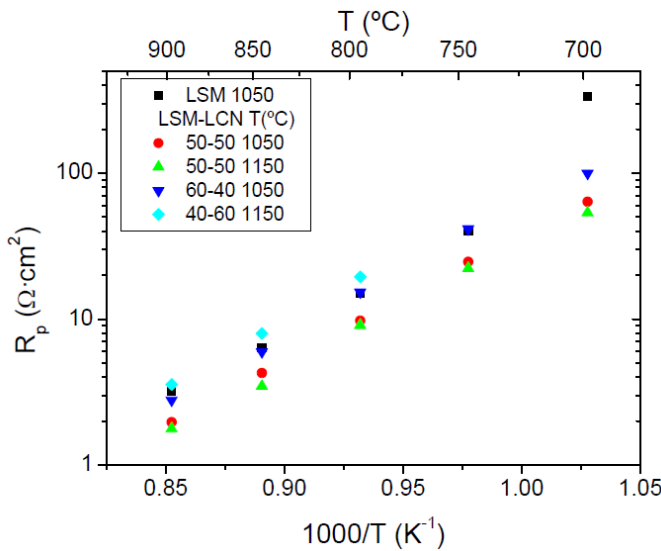


Figure 27. Polarization resistance of different cathodes compositions measured in wet air on LCN electrolytes of LSM and different LSM/LCN compositions.

When LCN was abandoned, EFFIPRO started the search for and testing of electron conducting cathode materials stable with and active for the new LWO electrolytes. These cathodes are largely different than the ones identified for LCN because of different chemical reactivity regimes. Figure 28 show examples of an early single phase  $\text{Pr}_2\text{NiO}_4$  cathode, which – along with other rare earth nickelates ( $\text{La}_2\text{NiO}_4$ -class oxides) - appeared as the best candidates. As one can see in **Figure 28** (left), the compatibility and adherence is excellent.

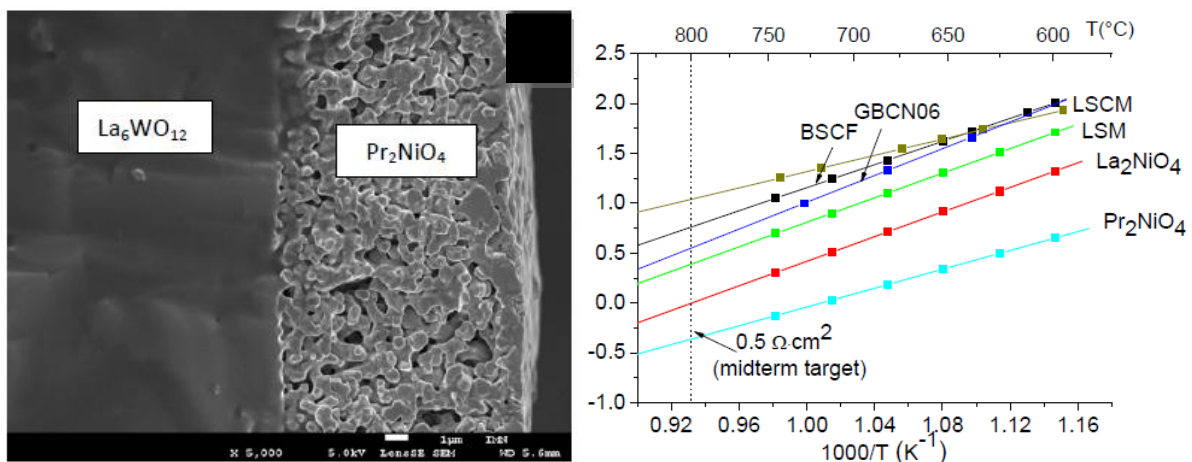


Figure 28. Left: Cross-section of pure  $\text{Pr}_2\text{NiO}_4$  electrode on LWO. Right: Log ASR of cathode polarisation vs  $1/T$  for some single phase cathodes on LWO electrolytes, in wet air.

The best combination comprising LWO and  $\text{Pr}_2\text{NiO}_4$  came down to below the  $0.5 \text{ ohm cm}^2$  midterm target for cathode polarisation when extrapolated to  $800^\circ\text{C}$ , see Figure 28 (right). The activation energies are now down to the region of 1 eV, as compared to 1.5 eV for LCN. One may speculate that the more mixed conductivity of LWO is the cause of the difference.

The studies of cathodes for LWO entered into a more detailed phase to elucidate fundamentals and improve the performance also towards the final target. Firstly, the chemical, mechanical and electrochemical compatibility was checked for  $\text{Pr}_2\text{NiO}_4$  (PNO) calcined at 600, 800, 1000 and  $1200^\circ\text{C}$ . It was shown that PNO pre-calcined at  $1000^\circ\text{C}$  or higher is stable for practical purposes in contact with LWO between  $800^\circ\text{C}$  (operation, where the thermodynamic stability of PNO is not high) and  $1200^\circ\text{C}$  (processing, where the kinetics of any reaction would be fast). The thickness of the PNO cathode layer on LWO was varied from  $12 \mu\text{m}$  to  $36 \mu\text{m}$ . The lowest area specific resistances (ASR) of around  $0.4 \Omega\cdot\text{cm}^2$  at  $700^\circ\text{C}$  were observed for PNO cathode powders calcined at 600 or  $800^\circ\text{C}$  with a thickness of  $12 \mu\text{m}$  and bonded to LWO at  $800^\circ\text{C}$  in symmetrical cells. While performing well, these were not stable, in accordance with the stability study above. The more stable  $\text{Pr}_2\text{NiO}_4$  powder calcined at  $1200^\circ\text{C}$  and thereafter ball-milled leads to just a little higher ASR values of  $0.47 \Omega\cdot\text{cm}^2$  and is therefore a preferable choice. These values are all close to final target value of  $0.2 \Omega\cdot\text{cm}^2$  at  $700^\circ\text{C}$  and a starting point for further optimisation.

It was in some cases possible to activate degraded surface kinetics by the application of net current.

We additionally studied  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM) and doped  $\text{La}_2\text{NiO}_4$  materials and their composites (cercers) with the electrolyte. The electrochemical polarisation resistance was determined and delineated using impedance spectroscopy versus temperature,  $p\text{O}_2$ ,  $p\text{H}_2\text{O}$ , and electrode-electrolyte composite composition. In general, the addition of the protonic pathways to the electronic cathode in the composite gives important improvement. The cercers were optimized by studying effects of different volumetric ratios between the two phases as well as the final sintering temperature. The addition of catalytic active Ce-Sm-O nanoparticles by infiltration resulted in a further improved performance of the studied cercer composite cathodes. Isotope exchange and  $p\text{O}_2$ -dependencies have given insight into the mechanisms at play, namely involving electron holes as electronic charge carrier and protons in the chemical part of the polarisation charge transfer. Effects of the H/D isotope exchange and of the Ce+Sm infiltration on the impedance spectrum are shown in Figure 29.

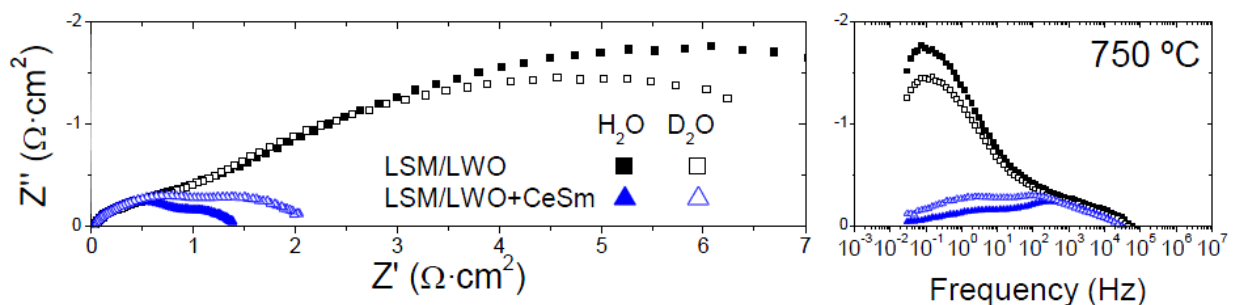


Figure 29. *Impedance spectra comparing impedances of LSM/LWO cercer cathodes with and without CeSm infiltration. Moreover, an H/D isotope exchange effect in the lower frequency semicircle shows that protons are involved in the chemical part of the polarisation of the cathode reaction.*

The best performances in this series were reached by using 5% Pr-doped  $\text{La}_2\text{NiO}_4$  (ASR of  $2.2 \Omega \cdot \text{cm}^2$  at  $700^\circ\text{C}$ ) and Ce+Sm infiltrated LSM/LWO 60/40 vol.% ( $1.2 \Omega \cdot \text{cm}^2$  at  $750^\circ\text{C}$ ), somewhat short of the results obtained with  $\text{Pr}_2\text{NiO}_4$  electrodes above.

Mischmetal strategies were evaluated but not found viable for cathode materials. This must however be assigned much to the limited resources and the need to focus on a new electrolyte and electrodes in the second half of the project, and the possibilities that exist for the future are not exhausted.

A survey of electronic conductivities of cathode materials was made. They are in the range of 20-50 S/cm, see Figure 30, somewhat short of the target of 75 S/cm for the cathode at project end. Finally, selected cathode cells were tested with respect to thermal cycleability and stability towards  $\text{CO}_2$ , with good results, see Figure 31, thereby meeting one of the project targets on robustness.

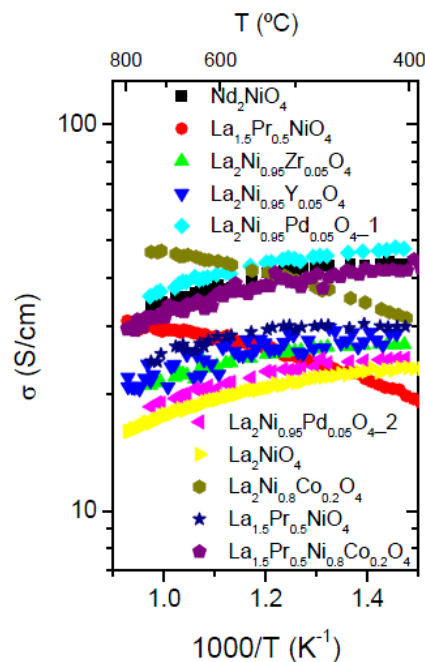


Figure 30. Conductivity of cathode candidate materials vs  $1/T$  between  $400$  and  $800^\circ\text{C}$  in air.

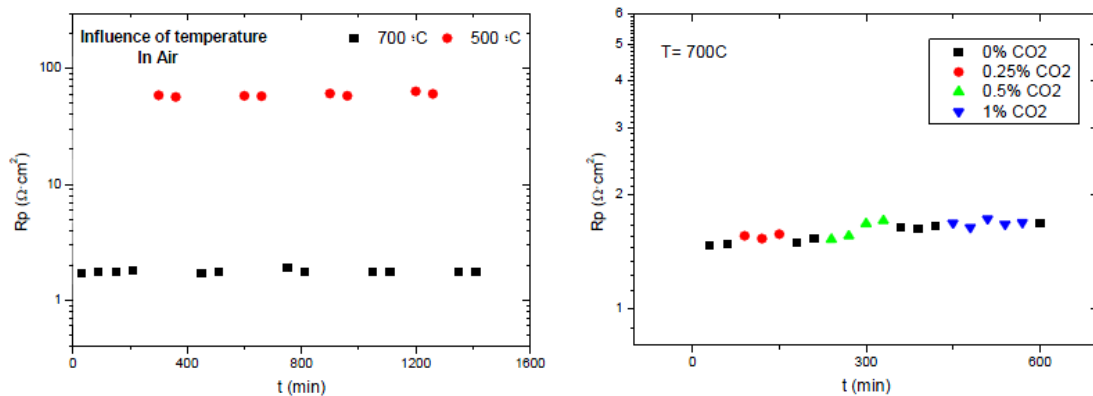


Figure 31. Checks of stability of electrolyte-cathode polarisation during thermal cycles and during exposure to  $\text{CO}_2$  contents well above those than in compressed natural air.

## Concluding remarks

Status at project closure is that out of 11 technical milestones, 6 were met, 3 partly met, and 2 missed by parameter factors of 2-3. This is shown in Table 2, which is an adapted version of Table 1 for the purpose. The project lists one patent, 11 international peer-reviewed articles, and 26 presentations. It is leading to several follow-up projects to make PCFCs an effective alternative for the emerging hydrogen economy.

Table 2. *EFFIRO final conditions, targets, and achievements.*

Property or conditions	Project target	Achievement	Comment
Temp. of operation	700 °C	700 °C	OK
Atmospheres	Moist H <sub>2</sub> /moist air	Moist H <sub>2</sub> /moist air	OK
Fuel utilization	> 90 %	> 90 %	OK; Corresponds to gases used.
Electrolyte $\sigma_{H^+,DC}$ , S/cm	0.0015	0.0015	OK. On target
Electrolyte thickness	3 $\mu\text{m}$	2.5 $\mu\text{m}$	OK; Surpasses target
Electrolyte ASR	0.2 $\Omega\text{cm}^2$	Estimated 0.17 $\Omega\text{cm}^2$	OK
$\sigma_{\text{anode}}$ , min., S/cm,	200	>200	OK; surpasses target
$\sigma_{\text{cathode}}$ , min., S/cm,	75	30-40	Factor 2 off target
Anode kinetics	0.2 $\Omega\text{cm}^2$	0.6 $\Omega\text{cm}^2$	Factor 3 off target
Cathode kinetics	0.2 $\Omega\text{cm}^2$	0.4 $\Omega\text{cm}^2$	Factor 2 off target
Thermochemical and – mechanical stability	No reactions between electrolyte, electrodes, CO <sub>2</sub> . Structures thermally cycleable without electrolyte cracks.	Interfaces stable. Performance stable during thermal cycling and CO <sub>2</sub> exposure	OK.



## 1.4. Potential impact

### Impact

#### Impact on technology of fuel cells and their introduction

EFFIPRO has been well disseminated and noticed on the international PCFC and SOFC arena in its latter half. It is considered successful and leading in the PCFC community, as a project that emphasises the importance of stable and affordable materials and cost-effective manufacturing processes. We see now many studies and projects in Europe and the US following in EFFIPRO's footsteps regarding materials choice and approach. We believe it is therefore important that the EFFIPRO partnership itself moves on into follow-up projects at the forefront of its science and technology, and also that the project as such is properly concluded in one or two review articles that sets the status and prevents future studies from re-inventing EFFIPRO ideas and learning. This is thus planned from the coordinator's side for the autumn of 2012.

EFFIPRO has gone further in the production of thin electrolyte films on porous electrode substrates than PCFC projects before, also longer than most SOFC projects. In this it took into use and developed several methods of achieving this, including electrophoretic deposition (EPD) and pulsed laser deposition (PLD) in addition to more well-proven ones more commonly used for thicker films.

Moreover, it gave as spin-off the acceptance that self-healing ceramic membranes will be essential not only for thin PCFC electrolytes, but also for SOFC electrolytes in general, as well as gas separation membranes. This has been supported by the User Group Forum, which comes mainly from SOFC industry. This process also gave birth to a number of ways to actually make membranes self-healing in the application "SEALEM" to the NMP call for self-healing materials 2011/2012.

During EFFIPRO we have learned that modestly conducting electrolytes as a rule cannot be co-doped to success, that high grain boundary resistance is an intrinsic property and thus hard to clean or engineer away, and that ternary line compounds (no cation nonstoichiometry) are hard to manufacture reproducibly. This has ruled out  $\text{LaNbO}_4$  as a potential candidate. Instead we have discovered that LWO materials have a forgiving range of cation stoichiometry, is remarkably stable, and has a higher proton conductivity. We have learned that mischmetal strategies for cost-reduction are possible but not straightforward. It seems we are on the verge of concluding that inherent oxygen deficiency and disorder counteracts grain boundary resistance and that we are understanding why – a major achievement if true, with potential consequences also for electrode development. We have learned a lot about compatible electrodes for PCFC electrolytes and how and why they work (or not). In parallel to EFFIPRO, it has become clear that  $\text{SrZrO}_3$  and  $\text{BaZrO}_3$  perovskites are more stable than we thought, that the high sintering temperature can be circumvented by sintering aids, that the grain size increased so as also to reduce grain boundary resistance. We thus now have the possibility to merge this progress with the learning from EFFIPRO for the next developments of robust PCFC technology. This is already being implemented in follow-up projects by project partners, where the possibilities of doped  $\text{BaZrO}_3$  and LWO systems go hand in hand.

EFFIPRO and its integrated parallel projects has demonstrated an arsenal of methods for manufacturing, characterising and testing materials and interfaces for SOFC in general and PCFCs in particular, e.g. spray pyrolysis, a range of deposition techniques, structural characterisation by XRD, neutrons, and Raman spectroscopy, SEM, high-resolution TEM, thermogravimetry, impedance





spectroscopy, isotope exchanges, transients of many kinds, many of them *in situ* with complete and probably unprecedented control of  $T$ ,  $pO_2$ ,  $pH_2$ , and  $pH_2O$ .

Many specific advances of EFFIPRO can be mentioned which may come to use in PCFC development and SOFC development in general: We have succeeded to make a 3 micron thick dense electrolyte on a 3<sup>rd</sup> generation large-grained and therefore stable and functional alloy support, by use of an intermediate ceramic electrode. We have shown that PLD may be a useful technique for making thin dense membranes for fuel cells. (While PLD is not generally considered up-scaleable to industrial level, this need not be true for thin electrolytes – all costs considered.) EPD has proven itself as a very versatile and efficient technique for layer and film deposition. *In situ* precipitation of nanoparticles (e.g. of Ni) on oxide electrodes has been demonstrated.

In view of the upcoming commercialisation of emission-free hydrogen cars, the need for hydrogen supplies, and the hydrogen society, electrochemical conversion will be more in demand in the future. Moreover, upgrading of fossil fuels, CCS, and use of biogas can be done better by use of ceramic membranes. Proton conductors can do the job in these cases, and in many of them in principle better than the more traditional and further developed oxide ion conductors, such as SOFC. No doubt, PCFC and SOFC and other pairs of technologies support each other towards breakthrough of ceramic fuel cells, electrolyzers, and gas separation membranes.

EFFIPRO is a first step towards such PCFC technology. It has for the most part met its ambitious goals. It is thus in our opinion keeping the pace towards PCFC impact in estimated 2020. Next stages of development would be design, manufacture, and tests of complete cells, upscaling/stacking, testing of operational parameters in comparison with for instance SOFC and PEMFC in various applications. This is part of various proposals that has been made – of which some are granted, some rejected, and some in the pipeline – to national research programme, EU NMP, and EU FCH calls.

In the meanwhile and at its present stage, EFFIPRO has given more momentum to the SME involved regarding powder production, and to Protia AS at UiO which is commercialising UiO technology and has projects on LWO for membranes. Regarding larger industries, EFFIPRO partners have had contacts especially with Topsoe Fuel Cells and Coorstek in the US in development of follow-up projects. A number of new industries – mostly SMEs on the materials and renewable energy arena in Europe – have also been drawn into new applications and the determination by EFFIPRO partners to develop PCFCs to the next stage.

## Cost

In terms of cost of fuel cell technology, SOFCs, and PCFCs in particular, we point at three outcomes of EFFIPRO: Firstly, of course, production routes may be improved by finding ways to using less man-hours and cheaper and more suitable precursors. One may note, e.g. from the LCN route that it needs not be necessary or even beneficial to fine tune a composition to a specific stoichiometry, but to understand how it can be made off-stoichiometric to safe-guard against variations. (Better always to have a secondary phase of harmless  $La_3NbO_7$  than to risk having detrimental  $LaNb_3O_9$ ). Secondly, mischmetal strategies should always be considered, but did not work out in the particular cases in EFFIPRO. Perhaps one may learn from this that mischmetal is best applied to a near-market technology rather than to early stage explorations - where there are enough other issues to be dealt with. Finally, we would like to repeat that EFFIPRO for the first time ever, demonstrated a 3<sup>rd</sup> generation (alloy-supported) PCFC. 3<sup>rd</sup> generation cells are considered the long-term most economic



alternative. Moreover, it happens to be particularly well-suited for PCFCs since the alloy on the alloy side here is exposed to drier hydrogen than in an SOFC, which should reduce oxidation of the alloy.

### **Benefits to related technologies**

EFFIPRO has contributed to optimisation of selected proton conductors, for their use both in the electrolyte (where proton conduction is prime target) and the composite electrodes (where also cost is a target). Moreover, up-scalable and affordable production methods for micrometer-range electrolyte films have been investigated. It has led to development and understanding of novel cathode materials, their kinetics and stability, and suitable cathode composites, microstructures, and application methods. Establishment of production and availability of kilogram-quantities of optimised powders for the components developed in the project is a welcomed addition to European PCFC and general SOFC research, making it less dependent on such delivery from outside EU. This is seen in the orders of related compounds that SME partner CerPoTech has outside of EFFIPRO.

In this way EFFIPRO contributes significantly directly or indirectly to a number of related technologies: PCFC technology can be reciprocated into steam electrolyzers (proton ceramic electrolysis cells, PCECs). By the proton conduction, these produce dry pressurised hydrogen directly, and are thus in principle more efficient than oxide ion conducting solid oxide electrolyser cells (SOECs) which produce wet hydrogen. Follow-up projects in this direction have been submitted to EU FCH by project partners.

Proton conduction can be combined with electron conduction for mixed conducting hydrogen permeable gas separation membranes. These can be used to extract hydrogen from reforming and shifting natural gas/steam reactors or from natural gas during catalytic dimerisation to higher hydrocarbons, even liquid ones directly. As an example, the UiO spin-off company Protia is working on a one-step gas-to-liquid (methane to benzene) process based on LWO-derived materials as mixed proton-electron-conducting membrane. EFFIPRO has contributed to knowledge of how to make such membranes thin enough on a stable, porous substrate. Equally interesting, proton conductors can be combined with electron conducting phases to make a permeable composite. EFFIPRO has investigated a number of such materials combinations, and provided a solid platform for the partners and the proton ceramic community to explore these possibilities.

The interest in carbon-neutral biogas has triggered calls and projects for reformers and fuel cells for biogas. Membranes can be used to enhance reforming and shift of the biogas in this context. However, biogas is particularly rich in sulphur, and many proton conductors tend as we know to be basic and react with acidic gases like  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . The work in EFFIPRO on more stable proton conductors and electrodes for these is therefore of great interest in such projects. One project “bioPCFC” is already launched nationally with partners in Norway.

As hydrogen as energy carrier is approaching (see also next part), there is interest in technologies for converting renewable energy to hydrogen for use, transport and storage. This comprises for instance solar thermal cycling processes. In the context of PCFCs it is however more interesting to discuss photoelectrochemical water splitting. This uses a semiconductor in contact with an electrolyte; light (UV or solar) splits water and produces oxygen on the semiconductor anode and hydrogen on a counter-electrode of e.g. platinum. It is in principle possible to use a solid-state proton conductor rather than a liquid electrolyte. This has certain advantages, such as less corrosion of certain photoanodes, higher operating temperature and utilisation of the full power of concentrated sunlight without need for cooling, fewer parts, and direct separation of the oxygen and hydrogen. Proton



conductors such as those developed in EFFIPRO and others operating at lower temperatures are presently being investigated for such purposes in national programmes.

### **Environment and climate**

Proton conducting fuel cells (PCFCs) with stable ceramic electrolytes may in the long run take over for standard SOFC concepts because they offer greater fuel utilisation and efficiency, simpler BOP, and intermediate temperature operation. EFFIPRO has taken one step in this direction by reaching many first targets and achievements for instance in proton conduction of stable electrolytes, thin films, substrate-electrode-electrolyte structures, electrode materials, and fundamental insight. The advantages are indisputable with hydrogen as fuel: PCFCs and related electrolyzers will be more efficient for transforming hydrogen to electricity and electricity to hydrogen. PCFCs will in this way at stage make an impact in a future hydrogen society.

Moreover, the advantage is also clear with highly reformed fossil fuels, where the high H<sub>2</sub> content of the reformat makes the cell work optimally, the stability towards residual CO and CO<sub>2</sub> is then crucial. And most of all, the PCFC operating temperatures (5-600 °C) are ideal for heat exchange with the newest reformer technologies. This will make fuel cells operate with typically 10 % higher efficiency and with higher maximum power reserve and reduced danger of stack-failure caused by irreversible anode oxidation of any single cell. Thus, emissions from use of fossil fuels may be reduced by up to 10% by use of PCFCs where SOFCs are making an impact.

### **Dissemination and use during the course of the project**

The project has published 9 peer-reviewed papers, 2 more are submitted, and at least 6 more are in preparation. It is presented regularly at conferences, a total of 26 at the writing of this report. It will be presented as a whole on the main event on proton conductors – SSPC16 in Grenoble September 2012. The project has a web-page at UiO, containing both open and closed (password-protected) information. The project reports its publications and deliverables to the participants portal of EU, and further has been able to follow the open access policy to about 90%. The portal and open access policy have been new to the partners and implementation has been a continuous learning process.

The project educates one PhD at UiO. The candidate has one paper submitted and 3 more in preparation. The thesis is expected submitted medio 2012 and defended ultimo 2012. The other three university partners have trained one post-doctoral researcher each.

EFFIPRO has so far led to one patent, by the group at UiO and researchers at SINTEF, on the development of electrodes for LWO electrolytes. The follow-up and use of this patent is handled by UiO's technology transfer office (TTO) Inven2.

Several of the partner institutions, notably the large industrial research institutes such as SINTEF, are using technologies developed in EFFIPRO for supporting and depositing thin dense ceramic films on porous substrates onwards in their work on not only fuel cells, but also electrolyzers and gas separation membranes. The latter is particularly important for oxygen transport membranes (OTM), hydrogen transport membranes (HTM) and CO<sub>2</sub>-permeable membranes, all for use in carbon capture and storage (CCS). The project has enabled SME partner CerPoTech AS to develop synthesis and production methods and implement cost-reducing actions. Some powders developed and delivered in EFFIPRO have become part of the product portfolio of CerPoTech. The developments in EFFIPRO are furthermore followed by Norwegian startup Protia AS which is commercialising technologies



based on proton conducting ceramics, and is a potential licensee of EFFIPRO patents. EFFIPRO further strengthens partners' ability to contribute significantly in collaboration with ceramics and SOFC manufacturing industries in Europe (e.g. Topsoe Fuel Cells) and the US (e.g. Coorstek).

EFFIPRO has been a pioneering project both in terms of the use of the novel proton conductors  $\text{LaNbO}_4$  and LWO, and in the application of thin films of proton conducting ceramics, and this is supported and followed up by national project applications, in parallel with and at the end of EFFIPRO. This covers in Norway, for instance, biomass-related fuel utilisation. It is also clear that much of the technology in EFFIPRO is transferable to steam electrolyser developments. National and European projects on this are emerging due to the need for distributed  $\text{H}_2$  production to serve tomorrow's hydrogen fuelled transport sector, notably in countries where there is periods of excess renewable electricity or sources of steam, e.g. from nuclear power plants or geothermally.

EFFIPRO partners have launched an application for a project "SEALEM" on to a call on self-healing materials in the EU 7FWP. This has background and inspiration from EFFIPRO. The project reached the 2<sup>nd</sup> stage of evaluation, but failed to be granted. It will be resubmitted as soon as possible to EU and/or national projects. If successful it will seek to remedy the inherent vulnerability to pinholes and cracks in thin ceramic membranes of many kinds and in several energy conversion technologies.

EFFIPRO partners have applied for and obtained a national project on biogas-fuelled PCFCs. Moreover, other partner constellations have applied to the FCH JTI for developing EFFIPRO technology into steam electrolyzers. It is planned to submit more project applications in the areas of fuel cells, electrolyzers, and gas separation membranes based on the support - functional layer - membrane architectures and methodologies developed in EFFIPRO in the near future.

## **Post-project dissemination, use, and exploitation**

### **Post-project dissemination**

The project has at closure recorded 9 journal publications printed or in print at the Participants Portal (SESAM) listed at the final date of the project. 2 more are submitted to journals and another 6 are listed as under preparation. The project has moreover listed 26 dissemination activities counting workshop organisation and posters, and multiple oral conference presentations. The project has listed one patent application. The project partners plan as a minimum to report their achievements in the following additional disseminations after project closure (including the 6 papers in preparation and another 4 papers):

- The overall project scientific outcome will be presented at Solid State Proton Conductors 16 (SSPC 16) Grenoble 2012 (leading conference on solid-state protonic conductors) plus in a follow-up paper on the same in Solid-State Ionics. Technology overview of LWO-based PCFCs as well as on routes of building support-anode-electrolyte structures will be presented at general conferences on SOFC and energy materials such as Electroceramics XII, plus 2-3 articles in e.g. J. Power Sources or Fuel Cells. Proton conduction in rare-earth-based pyrochlore and fluorite oxides will yield 2 additional journal papers (in preparation). The outcome of mischmetal approach to cost reduction of materials synthesis will be presented also at SSPC-16 as a talk or poster and possibly an article. Electrodes for LWO electrolytes will be presented in conference talks and posters, and three journal papers are in preparation.



- The PhD Thesis of Vasileios Besikiotis at UiO is expected submitted medio 2012 and defended ultimo 2012. It is mainly covering studies of hydration and proton conduction in pyrochlore oxides as well as development and studies of cathodes and anodes for PCFCs.
- All EFFIPRO publications will to the extent possible be given open access by uploading on open web sites. This is now true for approx. 90% of the published or submitted papers. EFFIPRO results will well after project conclusion be disseminated regularly to the scientific community and to relevant industries through informal interaction, conference attendance, and follow-up project applications.

*All in all, EFFIPRO is expected to have published around 25 peer-reviewed international articles by the end of 2012 and may expect to continue publication to reach approximately 30 in total. EFFIPRO will exceed 30 other dissemination activities including oral presentations at international conferences, organisation of workshops, and poster presentations. EFFIPRO will finally have led to 1 PhD Thesis and 1 patent application.*

### **Follow-up projects**

The partners of EFFIPRO are in collaboration with new partners comprising universities, SMEs, and industries in Europe and US to move forward to the next step in technologies based on stable ceramic proton conductors by submitting a large number of national and EU project applications, comprising:

- Self-healing ceramic membranes (“SEALEM”, NMP). This covers all types of ceramic membrane technologies (fuel cells, electrolyzers, gas separation membranes) and has 4 out of EFFIPRO’s 7 partners and 3 new. It has been invited and submitted to the 2<sup>nd</sup> round at the deadline of May 3rd.
- Integration of renewable energy sources in combination with PCFC technology aiming at biogas fuelling of sulphur tolerant PCFC in a national Norwegian research program in collaboration with 3 partners of EFFIPRO. The project has been granted in June 2012 and enlarges the fields of application of PCFC technologies.
- Use of stable proton conducting ceramics in various electrolyser concepts for hydrogen production. The coordinator of EFFIPRO has submitted one project to the FCH JTI for the May 24 deadline along with two other EFFIPRO partners and 8 new ones.

The new partnership created in EFFIPRO has therefore promoted strong collaboration within the consortium, which will be further strengthened in new European projects, which benefit of a solid participation of industry. Additionally, all partners of EFFIPRO are seeking for new funding within their respective national funding program to pursue their efforts in the development of PCFC technologies.

### **Use and commercial exploitation**

Developments in EFFIPRO are manifold and are addressing a number of scientific and technical bottlenecks in multiple technologies. They comprise:

- Know-how on fabrication of thin ceramic proton conducting electrolyte films on suitable support and electrode structures: this can be transferred to technologies based on multifunctional ceramic devices, such as SOFCs, gas separation membranes, high temperature electrolyzers, thermal barrier coatings, gas sensors, etc.



- Know-how on fabrication of porous alloy substrates coated with functional porous and dense ceramic layers enabling the pioneering realisation of alloy supported PCFC.
- Knowledge on degradation of thin films and the need for self-repairing mechanisms.
- Progress on understanding rate-limiting steps of anodes and cathodes on proton conducting electrolytes.

All this knowledge is used in the partners' further work and developments on PCFCs and – as mentioned above – in follow-up projects. The developments in EFFIPRO are particularly interesting for high temperature fuel cells and electrolyzers for hydrogen production. Hydrogen technology and the concept of hydrogen society have indeed been strengthened during the course of EFFIPRO, with the advances of H<sub>2</sub>-powered fuel cell cars. Equally important is the associated need for distributed production of hydrogen from electricity in various electrolyser concepts. In all of these, ceramic proton conductors offer in principle the most efficient technology, and high reactant steam pressures as well as integration with natural gas reforming makes the stability of the electrolyte – as focused on in EFFIPRO – an essential parameter.

The project has enabled partner CerPoTech AS to develop their synthesis and production methods and implement cost-reducing actions. This comprises uses of precursor chemicals, reduction of processing steps and introduction of entirely new methodology. The biggest potential for improvement has been found in the post-treatment of the synthesized powders. An example of the latter is the use of jet milling instead of ball milling. Jet milling has been evaluated during the EFFIPRO production of powders and will be further developed by CerPoTech after the project closure. Some of the powders developed and delivered in EFFIPRO have become part of the product portfolio of CerPoTech. EFFIPRO has so far led to one patent, by the group at UiO, and with co-authors at SINTEF on development of electrodes for LWO electrolytes. The use and follow-up of this patent depends on the research and evaluation that continues around the world on LWO which will clarify its competitiveness with for instance LNO and improved perovskite formulations. The developments in EFFIPRO are followed by Norwegian startup Protia AS which is commercialising technologies based on proton conducting ceramics, and is a potential licensee of EFFIPRO patents. EFFIPRO further strengthens its partners' abilities to collaborate with ceramics and SOFC manufacturing industries and research institutes in Europe (e.g. Topsoe Fuel Cells, Marion Technologies, Ikerlan, Protia, Höganäs) and the US (e.g. Coorstek) as well as energy companies (e.g. Abengoa, Carbon Recycling International). This is visible in the new project applications submitted nationally and to EU as a result of EFFIPRO's outcomes and partnerships.



## 1.5. EFFIPRO information, partners, and contacts

Web site: <http://www.mn.uio.no/smn/english/research/projects/effipro/>








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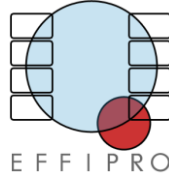
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### List of beneficiaries and contacts

No.	Beneficiary name	Short name	Country	Contact	Email
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3	Inst. Chemical Technology, U.P.Valencia/ CSIC 	CSIC-ITQ	Spain	José Serra	jsalfaro@itq.upv.es
4	SINTEF 	SINTEF	Norway	Rune Bredesen	rune.bredesen@sintef.no
5	Forschungszentrum Jülich 	JÜLICH	Germany	Wilhelm Meulenberg	w.a.meulenberg@fz-juelich.de
7	Fuel Cells and Solid State Chemistry Department, Risø National Laboratory for Sustainable Energy, Technical University of Denmark 	RISØ-DTU	Denmark	Nikolaos Bonanos	nibo@risoe.dtu.dk
8	Ceramic Powder Technology AS (CerPoTech) 	CERPOTECH	Norway	Marte Aspnes	marte.aspnes@cerpotech.com

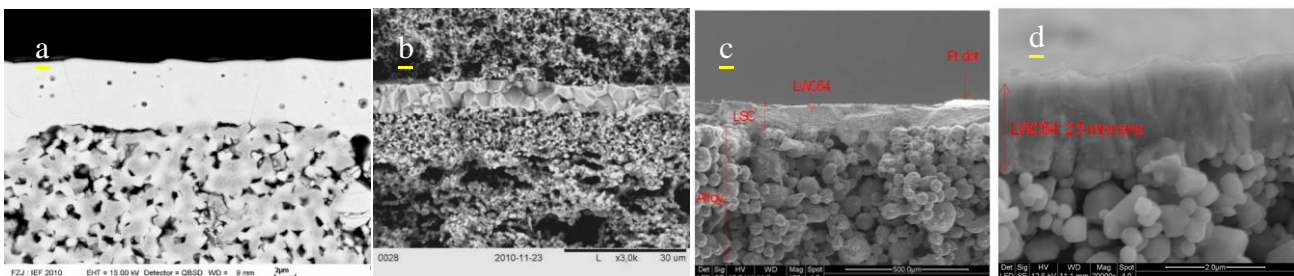
## 1.6. EFFIPRO Logo and highlights table and micrographs



EFFIPRO logo:

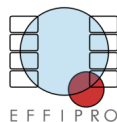
Table 3. *EFFIRO final conditions, targets, and achievements.*

Property or conditions	Project target	Project achievement	Comment
Temp. of operation	700 °C	700 °C	OK
Atmospheres	Moist H <sub>2</sub> /moist air	Moist H <sub>2</sub> /moist air	OK
Fuel utilization	> 90 %	> 90 %	OK; Corresponds to gases used.
Electrolyte $\sigma_{H^+,DC}$ , S/cm	0.0015	0.0015	OK. On target
Electrolyte thickness	3 $\mu\text{m}$	2.5 $\mu\text{m}$	OK; Surpasses target
Electrolyte ASR	0.2 $\Omega\text{cm}^2$	Estimated 0.17 $\Omega\text{cm}^2$	OK
$\sigma_{\text{anode}}$ , min., S/cm,	200	>200	OK; surpasses target
$\sigma_{\text{cathode}}$ , min., S/cm,	75	30-40	Factor 2 off target
Anode kinetics	0.2 $\Omega\text{cm}^2$	0.6 $\Omega\text{cm}^2$	Factor 3 off target
Cathode kinetics	0.2 $\Omega\text{cm}^2$	0.4 $\Omega\text{cm}^2$	Factor 2 off target
Thermochemical and – mechanical stability	Materials and interfaces stable and resistant towards thermal cycling and CO <sub>2</sub> exposure	Interfaces stable. Performance stable during thermal cycling and CO <sub>2</sub> exposure	OK.



*Anode-supported thin proton conducting electrolytes achieved in EFFIPRO: a) 7  $\mu\text{m}$  LCN on Ni-LCN cermet. b) LCN between supported functional anode and cathode. c) 3<sup>rd</sup> generation PCFC; coarse alloy support, fine LSC anode and thin dense LWO (hardly visible). d) Close-up of the same LWO on LSC.*

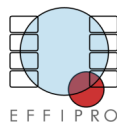




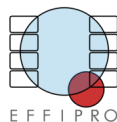
## 1.7. Publications

Table A1 contains all articles as listed/extracted from on the Participants Portal as of the writing of this report, starting with the published ones (most important first) and those in press, followed by the ones submitted, and finally those in preparation.

<b>A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES</b>										
NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers (if available)	Is/Will open access provided to this publication?
1	Electrochemical properties of composite cathodes for La <sub>0.995</sub> Ca <sub>0.005</sub> NbO <sub>4</sub> -based proton conducting fuel cells	Jose M. Serra	J. Power Sources	196	Elsevier	Amsterdam	2011	9220-9227	doi:10.1016/j.jpowsour.2011.07.041	Yes
2	Cathode materials for La <sub>0.995</sub> Ca <sub>0.005</sub> NbO <sub>4</sub> proton ceramic electrolyte	O. Joubert	Int. J. Hydrogen Energy	in press	Elsevier	Amsterdam	2011	in press	doi:10.1016/j.ijhydene.2011.07.069	Yes
3	Characterization of La <sub>0.995</sub> Ca <sub>0.005</sub> NbO <sub>4</sub> /Ni anode functional layer by electrophoretic deposition in a La <sub>0.995</sub> Ca <sub>0.005</sub> NbO <sub>4</sub> electrolyte based PCFC	F. Bozza	Int. J. Hydrogen Energy	in press	Elsevier	Amsterdam	2011	in press	doi:10.1016/j.ijhydene.2011.11.002	Yes
4	Compatibility of proton conducting La <sub>6</sub> WO <sub>12</sub> electrolyte with standard cathode materials	E. Quarez,	Solid State Ionics	in press	Elsevier	Amsterdam	2012	In press		No
5	Epitaxial Films of the proton-conducting Ca-doped LaNbO <sub>4</sub> material and study of their charge	A. Cavallaro, J. M. Serra	Solid State Ionics	in press	Elsevier	Amsterdam	2012	in press		Yes



	transport properties									
6	Adjusting the conduction properties of $\text{La}_{0.995}\text{Ca}_{0.005}\text{NbO}_{4-\delta}$ by doping for proton conducting fuel cells electrode operation	Jose M. Serra	Solid State Ionics	190	Elsevier	Amsterdam	2011	38-45	doi:10.1016/j.ssi.2011.03.008	Yes
7	$\text{La}_{5.5}\text{WO}_{12-\delta}$ Characterisation of Transport Properties under Oxidizing Conditions: A Conductivity Relaxation Study	Jose M. Serra	J. Physical Chemistry C	155	ACS		2011	11124-11131	doi:10.1021/jp2015066	Yes
8	Compatibility of $\text{La}_{26}\text{O}_{27}(\text{BO}_3)_8$ electrolyte with standard cathode materials for use in proton conducting solid oxide fuel cells	K.V. Kravchyk	J. Power Sources	196	Elsevier	Amsterdam	2011	7435–7441		No
9	Electrochemical properties of PSFC-BCYb composites as cathodes for proton conducting solid oxide fuel cells	Jose M. Serra	Fuel Cells	11	Wiley	New York	2011	81-90	doi:10.1002/fuce.201000090	Yes
10	Electrochemical properties of composite cathodes for $\text{La}_{5.5}\text{WO}_{12}$ proton conducting electrolytes	Jose M. Serra		submitted			2012			Yes
11	Conductivity and hydration trends in disordered fluorite / pyrochlore structures: A study on lanthanum cerate based compounds	Besikiotis, V.	Solid State Ionics	Submitted	Elsevier	Amsterdam	2012			Yes
12	Catalytic promotion through nanoparticle infiltration of LWO-based composite cathodes of PC-SOFC	Jose M. Serra, N. Bonanos	in preparation	in preparation			2012			Yes
13	Development and understanding of chromite anodes for LWO-based PC-	Jose M. Serra	in preparation	in preparation			2012			Yes



	SOFC									
14	Development of doped La <sub>2</sub> NiO <sub>4+δ</sub> cathodes for LWO-based PC-SOFC	Jose M. Serra	in preparation	in preparation			2012			Yes
15	Manufacturing of LaNbO <sub>4</sub> based proton conducting half cells via tape casting and screen printing	W. Schafbauer	in preparation	in preparation			2012			Yes
16	Ionic conductivity and hydration of the inherently oxygen-deficient La <sub>2</sub> Ce <sub>2</sub> O <sub>7</sub>	Besikiotis, V.	In preparation	In preparation			2012			Yes
17	Protonic defects and hydration enthalpy trends in pyrochlore structured oxides	T.S. Bjørheim, V. Besikiotis	In preparation	In preparation			2012			Yes
18	Critical issues of Metal Supported Fuel Cells	Y. Larring	Book Chapter	In preparation	Springer		2012			No
19	Development of proton conducting ceramic fuel cells on alloy substrates	C. Denonville	In preparation	In preparation			2012			No
20	On La <sub>2</sub> NiO <sub>4</sub> as cathode for lanthanum tungstate based proton conducting solid oxide fuel cells	R. Strandbakke, V. Besikiotis	in preparation	in preparation			2012			Yes