Proton ceramic fuel cells (PCFCs) 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, water the major product appears on the cathode side, and does not dilute the fuel or constitute a danger of oxidising the anode, contrary to regular solid oxide fuel cells (SOFCs). 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.

The need for PCFCs is emphasised by the approaching commercial introduction of hydrogen fuel cell cars
in 2015. While these are based on polymer electrolytes, the preference for higher temperatures and liquid water-free operation makes it likely that aspects of PCFC technology will be integrated in the long run. In parallel, there is a need for distributed production of hydrogen as well as the needs to use hydrogen as buffer for renewable energy peaks, calling not only for PCFCs but also related technologies such as proton ceramic electrolyser cells (PCECs) and mixed proton-electron conducting ceramic hydrogen separation membranes.

Proton conducting oxides have traditionally been Sr- or Ba-containing perovskites like acceptor-doped SrCeO3 or BaCeO3 which suffer from chemical instability towards reaction with acidic gases such as CO2 due to the basicity of the alkaline earth cation. EFFIPRO explores the use of novel Sr- and Ba-free stable oxides that may make an efficient PCFC also robust. The increased interest in use of biogas with its high contents of sulphur - further emphasises the need for chemically stable proton conductors.

EFFIPRO 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 cost-effective pilot scale powder production. It 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. EFFIPRO aims at developing anode supported electrolytes on ceramic-metal or alloy supports (second or third generation of fuel cells). The latter has not been realised for PCFCs elsewhere to date, and amplifies the range of innovation in the project. On the other side it comprises the electrode polarisation of the electrolyte-cathode assembly. On long term the three are each required to be less than 0.1 cm² 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 cm² at 800 °C at midterm and 0.2 cm² 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.

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. A further objective comprises cost reduction of manufacturing by process efficiency and if viable the use of mischmetal precursors. Finally, the materials, interfaces, and components are required to be stable towards thermal cycling and exposure to CO2 and other acidic gases.

Project results:

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, H2O 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 balance-of-plant (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 BaCeO3 or BaZrO3 which have suffered from poor stability towards CO2 due to Sr/Ba basicity, or high sintering temperatures and grain boundary resistance.
EFFIPRO has explored Sr/Ba-free oxides, notably Ca-doped LaNbO4 (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 cm2 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 CO2, 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 cerments. 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 La6-xWO12-3x/2 (LWO) class of materials. La54W10O111v (LWO54) was found to be most stable, also in CO2, with a proton conductivity of 0.0015 S/cm satisfying final target. Spray pyrolysis synthesis was developed, and cost-saving measures including mischmetal strategies investigated for this electrolyte as for the LCN system. LWO reacts with NiO, and EFFIPRO partners have filed patent for using Sr-doped LaCrO3 (LSC) as barrier and functional anode. The project made a 2.5 m LWO electrolyte by PLD on a porous LSC layer spray-deposited on an alloy support, the first so-called third generation PCFC structure reported. Other developments included Ni post-sintering infiltration and reductive precipitation of catalytic Ni nanoparticles from Ni-substituted LSC. Integration with parallel national projects has been fruitful, adding e.g. DFT calculations and atomic resolution microscopy to the anode development.

A number of potential cathode materials were screened and some scrutinised by a large range of in situ equilibrium and transient methods, e.g. Raman spectroscopy, impedance spectroscopy, thermogravimetry, and H/D and 18O/16O isotope exchanges. As cathode for LWO we investigated in depth substituted, infiltrated, and nanostructured LaMnO3 and La2NiO4, as well as the fundamentals of La2Ce2O7 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 cm2 in wet atmospheres at 700 °C, only factors 2-3 off project targets.

EFFIPRO 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.

Potential impact:

At project closure, 6 out of the 11 technical milestones have been met, 3 partly met, and 2 missed by parameter factors of 2 or 3. The project demonstrated the development and manufacture of two stable proton conducting oxides, Ca-doped LaNbO4 (LCN), and tungsten oxide La54W10O111v (LWO54) by cost-effective spray pyrolysis, and their application as thin films of 5 and 3m, respectively, on porous anodes supported on Ni-based cermet or alloy substrates. Layers and films have been made using electrophoretic deposition (EPD), pulsed laser deposition (PLD) and other techniques. The thin film of LWO54 has a proton conductivity of 0.0015 S/cm at the target temperature of 700 °C and thus reaches
the project goal of an area specific resistance (ASR) of less than 0.2 cm\(^2\). LWO54 was found to react with NiO during manufacturing, and a method to use Sr-doped LaCrO\(_3\) (LSC) as anode and barrier has been developed and patented. The anodes have been improved by precipitation of Ni nanoparticles from dissolved Ni during operation under reducing conditions or by post-sintering Ni infiltration techniques. Cathodes for LCN with acceptable performance could not be identified, while various La\(_2\)NiO\(_4\) and Pr\(_2\)NiO\(_4\) formulations with optimised processing were promising for cathodes for LWO54. All in all, cathode and anode polarisation ASRs reached 0.4 and 0.6 cm\(^2\), respectively, i.e. factors 2 and 3 off project target. The materials and interfaces were stable towards CO\(_2\) and thermal cycling, as requested.

The thin film of LWO54 on an LSC anode supported by an alloy substrate is the first so-called third generation PCFC demonstrated. The project moreover has yielded an unprecedented insight into anode and cathode rate limiting contributions by use of a large range of in-situ techniques in equilibrium or transient modes, including Raman spectroscopy, impedance spectroscopy, H/D and 18O/16O isotope exchanges, and thermogravimetry. Collaboration with parallel national projects has added, for instance, state-of-the-art DFT calculations and atomic resolution microscopy. The project has launched new hypotheses and understanding regarding use of solid electrolytes that may prove useful for SOFC, PCFC, and related developments perhaps even for solid-state Li-ion batteries. The project has educated one PhD and lists at closure one patent, 11 international peer-reviewed articles, and 26 presentations.

EFFIPRO has enabled more cost-effective and competitive production of advanced ceramic powders at SEM partner CerPoTech. The project has interacted with University of Oslo spin-off SME Protia, which is pursuing energy conversion and fuel upgrading technologies based on proton conducting ceramics, and larger industries in renewable energy, SOFC manufacturing, and ceramic products in Europe and US. Much of this is related to follow-up research and project applications to national and EU (FCH JTI and NMP) calls by various constellations of the EFFIPRO partnership and new actors. Many relate to hydrogen production and biogas uses, in addition to PCFCs as such. Some follow-up projects have already been granted and underway, others are in the pipeline.

All in all, EFFIPRO and its partnership constitute the expected solid base for further developments in PCFC and related technologies (electrolysers, gas separation membranes) based on proton conducting ceramics. It is estimated in 2020 to have an impact on fuel cells and their introduction not only in transport, but also in other energy conversion processes reducing the emissions from fossil energy and facilitating introduction of renewable energy.


**Related documents**

[140179851-8_en.zip](140179851-8_en.zip)

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