PROGRESS REPORT

Renewable Energies

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Introduction

Hydrogen is seen by many as a key energetic vector for the 21st century. Its utilization in fuel cells enables a clean and efficient production of electricity. The possibility to obtain hydrogen from various sources, along with several types of potential applications of fuel cells, have called the attention and investment of developed countries. European Union, United States, Canada and Japan have important programs that establish tied goals for the utilization of fuel cells in transport and distributed energy generation. Aware of the importance of this technology for the energetic future of Brazil, IPEN started 16 years ago the development of fuel cells for stationary and distributed energy applications. Preliminary studies were carried out at the Materials Research Center due to IPEN expertise on nuclear materials development. Based on both the good initial results and the proposition of the Brazilian Fuel Cell Program (ProH_2) by the Ministry of Science, Technology and Innovation (MCTI), IPEN decided to organize an institutional program on the subject, conducted at the Fuel Cell and Hydrogen Center – CCCH.

The objectives of the IPEN/CCCH program are based on the MCTI national program, contributing significantly to the national development in this area. The R&D Program was structured in a cross-cutting way involving human and infrastructure resources from many IPEN technical departments. The Center comprises three main areas of interests: PEMFC (Proton Exchange Membrane Fuel Cell); SOFC (Solid Oxide Fuel Cell); and H_2-PRODUCTION, mainly from ethanol reforming. More than 50 professionals were engaged at this development, although some in part time, including PhDs, MSc, and both undergraduate and graduate students.

Important scientific and technological results have been obtained and the main achievements can be evaluated by patents, published papers, graduate courses given, and the graduate student's thesis advisory. Since 2004, the PEMFC Laboratory was transferred to a new site, improving its research capabilities, which includes catalyst and MEA preparations and fuel cell stack test up to 5 kW electric power. In the period of 2005-2007, new laboratories of SOFC, Hydrogen, and Fuel Cell Systems have been implemented. In the period of 2014-2016, our attention turned also to scaling up, reliabilities studies and small demonstration projects.

The financial resources were based on scientific funds from federal and state government agencies (FINEP-MCTI- ProH_2, FAPESP, CNPq, and CAPES). Today, IPEN is considered as an important partner within the R&D networks established by the MCTI-ProH_2 Program. Partnership with emerging enterprises from CIETEC (Incubator Center) and others led to advances and autonomous technological domain in some areas.

The development of a FAPESP's Thematic Project (Process no 2014/09087-4, "Studies on the use of bioethanol in Proton Exchange Membrane and Solid Oxide Fuel Cells") started in 2016 at CCCH. This project consists in the use of bioethanol in Proton Exchange Membrane Fuel Cell (PEMFC) and Solid Oxide Fuel Cell (SOFC), either directly as a fuel or indirectly in the form of reformate hydrogen, has a number of technical barriers that require scientific and technological advances in order to provide high efficiency, durability, reliability and low cost to these devices. This project aims to address critical issues for the major scientific and technological challenges to advance the use of ethanol in fuel cells. For PEMFC, the main focus will be the development of anode catalysts, electrolytes, and membrane/ electrode/bipolar plates assemblies that allow a more efficient use of ethanol. For SOFC it will be investigated anode materials resistant to carbon deposits for the direct use of ethanol. Ethanol will be also studied as a source of hydrogen by developing catalysts for steam reforming and for purification by the preferential oxidation of carbon monoxide reaction (PROX-CO) of hydrogen-rich mixtures resulting from the steam reforming and shift processes. The success of this project will bring significant contributions to the advancement of the understanding of the electrochemical processes, in the development of devices that use a strategic biofuel and training of specialized human resources. CCCH also participates in Research, Innovation and Dissemination Centers (RIDCs) from São Paulo Research Foundation (FAPESP – Process no 2014/50279-4); this project aims to establish a world class Research Centre focused in Natural Gas investigations, innovation and dissemination of knowledge, where is intend to deal with the natural gas challenges according to three distinct, but complementary, research programs: Engineering, Physical and Chemistry and Energy Policies and Economics.

Proton Exchange Membrane Fuel Cell (PEMFC)

The activities of the PEMFC Group are focused on both the basic and technological developments of hydrogen fueled PEMFCs and the direct oxidation of alcohols (Direct Alcohol Fuel Cells – DAFC), such as methanol, ethanol, ethylene glycol and glycerol. Also, small molecules like formic acid, formate and ammonia have also been studied as combustible. The main goal concerns stationary and portable applications for distributed electric power generation Amongst the main research subjects are: the development of new methods of electrocatalysts production and new electrocatalysts systems; development, production, and characterization of new composite electrolytes for high operating temperatures (130°C); production, characterization and optimization of membrane electrode assembly (MEA); modeling and simulation of PEMFCs; unit cells tests in laboratory and pilot scales; development of low power fuel cell stacks, and education.

IN THE PERIOD OF 2014-2016, NEW STUDIES WERE STARTED AT CCCH:

- development of new electrocatalysts and anionic membranes for Alkaline Fuel Cells;

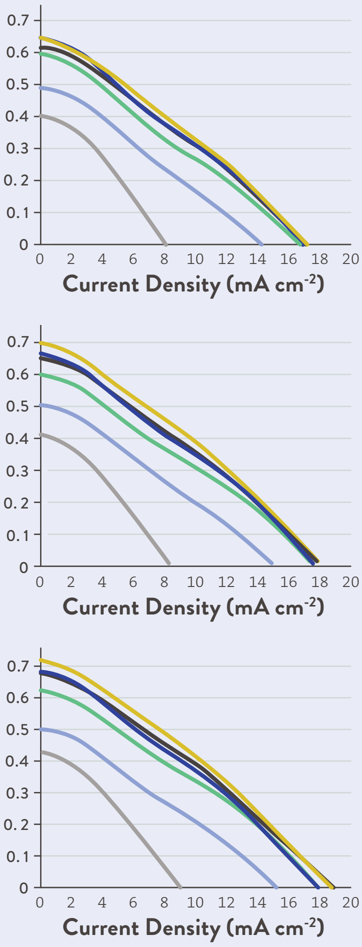
- a new equipment to deposit a catalytic ink by spray method was installed to prepare membrane electrodes assembly (MEA). This equipment has great precision to deposit a very thin catalytic layer reducing the Platinum loading on the anode and on the cathode, and avoiding the Pt losses in the MEA´s preparation;

- studies on simulation have been applied to represent the electrochemical phenomena occurring inside a fuel cell using a COMSOL Multiphysics program, which is a powerful simulation tool you can use to help understand and overcome PEM fuel cell design and construction.

Highlights 2014-2016

Direct Ammonia Fuel Cell performance using PtIr/C as anode electrocatalysts (Fig 1).

CELL POTENTIAL (V)



POWER DENSITY (MW CM-2)

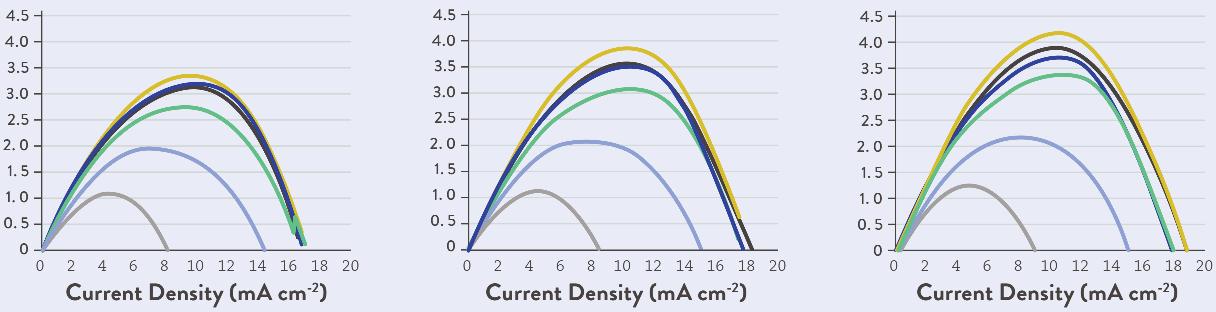


FIGURE 1. Polarization and power density curves of a 5 cm² DAFC at 40°C. (a) and (b) using NH4OH 1.0 mol L-1. (c) and (d) using NH_4OH 3.0 mol L-1. (e) and (f) using NH_4OH 5.0 (both in KOH 1 mol L-1). Ir/C (1 mg Ir cm-2), Pt/C BASF and PtIr/C (1 mg Pt cm-2) compositions used as anode, for cathode in all experiments was used Pt/C BASF (1 mg Pt cm-2).

Anodic oxidation of formic acid on PdAuIr/C-$Sb_2O_5 \cdot SnO_2$ electrocatalysts prepared by borohydride reduction electrocatalysts prepared by borohydride reduction (Fig 2).

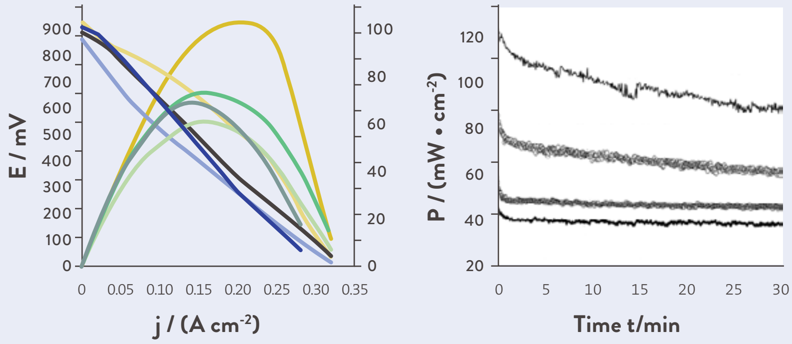


Figure 2. (a) Current time curves at 0. 5 V in presence of 1. 0 mol L-1 formic acid solution and 0. 5 mol L-1 H_2SO_4 solution for Pd / C-ATO and PdAuIr / C-ATO electrocatalysts at 25°C. (b) Curves (I-V) and the power density at 100°C using Pd/C-ATO and PdAuIr/C-ATO electrocatalysts Pd/C-ATO; PdAuIr / C-ATO(50:45:5); PdAuIr/C-ATO(70:20:10); PdAuIr/C-ATO(90:5:5)

Electrochemical and fuel cell evaluation of PtAu/C electrocatalysts for ethanol electro-oxidation in alkaline media (Fig. 3).

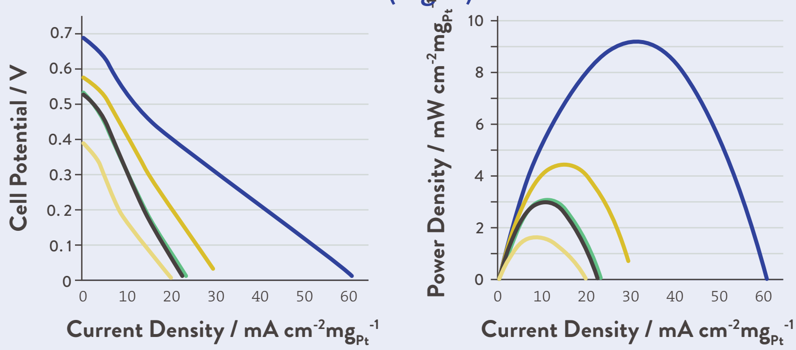


FIGURE 3. Direct ethanol fuel cell performance of the PtAu/C electrocatalysts, Pt/C and Au/C.

Effect of TiO_2 Content on Ethanol Electrooxidation in Alkaline Media Using Pt Nanoparticles Supported on Physical Mixtures of Carbon and TiO_2 as Electrocatalysts (Fig. 4).

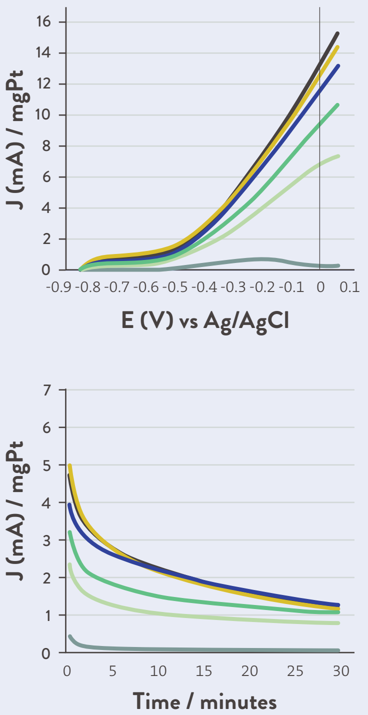
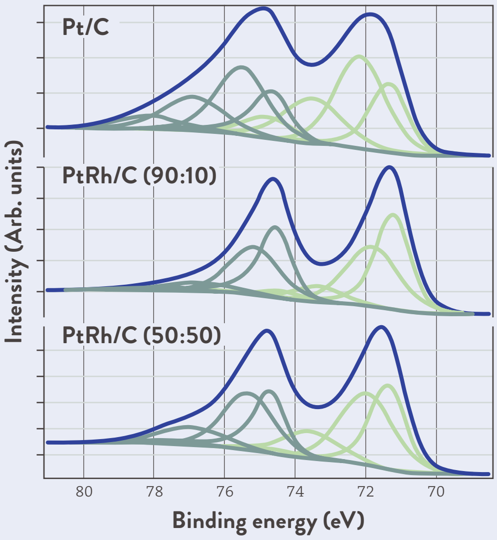
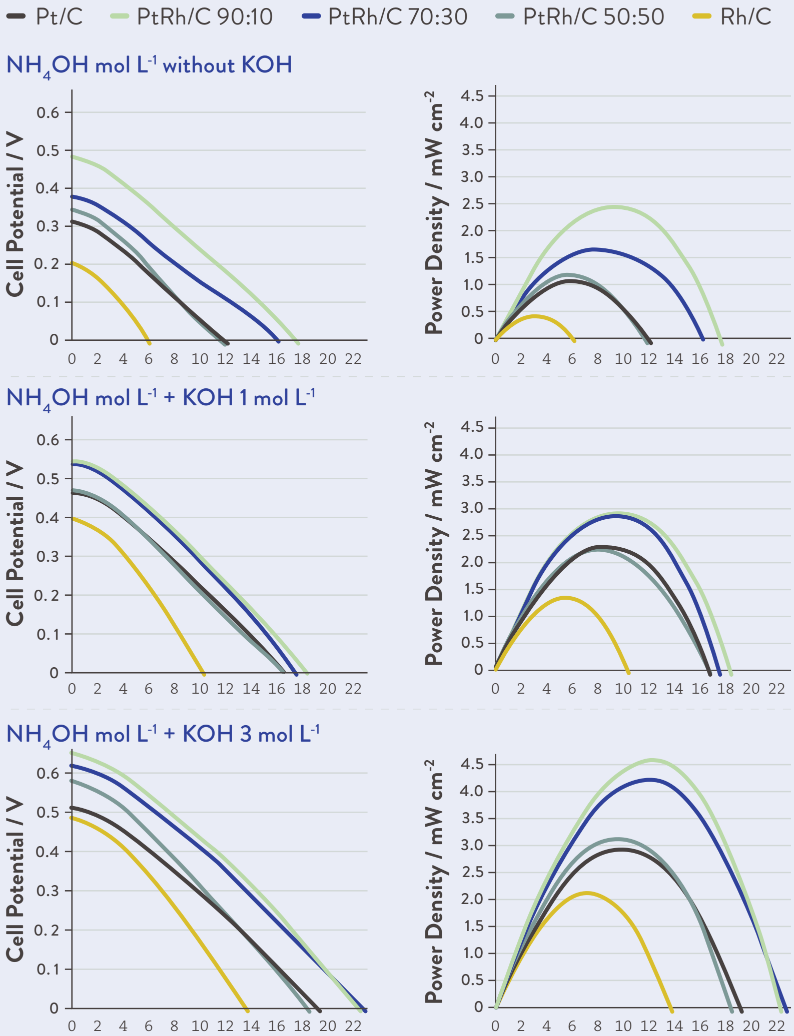


Figure 4. a Cyclic voltammograms of Pt/($C+TiO_2$) electrocatalysts in the presence of 1mol L^{-1} ethanol and 1mol L^{-1} KOH saturated with N_2 at a scan rate of 10 mV s^{-1}. b Current-time curves at −0.35 V in the presence of 1 mol L^{-1} ethanol and 1 mol L^{-1} KOH saturated with N_2 at room temperature.

Oxidation of ammonia using PtRh/C electrocatalysts: Fuel cell and electrochemical evaluation (Fig. 5).

Figure 5. (a) Fitted XPS Pt 4f core level spectra of the Pt/C, PtRh/C 90:10, PtRh/C 50:50 catalyst. (b) Polarization and power density curves of a 5 cm^2 DAFC with 2 mg metal cm^{-2} in both anode and cathode at 50°C and using 1 mol L^{-1} NH_4OH and KOH ranging from 0 mol L^{-1} to 3 mol L^{-1}.





Synthesis of hydroquinone with co-generation of electricity from phenol aqueous solution in a proton exchange membrane fuel cell reactor (Fig. 6).

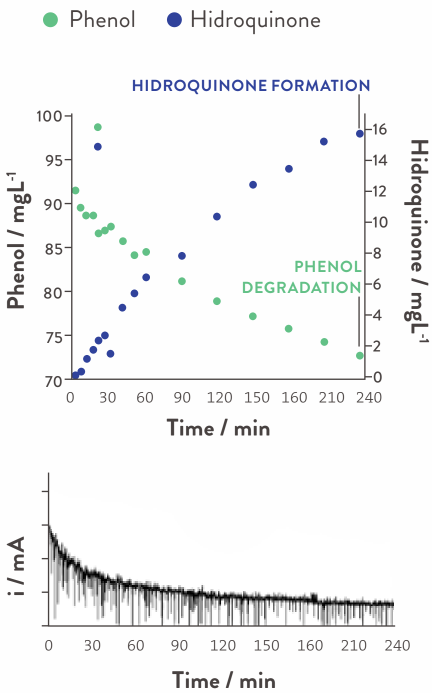
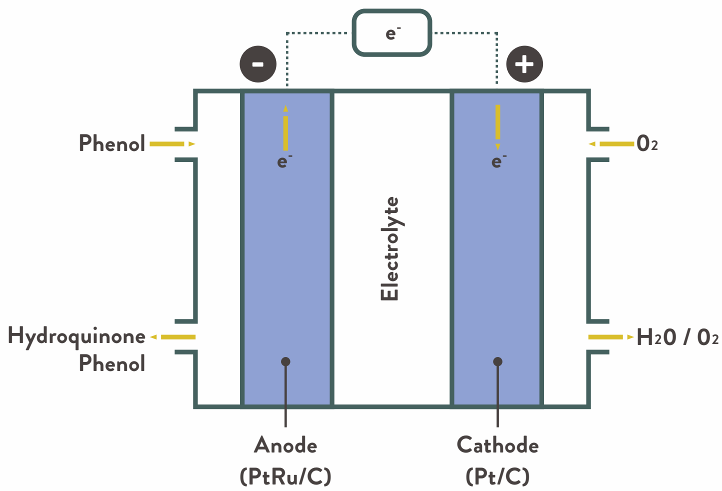


Figure 6. Scheme of the fuel cell used as flow reactor to produce hydroquinone. a) Phenol degradation with the hydroquinone production during the 4 hour experiment. b) The electricity co-generation during the hydroquinone production.



PdAu/C Electrocatalysts as Anodes for Direct Formate Fuel Cell (Fig. 7).

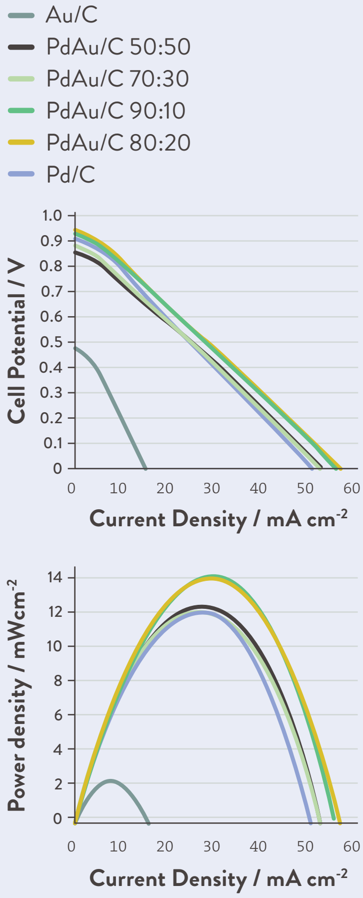


Figure 7. Polarization and power density curves of a direct formate fuel cell using PdAu/C in different atomic rations, Pd/C and Au/C electrocatalysts.

Electrochemical and in situ ATR-FTIR studies of ethanol electrooxidation in alkaline medium using PtRh/C electrocatalysts (Fig. 8).

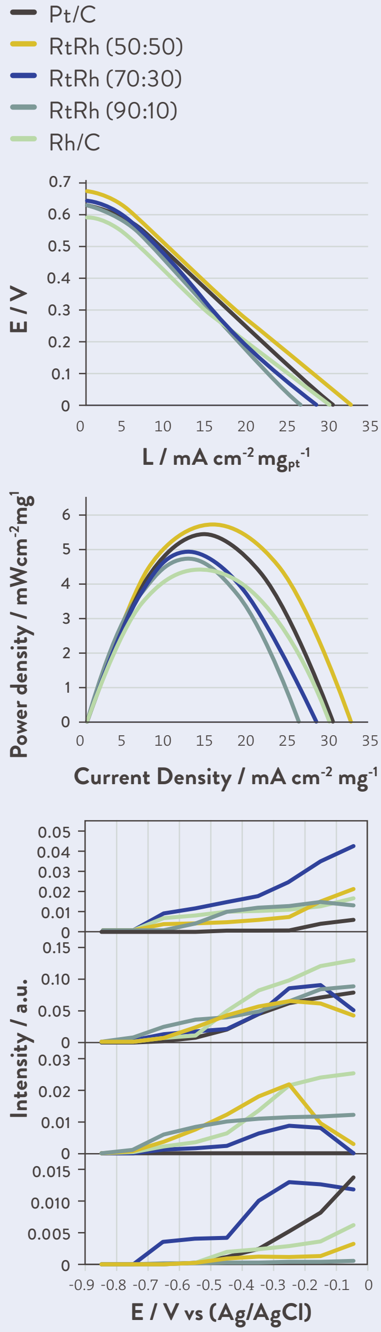


Figure 8. I–V Curves and the power density at 60oC of a 5 cm2 DAEFC using Pt/C, Rh/C and PtRh/C electrocatalysts anodes (1mgmetal cm-2 catalyst loading) and Pt/C E-TEK electrocatalyst cathode(1 mgPt cm-2 catalyst loading, 20 wt% Pt loading on carbon), Nafion 117 membrane KOH treated, ethanol (2.0 mol L-1) and oxygen pressure (2 bar). Integrated CO2, acetate, carbonate, methyl group, andacetaldehyde band intensity as a function of the electrode potentialfor Pt/C, Rh/C and PtRh/C electrocatalysts.

PtAu Electrocatalyst for Glycerol Oxidation Reaction Using a ATR-FTIR/Single Direct Alkaline Glycerol/Air Cell In Situ Study (Fig. 9).

- Pt/C
- PtAu/C 90.10
- PtAu/C 70.30
- PtAu/C 50.50
- Au/C

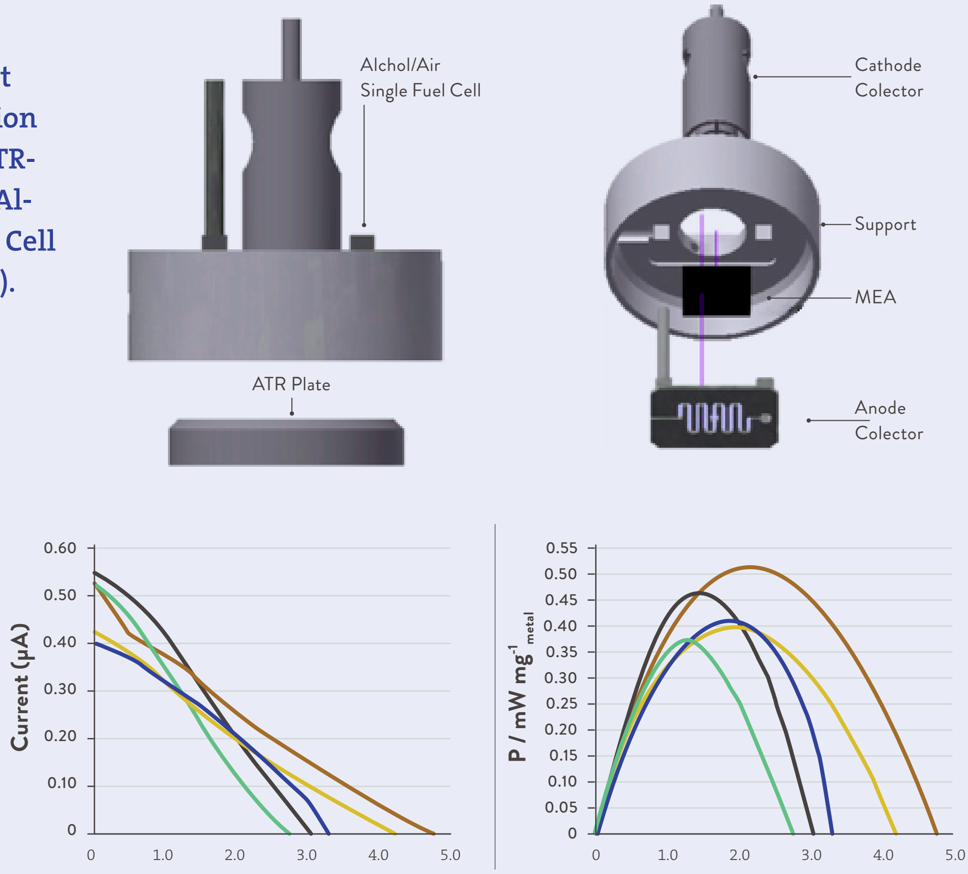


Figure 9. Polarization curves of single direct alkaline glycerol/air cell for Pt/C, Au/C, and PtAu/C electrocatalysts at atomic ratios 90:10, 70:30, and 50:50. (C) ATR-FTIR/alcohol/airsingle cell setu.

Synthesis of Pt nanoparticles with preferential (100) orientation directly on the carbon support for Direct Ethanol Fuel Cell (Fig. 10).

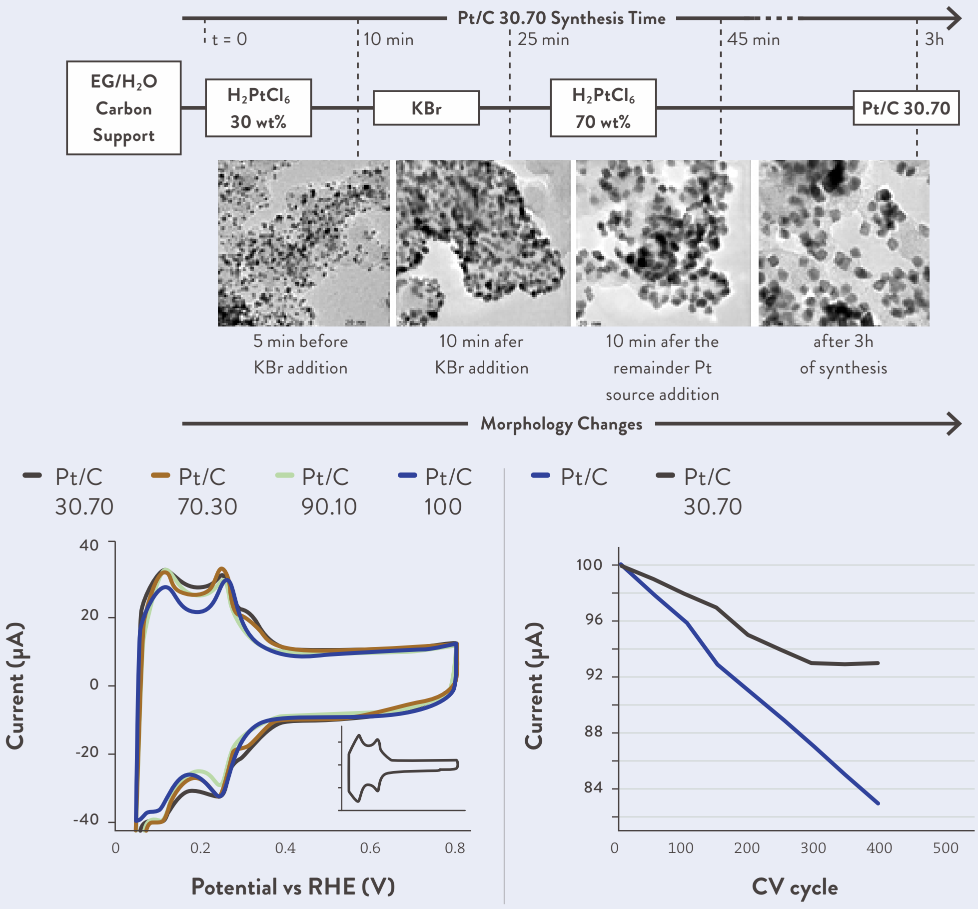


Figure 10. CVs of Pt/C electrocatalysts prepared with Br -:Pt ratio of 300 under different conditions: (a) H_2SO_4 0.5 mol L^{-1} electrolyte and scan rate of 50 mV s^{-1} and (b) ECSA loss with CV cycling.(c) Morphology development of Pt/C 30.70 electrocatalyst (collected at different synthesis times and analyzed by TEM).

The first study in fuel cell simulation was made on gas fluxes for different flow channels (Fig. 11), Nowadays the simulation has been made in a complete fuel cell (Fig. 12). In this case, many chemical phenomena are involved depending on which layer is on study, heat transfer, gas flux in porous media and flow channels, electrochemical reactions (Fig. 13).

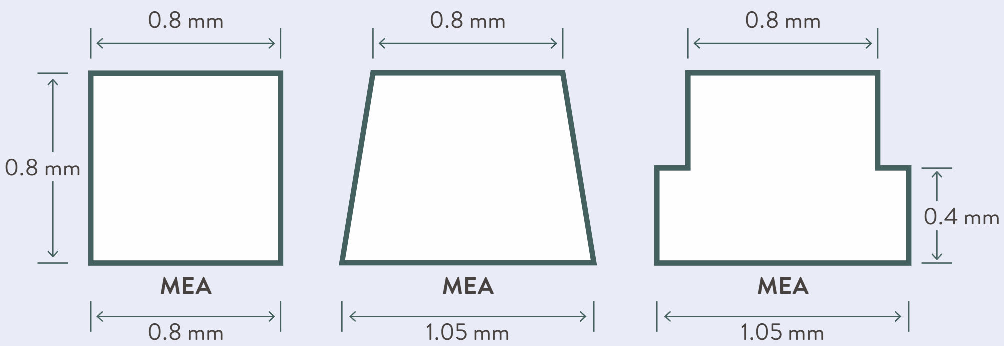


Figure 11. Channel cross sections and dimensions: (a) rectangular, (b) trapezoidal and (c) stepped.

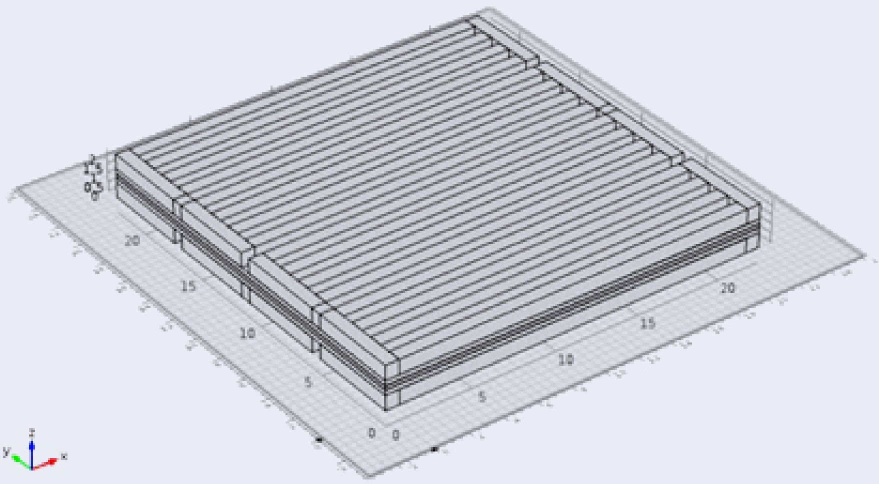


Figure12. A complete fuel cell with two gas flow channels, two gas diffusion layers, two catalytic layers and a membrane.

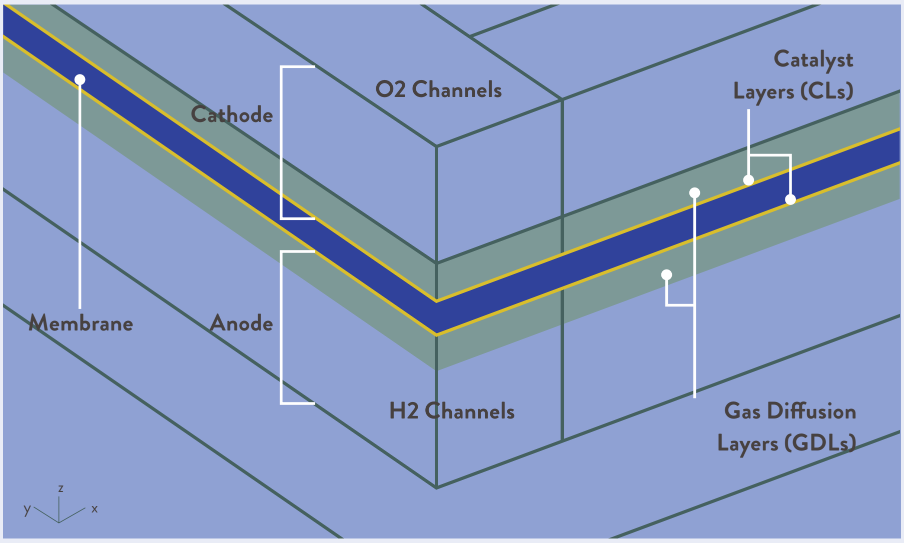


Figure 13. Detail of the layers of a fuel cell.

Fig. 14 represents the comparison of experimental and numerical polarization and potential curves used in the flooded agglomerate model.

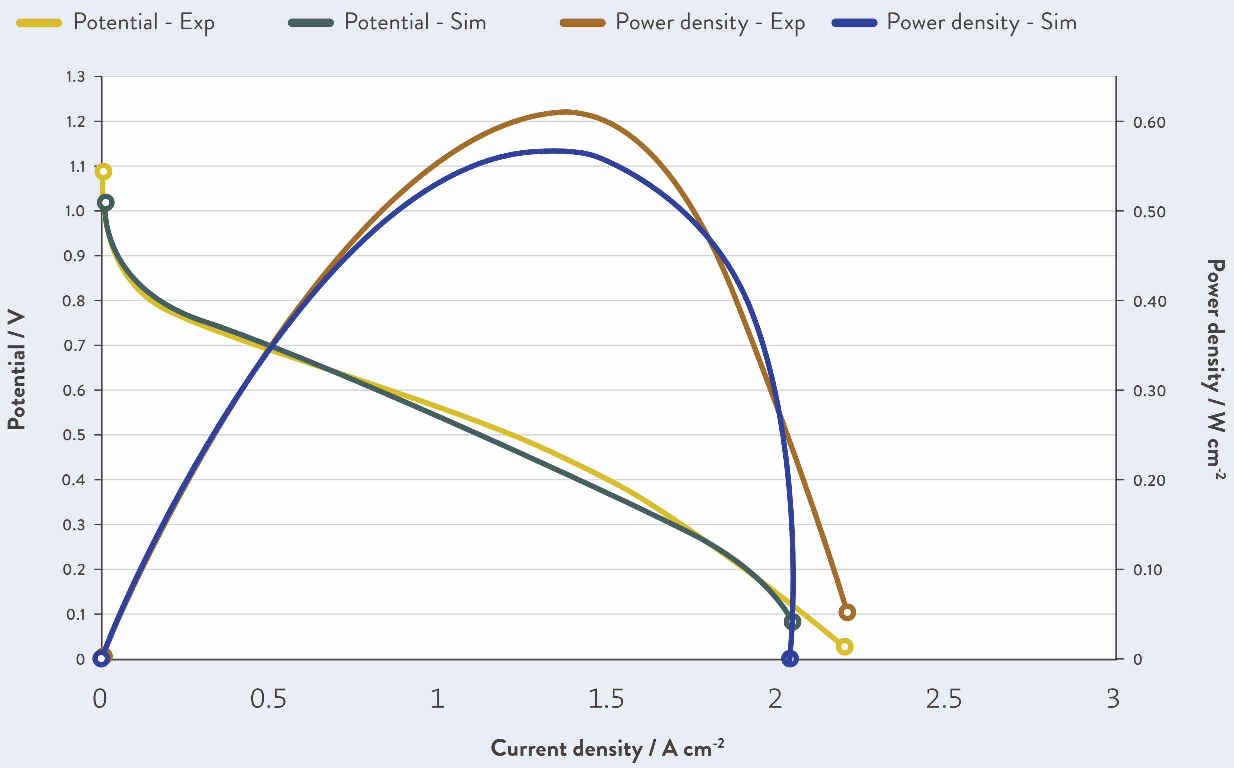


Figure 14. Experimental and numerical simulation (flooded agglomerate model) polarization curves for cells with rectangular channel.

Solid Oxide Fuel Cell (SOFC)

Solid Oxide Cells (SOCs) is a general classification for Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs) -SOFCs operated in electrolysis mode- are solid-state devices that can be used to i) convert between chemical and electrical energy and/or ii) drive chemical reactions. These capabilities make them attractive for energy conversion, energy storage, chemical sensing, chemical separation, and chemical synthesis applications. Most of the research focus has been given to the development of reversible SOCs devices capable of operating in both modes (fuel cell and electrolysis) for advanced application involving energy storage and generation in one device. SOFCs are the most efficient electrochemical devices to directly convert the chemical energy of fuels into electricity, thus they are regarded as promising power sources for several applications due to important characteristics such as: i) wide range of power outputs (from centralized power plants of MWatt to auxiliary portable units of a few Watt); ii) fuel flexibility, SOFCs potentially run on different fuels such as hydrogen, natural gas, and ethanol; and iii) high efficiency and carbon neutral energy generation with rather low noise and harmful emissions.

Basically, SOCs consist of two porous electrodes separated by a dense electrolyte. Such a ceramic cell requires complex fabrication technologies and each component must fulfill several criteria. Physical and chemical compatibility and stability at high temperature and oxidizing/reducing environments along with good electrochemical properties are important properties for materials used in these devices. Important goals in SOCs research include the development of fuel-flex anodes, capable of operating in different fuel, redox resistant, and tolerant to carbon deposits and sulphur contamination. The reduction of the operating temperature from 800-1000°C down to 500-800°C range, in order to minimize degradation of components, improve design flexibility, and lower material and manufacturing costs, is also a key issue for disseminating SOCs. Nevertheless, reducing the operating temperatures requires new materials for high-performance SOCs.

The main activities of the SOFC research group at IPEN have been the synthesis, processing, and characterization of the SOFC components, along with single cell testing, aiming at direct ethanol SOFCs. Ethanol is an available, efficient and cost competitive renewable fuel. Differently from hydrogen, which still requires an infrastructure for widespread use, ethanol brings strategic advantages such as easy storage and good distribution. Moreover, it allows SOFCs to run in a carbon neutral cycle.

Yttria-stabilized zirconia (YSZ) and nickel (Ni) composite is the standard anode for solid oxide fuel cell. This composite is the best anodes for hydrogen electrochemical oxidation, but it lacks of stability when carbon containing fuels are used. In order to use available fuels such as methane (natural gas) with the standard anodes, it is necessary to add an oxidant agent, typically water. However, adding water to the fuel stream adds complexity to the fuel cell system and decreases its efficiency. Therefore, developing new concepts of SOFC anode remains a one of the challenges to advance SOFC technology to commercialization. In this context, two main strategies can be identified. The first one is replacing the standard anode for more stable materials. Several compounds, mainly ceramic single-phase perovskites and alternative ceramic-metal composites, have been proposed, but so far none of them can reach the same performance of the Ni-YSZ anode running on hydrogen. Another alternative is to separate into different layers the catalytic and the electrochemical reactions taking place in the anode of the SOFC. Thus, the best composition can be selected for each function.

The main role of the catalytic layer is to promote the steam reforming of ethanol, generating hydrogen as the main decomposition product and promoting the internal reforming. Hydrogen obtained by the steam reforming in the catalytic layer is oxidized in the triple phase boundary of the Ni-based anode and electrolyte, generating electrons and steam. Thus, as long electric current is drawn from the SOFC the steam produced at the anode/electrolyte interface ensures the reforming of the ethanol in the catalytic layer. Therefore, the internal reforming requires no addition of water and the performance of fuel cells running in both hydrogen and ethanol are comparable as long an active catalyst is used. Fuel cells running on internal reforming of ethanol with catalytic layer were found to be stable over long periods of time.

The research carried out at IPEN in collaboration with University Grenoble Alpes (France) has pursued such anode configuration and promising results were obtained and reported in the Journal of the Electrochemical Society. SOFCs with a catalytic layer deposited on to the standard Ni-YSZ anode can run on ethanol with excellent stability and practically the same current output as in hydrogen, provided that an efficient catalyst is used. Moreover, we have demonstrated the fuel-flex SOFC concept, as shown in Fig.15. Such fuel cells are usually pointed out as fuel-flexible devices because

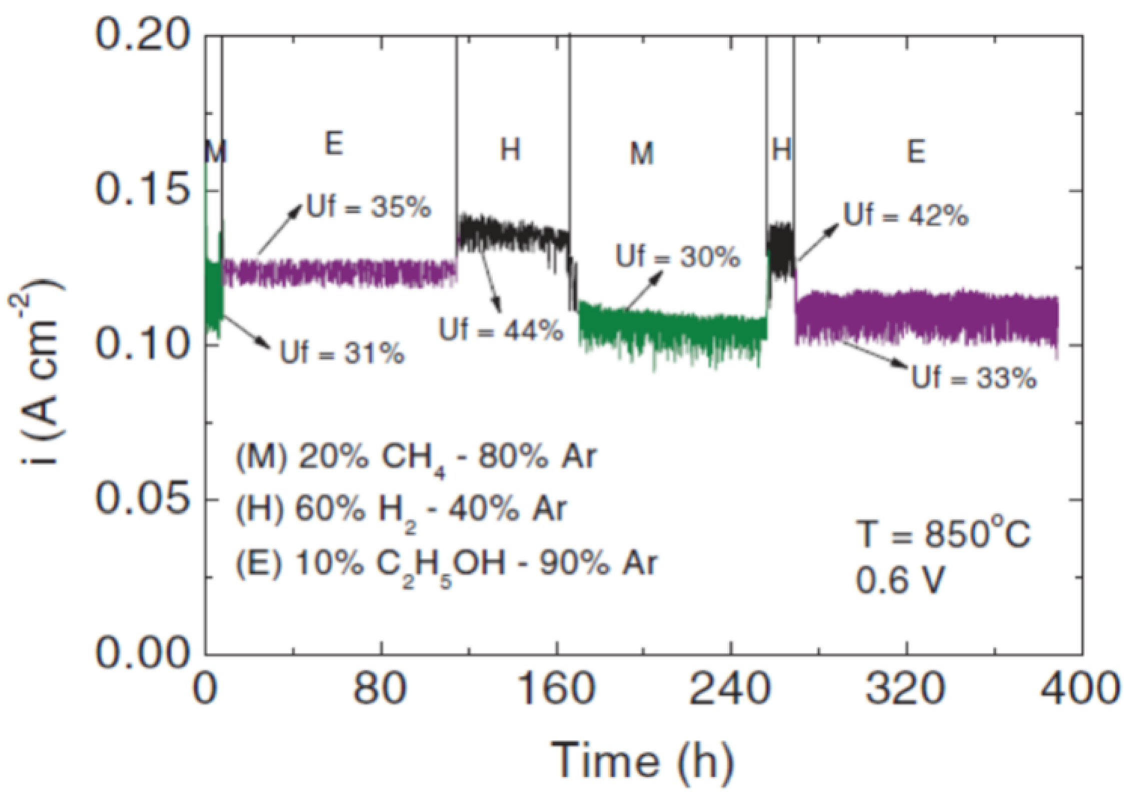


Figure15. Stability test of direct ethanol SOFC using a ceria-doped-based catalytic layer. The fuel-flex concept was demonstrated by sequentially switching fuels from H2, to ethanol (E) and methane (M).

the high operating temperature allows feeding with various fuels. However, reports of one SOFC using different fuels are rarely found. Thus, this is one of the few practical demonstration of a fuel cell running with different fuels with similar performance and good stability without adding water. More importantly, the post-test analysis revealed no detrimental carbon deposition as evidenced by electron microscopy analyses (Fig. 16).

Fundamental research on ceramic materials used in SOFC technology has been conducted at IPEN. In 2016, a collaboration with scientists from Technical University of Denmark resulted in the publication of a "hot paper" in the Journal of Materials Chemistry A. We have carried out studies trying to understand mechanisms of reaction between two important components in SOFC: YSZ and gadolinium-doped ceria (CGO). By comparing the resulting microstructures after sintering YSZ-CGO mixtures in both reducing and oxidant atmosphere, we have observed an inversion of the diffusion mechanisms that controls the solid solution formation between those two oxides. Fig. 17 shows scanning electron microscopy images of samples sintered in air and under H_2. In air, it is has been demonstrated that the main mechanism promoting the reaction between YSZ and CGO is the diffusion of Zr^{4+} into CeO_2. On the other hand, in reducing conditions, our results showed that the reduction of ceria promotes accelerated diffusion processes that do not result in densification of the composite, but rather in an extensive CGO-YSZ dissolution due to the diffusion of Ce^{3+} into ZrO_2.

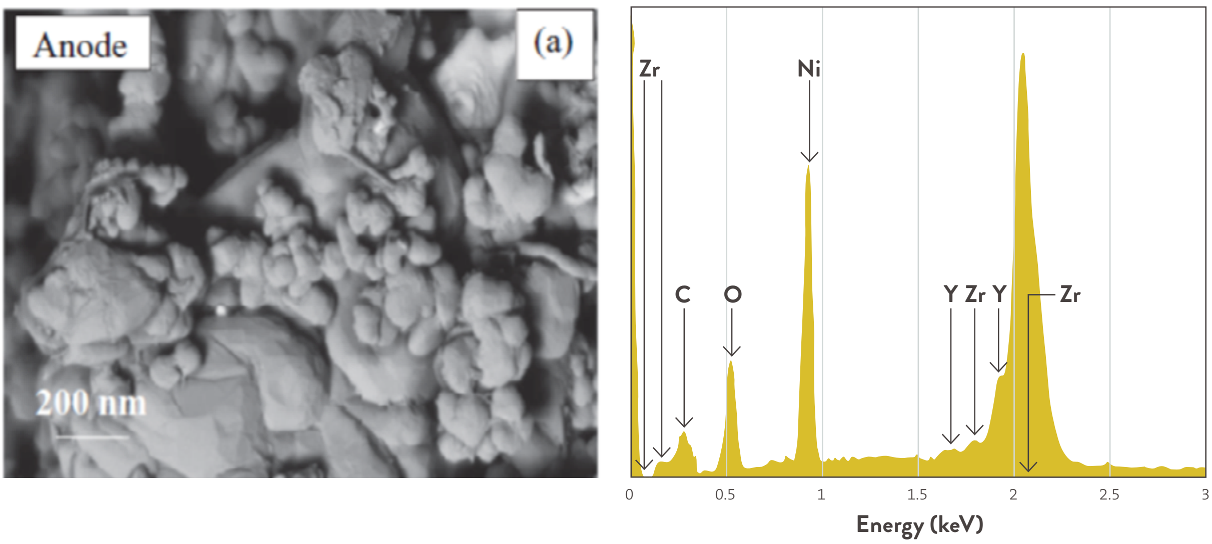


Figure 16. a) Scanning electron microscopy of the anode and b) energy-dispersive X-ray spectroscopy of the anode after 400 hours of ethanol/methane durability test.

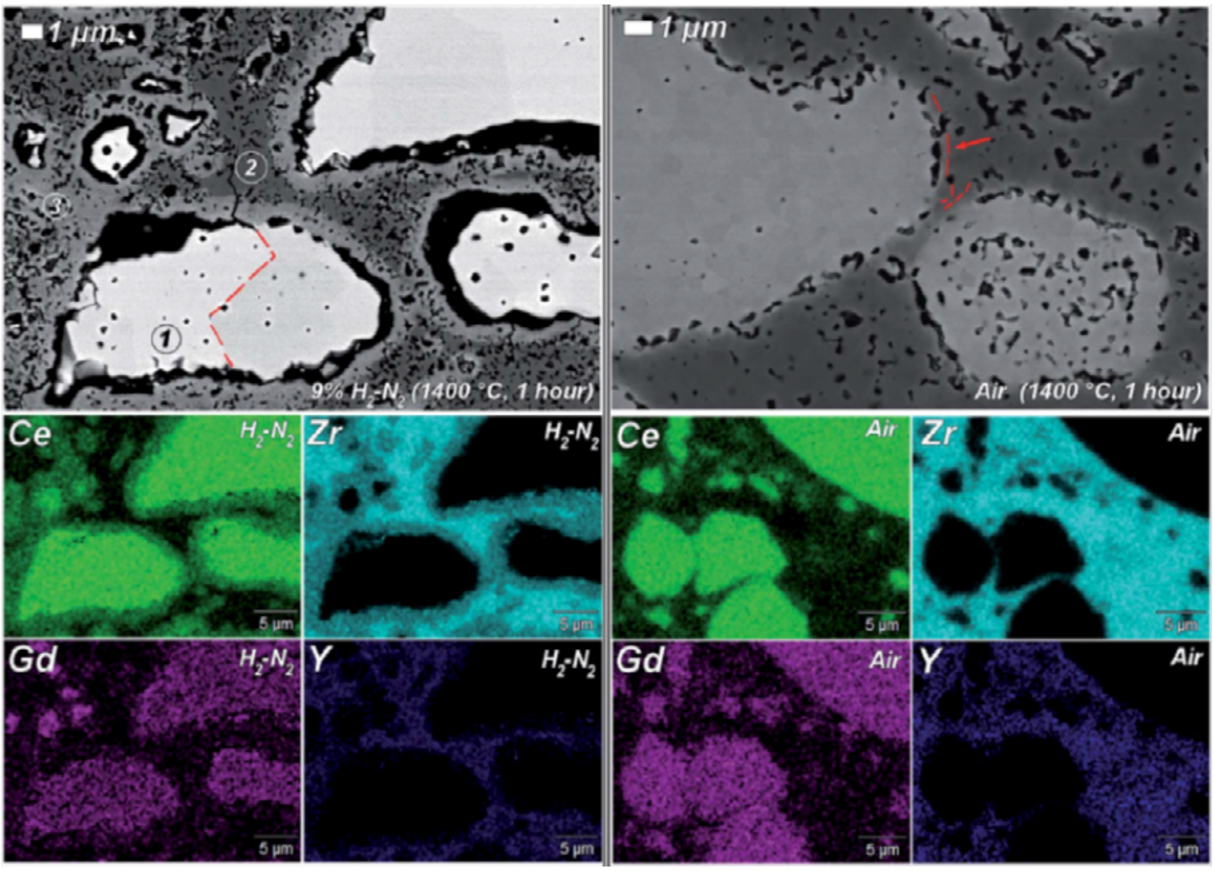


Figure 17. Scanning electron micrograph and the corresponding EDS analysis of the CGO/YSZ composite polished cross sections after sintering in air (right panel) and in 9% H_2–N_2 with reoxidation at 900°C in air (left panel).

Hydrogen

The Hydrogen Laboratory of CCCH began its activities in 2005 with the development of pilot plants for hydrogen production from ethanol through the processes of steam reforming, oxidative reforming and partial oxidation. Studies were also carried for obtaining hydrogen from biomass (coffee straw, sugarcane bagasse and cashew nuts) using a pyrolysis process. These studies played an important role in the implementation and development of the laboratory until 2013.

From 2014 onwards, the laboratory began a process of restructuring and renovation (Fig. 18), where it was decided to initiate studies at the bench-scale for hydrogen production and purification. The studies were focused on the development of nanostructured catalysts for ethanol steam reforming and for preferential oxidation of carbon monoxide in hydrogen-rich mixtures (CO-PROX process) in order to obtain high purity hydrogen suitable for use in low temperature fuel cells. To perform these studies bench-scale reactors and new equipments for catalysts characterization were installed (Fig. 19).

Figure 18. Renovation of the Hydrogen Laboratory Infrastructure.

Figure 19. Bench-scale reactor systems and equipments.

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