Renewable Energies

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 13 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 graduate students and undergraduate 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 concluded. 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 2011-2013 our attention turned also to scaling up, reliabilities studies and small demonstration projects. A new building for housing additional personal was built during this period.

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 an important partner within the R&D networks established by the MCTI-ProH_2 Program. Partnerships with emerging enterprises from CIETEC (Incubator Center) and others led to advances and autonomous technological domain in some areas.

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, such as methanol (DMFC - Direct Methanol Fuel Cell), ethanol (DEFC - Direct Ethanol Fuel Cell). 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.

Highlights 2011-2013

- Development of new electrocatalysts formulations like PtBi/C (Fig. 1a) and PdBi/C (Fig 1b) for direct ethanol electron-oxidation in alkaline medium.
- Development of new Pd Anode electrodes for Proton Exchange Membrane Fuel Cell (Fig 2).
- Studies on the effect of acetaldehyde and acetic acid on ethanol electro-oxidation using $PtSnO_2/C$ electrocatalysts (Fig. 3).
- Development of a single fuel cell/ATR-FTIR setup for studies in-situ of direct alcohols fuel cell (Fig. 4).
- Synthesis of Nafion-SiO_2 electrolytes for stable H_2/O_2 PEMFC operating at high temperature and low relative humidity: The effect of sol-gel solvent (Fig. 5).
- Theoretical-experimental studies of optimized components of high performance PEMFC (Fig. 6).
- Scaling up of Membrane-Electrode-Assembly (MEA) by sieve printing method, up to 250 cm^2 of electrode area. Delivery of MEAs to Electrocell company for demonstration in a 5 kW PEMFC Stack (Fig. 7).
- Development of a PEMFC stack of 5 kW electric power using technology developed at IPEN (Fig. 8).
- Reliability studies of PEMFC components.

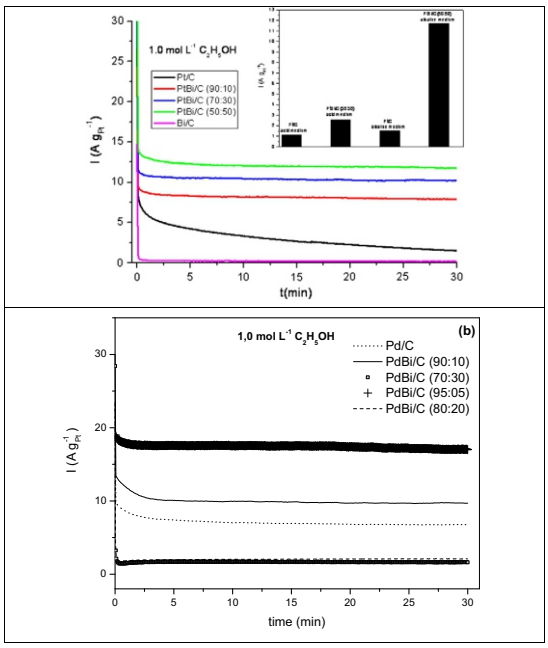


Figure 1. Current–time curves at−0.4 V in 1 mol L^{-1} ethanol solution in 1.0 mol L^{-1} KOH for Pt/C, Bi/C and PtBi/C electrocatalysts. (Inset) Current values at −0.4 V after 30 min for Pt/C and PtBi/C eletrocatalysts in alkaline and acid media.(b) Current–time curves at −0.4 V vs Ag/AgCl in 1.0 mol L^{-1} KOH solution containing 1 mol L−1 of ethanol for Pd/C and PdBi/C electrocatalysts.

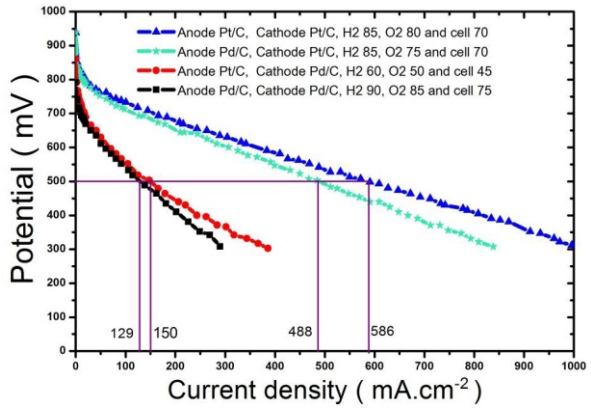


Figure 2. Polarization curves of MEAs with Pt/Pt, Pt/Pd, Pd/Pt and Pd/Pd (anode/cathode) electrodes. Active area of 5 cm^2. Anode 0.4 mg metal per cm^2 supplied with 160 mL.min^{-1} H_2 at 1 atm. Cathodes 0.4 mg metal per cm^2 supplied with 80 mL.min^{-1} at 1 atm. Both reactive gases saturated with high pure water. Temperatures of H_2, O_2 and cell that resulted in better performances are presented in the legend of the curves.

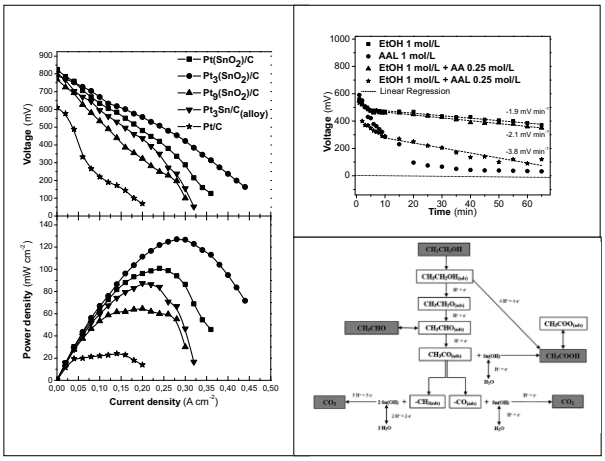


Figure 3. Electrical performance of DEFC using different PtSn/C electrocatalysts at the anode (100°C, 2 mg Pt cm^{-2} at the anode and cathode, 2mol L^{-1} of ethanol solution delivered at 2 mL min^{-1} in the anode) and the effect of acetaldehyde (AAL) and acetic acid (AA) on the fuel cell performance using $Pt_3(SnO_2)/C$ electrocatalyst.

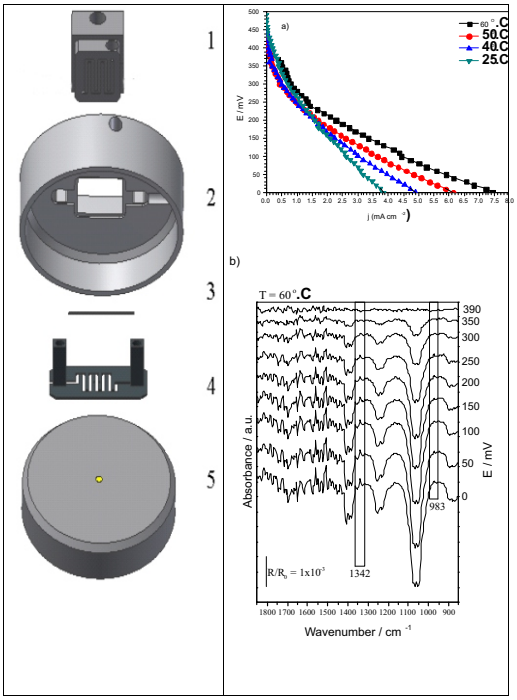


Figure 4. Single Cell/ATR-FTIR setup (1) cathode plate, (2) assembler, (3) MEA, (4) anode plate and (5) ATR plate. Polarization curves (a) and (b) *In Situ* ATR-FTIR spectra (60°C) taken at OCV to 0 V in 1 cm^2 DEFC using 20 wt.% Pt/C Basf electrocatalyst in anode and cathode (1 mg_{Pt} cm^{-2}). Nafion® 117 was used as the membrane. Ethanol 2 mol L^{-1} with 0.8 mL s^{-1} flux.

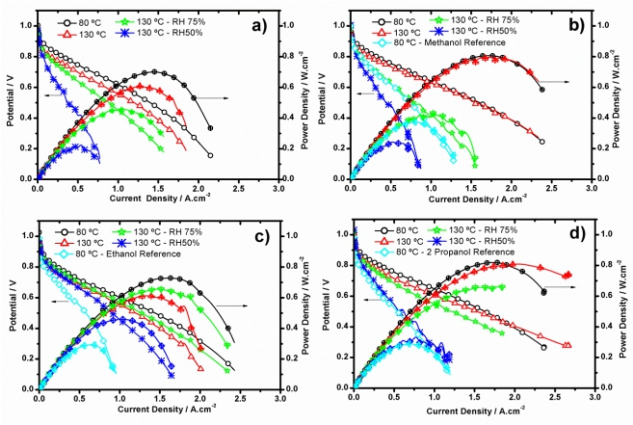


Figure 5. H_2/O_2 polarizations curves at 80ºC and 130ºC with RH=100%, and at 130ºC with RH 75% and 50% for: a) Nafion 115, b) Nafion-SiO_2 produced in methanol, c) Nafion-SiO_2 produced in ethanol, and d) Nafion-SiO_2 produced in 2-propanol. The polarization curves at 80°C of Nafion reference samples for the corresponding alcohol solvent are shown. The open symbols represent the polarization curves and the filled symbols correspond to the power density curves.

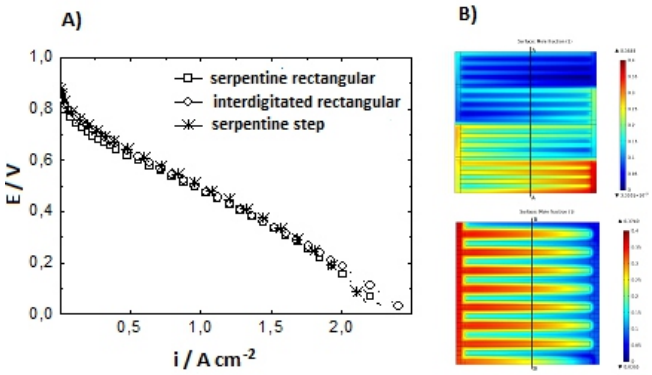


Figure 6. A) Experimental H_2/O_2 polarization curves for PEMFC using different flow channel patterns (interdigitated and serpentine) and channel designs (rectangular and step). B) Mole fraction of oxygen (O_2) in the catalyst layer midplane for serpentine (above) and interdigitated (below) patterns.

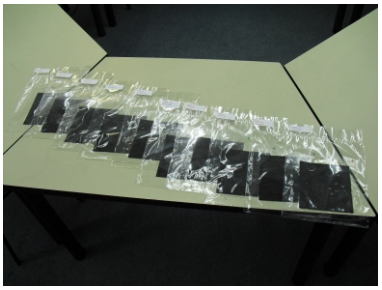


Figure 7. Membrane-Electrode-Assembly (MEA) with 250 cm^2 electrode area fabricated by sieve printing.

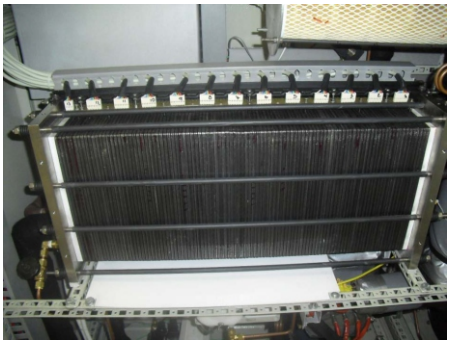


Figure 8. PEM fuel cell stack of 5 kW electric power, using technology developed at IPEN.

Solid Oxide Fuel Cell (SOFC)

Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs) (i.e., SOFCs operated in reverse) 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. SOFCs are the most efficient electrochemical device 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) carbon neutral energy generation with rather low noise and harmful emissions.

Basically, SOFCs consist of two porous electrodes separated by a dense electrolyte. Such a ceramic fuel 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 SOFC 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 800-1000ºC down to 500-800ºC range, in order to minimize degradation of components, improve design flexibility, and lower material and manufacturing costs, is also a key issue. Nevertheless, reducing the operating temperatures requires the development of new cathode and electrolytes for high-performance SOFCs.

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. The main SOFC components, including ceramic-metal composite anodes, lanthanum manganite cathodes, interconnect, and zirconia-based solid electrolytes, have been synthesized by different techniques. In addition, alternative materials have been studied, such as ceria-based electrolytes, ceramic anodes, and cobalt-ferrite cathodes. The synthesized materials are tailored according to the requirements of different processing techniques such as tape casting, spin coating, and spray deposition, in order to fabricate SOFCs.

Yttria-stabilized zirconia (YSZ) and nickel oxide (NiO) ceramic composite is the stander anode for solid oxide fuel cell. One of the possible alternative anode is the gadolinia-doped ceria (GDC) and nickel oxide cermet. Both materials have been synthesized by a coprecipitation technique. By using such technique it is possible to tailor the microstructure of the ceramic composite precursor of the cermet anode aiming at improved properties. In the Figure 9 it is shown the polished and thermally etched surfaces of sintered ceramic composites YSZ-NiO (Fig. 9A) and GDC-NiO composite (Fig. 9B).

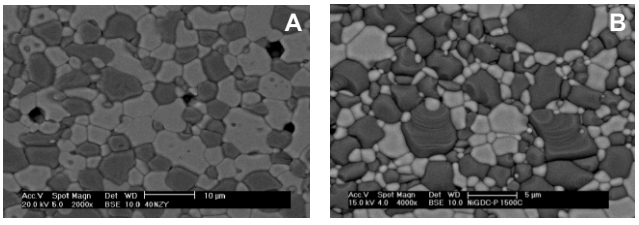


Figure 9. Scanning Electron Microscopy micrographs of polished and thermally etched surface of sintered ceramic composites of YSZ-NiO (A) and GDC-NiO (B).

Alternative cathode materials have been investigated for intermediate temperature SOFCs operating in the 500-800ºC range. The perovskite oxides $Ba_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ (BSCF) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ (LSCF) have been prepared by the citrate-EDTA and the polymeric precursor technique, respectively. The electrical conductivity was higher for ceramics sintered at 1000ºC for 1 h originating from particulates obtained at pH=6 synthesis (Fig. 10).

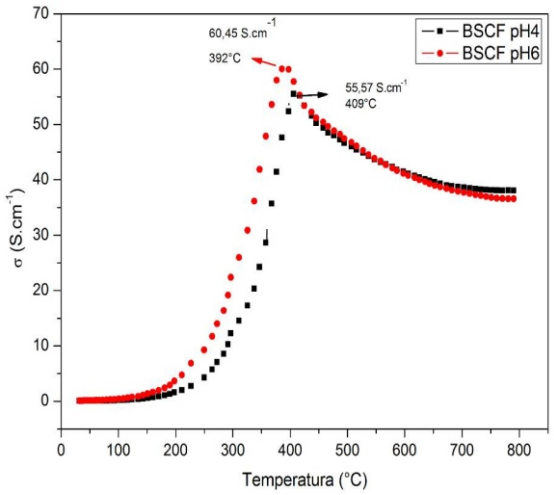


Figure 10. Temperature dependence of the electrical conductivity of the $Ba_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ ceramics synthesized at pH=4 and 6.

Ionic conductors that have high conductivity at lower operating temperatures are currently investigated. Previous studies have shown that the composition $La_{10}Si_6O_{27}$ apatite type exhibits high oxygen ionic conductivity, which is comparably higher than that of YSZ at 500°C. Thus, such apatite is a potential candidate for intermediate temperature SOFC electrolyte. Highly sinterable and weakly agglomerated powders have been obtained by a modified coprecipitation synthesis. Single phase and dense (> 90% of the theoretical density) samples were fabricated at relatively low sintering temperatures (≤ 1400°C), as shown in Fig. 11.

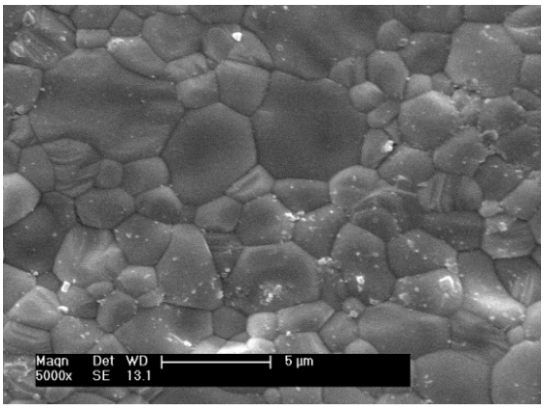


Figure 11. Scanning electron micrographs of the $La_{10}Si_6O_{27}$ sample sintered at 1400°C.

A great deal of attention has been given to the development of direct ethanol SOFCs. Bioethanol is an efficient renewable fuel readily available in Brazil and with enormous potential to carbon neutral energy generation in SOFCs. Important advances were achieved by using both ceramic anodes based on chromite-manganites ($La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$, LSCM) doped with a catalytic metal such as Ru. Upon heat treatment in reducing conditions Ru nanoparticles were observed to be formed on the surface of the LSCM ceramic particles (Fig. 12A). These materials were used as the outer layer of SOFC anode for direct (no water added) use of ethanol (Fig. 12B). Such fuel cells exhibited enhanced catalytic and electrochemical performance that resulted in enhanced performance in single SOFCs operating directly in ethanol (Fig. 12C).

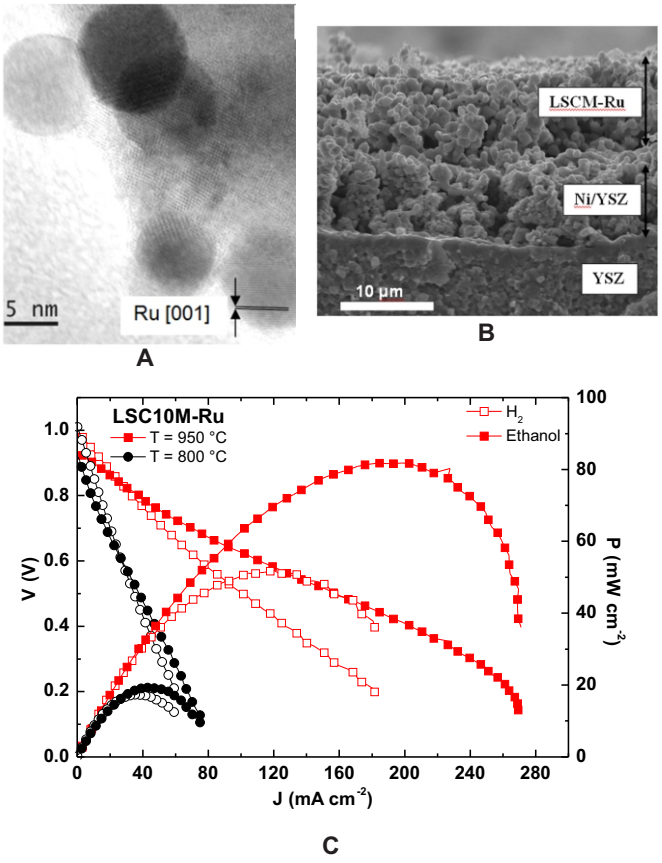
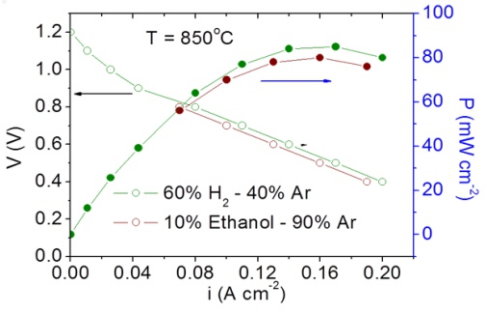
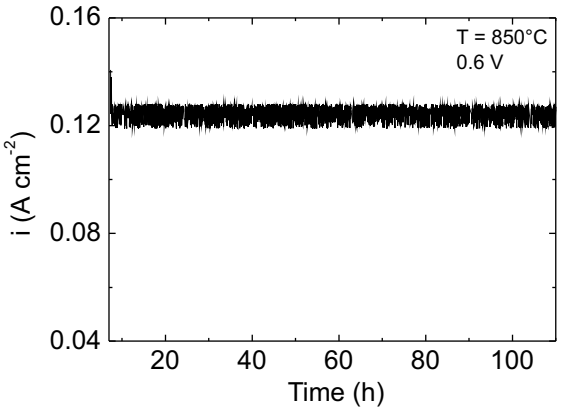


Figure 12. (A) Transmission electron microscopy of Ru-doped $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ showing Ru nanoparticles formed after heat treatment in reducing conditions. (B) cross section of single cell using Ru-doped $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ anode layer. (C) polarization curves of single cells using the ceramic anode operating in both hydrogen and ethanol.

A second approach for direct ethanol SOFC has investigated the deposition of an active layer over the standard Ni-base cermet anode (Fig. 13A). The main role of such catalytic layer is to promote the steam reforming of ethanol, generating hydrogen as the main decomposition product and promoting the gradual 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 gradual reforming requires no addition of water and the performance of fuel cells running in both hydrogen and ethanol are comparable Fig. 13B) as long an active catalyst is provided. More importantly, fuel cells running on internal gradual reforming of ethanol were found to be stable over long periods of time (> 100 hours, Fig. 13C). After stability tests fuel cells were analyzed by electron microscopy and no evidences of carbon formation was detected in the anodes.





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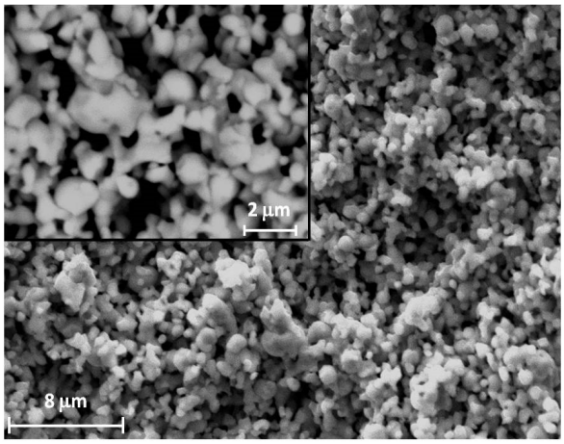

C

Figure 13. (A) Polarization curves of the SOFC operating in gradual internal reforming on both H2 and ethanol at 850°C. (B) stability tests under 0.6V polarization in dry ethanol at 850°C. (C) Scanning electron microscopy of the anode after 100 hours of operation under dry ethanol.

Hydrogen production

The widespread agricultural activities in Brazil have motivated the development of processes using biomass from agriculture and landfills as hydrogen sources. Such developments include steam reforming of bioethanol and gasification of biomass originated from agricultural residues such as sugarcane bagasse, coffee straw, and cashew nut shells. The main goal is the mitigation of environmental impact resulting from both agricultural activities and energy production.

Catalysts development

Obtaining suitable catalysts for processes such as ethanol steam reforming is an essential step for hydrogen production for fuel cells. Highly active catalysts for ethanol conversion using active metals such as nickel, cobalt, and copper supported on ceramic microspheres of zirconia, alumina, ceria or lantania (Fig.14) have been prepared and showed good hydrogen yield.

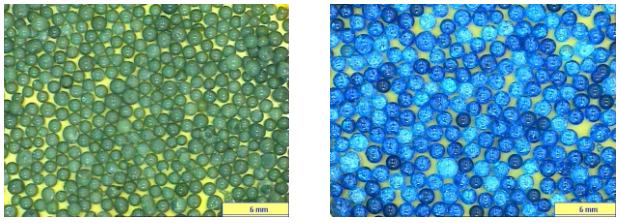

Figure 14. Co/Ni catalysts supported in ceramic microspheres.

Fuel cell systems

A 5 kW PEM fuel cell system was assembled using the technology developed at IPEN in collaboration with Electrocell (Fig. 15).

Figure 15. 5 kW PEMFC module constructed in collaboration with Electrocell using technology developed at IPEN.

Laboratory of PEMFC life cycle was expanded with the installation of new automated fuel cell test stations (Fig. 16).

Figure 16. New test stations for PEMFC life cycle evaluation.

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