Renewable Energies

Fuel Cell and Hydrogen laboratory

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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 different ways of obtaining hydrogen and the different types of fuel cells application 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 technology in transport and distributed energy. Aware of the importance of this technology for the energetic future of Brazil, IPEN started 10 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 and Technology (MCT), IPEN decided to organize an institutional program on the subject, conducted at the Fuel Cell and Hydrogen Center.

The objectives of the IPEN program are based on the MCT 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 program 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 observed by the patents, published international papers, the post-graduated 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 2008-2010 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-MCT- $ProH_2$, FAPESP, CNPq and CAPES). Today, IPEN is considered as an important partner within the R&D networks established by the MCT-$ProH_2$ Program. Partnership 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 Proton Exchange Membrane Fuel Cell (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), ethanol (DEFC). 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 composites 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; development of innovative radiation grafting techniques, combining direct and indirect processes; development of styrene grafted PP, PVDF, ETFE, FEP, PFA and PTFE films; development of sulfonated films of styrene grafted PVDF, ETFE, FEP, PFA and PTFE; polypropylene membrane base performed useful life of 300 hours, operating at 40°C; ETFE membrane based on fluorinated polymer performed useful life of 53 hours, operating at 80°C; and education.

Highlights 2008-2010:

- Development of new method for the preparation of skeletal-type PtSn/C electrocatalyst by chemical dealloying.
- Development of new electrocatalysts formulations like PtSn/CeO_2-C (Fig. 1) and Pt/Sb_2O_5.SnO_2-C for ethanol direct electron-oxidation.
- Scaling up of PEM-electrocatalysts production up to 50 g, including the formulations Pt/C and PtRu/C, using the IPEN alcohol-reduction process (Patent BR200304121-A), in cooperation with Evonik Brasil Ltda.
- Development of Nafion-Titanate Nanotube, Nafion-TiO_2 and Nafion-SiO_2 Composite Membranes for PEMFC and DEFC, operating at 130°C (Fig. 2).
- Scaling up of Membrane-Electrode-Assembly (MEA) by sieve printing method, up to 250 cm^2 of electrode area. Delivery of 100 MEAs to Electrocell company for demonstration in a 5 kW PEMFC Stack (Fig. 3).
- Modeling and Simulation of PEMFC and DMFC components using CFD techniques.
- Development of a PEMFC stack of 1 kW electric power using technology developed at IPEN (Fig. 4).
- Reliability studies of PEMFC components.

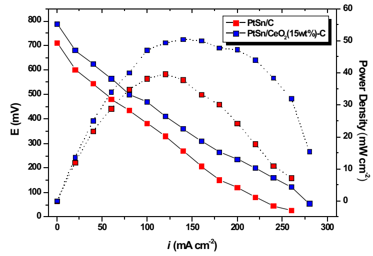


Figure 1. Electrical performances of a 5 cm^2 DEFC (Direct Ethanol Fuel Cell) at 100°C using PtSn/C and PtSn/CeO_2-C electrocatalysts anodes (1 mg Pt cm^{-2} catalyst loading) and Pt/C E-TEK cathode (1 mg Pt cm^{-2} catalyst loading, 20wt% catalyst on carbon), Nafion 117 membrane, ethanol flow rate of 2.0 mol L^{-1} and 2 bar oxygen pressure

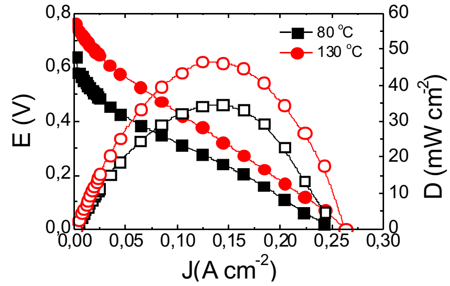


Figure 2. Polarization curve of a DEFC, using composite Nafion-TiO_2 membranes and PtSn/C electrocatalysts produced at IPEN, operating at 80°C and 130°C

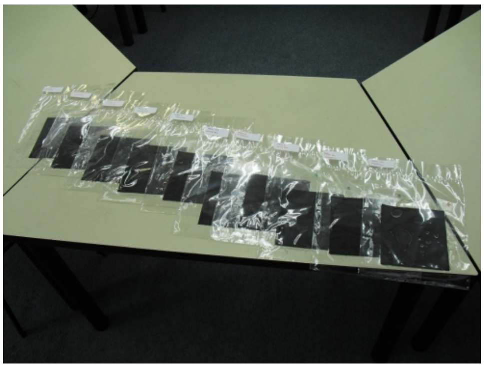


Figure 3. Membrane-Electrode-Assembly (MEA) with 250 cm^2 electrode area fabricated by sieve printing

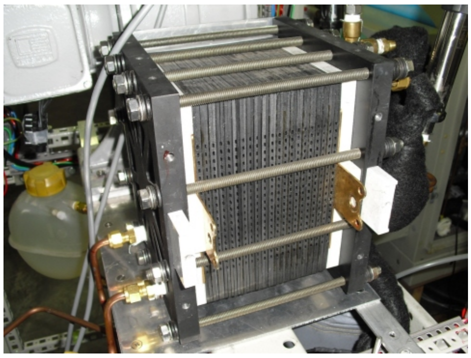


Figure 4. PEM fuel cell stack of 1 kW electric power, using technology developed at IPEN

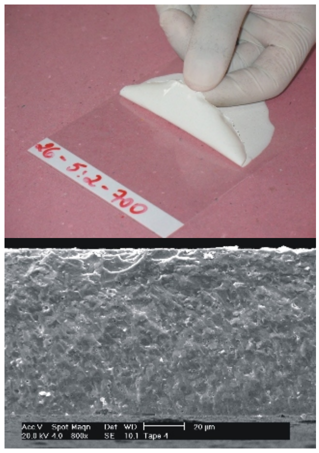
Solid Oxide Fuel Cell (SOFC)

Solid Oxide Fuel Cells (SOFCs) are the most efficient electrochemical device to convert the chemical energy of fuels into electricity. Such fuel cells are regarded as a promising power source 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) environmentally friendly energy generation with rather low noise and harmful emissions.

Among the various possible SOFC designs, the planar type is claimed to have the advantages of high power density per unit volume and low production costs. Two main configurations of planar SOFCs are under development worldwide: electrolyte supported and anode supported. Each of them has particular characteristics, but the anode supported cell is regarded as the most promising technology due to its low operating temperature. Essentially, 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 different criteria. Physical and chemical compatibility and stability at high temperature and oxidizing/reducing environments, and good electrochemical properties are key issues for the materials used for this technology. Important tasks in SOFC research are the development of fuel flex anodes and the reduction of the operating temperature from 800-1000ºC down to 500-800ºC range, in order to reduce degradation of cell components, improve flexibility in cell design, and lower the material and manufacturing costs by the use of cheaper and readily available materials.

The research activities at IPEN are primarily concerned with the development of the SOFC materials, aiming at the use of simple and low-cost methods for high-performance planar SOFC components. The activities of the SOFC research group at IPEN have been focused on the synthesis, processing, and characterization of the SOFC components, and single cell testing. Several different synthesis techniques have been used for the preparation of SOFC components. The main constituents of a SOFC have been investigated at IPEN, including ceramic-metal composites for anodes, doped lanthanum manganites for cathodes, zirconia based solid electrolytes and doped chromite interconnects. In addition, alternative materials for all components 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 ceramic layers for SOFC.

Ceramic electrolyte powders, such as yttria-stabilized zirconia (YSZ) and samaria or gadolinia-doped ceria, have been synthesized by chemical and hydrothermal techniques for SOFC component manufacturing. Such synthesis techniques allow the control of microstructural properties, such as grain shape and grain size distribution, that are important to achieve the necessary requirements for the processing of ceramic powders into SOFCs components. Tape casting is widely used for electrolyte and anode forming (Fig. 5) into layers for SOFC, and ceramic powders synthesized at IPEN were tailored for such technique. Figure shows a YSZ flexible green tape (Fig. 5a), and a cross section of the sintered (1500 °C) YSZ tape (Fig. 5b), evidencing a homogeneous and dense layer with thickness of ~80µm.

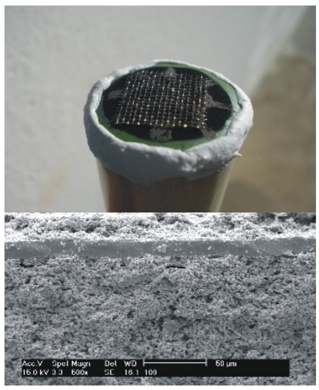


(a)

(b)

Figure 5. Yttria-stabilized zirconia tape for application as SOFC electrolyte: (a) after tape casting processing and (b) scanning electron micrograph of the cross section of the sintered YSZ tape

A spin coating method for the production of thin (10 µm) and dense yttria-stabilized zirconia (YSZ) was developed for the fabrication of anode supported SOFCs, as shown in Fig. 6a. Specially designed YSZ suspensions were developed in order to obtain 10 µm layers with a minimal number of deposition steps. The fabricated electrolyte layers are homogeneous and dense, with thickness within the desired range, as shown in the Figure 6b.



(a)

(b)

Figure 6. (a) Electrolyte supported SOFC (20 mm diameter, with Pt grid attached to the surface) sealed on the top of an alumina tube for single cell testing. (b) Scanning electron image of the fractured cross section of a single SOFC with spin coated dense YSZ electrolyte layer deposited by spin coating

In both electrolyte and anode supported SOFCs, controlling the morphology of the anodes is key issue for high performance devices. In order to fabricate an optimized microstructure with controlled grain size for both phases and porous, several techniques have been used for the production of the anode. The Figure 7 shows scanning electron micrograph of YSZ / NiO anode produced by combustion synthesis and sintered at 1300°C with pore former (rice starch) addition. The development of fuel flex anodes is a key point to advance the SOFC technology. In that context, direct ethanol SOFCs have been investigated. The main activities in this area are the development of active anodes for ethanol conversion, without coke formation, and the optimization of operating conditions for stable and high performance ethanol fueled SOFC. Preliminary tests of ethanol fueled SOFC evidenced the higher activity of ceria-based cermets than YSZ-based anodes at temperatures < 800°C.

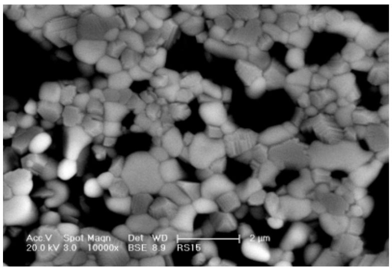
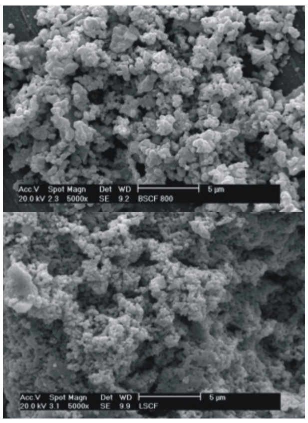


Figure 7. Scanning electron micrograph of porous ceramic yttria-stabilized zirconia / NiO composites for SOFC anode

New cathode materials have been investigated for intermediate temperature SOFCs operating in the 500-800ºC range. The perovskite oxides $Ba_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ have been prepared by the citrate-EDTA and the polymeric precursor technique, respectively. The micrographs in Fig. 8 show the morphology of single phase powders heat treated at 800°C.

(a)



(b)

Figure 8. Cathode materials for intermediate temperature SOFCs prepared by chemical synthesis methods. (a) $Ba_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, and (b) $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$

Hydrogen production

The widespread agricultural activities in Brazil led Hydrogen Production group to develop processes using biomass from agriculture and landfills as hydrogen source. Such efforts include bioethanol steam reforming, ammonia cracking of waste from chicken and eggs farming, and gasification of biomass originated from agricultural residues such as sugarcane bagasse, coffee straw, and cashew nut shells, always seeking out ways to mitigate environmental burden of energy production.

Catalysts development

Obtaining suitable catalysts for processes like ethanol steam reforming is an essential knowledge for hydrogen production for PEM fuel cells. Using active metals such as nickel, cobalt and copper supported onto either zirconia or alumina microspheres (Fig.9), the Hydrogen group prepares highly active catalysts for ethanol conversion showing good hydrogen yield.

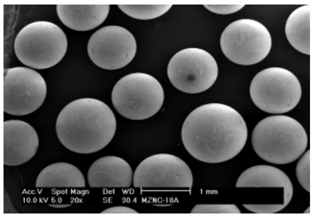


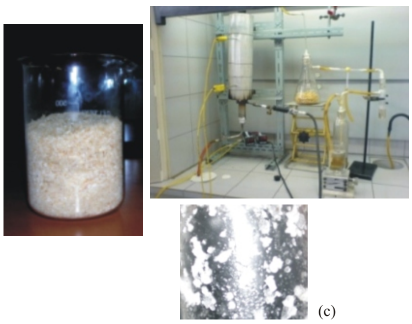
Figure 9. Cu/Ni catalysts supported on zirconia microspheres

Development of selective membranes for the purification of hydrogen

During ethanol reforming, secondary products such as CH_4, CO, CO_2 and oxygenated compounds like acetaldehyde, ethyl acetate, acetic acid are produced along with hydrogen. The purification of hydrogen can be achieved by using selective membranes made from ceramic or porous metallic substrates coated with palladium or silver-palladium alloys.

Development of gasification processes

Coffee straw, sugarcane bagasse and cashew nut shells are currently studied as viable sources for hydrogen production processes that include CO_2 capture techniques. (Fig.10)



(a) (b) (c)

Figure 10. (a) sugarcane bagasse; (b) gasificationsystem; (c) crystals obtained by CO_2 capture during gasification process

Project and construction of thermoreactors
Hydrogen Laboratory activities include prototyping and upscaling of laboratory thermoreactors using primary fuels and membranes for the production of high purity hydrogen (Fig. 11).

Figure 11. Ethanol reforming reactor

Fuel Cell systems

Activities of the Systems Group were substantially increased after personnel expansion by the enrollment of three additional permanent collaborators. A second unit for hydrogen and oxygen generator has been acquired to accommodate for ample production of such gases. Total production of ~30 m^3/h (20 m^3/h H_2 and 10 m^3/h O_2) should be enough to feed PEM fuel cell systems in excess of 20 kW (Fig.12).

Figure 12. Hydrogen and oxygen generators on their installation site

A 1kW PEM fuel cell system was assembled using the technology developed at IPEN (Fig.13).

Figure 13. 1kW PEMFC system made with IPEN technology

PEMFC life cycle testing facilities were expanded by the installation of two brand new test benches (Fig.14).

Figure 14. New test benches improved their previous versions by the inclusion of mass flow meters and a PLC controller

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Honor Mention and Awards

Best poster in the I Simposium Iberico of Hydrogen, Fuel Cells and Advanced Batteries (HYCELTEC 2008), held in Bilbao, Spain, from the 1st to the 4th of July, 2008. The paper "Graft polymerization of sulfonated styrene from carbon black surface and its use as electrocatalysts support for PEMFC and DMFC applications" was developed as a collaboration between the Instituto de Pesquisas Tecnológicas (IPT) and IPEN, and is co-authored by Marcelo Carmo, João Guilherme Rocha Poco, and Marcelo Linardi.