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 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 established 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 few years ago the development of fuel cells for stationary and distributed energy applications. Previous studies were carried out at the Materials Research Center due to IPEN expertise on nuclear materials development. Based both on the good initial results and on the Brazilian Fuel Cell Program proposition by the Ministry of Science and Technology (MCT), IPEN decided to organize an institutional program on the subject. The objectives and goals of the IPEN program are based on the MCT national program.

In July 2003 the Fuel Cell Program was formally established at IPEN in order to contribute to the national development in this area. The Program was structured in a cross-cutting way involving human and infrastructure resources from IPEN Technical Departments. Three main areas were developed: PEMFC (Proton Exchange Membrane Fuel Cell); SOFC (Solid Oxide Fuel Cell); and REFORM (H2 production from ethanol reforming).

More than 50 professionals were engaged at IPEN Program, although some in part time, including PhDs, MSc, and post-graduated students. Important scientific and technological results have been obtained and the main achievements can be observed by the submitted patents, the published international papers, the post-graduated courses given, and the graduate student's thesis advisory.

In October 2003, we organized the first IPEN Fuel Cell Meeting with participation of more than 150 attendees from IPEN and from all over the country. It was considered a very important event in the national scenario for the fuel cell development. In 2005 and 2007 the second and third IPEN Fuel Cell Meeting were realized with the same success as the first. In 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 1 kW of power. In the period of 2005-2007 news laboratories of SOFC, Hydrogen and Fuel Cell Systems have been implemented.

Due to the positive results obtained by the IPEN Fuel Cell Program, in 2007 a new center called Fuel Cell and Hydrogen Center was created. The financial resources were based on scientific funds from federal and state government (FINEP-MCT- ProH$_2$, FAPESP, CNPq and CAPES). Due to the good developments achieved, 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) led to advances and autonomous technological domain in PEMFC area.

Proton Exchange Membrane Fuel Cell (PEMFC)

The Proton Exchange Membrane Fuel Cell (PEMFC) Group aims the basic and technological developments of low power fuel cell for the direct oxidation of hydrogen, hydrogen/CO mixtures and alcohols (methanol, ethanol and ethylene glycol) concerning stationary applications, that means, distributed electric power generation. These includes: development of new methods of electrocatalyst production and new electrocatalyst formulations; development and production of new membranes (electrolytes) alternative to Nafion for special applications (Nafion-like) and High-Temperature operation (130^{o}C, composites); Membrane-Electrode-Assembly (MEA) production and optimization; unit cells tests in laboratory and pilot scales; development of low power fuel cell stacks; and finally education in related fields. Highlights 2005-2007:

- Development of new methods of electrocatalysts (carbon-supported Pt-based nanoparticles) preparation: radiolysis process (gamma and electron beam irradiation) and hydrothermal carbonization.
- Development of new electrocatalyst formulation PtSnNi/C for ethanol electron-oxidation, among others.
- Development of modified carbon supports with polymeric chains containing sulfonic groups that improves the three boundary phase of the fuel cell electrodes.
- Development of Nafion-Titanate Nanotube and Nafion-TiO_2 Composite Membranes for PEMFC Operating at High Temperatures.
- Development of Membranes Nafion-like.
- Development of Membrane-Electrode-Assembly (MEA) by sieve printing method and preparation of MEA with 144 cm^2 of electrode area (FIG. 1).
- Modelling and Simulation of Fuel Cell components (bipolar plates) using CFD techniques.
- Development of a fuel cell stack of 1 kW.

Figure 1. Sieve-printing apparatus for Membrane-Electrode-Assembly (MEA) production

Solid Oxide Fuel Cell (SOFC)

Solid oxide fuel cells are considered as promising potential electrical energy sources owing to their efficiency and release of environment friendly gaseous end products. Essentially, SOFC 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. Thermal and chemical compatibility, good electrochemical and mechanical properties, and thermal stability are key issues regarding this technology. One of the most important tasks in SOFC research is the reduction of operating temperature from 800-1000ºC down to 500-800ºC, to reduce degradation of cell components, improve flexibility in cell design, and lower the material and manufacturing cost by the use of cheap and readily available materials. Among the various designs of fuel cells, the planar type is claimed to have the advantages of high power density per unit volume and low production costs. The research activities at IPEN are primarily concerned with the development of the SOFC materials, aiming to the use of simple and low-cost methods for high-performance SOFC components. The activities of the SOFC research group at IPEN have been focused on the synthesis, processing, and characterization of the SOFC components. Along with the traditional solid oxide reaction, several different chemical techniques have been used for the synthesis of ceramic powders. The methods chosen for processing cells are largely dependent on the materials configurations as well as on macroscopic properties desired and their microstructural appearance. In order to improve the fracture toughness of cubic stabilized zirconia electrolyte, without compromising its electrical properties, composites containing up to 40 wt % of alumina, in a 9 mol % yttria-stabilized zirconia (9Y-CSZ) powders were synthesized by coprecipitation route and ceramic samples were prepared by pressing and sintering. SEM micrograph of sintered ceramic is shown in (FIG. 2). Studies about conditioning of YSZ powders have been realized to investigate effect of temperature and time of calcinations step and high energy ball milling on the physical characteristics of YSZ powders. The perovskites oxides $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_3$ and $Nd_{x-1}Sr_xMnO_3$ (x= 0,10, 0,30, 0,50)); (FIG. 3), have been prepared by the polymeric precursor technique and traditional solid oxide reaction, respectively, as a cathode materials for SOFC operating at intermediate temperatures (500-800ºC). The Strontium-substituted lanthanum manganite/yttria-

-stabilized zirconia (LSM/YSZ) composite samples were prepared for electrochemical performance of SOFC cathode to increase the three-phase boundary (TBP) sites.

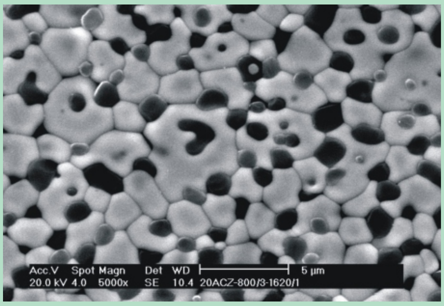

Figure 2. SEM micrograph of sintered zirconia alumina electrolyte

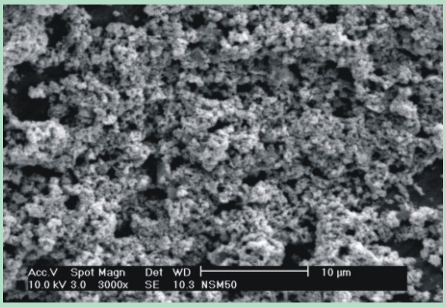

Figure 3. Scanning electron micrograph of the $Nd_{50}Sr_{50}MnO_3$ powders

Nickel oxide-yttria stabilized zirconia (8YSZ-NiO) anode materials were synthesized by combustion process involving metal nitrate-urea decomposition and by coprecipitation. The microstructural changes of the 8YSZ-NiO to occur in this composite when submitted to the reduction in tubular oven 800°C for periods between 5 minutes and 3 hours in controlled atmosphere with a mixture of 4% of hydrogen and 96% argon in atmospheric pressure.The chemical route has been also applied to the synthesis and characterization of zirconium titanate composites. Mechanical alloying processing has been investigated as a new SOFC anode preparation route. This method employs metallic Ni and YSZ co-milled powders leading to refined structures of dispersed constituent, which can improve the anode properties. Compacted powder sintering temperatures are reduced. The method can be designed with fewer processing steps. Thin films (green state of 500 microns) by tape casting process were attained as result of the rheological behavior studies of lanthanum chromite powders synthesized in ours laboratories (FIG. 4). Main application of this material is for interconnect devices. A laboratory setup was designed and put into operation for the development of SOFC. The whole project consisted of the preparation of the component materials: anode, cathode and electrolyte, and the buildup of a hydrogen leaking-free sample chamber with platinum leads and current collectors for measuring the electrochemical properties of single SOFC. Several anode-supported single SOFCs of the type (ZrO_2:Y_2O_3 + NiO) thick anode/(ZrO_2:Y_2O_3) thin electrolyte/($La_{0.65}Sr_{0.35}MnO_3$ + ZrO_2:Y_2O_3) thin cathode have been prepared and tested at 700 and 800°C after in situ H_2 anode reduction. The main results show that the slurry-coating method resulted in single-cells with good reproducibility and reasonable performance, suggesting that this method can be considered for fabrication of SOFCs. The wet powder spraying technique was also used for fabrication tests in LSM/YSZ interfaces.

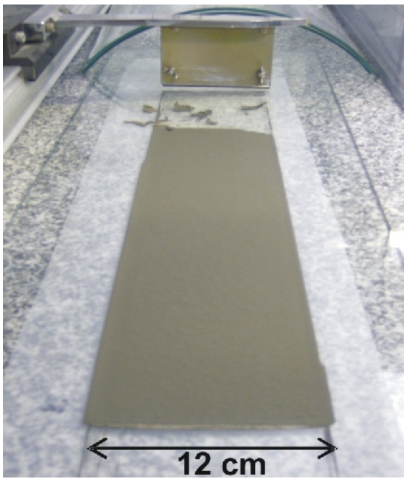

Figure 4. Tape of Lanthanum Chromite attained by tape casting process for SOFC interconector application

Hydrogen production

The biohydrogen can be withdrawn from various types of biomass as the organic municipal waste, sewage, animal excrement, tailings from forestry and agriculture. The great motivation for the development of hydrogen obtaining procedures, for use in fuel cells is to accelerate the learning of this technology to have a strong environmental character. In Brazil, particularly, there is a necessity for a national technology development based on bioethanol, in our particular market, which has different characteristics from other countries. Bioethanol is a liquid fuel, produced from renewable sources, considered less toxic than methanol and is handled, stored and transported easily. Brazil has the infrastructure for production and distribution of bioethanol throughout the national territory. The Hydrogen Group has been developed catalysts for ethanol steam reforming based on zirconia microspheres containing transition metals prepared by the sol-gel method. The catalysts exhibited good performances for hydrogen production. Researches on membrane reformers to obtain pure hydrogen from the mixture generated in the reforming process have been investigated as well the development of reactors for preferential oxidation and shift reaction. In 2006 was started up the research on the use of metal or ceramic membranes covered with palladium (FIG. 5), which will be integrated with a hydrogen reformer. In this process the reforming reaction and purification occur in a single stage (membrane reactor). The metallic membranes, palladium or their alloys especially, presenting itself as the most promising for the selective separation of hydrogen from reforming gases. The Hydrogen Group has conducted searches for obtaining these membranes with different substrates and recoveries with palladium.

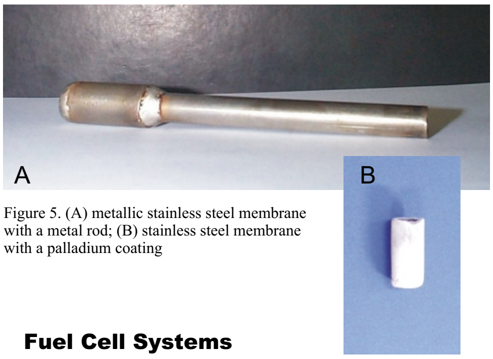

Figure 5. (A) metallic stainless steel membrane with a metal rod; (B) stainless steel membrane with a palladium coating

Fuel Cell Systems

The main objective of the group is to perform research, development, tests, certification of fuel cells and energy systems integration based on Fuel Cell technology. The Fuel Cell Systems Laboratory has been implemented and the following equipments and resources are installed:

- 50 kWe PEMFC Module with 3 stacks. (FIG. 6)

- PEMFC Life Cycle Test Stand. (FIG. 7)

- Electrolizer for hydrogen and oxygen generation with H_2 production capacity of 10.000 lt/h and O_2 production capacity of 5.000 lt/h both at 4 bar operation pressure.

- Gas piping line for hydrogen, oxygen and nitrogen. This piping line feeds the 50 kWe PEM Fuel Cell Module and the PEM Fuel Cell Life Cycle Test Stand.

Figure 6. 50 kWe PEMFC module

Figure 7. PEMFC life cycle test stand

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Honor Mention and Awards

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