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Role of Nuclear Based Techniques in Development and Characterization of Materials for Hydrogen Storage and Fuel Cells

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ROLE OF NUCLEAR BASED TECHNIQUES IN DEVELOPMENT AND CHARACTERIZATION OF MATERIALS FOR HYDROGEN STORAGE AND FUEL CELLS

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For further information on this publication, please contact:

Physics Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
email: Official.Mail@iaea.org

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FOREWORD

Hydrogen and fuel cells can greatly contribute to a more sustainable less carbon-dependent global energy system. The major components in a hydrogen economy are expected to include production, storage, transportation and conversion of hydrogen, e.g. in fuel cells. All these components present considerable technological challenges, in particular as they relate to materials development. The research efforts required to solve these challenges will need new materials and solutions, and not simply, incremental improvements of current technologies.

Nuclear methods are poised to play an important role in the improvement and development of materials by providing a major tool with which to characterize their properties and performance. A consultants meeting on application of 'Role of Nuclear Techniques in Development of Materials for Hydrogen Storage and Fuel Cells' was held by the International Atomic Energy Agency (IAEA) in Vienna, Austria, on 14-16 May 2008. The usefulness and importance of nuclear techniques to support materials oriented R&D for hydrogen storage in solid state materials and its conversion in fuel cells was recognised.

Two technical meetings on 'Role of Nuclear-based Techniques in Development of Materials for Hydrogen Storage and Fuel Cells were organized by the IAEA. The first was hosted by the International Energy Agency (IEA) in Paris, France, on 16–20 March 2009 and the second by University Trois-Rivières Quebec (UTRQ), Canada, from 23 to 26 August 2010. The meetings participants discussed the broad spectrum of nuclear techniques that can be effectively used for characterization of materials for hydrogen storage and conversion technologies.

This publication summarizes the outputs of the above meetings and selected contributions of the participants. The manuscript could be used by researchers planning to utilize nuclear techniques for the development of hydrogen storage and fuel cell materials. It also aims to disseminate knowledge and information to material scientists, physicists and chemists working towards characterizing and developing new materials.

The IAEA wishes to thank the participants for their contributions. An additional acknowledgment for the experts who helped to review this manuscript, specifically, S. Barroso from the Atomic Energy Research Institute (AEKI), Hungary, M. Steen from Joint Research Centre of European Commission, The Netherlands, J. Huot from Université du Québec à Trois-Rivières, Canada and S. Skinner from Imperial College London, United Kingdom. The IAEA officers responsible for this publication were A. Zeman and P. Salame of the Division of Physical and Chemical Sciences.

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CONTENTS

PRELIMINARY RESULTS OF THE DEGRADATION OF PLATINUM BASED CATALYST IN PEM FUEL CELLS USING PIXE*

M. GÜNTHER[a], M. DEBRAY[b], H. CORTI[a]
[a]Fuel Cell Group, Department of Physics of Condensed Matter
[b]Discret Nuclear Spectroscopy Group, Tandar Laboratory
Centro Atómico Constituyentes,Comisión Nacional de Energía Atómica (CNEA), Buenos Aires
Argentina
hrcorti@cnea.gov.ar

Abstract. This work reports the first results obtained on the dissolution and reprecipitation of platinum nanoparticles in the catalyst-membrane boundary of the MEA of a PEM fuel cell after 700 hours of operation under open circuit conditions. The formation of a platinum line on the membrane side near the cathode will be monitored using the PIXE technique in the ion beam facility at Tandar. The MEA used in the experiment was a commercial one (E-TEK), having a Nafion membrane and nanoparticulated Pt catalyst (loading 40%) on both, anodic and cathodic sides. Details of the sample preparation, the operating fuel cell parameters and the cutting procedure of the MEA previous to the ion beam analysis are described. The spatial resolution of the technique is discussed, along with the importance of the results for modelling the catalyst degradation in PEM fuel cells.

1. INTRODUCTION

Widespread application of hydrogen PEM fuel cells for vehicle and stationary purposes faces two major challenges: cost and lifetime. Although adding more catalyst or using thicker membranes could increase durability, increasing durability without increasing cost or losing performance seems to be the best option. For this reason, efforts are devoted to study the factors that determine a PEM fuel cell's lifetime [1].

Different processes can reduce the life of a PEMFC: dissolution and sintering of platinum or platinum alloys nanoparticles, membrane degradation and carbon-support corrosion. Besides that, the operation conditions such as impurities in the fuel or oxidant streams, pressure and temperature, load transients and start-up/shutdown cycles could also affect the fuel cell's durability.

The aggressive combination of strong acid and oxidizing conditions, high temperature and electrochemical potentials and reactive intermediate products affects the metal catalysts, proton-conducting membrane, and graphite used as catalyst support, gas diffusion layer (GDL) and bipolar plates. Thus, the durability targets of >5.000 hours for automotive fuel cells and >40.000 hours for stationary fuel cells, proposed by U.S DOE [2] are far of been reached.

The lack of standard durability protocols is a consequence of unknown mechanism of the deterioration processes occurring in the fuel cell. Most of the studies related to the chemical and physical degradation mechanisms of PEMFC membranes are performed on Nafion [3], while there have been limited studies on alternative studies on other proton conductive membranes such as those based on poly-benzimidazole (PBI) or modified PBI polymers. On

* Work performed within the framework of the IAEA Research Contract No. 15717/R0 ¨Study of the Degradation Mechanisms of the Membrane-Electrode Assembly of PEM Fuel Cells Using Ion Beam Analysis¨, part of the Co-ordinated Project: Application of Nuclear Methods in Microstructural Characterization and Performance Testing of Materials for Hydrogen Fuel Cell and Storage Technologies.

the other hand, most of the studies on the electrocatalyst stability were conducted on Pt nanoparticles supported on carbon (Vulcan) and mainly at room temperature. Little attention has been paid, so far, to the mechanism of degradation of new cathodic catalysts for the oxygen reduction reaction (ORR) [4].

High resolution Micro-PIXE (MPIXE) is now a well established technique for trace elemental analysis offering non-destructive multi-elemental 2D distribution capability and low detection limits. It allows simultaneous detection of multiple elements, with high quantitative accuracy coupled with an analytical sensitivity down to few ppm in plastics foils materials. Micro-Rutherford backscattering spectrometry (MRBS) provides information on matrix composition and thickness of the foil. The combination of MPIXE and MRBS therefore allows quantitative measurements of elemental concentration. STIM (Scanning Transmission Ion Microscopy) can be used in order to obtain an area mass density image for identifying structures, which are invisible under an optical microscope.

At the best of our knowledge, these techniques have never been used to explore the mechanisms of redistribution of metallic catalysts in contact with carbon support and proton conducting membranes. The aim of this work is to elucidate the mechanisms of degradation of Pt and Pt/Ru as anodic catalysts for PEMFC as well as Pt, and Pt alloys with Pd, Sn, Co and other metals for cathodic catalysts.

In order to accomplish this purpose the high resolution PIXE technique for direct measurements of metal concentration at different distances from the catalyst-membrane and catalysts GDL interphases will be used. The method to be used is similar to that described previously [5].

2. METHODS

2.1 The MPIXE technique

Most of the ion beam analysis (IBA) work done worldwide has been made so far with proton (1–3 MeV) and alpha particle (1–5 MeV) beams, probably due to their availability (most of the laboratories have small machines).Although protons and alpha particles have larger ranges compared to other ions with the same energy per nucleon (MeV/AMU) and are easy to focus to micron or submicrometer dimensions, heavier ions (_Z_ _e" _3_) have other characteristics_that make them very interesting for IBA applications.

The first one is related to the inner-shell vacancy production (or equivalently the X ray production) cross section. This cross section varies with the square of the projectile charge and the relevant energy parameter is the energy per nucleon of the projectile. In this approximation a beam of ^{16}O at 50 MeV is equivalent to protons of 3 MeV but with a cross section 64 times larger. Thus, measurements performed with a beam of ^{16}O at 50 MeV require 64 less time or beam current compared to one performed using 3 MeV protons.

Another advantage of the ^{16}O beam as compared to protons is the bremsstrahlung production. For protons, this contribution to the continuous background will always be present. On the other hand, in this case the membrane matrix is mainly composed of light N=Z elements (with the exception of ^{19}F), and this contribution disappears for ^{12}C and ^{16}O ions beams. For these reasons the heavy ion PIXE technique has clear advantages compared to low energy protons.

All these advantages are preserved in MPIXE where the quantities of sample material used in the analysis are much smaller and consistently the detection limits are higher. Due to the

superiority demonstrated for heavy ion PIXE, high energy heavy ion MPIXE (and other techniques of IBA, micromachining, etc.) was implemented at the Tandar accelerator, being one of few laboratories in the world which works with this technique.

In the standard PIXE the samples will be analyzed with normal size (2x2 mm^2) beams, with the surface of the membrane almost normal to the beam direction.

With our 20 MV tandem is possible to achieve high beam energies and hence larger depth within the analysed material. The possibility of achieving more energetic particles is crucial for the analysis of materials that are inhomogeneous in depth over the known thickness using the so called 'differential PIXE' which enables to get information on target stratum by performing PIXE on the same spot with different beam energies. Concerning this, a large number of test measurements at different beam energies on the various used membranes are needed in order to check the best experimental analysis conditions. In the same context, different ions (from protons to ^{16}O) might be use exploiting the possibilities offered by our tandem accelerator.

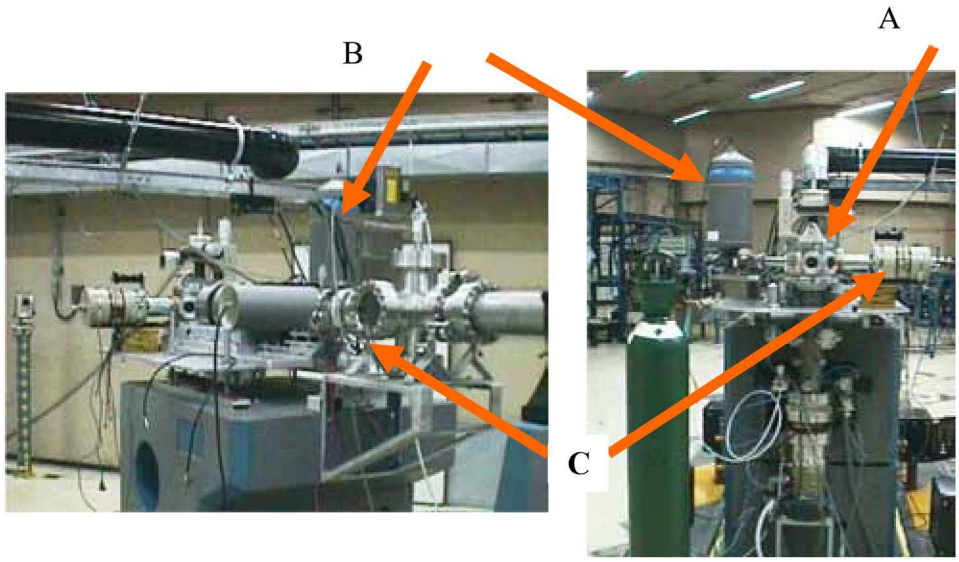

FIG. 1. View of the Tandar microbeam: irradiation chamber (A); detectors Si(Li) - 10 mm^2 (B), Si(Li) – 80 mm^2 (C).

Three techniques are currently being developed with the Tandar microbeam (Fig. 1) to address this problem. The first uses the transversal direct PIXE profile analysis of a cut membrane.

The second method is Rutherford Backscattering Spectrometry (RBS), for information on matrix composition and incident charge state. To detect back-scattered ions for RBS analysis an annular surface barrier detector is set on the beam axis. Scattering angle and counting rates can be controlled by changing the detector to sample distance.

The development of this technique comprises the optimization of the beam spot diameter, the analysis of thin-film depth profile standards at different energies to calibrate de methods and to determine optimum conditions, and finally, the quantitative analysis of the fuel cell MEAs.

2.2 Sample preparation and aging

During this period several MEAs are being prepared with membranes such as Nafion, PBI (polybenzimidazole) and ABPBI (modified polybezimidazole) obtained commercially or, as in the case of ABPBI, synthesized in our laboratory. However, the first PIXE assay is being performed with a commercial MEA (E-TEK) having a Nafion 117 membrane (thickness 170 μm) and Pt catalysts applied on the GDL and pressed on the membrane. The Pt loading on both side of the membrane was 0.5 $mg.cm^{-2}$.

A preliminary test of the MPIXE technique was performed using an E-TEK membrane having Pt on one side and Pt:Ru (atomic ratio 1:1) on the other side. This kind of catalyst is used in direct methanol fuel cell or in conventional hydrogen PEM fuel cells to improve the CO tolerance of the anode.

The MEA along with the GDL and the bipolar plates having channels to introduce the fuel (H_2) and the oxidant (air) were mounted on a monocell stack (Fig. 2). The temperature of the monocell was also controlled during the operation time using a PT100 thermoresistor.

The gases (H_2 and air) were humidified in order to control the water uptake of the membrane and their fluxes were maintained in 40 sccm for hydrogen and 100 sccm for air by using Alicat flow controllers. The complete setup for the MEAs aging process is shown in Fig. 3.

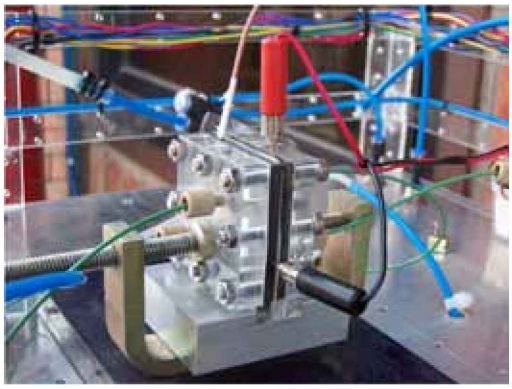

FIG. 2. View of the monocell with the gases input/outlet and the temperature sensor.

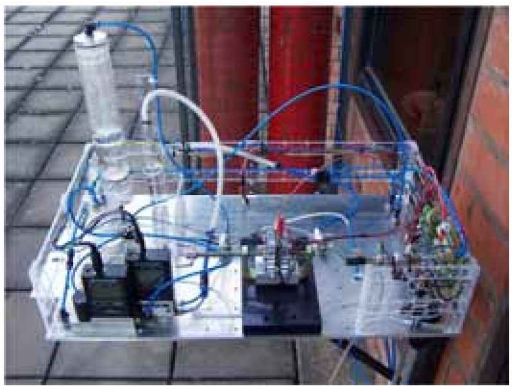

FIG. 3. View of the fuel monocell test station showing the humidifiers, flow controls and associated circuits.

The stack was maintained in open circuit condition to accelerate de dissolution and reprecipitation of Pt from the cathode side. Periodically the cell was connected to an Autolab PGSTAT112 in order to monitor the voltage vs. current curve time evolution.

Once the specified time of aging was reached, the MEA was removed and cut in pieces in order to prepare the sample for the IBA. One of the pieces was immersed in a plastic tube containing a liquid epoxy resin which is cured at moderate temperature. The imbibed membrane is cut in such a way that a transversal section of the membrane is exposed. Finally this side of the sample is polished with alumina.

3. RESULTS

3.1 Reference MEA.

The mechanism of Pt dissolution and reprecipitation within the membrane has been modelled using a thermodynamic and kinetic model that treats all the fundamental processes relevant for coarsening and mass loss in a MEA during normal operation of the fuel cell [8]. The model demonstrates the essential role of the particle size and hydrogen crossover on the degradation of the MEA.

The expected results of Pt degradation for a conventional MEA made with Nafion 117 and Pt nanoparticles supported on Vulcan XC-72 carbon are those reported by Zhang et al. [9], where a Pt band with thickness close to 1 μm or less is formed close to the cathode (several μm) after more than 1500 hours of OCV operation (that is, accelerated test) at 95 °C and 3 bar of pressure H_2/O_2.

In order to have a reference for our ageing tests and to probe that the PIXE technique with allows the characterization of Pt and bimetallic catalyst we performed an IBA with a ^{16}O beam on commercial (E-TEK) MEA with Pt and Pt:Ru (1:1) catalyst on each side of the membrane.

The results, shown in Figure 4, where the Pt side is up and the Pt:Ru side is down, indicate that the both membrane-catalyst layer are well defined. The larger thickness of the Pt:Ru layer is probably due to the tilt of the sample respect to the irradiation direction (a problem which can be avoided in future experiments) and to metal dragging during the cut of the sample

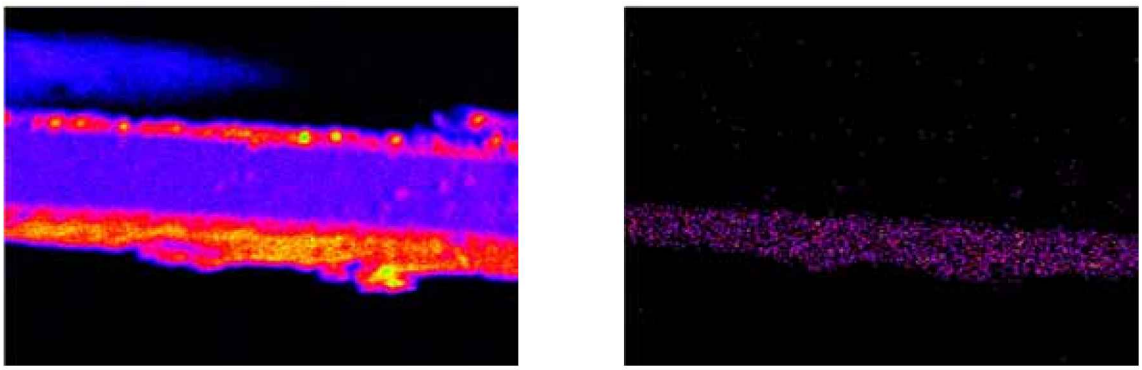

FIG. 4. 500 μm x 500 μm PIXE bidimentional images of the line Pt Lα (left) and the line Ru Kα. (right)

3.2 Aging sample

A commercial (E-TEK) MEA with Pt on both sides is being aged in the test facility described in Section 2.2. The test conditions are:

Temperature: ambient

Pressure (H_2/air) : 0.1 Mpa

Fluxes: 40 sccm for hydrogen and 100 sccm for air

In Fig. 5 it is shown the evolution of the OCV after 720 hours of aging. In average the cell voltage has decreased 10% from the initial value, which is a clear indication of MEA degradation.

In the next phase, MPIXE analysis will be completed. The results will be compared with that obtained by SEM analysis on the same MEA.

The MRBS technique will be also employed and compared to the MPIXE results. It is expected that MRBS could help us to determine the extension of the degradation in case the Pt band is well formed but its thickness is small enough to be determined by PIXE. On the other hand, if the Pt degradation does not result in the formation of a Pt-band, but small particles distributed in the membrane, MPIXE, would be the preferred technique due to its high sensitivity.

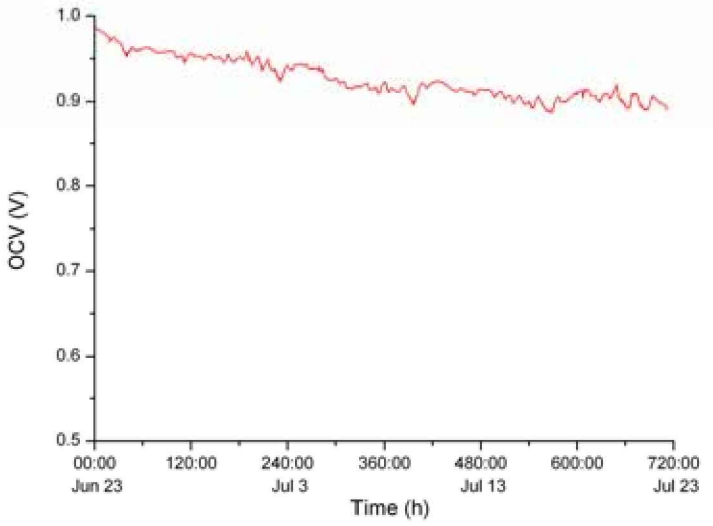

FIG. 5. Open circuit voltage of a commercial Pt/Nafion/Pt MEA as a function of time

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