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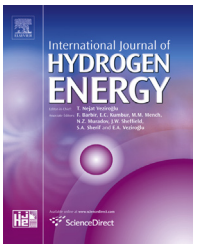

Life test of a high temperature PEM fuel cell prepared by electrospray

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ABSTRACT

A life test has been conducted to a PBI-based membrane-electrode assembly (MEA) in which the anode and cathode catalyst layers were prepared by electrospray and results were compared with a previous study in which the catalyst layer was prepared by air-brushing. During the study, the average and local current density were continually monitored and several diagnostic techniques were periodically applied, including polarization curves, cyclic voltammetries, electrochemical impedance spectroscopy and computational fluid dynamics modelling (CFD). Results show that significantly better fuel cell performance is achieved by the electrosprayed MEA, by about 40%, as compared with the MEA prepared by traditional airbrushing with the same catalyst loading. According to the experimental measurements, the higher electrochemical active surface area and more favourable mass transport are the main responsible for the improved yield. Modelling estimations agree with experimental observations and corroborate better mass transport properties of the catalyst layer when using electrospray. This can be explained by a more appropriate morphology of the layer. No evidence of positive effects on the lifetime of the fuel cell was found out. At the end of the lifetest, the local concentrations of platinum (Pt) and phosphorus (P) in the degraded MEA were analysed and a correlation between Pt loading profile and local current distribution could be established.

Introduction

One of the main problems that limit the introduction of fuel cells in the market and their massive commercialization is their high price. Therefore, institutions such as the European Commission and the Department of Energy of the U.S.A include in their guidelines the reduction of production cost as one of the key points for fuel cells to be commercialized in the near future [1,2]. In the case of PEMFC there is an item of the investment cost of great relevance: the catalyst. Doing a rough estimation, platinum may represent around 40% of the total cost of a PEM fuel cell, in both low and high temperature technologies.

The reduction of Pt loading without severely affecting fuel cell performance is possible by several means, being one of them the improvement of electrode preparation and Pt deposition [3]. There exists a number of different methods to prepare electrodes (tape-casting, spraying, painting, sputtering, filtering, etc.) for a PEM fuel cell [4–9] and all of them aim

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at achieving a proper morphology and structure in order to attain better catalyst utilization. Amongst them, one of the most promising is the electrospray deposition of a catalyst ink onto the gas diffusion layer.

The electrospray deposition technique, which was applied to the preparation of electrodes for low temperature PEM fuel cells by Baturina and Wnek [10] and Benítez et al. [11,12], consists of the generation of an aerosol phase from a suspension of particles, thanks to the action of a strong electric field. When it is employed to make PEMFC electrodes, the electric potential is applied between an ejector needle and the substrate where the catalyst layer needs to be deposited. A suspension containing the different components of the catalyst layer (ink) is transferred into an aerosol, which is formed by highly disperse charged particles that deposit on the substrate under the electrostatic interaction. Under appropriate conditions, a film with high catalytic performance and porous dendritic morphology can be obtained. Such film is characterised by a highly porous structure in the meso- and macroporosity range, with pore volumes per gram of carbon of up to 12 cm^3/g_C, against 1.8–2.5 cm^3/g_C for standard airbrushed layers, as measured with mercury porosimetry [13]. Model estimations of the catalyst layer porosity in this work corroborate the important porosity increase with electrosprayed films. A recent localized reference electrode study has shown that the high porosity of the catalyst layer favours lateral homogeneity of cell response as a consequence of improved mass transport within the cell [14]. Ultra-low platinum loadings have been used with promising results in Nafion-based fuel cells [15–17], obtaining a comparable performance to electrodes prepared by sputtering.

Most studies with electrosprayed catalyst layer have been mostly dedicated to their application in low temperature PEMFC. The first study, to our knowledge, on the use of electrospray-prepared electrodes in PBI-based PEM fuel cells has been communicated in Ref. [18] showing improved performance with respect to conventional layers prepared with airbrushing. The porous morphology of the electrosprayed layers improves reactants accessibility and transport within the catalyst layer also within a PBI based cell. However, no information was reported about the stability of this cell type when using electrosprayed catalyst layer. A change in stability is to be expected with catalyst layer morphology, since degradation processes like carbon corrosion and platinum dissolution, also depend on mass transport properties under certain conditions. For instances, in a cell operated under high current density, corrosion reactions may exacerbate by localized starvation phenomena and lateral inhomogeneities that appear as a consequence of slow mass transport. Such phenomena are especially acute in low temperature PEMFC due to the presence of liquid water that must be transported through the porous medium at a high rate [19–21]. In PBI cells working at higher temperatures, water transport in the vapour phase may be faster, although corrosion reactions are accelerated by the higher working temperature. It is, therefore, of high interest to analyse if there is an effect of the electrosprayed layer on the durability of this type of cell.

In this paper, we aim at studying the break-in and degradation (typical life test) of a PBI PEM fuel cell whose electrodes have been prepared by the electrospray technique, identifying the reasons that cause it by means of experimental characterization (including current density distribution, electrochemical characterization with different techniques and physico-chemical characterization of the MEA after the life test). Experimental results are complemented with modelling based on computational fluid dynamics, as developed in previous works [22–24].

It is also of interest to compare the results obtained in this study with those of the life test study performed to the MEA presented in Ref. [25], prepared by manual airbrush.

Experimental and modelling

MEA preparation

To prepare the membrane-electrode assembly (MEA), two 49 cm^2 square electrodes with 0.25 mg cm^{-2} Pt loading, the same as that used in Ref. [25], were fabricated. In the first place, a microporous layer constituted by carbon black (Vulcan XC-72) and polytetrafluoroethylene was manually sprayed onto a piece of carbon fibre paper (TORAY TGPH-90) until the desired carbon loading was achieved. Next, the catalyst layer was deposited using the electrospray technique [13]. In order to prepare the catalytic ink, Pt/C (E-TEK 40 wt. % Pt on carbon Vulcan XC-72) and polybenzimidazole (PBI) were dispersed into a dimethylacetamide solution. Then, the electrodes were assembled by hot-pressing them with a PBI membrane in between. This membrane had previously been casted from a PBI solution and immersed into a 75 wt. % H_3PO_4 bath until a doping level of around eight molecules of acid per polymer repeating unit was reached.

Fuel cell set-up

The so-prepared MEA was inserted between two graphite end plates where 4-step serpentine flow channels are mechanized. A sensor plate for current distribution measurement (S++, Germany) was placed behind the end plate of the

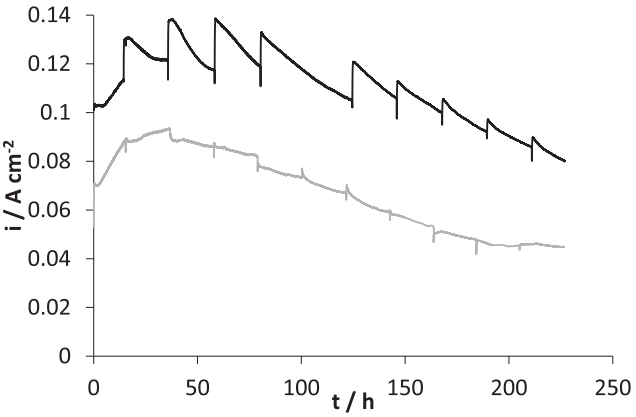

Fig. 1 – Evolution of the average current density at E_{cell} = 0.60 V during the lifetime of the fuel cell. T = 150 °C; P=Ambient pressure; Q_{H_2} = 100 mL min^{-1} (STP); Q_{O_2} = 100 mL min^{-1} (STP). Electrospray: solid black line; Airbrush: solid grey line.

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