Recent Advances in the Development of Unitized Regenerative Fuel cells based on PEM technology

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Abstract

Unitized Regenerative Fuel Cells (URFC) are reversible electrochemical devices which can alternatively operate as a water electrolyser or a H_2/O_2 (air) fuel cell. Results reported in this communication are related to R&D on bi-functional electrocatalysts and stack development. Pt-Ir mixtures have been used as anodic catalyst for water and hydrogen oxidation. Carbon-supported platinum has been used for hydrogen evolution and oxygen reduction. A two-cell stack with 250 cm^2 active area electrodes has been assembled and successfully tested. Electrochemical performances are close to those obtained with conventional water electrolysers and H_2/O_2 fuel cells. Typical cell voltages of 1.55 and 0.70 V have been recorded at a current density of 0.2 $A.cm^{-2}$, during respectively water electrolysis and H_2/O_2 fuel cell operation.

1   Introduction

Proton Exchange Membrane (PEM) technology can be used for the development of unitized regenerative fuel cells (URFCs) operating either as water electrolysers (WE) or as H_2/O_2 fuel cells (FC) [1-4]. In conventional PEM water electrolysis technology, platinum is used as electrocatalyst for the hydrogen evolution reaction (HER) at the cathode and iridium (metal or oxide) is used as electrocatalyst for the oxygen evolution reaction (OER) at the anode. In conventional H_2/O_2 PEM fuel cell technology, platinum is used as electrocatalyst for both the hydrogen oxidation reactions (HOR) at the negative and for the oxygen reduction reaction (ORR) at the positive. Platinum group metals can thus be used as electrocatalysts in PEM-URFCs, but there are some specific problems to be handled to turn efficient water electrolysis cells and fuel cells into efficient URFCs. Potentially, there are two different designs for reversible cells: (i) one is using truly reversible oxygen and hydrogen electrodes and (ii) the other is using electrodes which do not change their redox function when the mode of operation is switched from electrolysis to fuel cell. Results reported here concern the second design which was found to be the most efficient although gas management is more complicated [5]. As in electrolysers and fuel cells, reversible cells can be stacked into a stack to adjust the gas and electric power productions of the URFC to process requirements. Basic components of PEM reversible cells are (i) solid polymer electrolyte (membrane), (ii) anodic and cathodic electrocatalytic layers, (iii) gas diffusion electrodes (GDE), and also separating bipolar plates. The purpose of the work reported in this communication was double. First, to develop efficient PEM-URFCs with low platinum-group-metals loadings and improved life time performances during cycling. To achieve this goal, bi-functional electrocatalytic layers and specific GDEs were developed and optimized for operation in both electrolysis and fuel cell modes. Then, to obtain a proof-of-concept using large surface area electrodes (250 cm^2) and

stack configuration (2 cells). These results were obtained in the course of the GenHyPEM STREP program supported by the European Commission.

2   Results and Discussions

2.1   Lab-scale results
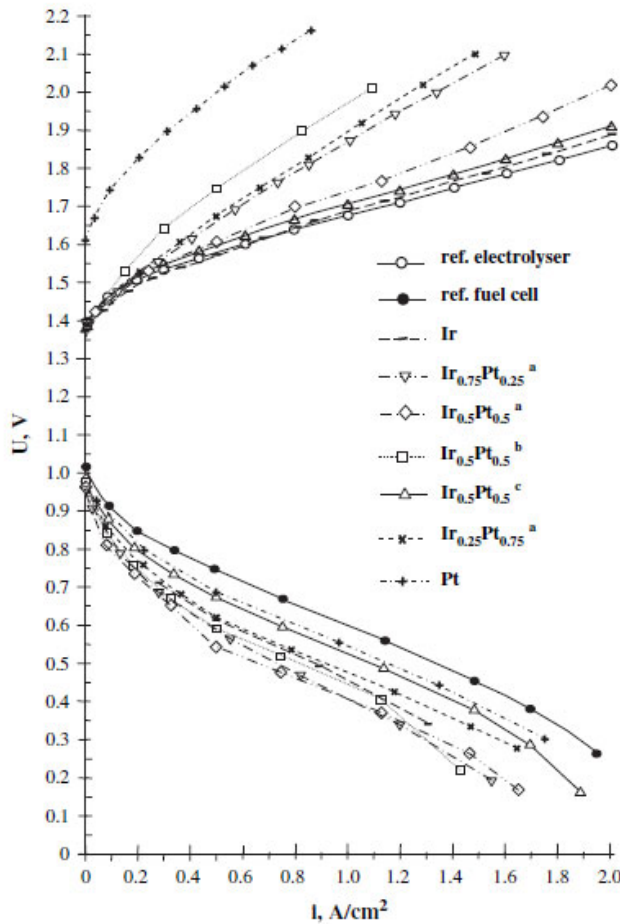
Figure 1:   Current–voltage relationships measured using a reference electrolysis cell (o), a reference PEM fuel cell (●), and reversible cells with anodes made of various Ir_xPt_y catalytic compositions. S=7 cm².

Membrane electrode assemblies (MEAs) used for operation in the PEM-URFC were firstly optimized at the lab scale (7 cm² monocell), using different catalysts. Typical polarization curves measured on a conventional PEM-WE cell (o) and on a conventional H_2/O_2 PEM-FC (●) are plotted in figure 1 for reference. Current-voltage polarization curves measured in both WE and FC modes using a URFC monocell are also plotted in figure 1. Pt40/Vulcan®XC-72 mixtures were used at the cathode (for the HER and the ORR) and Pt-Ir mixtures of various compositions have been tested as bi-functional electrocatalysts at the anode. As a general trend, homogeneous Pt-Ir mixtures did not provide satisfactory results, electrochemical performances being largely inferior to those measured on references cells. Best performances were obtained using a first thin and porous layer of metallic iridium deposited

directly against the SPE and a second layer of platinum placed on top. Using this two-layer structure, best current-voltage performances were obtained using 50 wt.% Pt and 50 wt.% Ir, both in WE and FC modes. As can be seen from figure 1, when proper catalytic compositions are used, electrochemical performances close to those measured on individual electrolysis cells and fuel cells are measured.

2.2   Two-cell stack performances

A two-cell stack URFC with two MEAs (250 cm^2 each) has been developed and tested. Nafion 117 was used as solid polymer electrolyte. A 3 mm thick titanium foil was used as bipolar plate to separate the two cells. Internal cell design has been optimized to improve the hydrodynamics of water-gas mixtures (electrolysis operation) and distribution of gases (fuel cell operation). During water electrolysis experiments, the URFC was directly powered using a 250A-50V DC power supply. A specific automated test station was used to measure stationary polarization curves. During H_2/O_2 fuel cell experiments, humidified H_2 and O_2 gases were provided by a PEM water electrolyser in the 1 to 10 bar pressure range. It was thus possible to adjust gas flows and input pressures to analyze their impact on the performances of the URFC. Typical polarization curves measured on this two-cell stack are plotted in figure 2 (circles). They are compared to those obtained on conventional cells of similar size. Although less efficient performances were obtained with the stack, encouraging results were measured under steady state conditions.
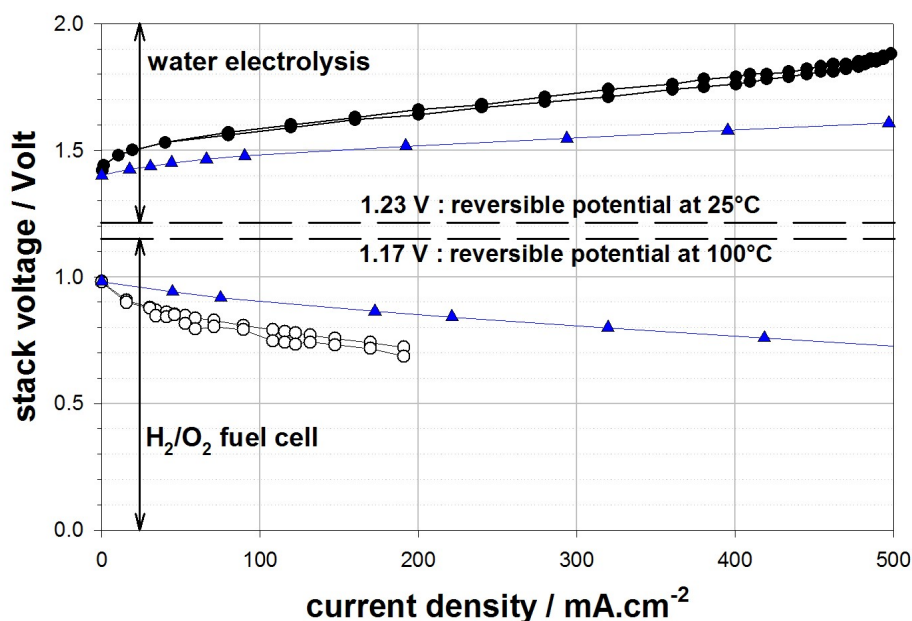

Figure 2:   Individual polarisation curves measured on the two-cell PEM URFC (S = 250 cm^2): (●) water electrolysis; T = 51°C; (o) H_2/O_2 fuel cell; T = 80°C; (▲) WE and FC reference curves; T = 80°C.

2.3   Alternative WE and FC operation

The development of URFCs that can maintain their performances during a significant number of alternative cycles is also very challenging. A simple experimental protocol has been used to assess the capability of the URFC stack to maintain its electrochemical performances on the long-term ($\approx$ 100 cycles, 30 minutes long at *ca.* 500 mA.cm^{-2}). Results, the detail of which cannot be reported within the format of this communication, show that electrochemical performances in stationary conditions of operation remain mostly stable. However, several minutes are required to stabilize performances after switching from WE to FC modes and conversely.

3   Conclusion and Perspectives

Some results obtained on Unitized Regenerative Fuel Cells in the course of the EC-supported GenHyPEM project are presented in this paper. The development and characterisation of electrodes where similar redox processes (reduction or oxidation) are taking place during water electrolysis and fuel cell experiments have been privileged. Lab-scale results obtained on 7 cm^2 reversible cells with optimized electrocatalytic compositions are encouraging, showing rather high electrochemical performances close to those obtained on conventional water electrolysis and H_2/O_2 cells. Best cell performances, both in electrolysis and fuel cell modes, were obtained with Pt-Ir black bi-layers, when the Ir-layer is directly facing the membrane. The use of porous titanium as anodic gas diffusion electrode during fuel cell experiments provides similar current-voltage performances to those obtained with conventional carbon cloth electrode. Carbon cloth or paper demonstrated a sufficient stability at the cathode. Stable and reproducible results have been obtained over several tens of cycles, alternating water electrolysis and H_2/O_2 experiments at a constant current density of 500 mA.cm^{-2}. The possibility of using other electrocatalysts (Pt and mixed oxides, such as nanostructured $Ru_xIr_ySn_{1-x-y}O_2$) is still under investigation. A two-cell stack with 250 cm^2 MEAs has been developed and tested. Encouraging performances have been obtained during both water electrolysis and fuel cell experiments. Experiments have been conducted over a limited ($\approx$ 100) number of operating cycles. No significant loss of performances was observed though.

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