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SOLUTION-CAST NAFION™ COMPOSITE MEMBRANE DURABILITY STUDY

Alfonso Pozio, Alessia Cemmi, Francesco Mura, Rodrigo Ferreira Silva
ENEA Casaccia Research Center TER, Via Anguillarese 301, 00123, S. Maria di Galeria, Rome (Italy)

ABSTRACT

Perfluorosulfonate ionomer dispersions in dimethylformamide solvent have been used to produce solution-cast membranes. Further, modified composite membranes have been prepared with the addition of low amount of silicate.

In order to investigate the durability of such membranes vs commercial ones at low humidification conditions, long-term fuel cell experiments have been carried out. Results show that the addition of a low quantity of silicate in the polymeric membrane allows PEFC to operate at low humidification conditions, giving higher performances than those of unmodified Nafion™ 112 membrane and lowering system degradation.

1. INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) based on proton exchange membranes (PEMs) are considered as the leading candidate to replace the traditional power sources like the internal combustion engines and also find application in the cogeneration power for both stationary and portable systems. In the cell, fuel is oxidized at the anode, oxygen is reduced to water at the cathode and electrical energy is delivered with very high yield in a production process having near-zero emissions. At present, one of the most common perfluorosulfonic acid based membranes employed in fuel cells is Nafion©, a registered mark of Du-Pont©. This membrane has many desirable properties including good chemical stability, high mechanical strength, and high ionic conductivity under high humidity conditions. However, the proton conductivity of Nafion© is strongly dependent on water content, and decreases considerably at low relative humidity (RH), leading to large relative losses and a reduction in cell voltage and efficiency.

Operating a fuel cell at low relative humidity results in several advantages and, therefore, there is a growing interest to develop and commercialize PEFCs that work under these conditions. In the field of membrane research for fuel cells, the key issue is to find alternative polymer electrolytes to Nafion©, which are capable to overcome its disadvantages as well as to lead to stack cost reduction.

In this regard, a very interesting approach is the formation of inorganic-organic composite membranes. Recent literature describes the synthesis of composite membranes formed by the recasting process and modified by in situ polymerization of embedded polymer precursors [1], and by the addition of heteropolyacids [2,3] or phosphate particles [4,5]. Impregnation of Nafion© ionomer into porous PTFE membranes has also been carried out [6].

Composite membranes containing montmorillonite (MMT) have already been cited elsewhere [7]. Montmorillonite can provide an excellent barrier effect for the permeation of small molecules. If a comparison is made with commercially available Nafion© membranes, the addition of a small amount of montmorillonite salts to perfluorosulfonic acid (PFSA) membranes leads to a decrease of conductivity [7]. However, we have succeeded in preparing Nafion©/MMT composite membranes that have the same conductivity of commercial membranes [8].

In the present work, we aimed at investigating the durability of such membranes at low humidification conditions. Assemblies containing composite and commercial membranes were tested in a fuel cell work station.

2. EXPERIMENTAL

Membrane-electrodes assemblies (MEAs) have been prepared using 30 wt.% Pt/C deposited on gas diffusion layer, both for cathode and anode, with different polymeric electrolyte membranes (Nafion™ 112, Solvay Hyflon™ Ion E87-05 and modified Nafion™). These systems have been tested for more than 500 hours in a 2-cm^2 active area single cell station, fed with humidified H_2/O_2 gases (at room temperature), under a pressure of 2 abs bar and a stoichiometric ratio of 1:2. MEAs have been submitted to a galvanostatic polarization by means of a programmable power supply interfaced with a computer for data acquisition; all measurements have been carried out in the same operative conditions. The overall ohmic resistance has been measured by electrochemical impedance spectroscopy (EIS).

Cell tests have been carried out with temperature ranging from 25°C to 50°C, and current density values varied pe-

riodically between 0 mA cm^{-2} and 240 mA cm^{-2} in order to simulate periodic start-up and to study the effect of these parameters on the membrane ageing. Then, voltage vs current density plots have been recorded daily.

In addition, cathodic and anodic exhausted water has been periodically collected in plastic containers to measure the conductivity by means of a Crison mod. 525 conductivity meter.

3. RESULTS AND DISCUSSION

In Fig. 1, the cell voltage vs. time of a MEA with a Nafion© membrane related to the particular conditions of high humidity, with anodic temperature at 80°C and cathodic at 65°C are presented. It is interesting to note that the MEA performance at 70°C at a current density of 142 mA cm-2 decreases at a rate of only -2.3 µV/h after 2000 h.
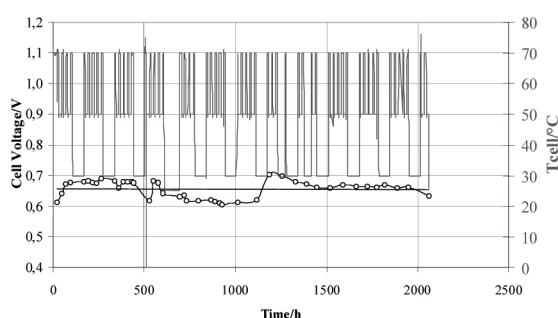
Fig.1: LONG TERM TEST FOR HUMIDIFIED NAFION.

In Fig. 2 the cell voltage vs. time of a MEA with a Nafion© 112 membrane curves related to the particular conditions of low humidity, with anodic temperature at 19°C and cathodic at 19°C, are presented. In this case, the MEA performance at 50°C at a current density of 240 mA cm-2 decreases at a rate of -154 µV/h after only 600 h.
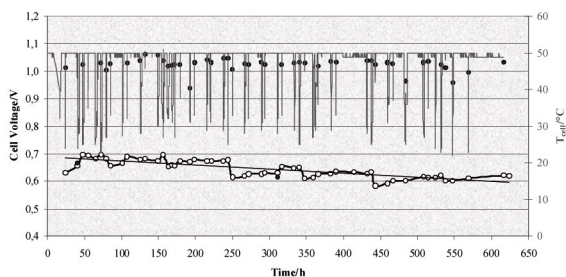
Fig.2: LONG TERM TEST FOR NAFION 112 AT LOW HUMIDIFICATION.

In Fig. 3 the cell voltage vs. time of a MEA with a Nafion© modified 112 membrane curves related to the particular conditions of low humidity, with anodic temperature at 19°C and cathodic at 19°C, are presented. In this case, the MEA performance at 50°C at a current density of 240 mA cm-2 decreases at a rate of 73 µV/h after 600 h.
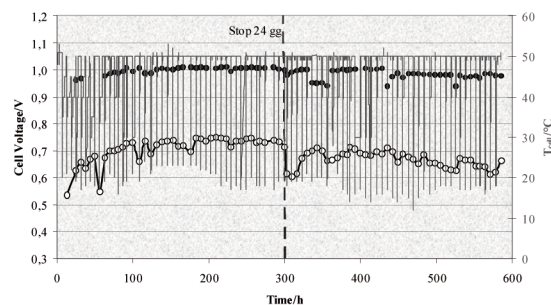
Fig.3: LONG TERM TEST FOR NAFION/ MONTMORILLONITE AT LOW HUMIDIFICATION.

4. CONCLUSIONS

The optimization of the recast Nafion®-based membrane synthesis was verified for long-term tests. Recast Nafion®-based composite membranes with hygroscopic properties were realized. Performance enhancement at low gas humidification was demonstrated for a comparison with commercial membranes.

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