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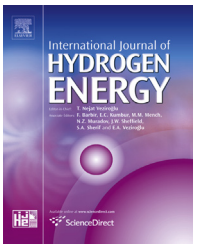

Perfluorosulfonic acid membrane degradation in the hydrogen inlet region: A macroscopic approach

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ABSTRACT

This study focuses on the characterization of two complete stacks of a proton exchange membrane fuel cell that have operated in stationary mode for 12,860 h. We compare cell voltage, and *in situ* and *ex situ* leak tests with local cell performance from a segmented cell, showing large differences in degradation between the stacks. Cells near the warmest region show more membrane degradation in the hydrogen inlets. We build a membrane thickness profile over a large area from thousands of optical microscopy images, covering seven channels and lands around the hydrogen inlet region, and identify a dramatic difference between channels 1 and 2, where dry hydrogen enters, and channel 3, where hydrogen has travelled 26 cm. Using a polytetrafluoroethylene reinforced membrane, we discriminate thickness variation for each layer and we show that degradation commences from the anode side.

Introduction

Proton exchange membrane fuel cells (PEMFC) remain a promising technology in the field of renewable energy. Their emergence is strongly dependent on their cost, reliability and durability. Performance is affected by premature aging of the catalysts, whereas durability is primarily governed by membrane failure leading to high gas crossover and fast chemical decomposition around pinholes. Many articles focus on single parameter effects on the degradation of membrane electrode assembly (MEA) components and are of interest for manufacturers to improve materials. In practical applications, aging is often disregarded, largely due to the difficulty of integrating real systems and analysing complete stacks. Collaboration between three laboratories and Axane, a fuel cell manufacturer, has allowed the effects of real life and long term operations to be analysed at different scales (MEA, catalyst layers, membrane). Subsequently, system lifetime was improved from 1500 to 13,000 h [1,2], largely due to the use of

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polytetrafluoroethylene (PTFE) reinforced perfluorosulfonic acid (PFSA) membranes [3–6]. PFSA reinforced membranes have better mechanical properties [7] and better resistance to crack initiation and propagation [8]. Moreover, they are less sensitive to swelling and less impacted by mechanical fatigue induced by humidity cycling, described by many authors as harmful [9–13].

However, for all the membranes used, stack management should be perfectly controlled to avoid aging heterogeneities between as well as inside cells [2,14,15]. Aging heterogeneities may arise from a bad thermal/or water management, and/or stack design and assembly [16,17]. To understand the origin of heterogeneities, fast, simple, macroscopic and non-invasive techniques should be performed at fuel cell end of life [1,2,18,19]. This macroscopic approach is a first step towards individual cell defect cartography. In recent years, degradation mapping of the cells has shown that gas inlets/outlets are the main fuel cell weakness [20]. Depending on the fuel cell configuration and operating conditions, the results may differ. The cathode catalyst layer is more degraded at the anode outlet or cathode inlet region, where the fuel is in starvation and at high potential to the cathode [21,22], whereas membranes are favourably degraded in the anode inlet region [13,23–25]. Several reasons have been proposed for the inlet region effects, such as higher hydrogen crossover [26–29], dry or low gas humidity [25,30–32], higher partial pressure difference between the anode and cathode sides [33], air starvation [34], and $H^{\bullet}$ radical formation [35,36]. Solutions to prevent such defects are beginning to appear [37]. Identifying defective areas inside a cell is relatively straight forward, whereas identifying the degraded side in the membrane is a much more difficult task. However, being able to characterize the membrane in the cross-section and identify the degradation mechanisms as a function of the side would answer many questions. Recently, techniques combining microscopy and spectroscopy, over a narrower spectral analysis region, have been developed. *Danilczuk* et al. used Fourier transform infrared spectroscopy (FTIR) microscopy to show that the anode was more degraded than the cathode side, with more C–H and C=O bands on that surface [38]. Raman spectroscopy has also been used to detect if membranes were more degraded around the Pt band [39]. Another technique consists of sticking two identical membranes together prior to aging tests, then separated and separately characterized, to simulate aging mechanisms on each side [40]. Depending on the tests or operating conditions, degradation may occur preferentially at the anode [31,41] or cathode [30].

Membrane degradation by radical attacks is described as an unzipping process of the main chain and a side chain cleavage that reduces membrane thickness. Measuring the membrane thickness is relatively simple and is routinely employed to estimate membrane degradation. Membrane images are generally obtained from scanning electron microscopy (SEM) [25,42] or optical imagery (OM) [13], and some authors use infrared imagery to study degradation around pinholes [2,40,43], providing a deeper understanding of the mechanisms that lead to membrane failure. However, as mentioned by *Rodgers* et al. [44], conclusions about thickness based on a piece of membrane of few hundred of μm are not necessarily representative of the rest of the MEA. In this study, we analysed a complete system returned from the field after 12,860 h of real operation, at macroscopic scale. Numerous membrane failures were revealed in the dry hydrogen inlet area. Membrane thickness profile on a macroscopic range (≥1.5 cm covering seven channels and lands) was made by OM. The three layers of the PTFE-reinforced membrane were individually studied and the degradation side identified.

Experimental

Fuel cell aging

Fuel cell aging has been performed in the field in real conditions with a system composed of two stacks of 55 cells with power range 1.5–2 kW. Anode and cathode bipolar plates were designed to operate in a counter-flow mode which produces optimum cell performance [45]. Current density was 0.26 A/cm^2 for 12,860 h at 60–65 °C. MEAs were identical with a specific active area of 86 cm^2. The membrane was a PTFE/PFSA composite long side chain membrane with average thickness 30 μm. The catalyst layers were Pt/C type and similar for all cells. The electrocatalytic materials, the chemical nature of the ionomer contained in the catalytic layers, and the proton-exchange membrane are proprietary and cannot be described here in detail. The anode side was in dead-end mode and pure and dry hydrogen was fed into the inlet at 350 mbar above atmospheric pressure (stoichiometry of 1.1). The cathode was fed with humidified air at 60% relative humidity (RH) at relative pressure of 100 mbar (stoichiometry of 2.5). Air and hydrogen compartments were frequently purged to remove excess water and accumulated nitrogen from air at the end of the anode side. Individual cell voltages and leaks were measured at end of life. Stacks were then disassembled, and each MEA analysed by infrared imagery.

Leak test protocols

In situ *leak test*

Leak test by pressure drop was performed *in situ* prior to stack disassembly. The external gas collectors were individually removable, and an external device developed by Axane was plugged into the collectors. The outlets were closed and air supplied at the inlet to reach relative pressure of 250 mbar, and the pressure drop measured over 30 s. A rapid drop of the pressure was evidence of a gas leak in the membrane. The measurement was performed on the anode, cathode, or both compartments simultaneously to separate internal (membrane) and external (e.g. gasket) leaks.

Ex situ *leak test*

A bubble mapping device was employed to detect pinholes inside membranes. The device had 40 segments (1.5 × 1.5 cm). The bubble positions were identified by the segment number for the 110 MEA of the stack. In addition, infrared imagery was used to more precisely map and localize membrane failures [46]. Post mortem analysis was performed on the 110 MEAs using an infrared (IR) camera (Thermovision A320 from FLIR Systems). A cell was constructed to fit the dimensions of the MEA with the cathode side facing the camera lens. Hydrogen

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