Long-term testing of a high-temperature proton exchange membrane fuel cell short stack operated with improved polybenzimidazole-based composite membranes

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HIGHLIGHTS

- Scale-up of composite PBI based membrane high temperature PEM fuel cell technology.
- Feasibility of a modified titanium-PBI based membrane system operating in static and dynamic modes.
- Reduction of phosphoric acid leaching from stack, operating with TiO_2 composite PBI based membranes.
- The PBI based HT-PEMFC with composite membranes has shown high durability (>1000 h).

GRAPHICAL ABSTRACT
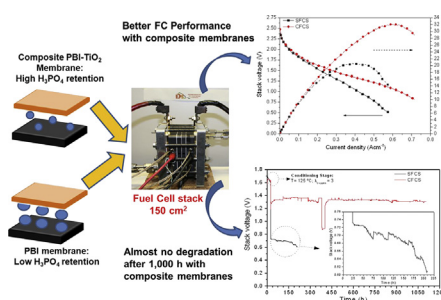
ABSTRACT

In this work, the feasibility of a 150 cm^2 high-temperature proton exchange membrane fuel cell (HT-PEMFC) stack operated with modified proton exchange membranes is demonstrated. The short fuel cell stack was manufactured using a total of three 50 cm^2 membrane electrode assemblies (MEAs). The PEM technology is based on a polybenzimidazole (PBI) membrane. The obtained results were compared with those obtained using a HT-PEMFC stack with unmodified membranes. The membranes were cast from a PBI polymer synthesized in the laboratory, and the modified membranes contained 2 wt.% micro-sized TiO_2 as a filler. Long-term tests were performed in both constant and dynamic loading modes. The fuel cell stack with 2 wt.% TiO_2 composite PBI membranes exhibited an irreversible voltage loss of less than 2% after 1100 h of operation. In addition, the acid loss was reduced from 2% for the fuel cell stack with unmodified membranes to 0.6% for the fuel cell stack with modified membranes. The results demonstrate that introducing filler into the membranes enhances the durability and stability of this type of fuel cell technology. Moreover, the fuel cell stack system also exhibits very rapid and stable power and voltage output responses under dynamic load regimes.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are potential candidates for power plant generation/cogeneration, transportation and portable power applications. The target lifetime requirements for electrochemical fuel cell stacks are 40,000 h (continuous operation) for power generation, 3000—5000

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operating hours over a 5-year period for transportation, and 1000 h (intermittent operation) for portable power applications. To assess the lifetime of fuel cell systems, studies are typically conducted using individual fuel cells and fuel cell stacks, which are scaled-up to different degrees. However, a single fuel cell must be scaled up to the size of a fuel cell stack to achieve the voltage and power output levels required for a real application [1–3].

Nafion® membrane fuel cell technology has been widely studied in recent decades and is currently in its premarket phase. One problem associated with low-temperature (LT-) PEMFC systems (operating temperatures below 100 °C at $P = 1$ atm), i.e., Nafion®-based fuel cells, is that some efficiency and power density are lost in the area of the electrode that is scaled up. One reason for this may be the increased difficulty in removing water from larger cells. Water tends to condense within the flow channels or form droplets on the substrate and/or diffusion layer of the fuel cell electrodes, which consequently impedes the diffusion of the reactants to the active sites and the removal of the products from the active sites. The net result is an increase in the mass transport overpotential [1]. The removal of heat is also problematic for this type of fuel cell, particularly at high power densities, which produce greater quantities of heat because the temperature gradient between the fuel cell and the environment is small [2]. Thus, the development of this LT-PEMFC technology is currently focused on overcoming design issues to improve water and heat management, among others.

For high-temperature (HT-) PEMFC systems, water management and heat removal are not concerns. This technology operates at temperatures above 100 °C. Therefore, water is in its gaseous phase at atmospheric pressure and can be easily removed from the system. Furthermore, the temperature gradient between the fuel cell and the environment is larger, which means that the removal of heat is easier and is an advantage over LT-PEMFC systems. The waste heat can be used for the processing of fuel and/or for heating, thereby enhancing the overall efficiency of the system [3–5].

Polybenzimidazole (PBI)-based HT-PEMFC technology, unlike Nafion®-based technology, is currently still in the research stage. However, some research groups have attempted to scale up this type of technology [3] and have reported that the rate of H_3PO_4 loss is the main drawback. In 2006, Staudt et al. [6] tested a 5 kW PBI-based PEM fuel cell stack for 800 h. They estimated a H_3PO_4 loss rate of 216 ng cm^{-2} h^{-1} at 160 °C. Similar measurements were performed by Yu et al. [7] in 2008 under both steady-state and dynamic (load, thermal and shutdown/start-up cycling) conditions on a single PBI-based PEM cell. A voltage degradation rate of 4.9–6.3 μV h^{-1} at 160 °C was reported under steady-state operation. Over the temperature range from 80 to 160 °C, the H_3PO_4 loss rate was less than 10 ng cm^{-2} h^{-1}. This result was very promising and corresponded to a total acid loss of 2.6% after 40,000 h of steady-state operation.

In 2009, Andreasen et al. [8] reported the characterization of a 1 kW PBI fuel cell stack using electrochemical impedance spectroscopy (EIS). They found that the impedance of the fuel cell stack was dependent on the impedance of each cell of the fuel cell stack. Consequently, equivalent circuit models for each cell could be used to predict the impedance of the fuel cell stack for different temperature profiles. The information available in such models could therefore be used to predict the performance of the fuel cell stack, e.g., systems in which different electronic components introduce current harmonics.

In 2010, Moçotéguy et al. [9] tested, in dynamic mode, a H_3PO_4/PBI, Celtec-P based HT-PEMFC for Micro-CHP (Combined Heat and Power) applications. The long-term test of the 500 W fuel cell stack used synthetic reformate (70% H_2 + 29% CO_2 + 1% CO) and air at 160 °C for 674 h. The decrease in the performance of the fuel cell stack was limited to 7.6%, and its electrical efficiency decreased

from 30.6 to 28.3 %. Four initial stop/start cycles weakly impacted the performance, and some specific cells (primarily associated with a lower initial open circuit voltage, OCV) exhibited significantly higher degradation rates.

In 2011, Lee et al. [10] reported the insertion of a sub-gasket during the hot-pressing procedure for manufacturing the MEA to avoid deterioration of the PBI membrane during fabrication and operation of the fuel cell. The use of this sub-gasket resulted in higher fuel cell stack performance than did the use of a pristine MEA. The 20 W fuel cell stack, which incorporated 7 MEAs, was operated for 1200 h without a noticeable performance loss.

The aim of this work is to assess the behavior of a 150 cm^2 HT-PEMFC stack that is based on PBI membranes that contain 2 wt.% TiO_2. The use of TiO_2 composite membranes as an electrolyte material could potentially enhance the performance and stability of the fuel cell. Moreover, the use of TiO_2 as a filler also increases the acid-doping level in the PBI membrane [11–13], thereby enhancing proton conductivity. To confirm these benefits, the fuel cell short stack with the composite membranes was evaluated using a 1000 h life test. Moreover, the behavior of this system was compared with that of a HT-PEMFC stack with the same size but operated using standard PBI membranes, whose behavior was previously reported in a preliminary study [14]. A life test consists of operating the fuel cell stack at a constant current density over a long period with several shutdowns and start-ups. During the life test, several dynamic load tests are performed. These tests allow us to determine the speed of response to a particular sequence of changes in the loading.

2. Experimental procedure

2.1. Manufacturing of the MEA and fuel cell stack

The first step for manufacturing the MEA (membrane electrode assembly) was synthesizing the polymer powder. The m-PBI polymer (308 g per monomer) was synthesized in the laboratory according to a procedure described in a previous work [15]. All of the membranes used in this study were derived from a polymer with an intrinsic viscosity of 1.15 dL g^{-1}. Next, the polymer was dissolved in N,N-dimethylacetamide (DMAc) to produce a 2.2 wt.% PBI solution. To manufacture the composite membranes, 2 wt.% TiO_2 powder (Merck) with a mean particle size of 1.14 μm was added to the polymer solution. Both standard and composite membranes were cast using the following procedure. First, the polymer solution in DMAc was spread onto glass plates. The plates were then placed in an oven at 90 °C for approximately 15 h. This heat treatment caused the solvent to evaporate; next, the membranes were detached from the plate and washed with Milli-Q water to remove trace solvent. The membranes were then immersed in an 85 wt.% H_3PO_4 bath (PA-ACS-ISO, Panreac, Spain) for a minimum of five days to ensure steady-state conditions for the H_3PO_4 absorption process under ambient laboratory pressure and temperature [16].

The doping levels in the composite PBI membranes were 14.5 ± 0.3 mol H_3PO_4 per monomer and 10.8 ± 0.3 mol H_3PO_4 per monomer for the PBI membranes. For acid-doped PBI membranes, high doping levels lead to high proton conductivity values and weakened mechanical properties. In previous investigations [12], the mechanical properties of the 2 wt.% TiO_2 composite PBI membrane and standard PBI membrane were studied. For a non-doped PBI membrane, the tensile strength was 446 MPa, whereas for a PBI membrane doped with 11.3 mol H_3PO_4 per monomer, the tensile strength was 22.2 MPa. Similarly, a 2 wt.% TiO_2 composite PBI membrane doped with 15.3 mol H_3PO_4 per monomer exhibited a tensile strength of 6.4 MPa.