INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–8

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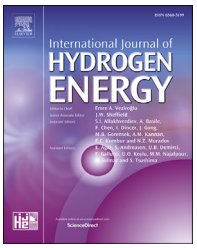

Direct methanol fuel cell stack for auxiliary power units applications based on fumapem® F-1850 membrane

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ARTICLE INFO

Article history:
Received 6 March 2017
Received in revised form
12 July 2017
Accepted 17 August 2017
Available online xxx

Keywords:
Direct methanol fuel cell
Bipolar stack
Methanol cross-over
Polymeric membrane

ABSTRACT

Direct methanol fuel cells (DMFCs) have been actively investigated from both fundamental and applied points of view due to their interesting perspectives for the application in the fields of auxiliary power supply and portable power sources. However, research efforts are still needed to solve the drawbacks presently affecting these devices, such as methanol cross-over constraints, high costs of materials, etc. The present paper addresses these issues by using a new FUMATECH proton exchange membrane (fumapem® F-1850), characterized by a nominal equivalent weight of 1800, as the electrolyte, and low electrode noble metal loadings compared to the state of the art. A membrane-electrode assembly (MEA) based on this membrane was investigated in a small area (5 cm^2) direct methanol fuel cell at 60 °C and compared to a benchmark Nafion® 115 membrane in terms of performance and methanol cross-over. The F-1850 membrane showed a lower methanol cross-over rate than Nafion® 115, despite a lower thickness of the fumapem® membrane. This allowed to obtain a higher performance (74 vs. 64 mW cm^{-2}) for the F-1850 membrane compared to Nafion® at ambient pressure. To study the scalability of the DMFC device and related components, the new membrane was integrated in large-area MEAs (100 cm^2) and investigated in a 5-cell and 10-cell pressurized stack based on a bipolar design. The stack was tested at 75 °C, 5 M methanol solution at the anode and pressurized oxygen (2 atm. rel.) at the cathode, giving a normalized power density per cell of about 130 mW cm^{-2}. The results obtained with the 10-cell stack showed a good agreement with the performance recorded with the 5-cell stack, confirming the scalability of the DMFC device.

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http://dx.doi.org/10.1016/j.ijhydene.2017.08.109

Introduction

Direct methanol fuel cells (DMFCs) are almost ready for commercialization, but the high costs associated with noble metal catalysts and the commonly used perfluorosulfonic polymer electrolyte membranes hinder the widespread diffusion of these devices [1–3]. Up to now, the Nafion® membrane, a perfluorosulfonic acid solid polymer electrolyte produced by DuPont, is the most widely used in H_2/air and direct methanol fuel cells due to its high proton conductivity (up to 80 °C), suitable mechanical properties and good chemical and electrochemical stability. However, Nafion® membranes exhibit some negative aspects such as: high H_2 and methanol crossover, fast dehydration with loss of proton conductivity at temperatures above 100 °C and loss of fluorine ions in the exhaust gas due to ·OH radicals attack [4–6]. Accordingly, research efforts are needed to develop alternative membranes, which should be cheaper than Nafion® and with similar or higher conductivity and lower fuel cross-over in the temperature range of interest (25–100 °C) [7–9].

Reduction of methanol crossover can be achieved by using cross-linking procedures or adding nanosized inorganic fillers inside the membrane to increase the tortuosity path as well as by tuning the ion exchange capacity (IEC) [10–13]. Another approach considers the variation of the chemical properties of the polymer network surrounding the ionic groups to modulate the degree of dissociation as well as the degree of interpenetrated networks [14–16]. These approaches can reduce the level of methanol permeability while keeping the proton conductivity at suitable levels.

Several polymer membranes characterized by different chemistry (sulfonated polyethersulfones [17], sulfonated polysulfones [18], sulfonated polyetherketones [19], sulfonated polyimide [20], sulfonated or acid doped polybenzimidazole (PBI) [21–23]) were investigated with the aim to reduce methanol cross-over in direct methanol fuel cells [24]. FUMATECH developed a range of low IEC (high equivalent weight) membranes designed for low methanol crossover that were based upon long side chain (fumion® F) PFSA blends [24–26]. In the framework of a European Community FP7 collaborative FCH JU Project, DURAMET (www.duramet.eu), a FUMATECH membrane with a nominal equivalent weight (EW) of 1800 g mol^{-1} was investigated and compared to a benchmark Nafion® 115 membrane (from Ion Power) in terms of performance and methanol cross-over. The main results obtained in a 5-cm^2 single cell are reported in the present paper. The same membrane has been integrated in large-area MEAs (100 cm^2) and investigated, for the first time, in a 5-cell and 10-cell stack based on a bipolar design, which consists of a number of repeating units of membrane-electrode assemblies (MEAs) and bipolar plates, developed within the project [27]. A bipolar plate separates each MEA, provides an in-series electrical connection between the cells and supplies reactants to each cell through flow channels manufactured on both sides of the plates. Compared to a monopolar design [28–31], the stack based on a bipolar configuration has a lower internal resistance and, thus, is suitable for larger stacks. The stack equipped with the FUMATECH membrane has been investigated at 75 °C feeding a high methanol concentration (5 M) in order to minimize the size of the fuel reservoir and increase the energy density of the system.

Experimental

The fumapem® F-1850 membrane is a proton exchange membrane based on a perfluorosulfonic acid-type polymer (fumion® F), developed at FUMATECH laboratories. The fumapem® F-1850 membrane has an equivalent weight (EW) = 1800 g mol^{-1} and a thickness of 50 μm [24]. This membrane was integrated in a membrane–electrode assembly and investigated in a 5-cm^2 single cell in terms of performance and methanol crossover. The electrodes consisted of catalytic layers based on 15 wt% Nafion ionomer (Ion Power, 5 wt% solution, 1100 EW) and 85 wt% catalyst, and commercial backing layers (E-TEK). A Pt–Ru/C catalyst (1:1 atomic ratio) was used as the anode catalyst; a Pt/C catalyst was used at the cathode for all MEAs. The loadings were 2 $mg_{(Pt + Ru)}$ cm^{-2} for the anode and 1 mg_{Pt} cm^{-2} for the cathode. MEAs have been assembled in situ. The compression was kept constant for all the MEAs at 15 kg cm^{-2}. No thermal treatment was carried out during the MEA assembling. The MEA based on fumapem® F-1850 membrane have been investigated at 60 °C and compared to an MEA equipped with the benchmark Nafion® 115 membrane. The MEAs were tested in a Fuel Cell Technologies, Inc. DMFC test station. For polarization curves, a 2 M methanol solution was fed at the anode with a flow rate of 3 mL min^{-1}, whereas oxygen was fed at the cathode with a flow rate of 100 mL min^{-1} under atmospheric pressure.

After the screening in the 5-cm^2 single cell, the fumapem® F-1850 membrane was used as the electrolyte in a stack based on bipolar plates, developed for APU applications, with an active electrode area of 100 cm^2. It was operated with a gradient pressure of 2 atm between the cathode and anode compartments. The anode was fed with a 5 M methanol solution. Two stacks were tested consisting of 5 or 10 cells. The MEAs used in the stack consisted of 5-layers: two anodic and cathodic Gas Diffusion Layers (GDLs) from SGL Carbon (SGL35DC) and a Catalyst Coated Membrane (CCM, three layers). The catalyst loading was 1.8 $mg_{(Pt+Ru)}$ cm^{-2} at the anode and 1.2 mg_{Pt} cm^{-2} at the cathode.

DMFC tests were carried out by connecting the fuel cell stack to a fuel cell test station (Hydrogenics). Polarization curves were acquired in the galvanostatic mode by increasing the current in steps and recording the corresponding potential. Chronopotentiometric curves for the DMFC bipolar stack were registered at a constant current of 20 A.

A Varian micro gas-chromatograph was used to analyse the gas stream of the cathode outlet after condensing the liquid fraction. An Agilent bench gas-chromatograph equipped with flame ionization detector was used for the liquid fraction.

Results and discussion

The fumapem® F-1850 membrane was first investigated in terms of polarization behaviour under fuel cell conditions in a 5-cm^2 single cell and compared to the benchmark Nafion® 115

Please cite this article in press as: Baglio V, et al., Direct methanol fuel cell stack for auxiliary power units applications based on fumapem® F-1850 membrane, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.08.109