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

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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.

Keywords: Direct Methanol Fuel Cell; bipolar stack; methanol cross-over; polymeric membrane.

1. 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 °C-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.

2. 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} $\cdot cm^{-2}$ 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). Polarisation 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.

3. Results and discussion

The fumapem® F-1850 membrane was first investigated in terms of polarization behavior under fuel cell conditions in a 5-cm^2 single cell and compared to the benchmark Nafion® 115 membrane. An estimation of the methanol crossover was carried out by analyzing of the exhaust gas at the cathode side of the DMFC single cell at different current density values. The CO_2 produced by the oxidation of the methanol permeated to the cathode was analyzed using an online micro-gas chromatograph. Furthermore, sampled aliquots of the condensed cathode stream were analyzed by a bench gas-chromatograph. Only traces of unreacted methanol were detected in the condensed stream from the cathode. As observed in Table 1, in which several characteristics of the fumapem® F-1850 membrane are reported and compared with Nafion® 115, methanol crossover slightly decreases with the operating current density. Under different operating current densities, the fumapem® F-1850 membrane shows a lower methanol cross-over rate than Nafion® 115, despite the lower thickness of the fumapem® F-1850 membrane used in this work (Table 1). This is an important aspect for the large scale application of this membrane, since it means an increase of fuel utilization and energy density (allowing the use of high methanol concentration at the anode) and a reduction of costs in terms of raw materials compared to a benchmark perfluorosulfonic acid membrane characterized by a larger thickness.

Table 1. Characterization data of the fumapem® F-1850 membrane compared to Nafion® 115.

Membrane properties	**Unit**	**F-1850**	**Nafion® 115**
EW (theoretical)	$g \cdot mol^{-1}$	1800	1100
IEC (exp.)	$mmol \cdot g^{-1}$	0.5	0.9
Thickness (dry)	µm	50	125
Solvent uptake in MeOH at 25 °C	Wt %	30	54
Length increase Δl in MeOH at 25 °C	%	18	31
Conductivity in H_2O at 25 °C	$mS \cdot cm^{-1}$	58	62
Methanol cross-over at 60 °C and 0 mA cm^{-2} (OCV) with 5 M alcohol concentration	$mol \cdot cm^{-2} \cdot min^{-1}$	$3.48 \cdot 10^{-5}$	$4.64 \cdot 10^{-5}$
Methanol cross-over at 60 °C and 40 mA cm^{-2} with 5 M alcohol concentration	$mol \cdot cm^{-2} \cdot min^{-1}$	$1.99 \cdot 10^{-5}$	$4.21 \cdot 10^{-5}$
Methanol cross-over at 60 °C and 125 mA cm^{-2} with 5 M alcohol concentration	$mol \cdot cm^{-2} \cdot min^{-1}$	$1.89 \cdot 10^{-5}$	$4.13 \cdot 10^{-5}$

The DMFC performances in a 5-cm^2 single cell, for the MEAs equipped with the F-1850 and Nafion® 115, are reported in Fig. 1. Nafion 115 membrane (125 µm in thickness) is the state-of-the-art electrolyte for DMFCs, since it presents the best compromise in terms of reduction of methanol cross-over and suitable cell resistance. Thus, in this paper, we have selected Nafion 115 as reference membrane in order to assess the reliability of the fumapem® F-1850 membrane in comparison with this reference. As a preliminary screening and in order to compare the results with the literature, a 2 M methanol solution was used at the anode compartment and oxygen at the cathode. The MEA based on F-1850 membrane showed an open circuit voltage (OCV) similar to the Nafion®115-based cell, despite the significantly lower thickness of the membrane in the former MEA. Since the OCV is an indication of the permeability characteristics of a membrane, the value of 0.77 V reached at 60°C, with 2 M methanol solution at the anode, suggests low methanol cross-over characteristics of the membrane, as confirmed by the measurements recorded with high methanol concentration (5 M) reported in Table 1. The performance obtained with the MEA based on F-1850 membrane is better than that with Nafion® 115 both in terms of maximum power and current density. Moreover, these results are in line with literature reports dealing with the use of Nafion NR 212 or recast Nafion with similar thickness of the F-1850 membrane or commercial membrane-based MEAs [32-36], taking into account that low catalyst loadings were used in the present work.

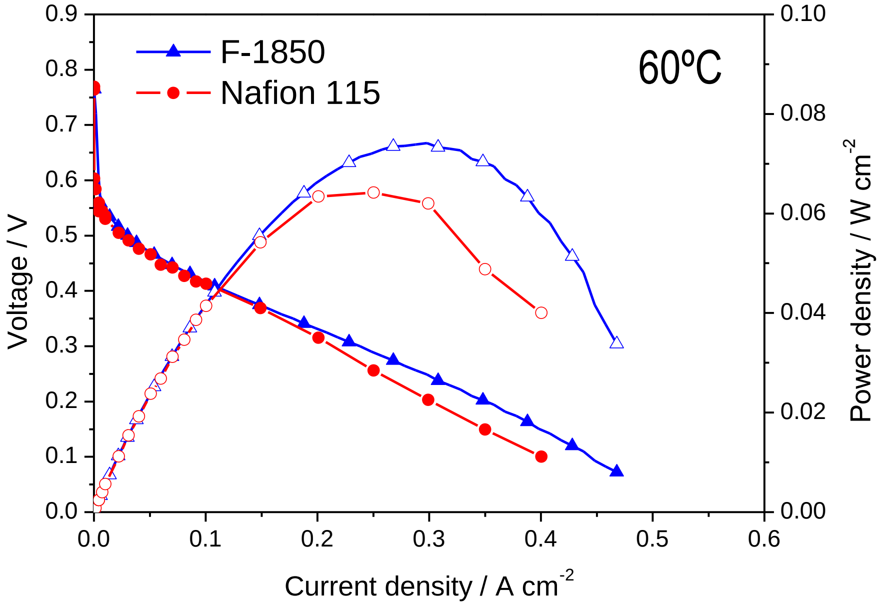


Fig. 1. Polarization and power density curves for the MEAs equipped with the F-1850 and Nafion 115 membranes at 60 °C, 2 M methanol.

The stack was initially assembled with 5 cells and subsequently with 10 cells; some pictures of the assembling steps, with current collectors, graphite plates and clamping plates, are reported in Fig. 2 together with the complete stack. More details about the stack properties and configuration are reported in a previous report [27].

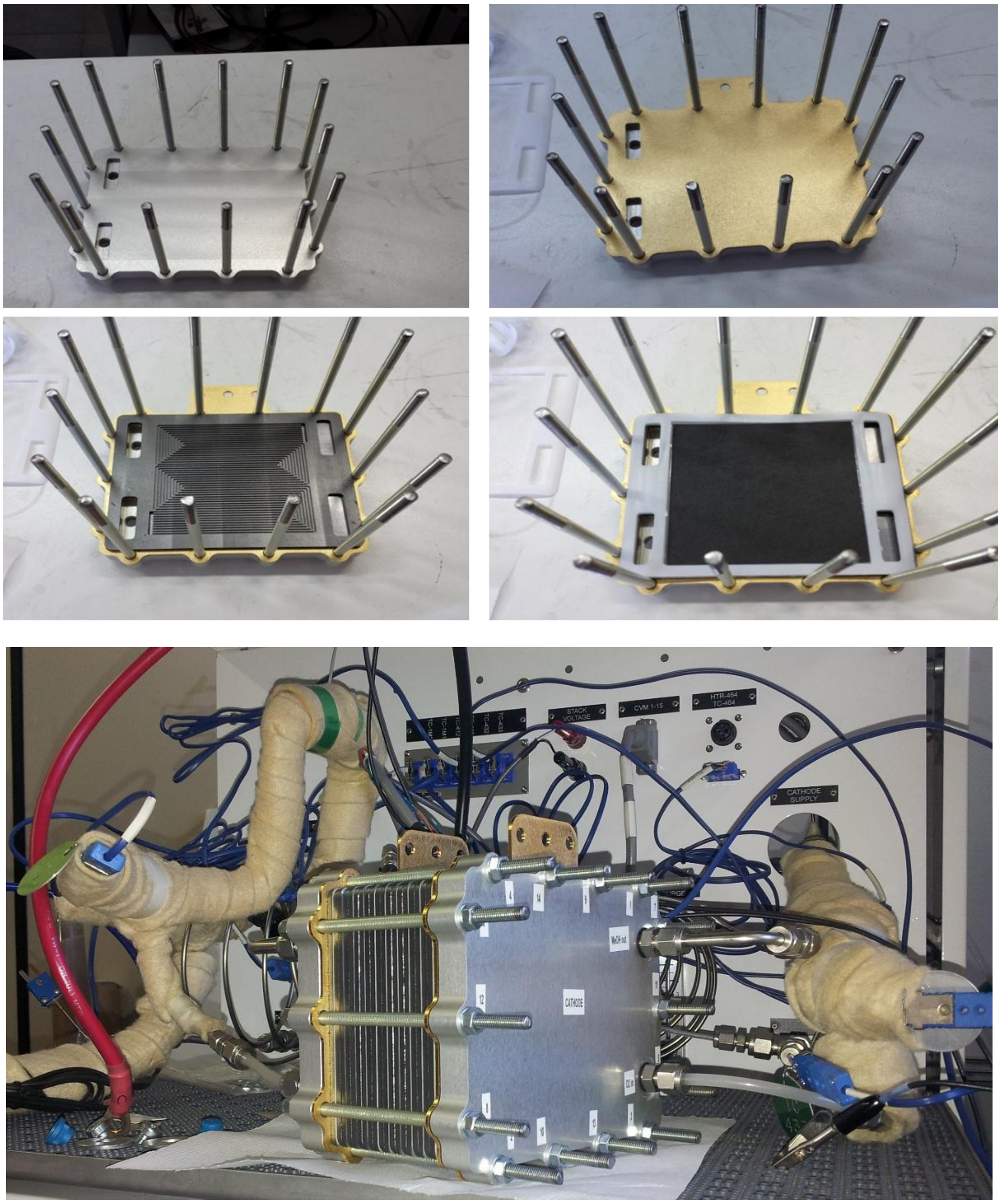
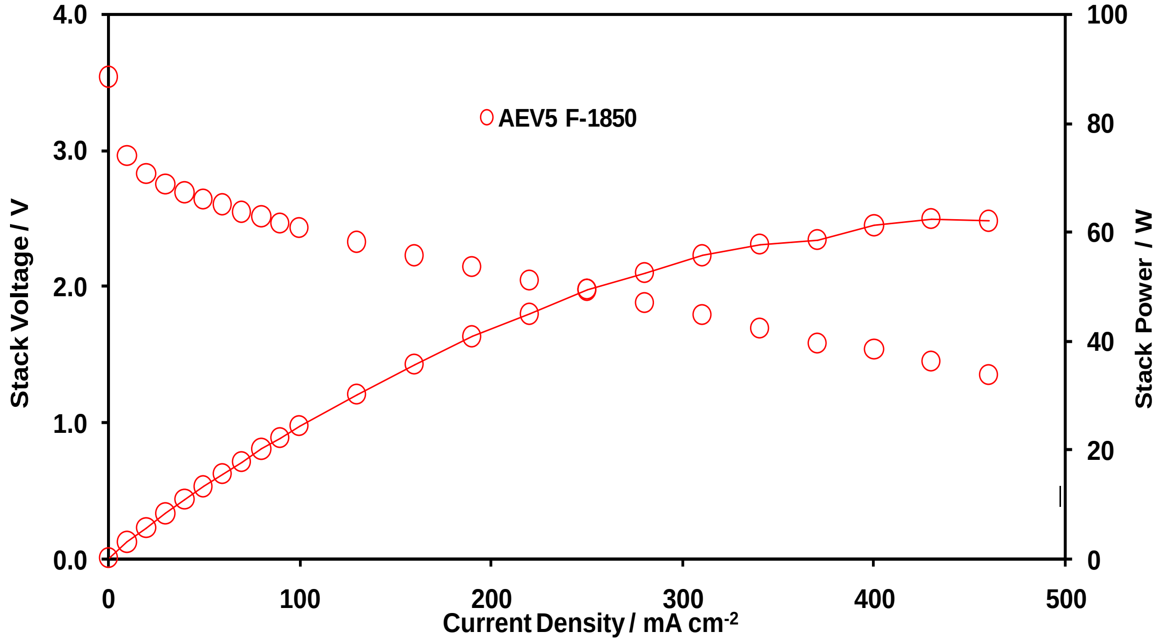


Fig. 2. Pictures of bipolar-plate-based stack assembling and the final 10-cell stack based on fumapem® F-1850 membrane.

The 5-cell stack was electrochemically investigated by feeding a 5 M methanol solution to increase the energy density of the system and reduce the volume of the fuel reservoir. The 5-cell stack produced a maximum power of 63.5 W at 470 mA cm^{-2} and 1.35 V (Fig. 3, top). In terms of normalised power density, it corresponds to about 130 mW cm^{-2} with an averaged cell voltage of 0.27 V (Fig. 3, bottom). The normalised performance is lower than that reported in a previous paper for the same stack equipped with Nafion® 115 membranes [27]. This is attributed to the different operating temperatures of the two stacks (75°C in the present case, 90°C in the previous paper [27]). Since the stack was self-heating, the actual operating temperature depended on the methanol cross-over properties of the membranes and on the irreversibility of the electrochemical reactions [37]. The heat released by the stack generally increases with the irreversibility of the electrochemical process at high currents but also decreases with the reduction of methanol cross-over. Methanol cross-over is lower at high current density compensating in part the previous effect [37]. Being the FUMATECH F-1850 membrane characterized by a lower methanol permeability than Nafion® 115 membrane, as reported above, the stack could not reach 90°C, as in the previous work [27]. The temperature of 75°C was regulated by selecting proper recirculation rate for the methanol solution fed to the anode, which also worked as cooling system.

There are several reports in the literature concerning with the investigation of DMFC stacks based on a bipolar configuration. Most of the achievements in this field have been reported in a review paper by Li and Faghri [38]. Dohle et al. [39] developed a DMFC stack consisting of 71 cells with an electrode area of 144 cm^2, with stainless steel and gold-plated stainless steel current collectors. The fuel cell stack achieved a power density of 30.4 mW cm^{-2} at 64 °C with 1 M methanol solution and air under ambient pressure and 150 mW cm^{-2} using oxygen at 3 bar absolute pressure with 1 M methanol solution at 80 °C. Jiang et al. [40] designed a DMFC stack with a metal foam flow field, reaching an average power output of 26 mW cm^{-2}. Buttin et al. [41] demonstrated a 150 W DMFC stack with five cells by feeding 1 M of methanol and air at 3 atm, with an average power density of about 140 $mWcm^{-2}$ at 110°C. Gogel et al. [42] showed that a DMFC stack made up of 12 cells using Nafion® 105 could be operated in a temperature range of 70°C and 90°C and exhibited a power density about 60 mW cm^{-2} at 0.5V. A 50 W stack was developed at KIST by Kim et al. [43] feeding 2 M methanol. The maximum power density was found to be 85 mW cm^{-2} in air and 154 mW cm^{-2} in oxygen. Oedegaard and Hentschel [44] developed a DMFC stack consisting of twelve cells with a 49 cm^2 active area for each cell. The normalized power density per cell was 50 mW cm^{-2} with 1 M methanol solution and air supplied at 60 °C.

The novelty of the present work relies on the use of a cheaper membrane, with lower methanol permeability compared to Nafion® commonly used in the previous described papers. The low methanol crossover characteristics allowed the use of a concentrated methanol solution (5 M), which means longer times of running before refuelling. A suitable performance was achieved under these operating conditions that favourably compares to Nafion®-based stacks reported in the literature and operating with lower or similar methanol concentration.



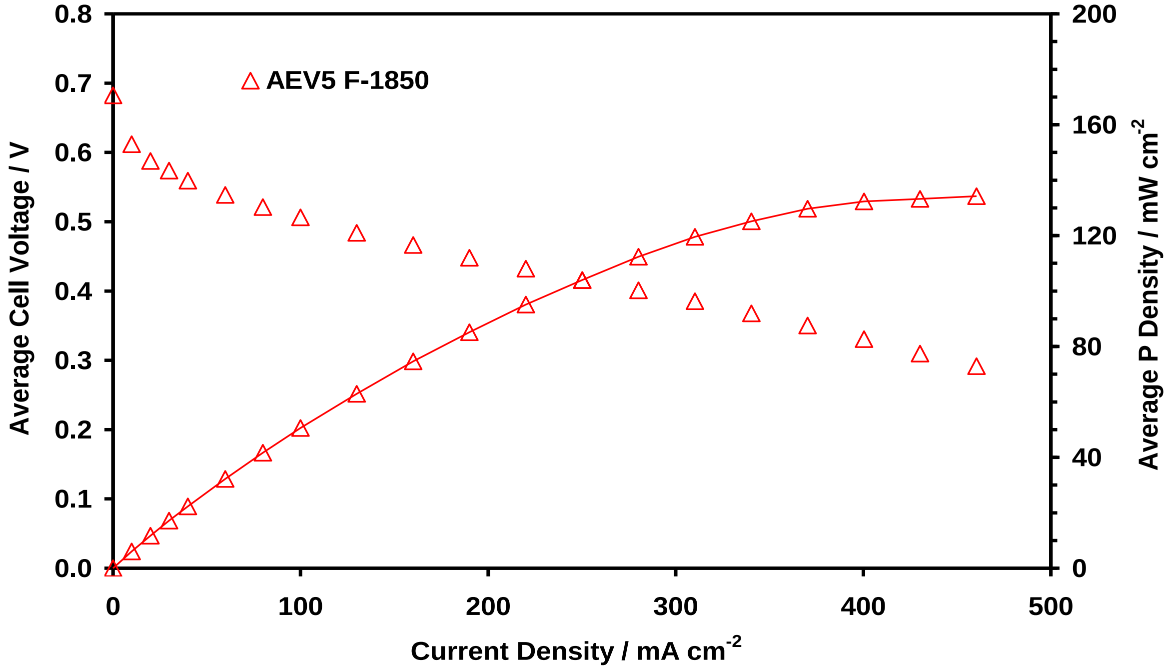


Fig. 3. Polarisation curves for the overall stack (top) and normalized cell performance (bottom). Self-heating 5-cell stack fed with 5 M methanol solution. The internal temperature reached about 75°C. Stoichiometry: λ=4 both for fuel and oxidant.

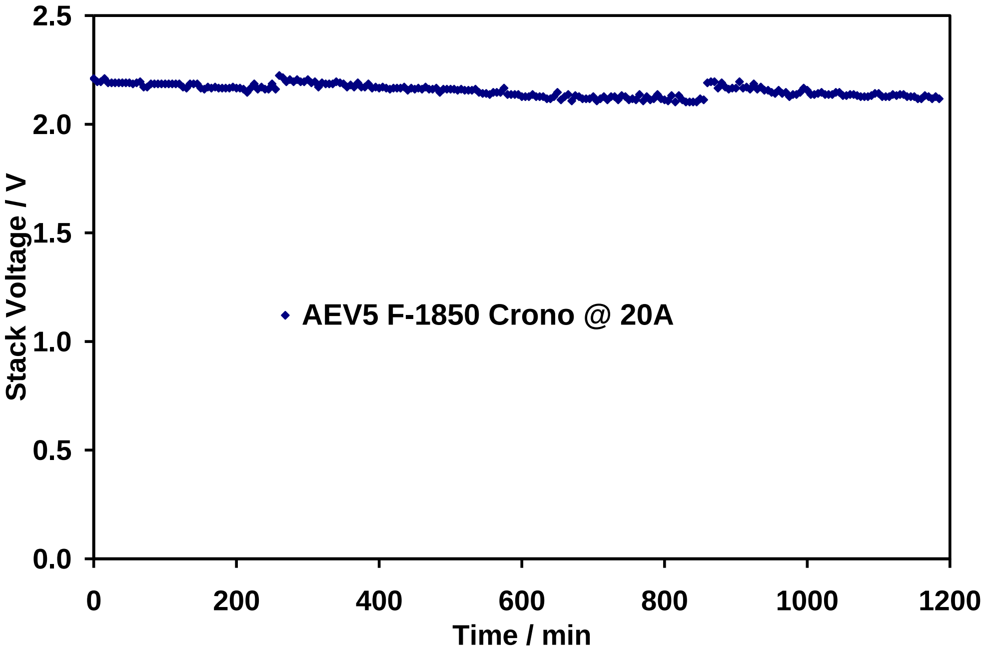


Fig. 4 Time-test at 20 A with shut-down/start-up cycles for the 5-cell stack, operating under self-heating mode (ca. 75°C) and fed with 5 M Methanol.

A short time test (about 1200 minutes) with two shut-down and start-up events (at 260 and 860 min) was carried out by imposing a constant current of 20 A (Fig. 4); the 5-cell bipolar stack delivered an averaged power of about 45 W at a mean voltage of 2.3 V. During operation, some recoverable voltage losses were registered. This was interpreted as due to an increased coverage of CO-like species at the anode surface and the cathode poisoning by methanol cross-over. These losses were almost recovered after each shut-down/start-up cycle, as reported also in the literature for systems operating for longer times [45, 46].

After the positive results obtained with the 5-cell stack, a 10-cell stack based on the same membrane was manufactured and investigated under similar operating conditions. A comparison of the polarisation behaviour of the 5-cell and 10-cell stacks, in which minimal differences were recorded, is shown in Fig. 5. The behaviour of the 10-cell stack appears even better than that based on 5 cells, in particular in the activation region. This could be explained in terms of the internal temperature of each MEA, which was slightly larger than 75°C for the 10-cell stack. The results showed that the bipolar stack is characterised by appropriate modular properties.

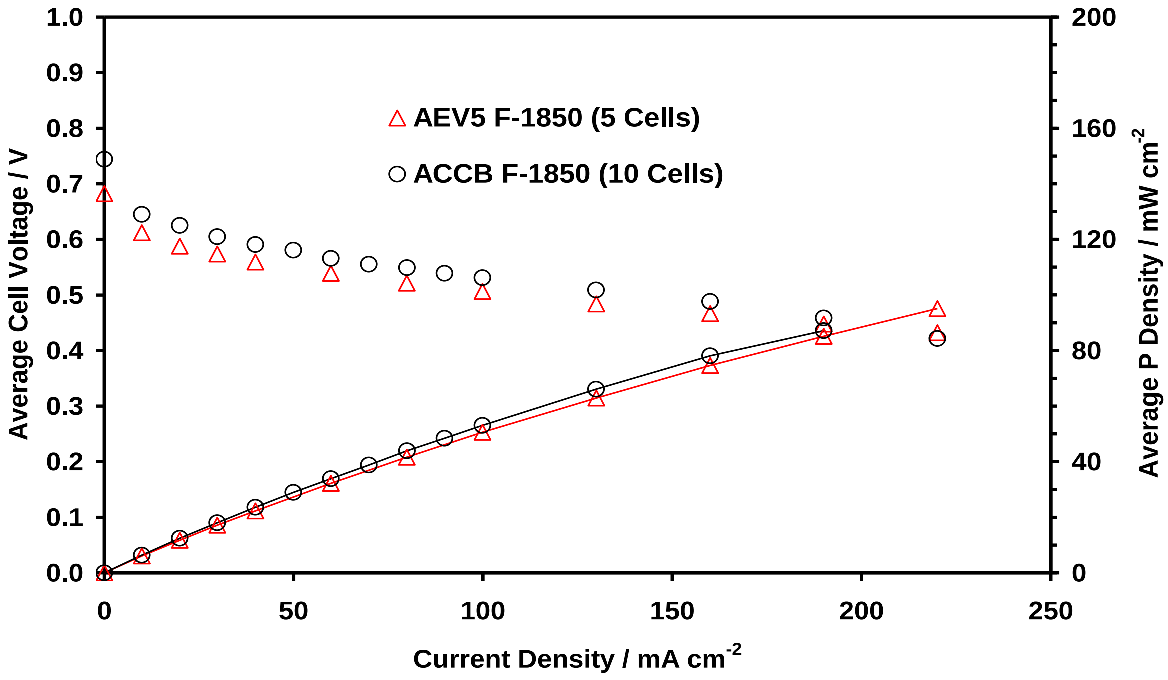


Fig. 5. Comparison between 5-cell and 10-cell stack polarisations.

4. Conclusions

A FUMATECH membrane based upon long side chain PFSA blend, with a nominal EW of 1800 g mol^{-1}, designed for low methanol crossover, was investigated in a direct methanol fuel cell and compared to a benchmark Nafion® 115 membrane. The new membrane showed lower methanol permeability resulting in an enhanced DMFC performance. MEAs based on the FUMATECH membrane were investigated in a pressurized, self-heating DMFC stack showing excellent power densities (130 mW cm^{-2}) that favourably compare to the literature reports on Nafion®-based DMFC stacks. The system also showed excellent modular properties. The FUMATECH membrane, thus, appears as a suitable alternative to Nafion® for application in DMFC stacks designed for auxiliary power units.

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