

Investigation of grafted ETFE-based polymer membranes as alternative electrolyte for direct methanol fuel cells

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Abstract

Low cost ethylene-tetrafluoroethylene (ETFE)-based grafted membranes have been prepared by a process based on electron beam irradiation, subsequent grafting, cross-linking and sulfonation procedure. Two different grafted membranes varying by their grafting and cross-linking levels have been investigated for applications in direct methanol fuel cells (DMFCs) operating between 90 and 130 °C. DMFC assemblies based on these membranes showed cell resistance and performance values comparable to Nafion 117. Stable electrochemical performance was recorded during 1 month of cycled operation. Tailoring of grafting and cross-linking properties allows a significant reduction of methanol cross-over while maintaining suitable conductivity and performance levels.

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1. Introduction

Polymer electrolyte based fuel cells, including direct methanol fuel cells, have good potentialities for a wide application in the next future as electrical power generators due to their low environmental impact [1]. The fields in which these devices may find application involve transportation, portable power sources and distributed generation of clean energy. One of the main drawbacks which has limited the market penetration of these systems is the cost of the polymer electrolyte membrane. In fact, commercially available fuel cells stacks are based on Nafion (DuPont) or similar high cost perfluorosulfonic membranes which contribute to a significant extent to the cost of the entire device. A recent technical cost analysis of polymer electrolyte fuel cells systems [2] has evidenced that the electrolyte affects significantly the cost of the fuel cell stack. Beside these aspects, application of Nafion membranes in direct methanol fuel cells is affected by significant cross-over levels which reduce the fuel efficiency of these devices. Thus, DMFCs lose part of their advantages with respect to internal combustion systems. Some technical solutions have been pro-

posed to address this latter drawback. Most of them involve modification of perfluorosulfonic membranes by addition of ceramic oxides [3–6], deposition of Pt nanoparticles inside inner polymer channels [7], coating the surface with barrier polymer [8], or deposition of sulfonated polyvinyl alcohol [9,10] etc. All these efforts have shown that it may be possible to reduce methanol cross-over but it can not be completely eliminated while maintaining high conductivity levels. Such evidences may be explained by the fact that an efficient proton transport in the temperature range from 50 to 130 °C requires suitable water contents and water transport inside the polymer electrolyte [11,12]. As methanol is highly soluble in water, its mass transport through the membrane may be eliminated only at expenses of the electrolyte conductivity. Alternatively, membranes such as phosphoric acid impregnated-polybenzimidazole (PBI) which do not need water transport to maintain high proton conductivity may constitute a valid approach [13,14]. However, these electrolytes still present significant methanol cross-over effects and suitable life-times for devices based on such membranes have not been yet demonstrated. In principle, the water uptake properties of sulfonic acid-based membranes may be modulated by selecting a proper concentration and distribution of sulfonic groups inside the polymer. Such objective is generally pursued in the preparation of grafted polymer membranes [15,16].

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A research activity has been carried out in the last decades in our laboratories to single out a cheap process to produce ion conducting electrolytes with flexible properties for application in electrodialysis. Application of the radio-chemical grafting technique to the production of DMFC membranes has been explored in the framework of the NEMECCEL European program. Depending on the particular application, the material properties may be properly tailored by varying a few parameters in the synthesis while maintaining the process characteristics and plants for large scale production. The main efforts are addressed to reduce the cost of production through a flexible preparation process and the proper selection of cheap base materials. For this purpose ETFE (ethylene-tetrafluoroethylene, C₂H₂ and C₂F₂ groups with 1/1 ratio and nearly perfect alternance) films have been selected as substrate material; the films are radio-chemically grafted with styrene and subsequently sulfonated in order to obtain sulfonic acid anchored groups. The present cost of the base irradiated ETFE material (about 25 € per square meter) favorably compares with the average industrial cost of the commercial perfluorinated sulfonic membranes (about 400 € per square meter). In order to improve the mechanical strength properties of the polymer, increase the thermal resistance and reduce the cross-over of gases or liquids (such as methanol) through it, while maintaining suitable conductivity, appropriate cross-linking is achieved during the grafting step by adding a cross-linking agent. This procedure has been optimized for this application with the main effort addressed to reduce methanol cross-over. Two membranes have been selected varying in terms of grafting degree and cross-linking. The relative characteristics of conductivity and system efficiency have been discussed and compared to Nafion. Furthermore, some aspects related to cycled system operation which are of particular interest for applications as power sources in portable and mobile systems have been investigated.

2. Experimental

2.1. Membrane preparation

Two different membranes, referred to as NEM 20 and NEM 21, varying by the degree of grafting and cross-linking have been studied. The membranes were prepared using a 100 μm ETFE film as starting material. The films were irradiated up to a dose of 80 kGy under an 1.5 MeV electron beam in the presence of air. The activated films were stored for future use.

The grafting of the membranes was performed by maintaining the irradiated films during 6 h at 75 °C in nitrogen purged styrene in which divinylbenzene (DVB) had been added as cross-linking agent. The quantity of cross-linking agent is expressed as the percentage of the volume of DVB versus the styrene volume. After grafting, the membranes have been washed until to obtain a constant weight in methanol and dried during 24 h at 80 °C to measure the grafting level (GL). The grafting level was defined as follows: $GL(\%) = [(W_g - W_i)/W_i] \times 100$, where W_i is the initial weight of the film and W_g the weight of the dry grafted film (Table 1).

Prior to the sulfonation step the membranes were swelled in dichloroethane (DCE) during 24 h. Sulfonation was made at a temperature of 23 °C in DCE, to which chlorosulfonic (CSA) acid had been added to a level of 10% by weight. Samples have been maintained in the sulfonation solution for 16 h before to be washed free of DCE in ethanol. Hydrolysis of the chlorosulfonyl groups was carried out during 16 h in a 0.5 M NaOH solution at 60 °C. The ion exchange sites were turned to the acidic form by washing the membranes with demineralized water, leaving the samples in a 1 M HCl solution for 16 h and finally washing the samples with demineralized water until no further acid was released. Five square meters of both membranes were produced at a pilot scale. Value of exchange capacity and water content were checked after final washing of the samples (Table 1). Exchange capacity was expressed in meq. per gram of dry membrane and the water content as the percentage of weight gain between the dry membrane and the weight of the same sample swelled in demineralized water at 60 °C for 16 h. In the wet form, the thickness was similar for both membranes i.e. 150 ± 10 microns. Both membranes were further purified before being tested in the DMFC by washing with acetone, rinsing with distilled water and then boiling in bi-distilled water for 24 h. Nafion 117 membrane was purchased by DuPont. Nafion membrane was purified by using a widely employed procedure reported in the literature [17].

2.2. Membrane-electrode assembly (MEA)

The catalysts for methanol oxidation and oxygen reduction were 60% Pt-Ru (1:1)/Vulcan XC 72 (E-TEK Inc.) and 30% Pt/Vulcan XC 72 (E-TEK Inc.), respectively. The physicochemical characteristics of these materials were previously investigated [18]. The reaction layers were prepared by directly mixing in an ultrasonic bath a suspension of Nafion[®] ionomer in water with the catalyst powder (catalyst/ionomer = 67/33 wt.); the obtained paste

Table 1
Physico-chemical properties of grafted Solvay membranes

Sample	Grafting level (%)	Cross-linking agent concentration	Thickness wet (μm)	Exchange capacity (meq./g)	Water content (%)
NEM 20	42	8	160 ± 5	1.88	26.0
NEM 21	31	6	150 ± 5	1.49	22.5

was spread on carbon cloth backings [18]. Pt loading was 2 mg cm^{-2} in both electrodes. The MEA was manufactured by pressing the electrodes onto the polymer membrane at 130° and 50 atm [18].

2.3. Single cell

The MEA was loaded into a single cell test fixture (Globe Tech Inc.) which was connected to an HP 6060B electronic load. Aqueous solutions of methanol, as well as humidified oxygen or air were preheated at 100°C and fed to the cell. In presence of oxygen feed at the cathode, the methanol concentration in the anode feed was 2 M, whereas, 1 M methanol was fed to the anode when air was selected for the cathode feed. The operating temperature of the cell was varied between 90 and 130°C . Cathode back pressure was fixed to 2 atm relative, whereas anode back pressure was increased from 0 to 2 atm relative as the temperature was increased from 90 to 130°C .

The methanol cross-over was determined by measuring the CO_2 content in the outlet cathode stream by an Infrared detector while cell was under operation with 1 M methanol and air feed. The liquid fraction in the cathode stream was first condensed at low temperature, whereas the gas escaping from the condenser was further purified by passing it through a magnesium perchlorate bed before being analyzed by the infrared sensor. Chromatographic analyses of the condensed liquid fraction have revealed small amounts of unreacted methanol. Accordingly, almost all methanol molecules crossing the membrane are oxidized to CO_2 at the cathode (>95%) [3]. Furthermore, the proper estimation of methanol cross-over from this measurements may be affected by the CO_2 permeation from the anode. Although CO_2 permeation through thin membranes such as Nafion 112 is significant, it

should play a minor role for the present membranes that are characterized by larger thickness and suitable cross-linking. The effects due to unreacted methanol and CO_2 permeation from the anode should compensate each other. Thus, the estimated error in the present cross-over measurements should not be larger than 5%.

3. Results and discussion

3.1. Cell resistance analysis

One of the pre-requisite of a proton conducting membrane to be used in different applications is a suitable conductivity compatible with power generation requirements of the device. At present, our main efforts are focused on the application of these proton conductors in fuel cells operating between 90 and 130°C , i.e. for application in electro-traction and in distributed power sources. However, more insights on the membrane applications could be obtained by determining the conductivity in a wide temperature range. An estimation of the membrane conductivity can be made by directly measuring the resistance of a fuel cell based on a MEA (membrane-electrode assembly) equipped with the electrolyte under investigation. The cell resistance was thus measured for MEAs based on NEM 20 and NEM 21 Solvay membranes in the range between 30 and 130°C (Fig. 1).

Two different experimental approaches were used to determine the resistance characteristics in the overall range of temperature. In the low temperature range up to 90°C an impedance bridge was used and the resistance value was determined at 1 kHz under open circuit. From 90 to 130°C , the fuel cell was normally operated and the resistance value was obtained by the current interruption method at 300 mA cm^{-2}

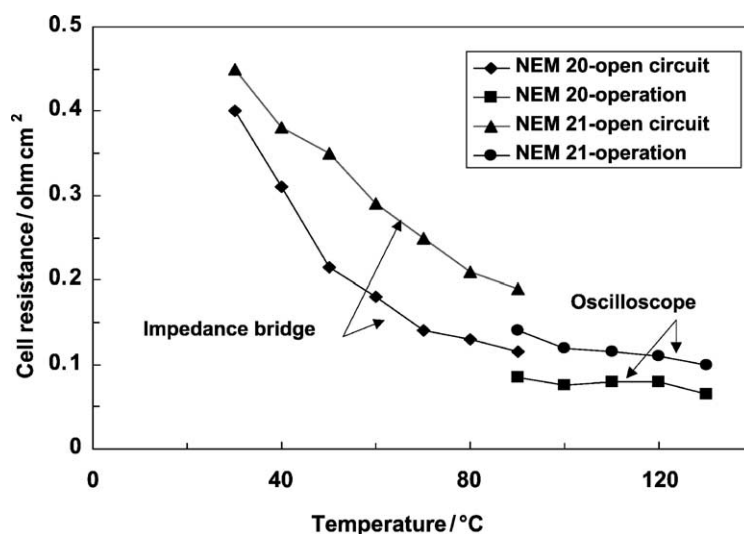


Fig. 1. Variation of cell resistance for two MEAs based on grafted Solvay membranes as a function of temperature. Cell resistance values have been monitored up to 90°C by an impedance bridge in absence of reactants. From 90 to 130°C , the cell resistance was determined under DMFC operation by the current interrupter method.

by using an oscilloscope. Since the higher the current density the cell is operated the larger is the voltage drop corresponding to a particular cell resistance, suitable current densities are needed to achieve a good signal to noise ratio. Furthermore, operation of the fuel cell above 100 °C requires the selection of high current densities to allow membrane hydration at the cathode side by the water produced in the electrochemical reaction. The selected current should be compatible with the cell polarization characteristics at different temperatures. Yet, selection of high currents is not possible at low temperatures. In these conditions, the sensitivity of the impedance bridge appears more appropriate.

An exponential decay of cell resistance is observed with increasing temperature for both NEM 20 and NEM 21 membranes with cell resistance decreasing from 0.4 to 0.45 ohm cm² at 30 °C to 0.1 to 0.05 ohm cm² at 130 °C. The cell resistance of the membrane with a low degree of grafting (NEM 21) is approximately 0.05 ohm cm² larger than the membrane with higher exchange capacity. A slightly discontinuity is recorded at 90 °C passing from the impedance bridge to the oscilloscopy-determined resistance. This effect is probably due to the in situ purification and better humidification of the electrolyte when protons co-ordinating water molecules migrate from the anode to the cathode under an applied current. Water produced at the cathode under operation also facilitates humidification of the membrane at the elevated temperatures. The recorded cell resistance values (0.4 ohm cm² at 30 °C and 0.1 ohm cm² at 130 °C) appear suitable for membrane application both in portable and mobile applications. Assuming negligible resistance values for graphite plates and carbon cloth-based electrodes, the membrane conductivity at various temperatures may be calculated. These conductivity values could be slightly under-estimated since there is always a small contribution from the contact resistance even when there is a good adhesion of electrodes to the electrolyte as in the present case, favored by the high temperature and pressure MEA fabrication process. However, it should be also considered that after cell tightening a slight reduction in the membrane thickness may occur. In effect, membrane conductivities determined at low temperatures in a classical conductivity cell using smooth Pt electrodes and a thermostated bath do not significantly deviate from those determined in the fuel cell at the same temperatures. This work focused on the investigation of the membrane properties in relation to their

practical application; thus, we have determined the conductivity in situ. The conductivity values range between about 0.03 and 0.23 S cm⁻¹ as the temperature varies from 30 to 130 °C (Table 2). The exponential decrease of cell resistance in the investigated range indicates a temperature-activated proton conduction mechanism, an Arrhenius diagram is reported in Fig. 2. An activation energy of around 0.2 eV for proton conduction is observed for both NEM 20 and NEM 21 membranes; this value is similar to that observed with commercial perfluorosulfonic membranes indicating no significant deviation from the widely accepted proton conduction mechanism of Nafion.

3.2. Single cell results

DMFC polarization curves have been recorded, between 90 and 130 °C with air-feed operation and with 1 M methanol fuel fed to the anode for both NEM 20 and NEM 21 membranes (Figs. 3 and 4). Higher power densities have been recorded especially in the high temperature range for the NEM 20 membrane, which is characterized by a higher degree of grafting; larger open circuit values have been observed for NEM 21 characterized by a lower level of grafting. All cells show significant activation control at very low current densities and mass transfer control at high current densities. Larger diffusion limiting currents have been recorded for NEM 20. The maximum power density in the case of NEM 20 varies from 0.12 W cm⁻² at 90° to 0.23 W cm⁻² at 130 °C. Similarly, at a cell voltage of 0.5 V, the current density at 130 °C (0.4 A cm⁻²) is twice that measured at 90 °C (0.2 A cm⁻²). At 0.5 V cell voltage, the polarization characteristics are mainly controlled by the ohmic resistances at all temperatures reported. Cell resistance measurements reported in Fig. 1 show a slight decrease of cell resistance from 90 to 130 °C which does not account alone for such increase in fuel cell performance. Thus, it is rationalized that, beside membrane conductivity, the activation processes of electrode reactions with temperature, especially methanol oxidation, play a significant role at these potentials. Similar evidence results from the analysis of the polarization characteristics of NEM 21. The maximum power densities increase from about 0.09 W cm⁻² at 90° to 0.17 W cm⁻² at 130 °C, whereas the current density at 0.5 V (cell voltage) increases from 0.12 A cm⁻² at 90 °C to 0.29 A cm⁻² at 130 °C. The lower performances observed for NEM 21 are

Table 2
Methanol cross-over and conductivity characteristics of DMFC MEAs based on grafted Solvay membranes

Temperature (°C)	Cross-over NEM 20 10 ⁻⁶ moles min ⁻¹ cm ⁻² @ 300 mA cm ⁻²	Cross-over NEM 21 10 ⁻⁶ moles min ⁻¹ cm ⁻² @ 300 mA cm ⁻²	Conductivity NEM 20 S cm ⁻¹	Conductivity NEM 21 S cm ⁻¹
90	5.5	2.3	0.17	0.11
100	8.3	3.5	0.20	0.125
110	10.5	4.9	0.19	0.13
120	–	–	0.20	0.14
130	12.2	6.3	0.23	0.15

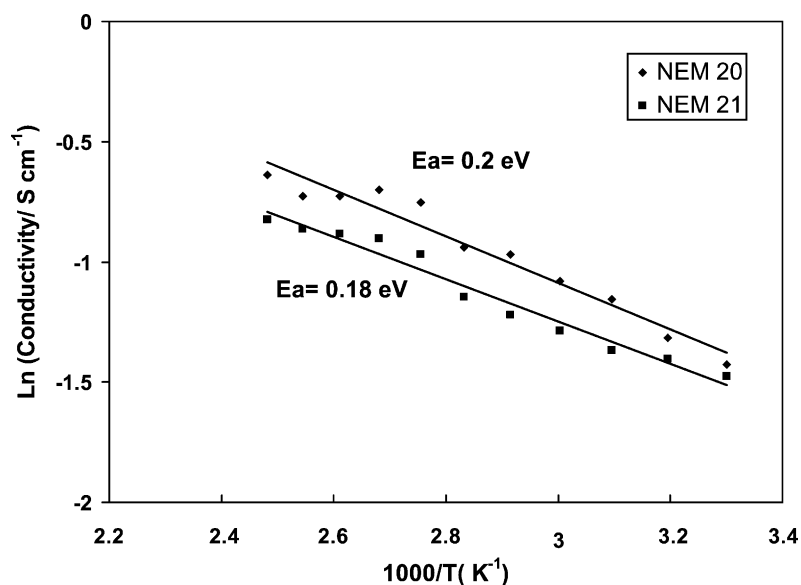


Fig. 2. Arrhenius plot of conductivity for the MEAs based on grafted Solvay membranes.

in part attributed to the lower conductivity values. As example, at 130 °C and 0.6 A cm⁻², an increase of cell resistance of 0.05 ohm cm² would result in a loss of power density of 0.03 W cm⁻². Yet, the observed difference in power density between NEM 20 and NEM 21 is almost 0.06 W cm⁻² (see Figs. 3 and 4, power density curves at 130 °C). We suggest, as speculative hypothesis, that the larger proton conduction in the NEM 20 membrane may activate the electrode reactions at the interface.

For some applications requiring high power densities (e.g. for spacecrafts), the use of pure oxygen as oxidant may be of interest. DMFC polarization and power densities in presence of oxygen feed for the membrane NEM 20 are reported in Fig. 5. A potential decay of about 0.25 V is observed in the activation controlled region at very low current densities, as in the case of air feed, indicating that the methanol oxidation reaction is largely contributing to the activation behavior. On the other hand, the significantly larger diffusion limiting current recorded in the presence of oxygen compared to the air feed would indicate that mass transfer limitations at high currents may in part derive from the low concentration of oxygen molecules close to the catalytic sites under air feed operation. Diffusion of oxygen molecules inside the cathode under cell operation is probably limited by water flooding at high currents. Beside these aspects, the lower methanol concentration (1 M) selected in the presence of air feed should also contribute to the mass transport limitations at high currents. The preferred methanol concentration for the anode feed to achieve the best electrical performance is a function of the cathode stream composition. In fact, methanol passing the membrane produces lower cathode poisoning effects in presence of oxygen than air. As speculative hypothesis, one may suggest that the chemisorption of methanol on the cathode surface is less favored (or less irreversible) in the presence of an high oxygen partial pressure. It is well

known that methanol chemisorption on the cathode surface produces a mixed potential and its consequent oxidation to CO₂ decreases the overall cell performance through such parasitic chemical reaction.

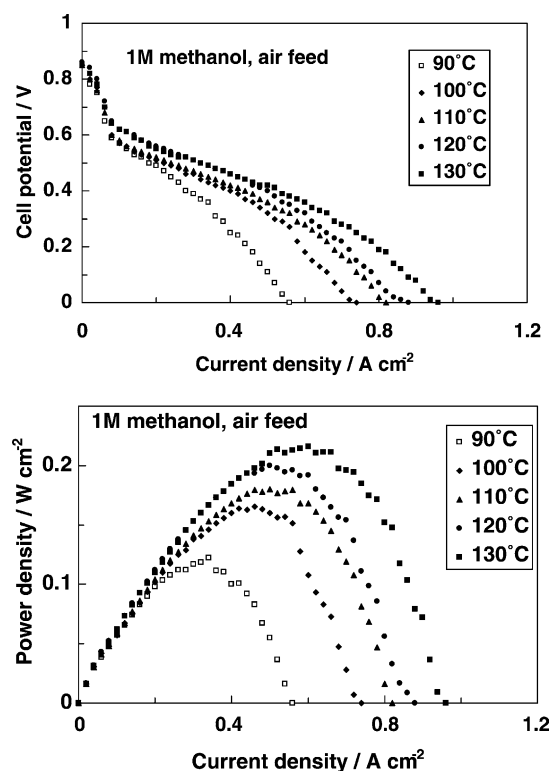


Fig. 3. DMFC polarization and power density curves at various temperatures for a MEA based on Solvay NEM 20 membrane under air feed operation. Methanol feed 1 M; methanol back pressure increasing progressively from 0 to 2 atm relative as temperature increases from 90 to 130 °C. Air pressure fixed at 2 atm relative.

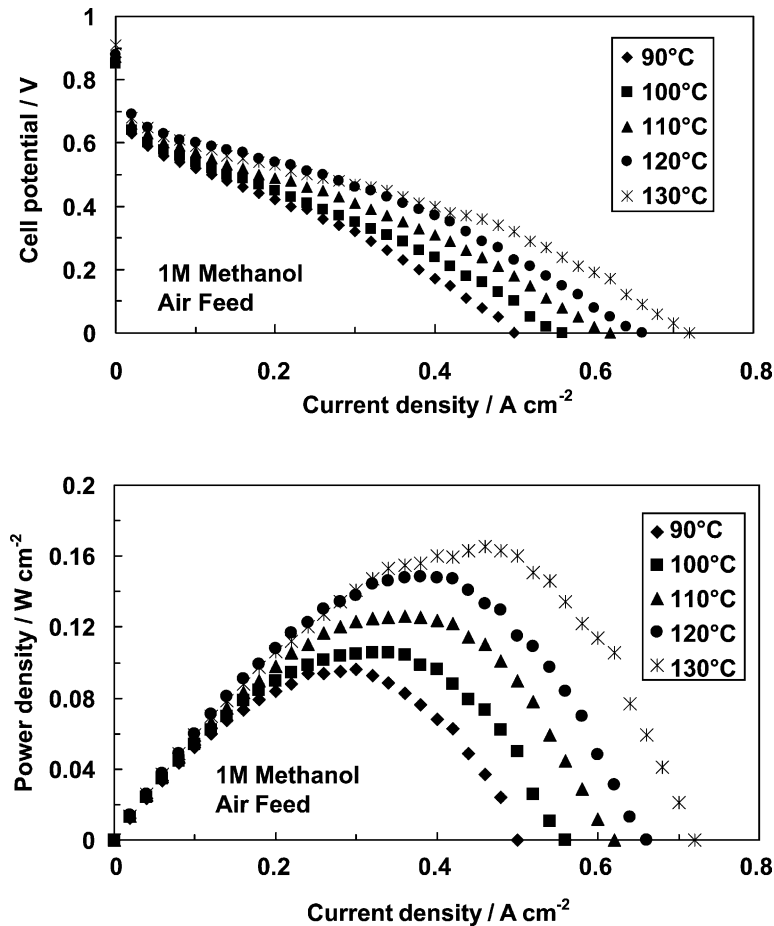


Fig. 4. DMFC polarization and power density curves at various temperatures for a MEA based on Solvay NEM 21 membrane under air feed operation. Methanol feed 1M; methanol back pressure increasing progressively from 0 to 2 atm relative as temperature increases from 90 to 130 °C. Air pressure fixed at 2 atm relative.

Using oxygen as oxidant, current density at 0.5 V and maximum power density become twice passing from 90 to 130 °C as in the case of air feed. This would also imply that the methanol oxidation is governing the activation behavior.

For application of DMFCs in electro-traction and distributed power sources, the highest operation temperature of 130 °C is more appealing since it allows to achieve high power densities with better voltage efficiencies and may reduce heat and water management constraints. A comparison of the polarization characteristics of NEM 20 and NEM 21, as well as between the most performing membrane (i.e. NEM 20) and Nafion 117 at the maximum operating temperature are reported in Figs. 6 and 7, respectively. The NEM 20 membrane shows a performance about 25% superior to the NEM 21, both in terms of maximum power density and current density at a cell voltage of 0.5 V. On the other hand, the NEM 21 membrane is characterized by 70 mV higher open circuit voltage (0.92 V versus 0.85 V) which indicates lower cross-over as it would be expected by the lower grafting level and exchange capacity. The NEM 20 has the same open circuit voltage as Nafion 117 and performance about

15% less in terms of maximum power density and current density at 0.5 V cell voltage.

3.3. Methanol cross-over

The achievement of high cell power density output is not sufficient for a successful application of a proton conducting electrolyte in electrochemical devices. Other relevant aspects beside the cost are the system efficiency and long term stability. The DMFC efficiency (excluding auxiliaries) is determined by the product of voltage efficiency by fuel efficiency; this latter is strongly related to fuel cross-over [19]. A comparison of the methanol cross-over levels measured under fuel operation at various temperatures and at a current density of 300 mA cm⁻² is reported in Table 1. It is observed that cross-over values are quite lower with NEM 21 compared to NEM 20. The latter membrane has cross-over values comparable to Nafion 117 under same conditions. Generally, beside the temperature, other experimental conditions influence the cross-over; as example, the current density determines the methanol concentration gradient at the interface and the

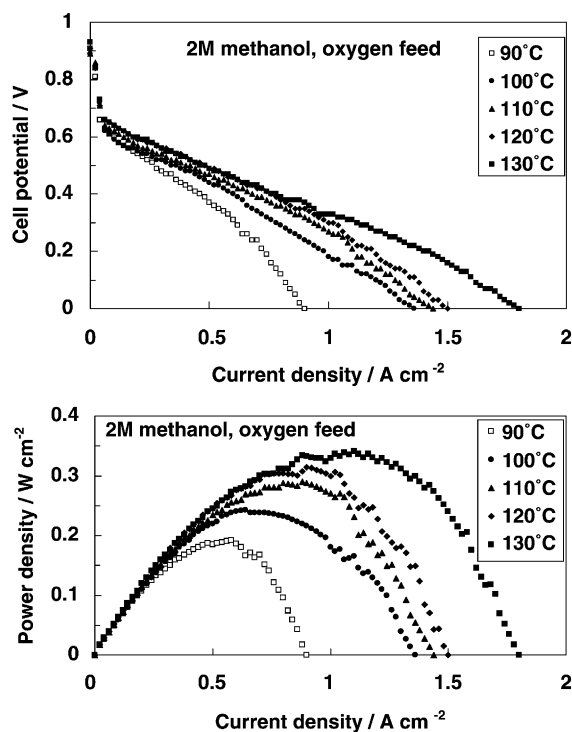


Fig. 5. DMFC polarization and power density curves at various temperatures for a MEA based on Solvay NEM 20 membrane under oxygen feed operation. Methanol feed 2M; methanol back pressure increasing progressively from 0 to 2 atm relative as temperature increases from 90 to 130 °C. Oxygen pressure fixed at 2 atm relative.

electro-osmotic drag. The cell flow fields, as well as anode and cathode pressure, influence the diffusion of methanol through the membrane. Accordingly, a proper comparison with the values reported in the literature is not always possible.

Fuel efficiencies are inversely related to the cross-over values and they are significantly higher for NEM 21 compared with NEM 20 and Nafion under the same conditions.

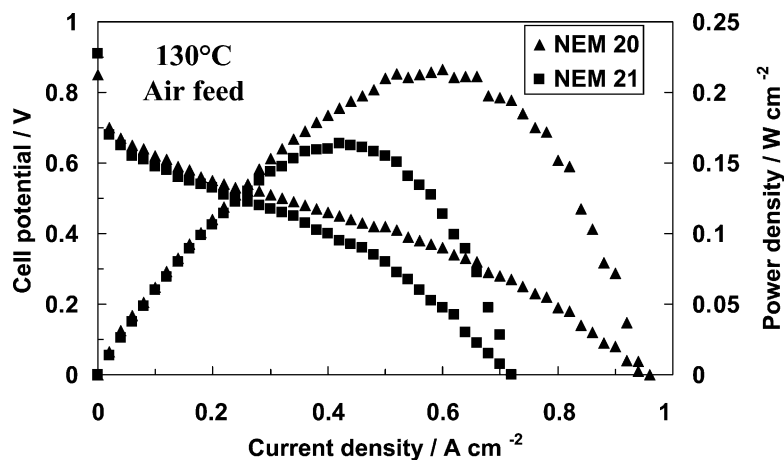


Fig. 6. Comparison of DMFC performance at 130 °C for MEAs based on Solvay NEM 20 and NEM 21 membranes under air feed operation. Operating conditions as in Fig. 3.

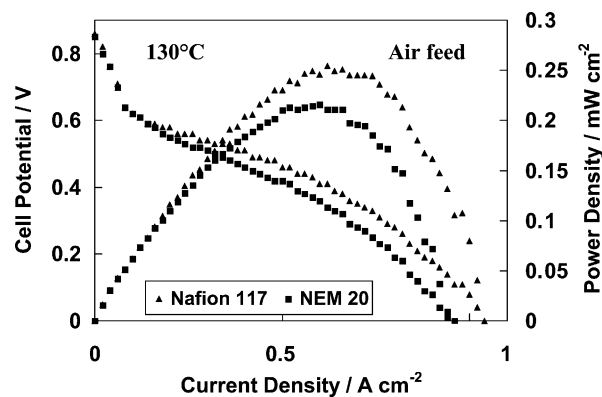


Fig. 7. Comparison of DMFC performance at 130 °C for MEAs based on Solvay NEM 20 and Nafion 117 membranes under air feed operation. Operating conditions as in Fig. 3.

3.4. Cycled operation

NEM 20 and 21 show good electrochemical and thermal stability characteristics. However, the NEM 21, characterized by a lower grafting level, showed stronger mechanical strength characteristics. Preliminary stability experiments were focused on NEM 21 due to its high fuel efficiency and optimal mechanical properties. In general, cycle-operation characteristics are of significant relevance for applications in mobile and portable systems where discontinuous operation is required. Accordingly, a M&E assembly based on MEM 21 membrane was subjected to 1 month operation with day cycles of start up during the morning and shut down in the night. In 1 month the cell was operated 20 days and about 8 h per day, including slow start up and shut down procedures. The recorded cell current density, at the cell voltage of 0.4 V, is reported in Fig. 8a and b. For such experiments, mild operating conditions were chosen, i.e. 110 °C cell temperature, 1 atm anode back pressure, 2 atm cathode back pressure. Each day after operation, the cell was discharged by feeding water at the anode before

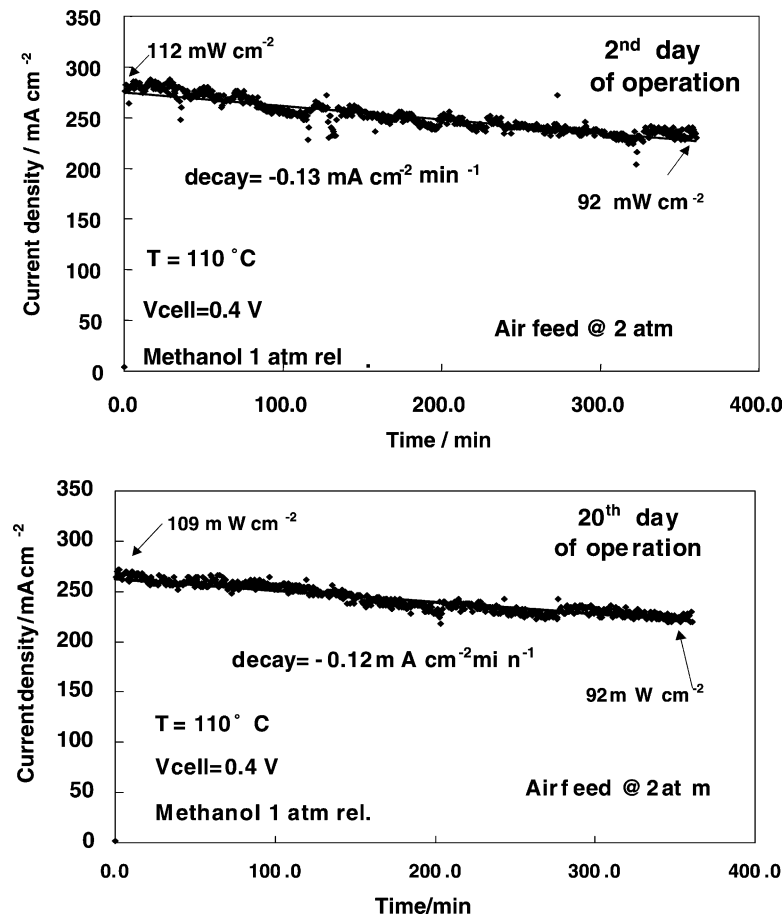


Fig. 8. Variation of DMFC current density for a MEA based on Solvay NEM 21 membrane under air feed operation as a function of time during a day operation under potentiostatic control. Cell voltage 0.4 V, temperature 110 °C, methanol 1 M, 1 atm relative; air feed 2 atm. The cell was subjected to cycled operation; the reported experiments are relative to the 2nd and 20th day of operation.

decreasing the temperature. After cell conditioning, a steady-state performance was obtained the second day of operation. The initial current density was about 0.28 A cm⁻² with a corresponding power density of 112 mW cm⁻². At the end of the day, the power density was 92 mW cm⁻² with a linear decay of performance of -0.13 mA cm⁻² min⁻¹ at 0.4 V and 110 °C. A similar behavior was recorded during the other days of operation. The cell regained the initial performance each day after the start up and showed the same decay during the day. This decay is likely to be associated to anode poisoning by methanolic residues during continuous operation. The cell discharging procedure at the end of each day, operated by feeding water at the anode, probably clears the anode catalyst surface from strongly adsorbed methanolic residues allowing the cell to regain the initial performance the next day. Specific tests were carried out on other assemblies, including Nafion membranes, with cell discharging in water after a few hours of potentiostatic operation. A regain of the initial performance was observed. Accordingly, such behavior is characteristic of the electrode reactions and not of the membrane. The experiment carried out after 20 days of cycled operation is shown in Fig. 8b. The initial performance was slightly lower (109 mW cm⁻²)

but it reached the same value of 92 mW cm⁻² at the end of the day, as in the second day experiment.

Optical microscope observation of the NEM 21-based M&E cross-section after cell dismantling showed good adhesion of electrodes to the membrane confirming the mechanical stability of the system under cycle-operation conditions. As pointed out above, these experiments were carried out under mild operating conditions; at present, no investigation of life-time characteristics and system stability under high temperature (130 °C) and high pressure conditions has been carried out. Experiments under such conditions were performed only for a few days mainly to preserve the experimental apparatus; these revealed similar characteristics but lower current density decay. Probably, the increased operation temperature enhances the anode tolerance towards the poisoning effects due to the reaction intermediates.

4. Conclusions

Low cost ETFE based membranes have been demonstrated to be a suitable alternative to Nafion or similar

commercial perfluorosulfonic membranes for application in DMFC systems. Performances and methanol cross-over values comparable to Nafion 117 have been recorded for highly sulfonated grafted membranes based on a low cost perfluorinated polymer. Tailoring of grafting and cross-linking properties of these membranes allows a significant increase in the fuel efficiency of the device by decreasing methanol cross-over, while maintaining suitable performance levels. Cycled cell operation experiments indicate good stability of the MEAs based on grafted membranes for those systems requiring discontinuous power generation.

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