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Effect of hot pressing on the performance of direct methanol fuel cells

C. SONG and P.G. PICKUP*
Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7
*(*author for correspondence, Fax: + 709 737 3702, e-mail: ppickup@mun.ca)*

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Abstract

The effects of hot pressing of electrodes onto Nafion® membranes in the preparation of membrane and electrode assemblies for direct methanol fuel cells have been investigated. Hot pressing does not significantly influence the cell resistance or methanol crossover, but it can decrease cell performance by restricting mass transport in the anode catalyst layer. It also increases the time required for the cell to reach optimum performance. Best performances were obtained with membrane and electrode assemblies that had not been pressed. It was also found that membranes that had not been subjected to hot pressing could easily be re-used, making recycling of membranes and catalysts more feasible.

1. Introduction

Direct methanol fuel cells (DMFC) have advantages over hydrogen fuel cells because methanol is easily prepared, handled and stored [1–3]. The key component of a DMFC is the membrane electrode assembly (MEA), which comprises a polymer electrolyte membrane, and catalyst coated porous electrodes for methanol oxidation (anode), and oxygen reduction (cathode). Typically, the membrane is Nafion®, or a similar perfluorosulfonic acid based polymer, the anode catalyst is a Pt–Ru alloy, the cathode catalyst is Pt black, and the electrodes are carbon fiber paper or carbon cloth. To date, three main methods have been used to prepare MEAs [4, 5]. Initially, the catalysts were mixed with a PTFE suspension, spread onto the porous carbon support (paper or cloth), and sintered to produce electrodes that were then hot pressed onto each side of the Nafion® membrane. More recently, the preferred method (decal method [6]) has been to form the catalyst layers on Teflon supports using a Nafion® containing ink and then transfer these to the membrane by hot pressing. The Teflon support is then peeled away and the catalyst coated membrane is sandwiched between the porous carbon supports. Alternatively, the catalyst ink can be painted or sprayed directly onto the membrane [4].

Hot pressing is used in most methods for the preparation of MEAs, but its effects on the properties of the MEA and its components have not been extensively studied. Wilson and Gottesfeld [4] reported that MEAs prepared by painting the catalyst onto the membrane exhibited only slightly inferior performances if they were not hot pressed. Their procedure involved painting of a catalyst ink onto a Nafion® membrane in the Na^+ form, hot pressing between Teflon plates, and subsequent treatment with acid to convert the membrane to the H^+ form. The catalyst coated membrane was then put directly into the fuel cell between two carbon paper electrodes. It now appears to be common practice to use catalyst coated membranes without hot-pressing them onto the porous carbon support [7, 8].

Although catalyst coated membranes are commonly used, catalyst coated electrodes are also still widely used, and their commercial availability makes it important that their use continues to be developed and optimized. The need for hot pressing them onto the membrane does not appear to have been questioned or investigated, although it is clearly an important issue. Avoiding the hot pressing step would have a number or advantages, including reducing equipment/processing requirements and simplifying the recycling of materials. Surprising, we have also found that it can lead to better fuel cell performance.

The temperature used for hot pressing is usually about 130 °C, slightly above the glass transition temperature of Nafion®, with pressures ranging from 2 to 350 kg cm^{-2} [9–11]. The goal of hot pressing is to provide better contact between the catalysts and the membrane. However, the high pressures that are often used can damage components of the MEA. Kuver reported that carbon cloth can be mechanically damaged by pressures exceeding 100 kg cm^{-2} [9]. Hot pressing also causes dehydration of the Nafion® membrane, which may inhibit start-up of the fuel cell and lead to an irreversible performance loss [12].

Dehydration of Nafion® membranes is a serious problem in the operation of fuel cells at elevated temperatures (>100 °C) [13]. Additionally, there may be losses of porosity and activity in the catalyst layers.

The effects of hot pressing on the performance of hydrogen fuel cells appear to be minor [4], but they may be more significant when other fuels, particularly liquid fuels such as methanol, are used. In this paper we report on the effect of hot and cold pressing on the performance of MEAs in a direct methanol fuel cell. We have found that the best performances can be achieved without employing a pressing procedure. Furthermore, the membranes of MEAs that have not been pressed can easily be reused in new MEAs, without loss of performance.

2. Experimental details

Nafion®115 membranes (DuPont) were cleaned in 10% H_2O_2(aq), 1 M H_2SO_4(aq) (1 h at 60–80 °C in each solution) and water. Anodes and cathodes consisting of 4 mg cm^{-2} Pt/Ru black and 4 mg cm^{-2} Pt black, respectively, and 15% Nafion® and 14% PTFE on Toray carbon fibre paper, were donated by the H Power Corporation. Additional cathodes with 0.4 mg cm^{-2} Pt and 0.9 mg cm^{-2} Nafion® loadings were prepared by spraying an ink containing a carbon supported Pt catalyst (20% Pt; Etek), Nafion® (5% solution; Aldrich) and isopropanol (Fisher) onto Toray carbon fiber paper with a spray gun (Paasche Airbrush Company). These electrodes were heated in an oven at 130 °C for 30 min.

2.1. *Preparation of MEAs*

The membrane and electrodes (5.3 cm^2) were placed into a brass die and pressed for 3 min at either ambient temperature or 130 °C with a Carver Laboratory Press (model M). Pressures of either 43 or 155 kg cm^{-2} were used. Half-pressed MEAs were prepared by pressing either the anode or cathode onto the membrane, with a PTFE sheet on the other side.

2.2. *Fuel cell experiments*

MEAs were evaluated in a commercial (Fuel Cell Technologies) 5.3 cm^2 active area cell fed with 1 M aqueous MeOH at 0.15 ml min^{-1} and dry air at a fixed flow rate of 75 ml min^{-1}, corresponding to stoichiometries of 1.4 mol MeOH/6 mol electrons and 3.8 mol O_2/4 mol electrons at 200 mA cm^{-2}. Experiments were conducted at 60 ± 1 °C. In some experiments the electrodes and membrane were put into the cell without prior pressing. The pressure of about 15 kg cm^{-2} ($\simeq$1.5 MPa) exerted during cell assembly was found to be sufficient to provide good contact between the electrodes and the membrane.

Polarization data were recorded using a Princeton Applied Research (PARC model 273) electrochemical analysis system after operation of the cell at 76 mA cm^{-2} until the voltage was stable (typically 30 min). The voltage at each current density was allowed to stabilize (typically about 3 min) before measurement. Cell resistances were measured as the high frequency intercept from impedance spectroscopy (100 kHz–100 mHz; 10 mV a.c. amplitude) at the open circuit potential. High frequency resistances were not significantly different when measured with the cell under load.

Methanol crossover was measured by using a steady state electrochemical method similar to that described by Ren et al. [14]. The cathode compartment of the fuel cell was flushed with nitrogen to remove O_2, and the fuel cell cathode (now the anode in the experiment) was set at a potential of 0.7 V relative to the fuel cell anode (containing aqueous methanol; and now acting as a dynamic hydrogen electrode) for 50 s to oxidize methanol that had accumulate within the cathode. The potential was stepped to 0.9 V for 100 s, and then to 0.8 V for 100 s. The steady state currents at these potentials were always very close, confirming that they represent the limiting current. Their average was taken as the methanol crossover current, which is proportional to the flux of methanol across the membrane. A correction for electroosmotic drag was not applied.

2.3. *Recycling of Nafion® membranes*

When the fuel cell was disassembled, the electrodes could easily be separated from the membrane if they had not been pressed onto it prior to cell assembly. However, some of the catalyst always remained on the membrane. In order to reuse the membrane, the remaining catalyst was removed chemically by heating in a 1:1 mixture of concentrated HCl and HNO_3 for 15 min and/or physically by scrapping with a scalpel. Usually, a combination of both treatments was used, followed by heating of the membrane in 1 M H_2SO_4(aq) for 1 h, boiling in deionized water for 1 h, and storage in deionized water overnight before use.

3. Results

3.1. *Effect of hot pressing on optimum performance*

Figure 1 compares the optimum performances (attained after 1 to 3 days in the cell; see below) of two hot pressed MEAs with that of an MEA that was not pressed. Maximum power densities, cell resistances, and methanol crossover currents for these MEAs are reported in Table 1. The performance of the MEA that was hot pressed at 155 kg cm^{-2} ($\simeq$15.5 MPa) (MEA a) was much worse than that of the MEA that was not pressed (MEA c). However, the MEA pressed at a lower pressure of 43 kg cm^{-2} (MEA b) exhibited similar performance to that of the unpressed MEA. Methanol crossover currents were similar for all three MEAs, but

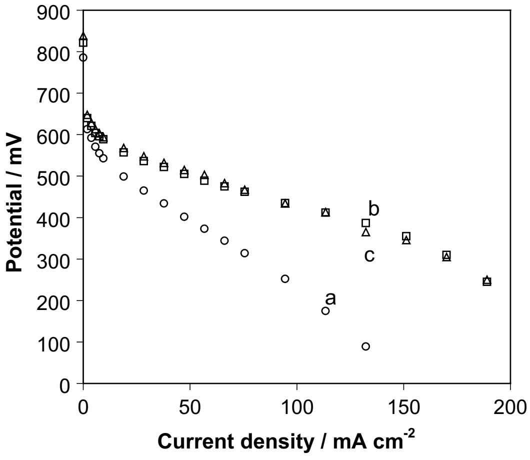

Fig. 1. Polarization curves for DMFCs with hot pressed (3 min at 130 °C and 155 kg cm^{-2} (○) or ; 43 kg cm^{-2} (□)) and unpressed (△) MEAs with cathodes containing 4 mg cm^{-2} Pt black.

the MEA pressed at 155 kg cm^{-2} ($\simeq$15.4 MPa) gave a significantly higher cell resistance than the others. However, although the differences between curve (a) and curves (b) and (c) in Figure 1 appear to be ohmic, the resistance difference of 0.017 Ω between the MEAs accounts for only a 9 mV difference in cell potential at 100 mA cm^{-2}, and so does not explain the large performance differences (e.g., 200 mV at 100 mA cm^{-2}). Clearly, the differences must be due primarily to changes in the rates of mass and/or ion transport processes in the electrodes, which also result in differences in the slopes of polarization curves [15].

The differences in performance illustrated in Figure 1 are typical of results obtained in a number of other experiments, and with a variety of different cathodes. Data for MEAs with low loading cathodes prepared with a carbon supported catalyst are included in Table 1. Again, hot pressing at 155 kg cm^{-2} ($\simeq$15.5 MPa) produced a large decrease in performance, but did not significantly influence crossover or ohmic losses.

In another experiment (entry 8 in Table 1) an MEA was pressed at 155 kg cm^{-2} and ambient temperature (∼22 °C). Its performance was also significantly inferior to that of an unpressed MEA, confirming that the pressing pressure is the main parameter influencing cell performance.

3.2. *Activation of DMFCs*

Further insight into to effects of hot pressing can be obtained by looking at the time dependence of the cell performance. It was found that the performances of all MEAs used in this work improved with time over the first few days of experimentation. The polarization curves shown in Figure 2 illustrate this for an MEA hot pressed at 43 kg cm^{-2}(4.3 MPa). The performance, resistance and crossover of the cell was evaluated on three consecutive days, with the cell operating for about 2–4 h each day. Table 2 summarizes the properties of the cell at different times. The performance of the cell improved considerably over the first two days, and then showed no significant further improvement. The resistance of the cell decreased slightly during this period, and methanol crossover increased, suggesting that the membrane only slowly reached full hydration. However, these minor changes can not explain the large changes in cell performance.

The greatest increases in performance observed in this experiment occurred when the cell was left overnight at ambient temperature with 1 M methanol in the anode compartment. Shutdown and restarting of the cell on day two did not improved its performance greatly (20 and 24 h curves in Figure 2), while overnight shutdown did (44 h curve).

A similar MEA that had not been hot pressed reached optimum performance much more quickly (Figure 3 and Table 2), indicating that hot pressing greatly increases the time required for 'activation' of an MEA.

In addition to the different rates of activation observed for pressed and unpressed MEAs, there is also a significant difference in the nature of the changes in the polarization curve. The polarization curves for the unpressed MEA (Figure 3) are approximately parallel,

Table 1. Summary of the properties of MEAs discussed in this paper

Description	Cathode Pt /mg cm^{-2}	Pressure /kg cm^{-2}	Peak power /mW cm^{-2}	Crossover /mA cm^{-2}	Resistance/Ω
a	4	155	24	91	0.048
b	4	43	54	96	0.033
c	4	not pressed	52	91	0.031
d	0.4	155	21	94	0.038
e	0.4	not pressed	38	96	0.036
Pressed anode	4	155	47	91	0.034
Pressed cathode	4	155	47	105	0.031
Cold pressed	4	155	33	100	NM
Recycled Nafion® (mechanically cleaned)	4	not pressed	54	103	0.034
Recycled Nafion® (acid and mechanical cleaning)	4	not pressed	57	106	0.031

NM = not measured.

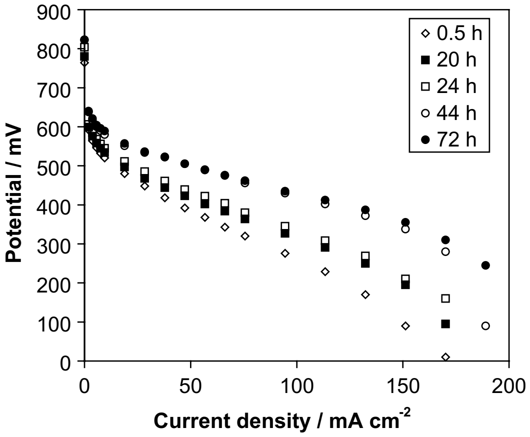

Fig. 2. Polarization curves at different times for a DMFC with a hot pressed (3 min at 130 °C and 43 kg cm^{-2}) MEA (MEA b). The cell was operated for 2–4 h each day, with MeOH(aq) left in the anode compartment at ambient temperature when the cell was not operating.

Table 2. Activation of MEA b (hot pressed at 43 kg cm^{-2}) and MEA c (not pressed)

	Time/h	Resistance/Ω	Crossover/mA cm^{-2}
MEA b	0.5	NM	NM
	24	0.041	83
	44	0.038	97
	72	0.033	96
MEA c	0.5	0.037	93
	20	0.031	91

NM = not measured.

indicating that activation mainly involved an increase in the exchange current (electrochemical kinetics). In contrast, the polarization curves for the pressed MEA (Figure 2) also show an increase in slope indicating that there were changes in the rates of mass and/or ion transport processes [15].

3.3. *Half pressed MEAs*

To investigate the effects of hot pressing on the individual electrodes, MEAs were prepared in which only one of the electrodes was hot pressed onto the membrane. The other electrode was put in place during cell assembly. Figure 4 shows polarization curves for two such 'half-pressed' MEAs; further details are included in Table 1. The two half pressed MEAs exhibited almost the same performances, and both were slightly inferior to a similar MEA that had not been pressed. Both showed normal resistances and crossover currents. It is clear from these results, that the poor performances of MEAs in which both electrodes are pressed at 155 kg cm^{-2} ($\simeq$15.5 MPa) is due to a combination of effects at both electrodes, and that these effects can be more than additive.

Although the two half-pressed MEAs discussed above exhibited similar performances, their activation rates were significantly different. The MEA in which the cathode was pressed, but the anode was not, showed activation behavior similar to that of an MEA that had not been pressed (cf. Figure 3). It reached optimum performance in just one day, without a significant change in the slope of the linear region of the polarization curve. In contrast, the MEA prepared with a hot pressed anode, and unpressed cathode, behaved like a fully pressed MEA (cf. Figure 2), exhibiting slower activation and a decrease in the slope of the polarization curve.

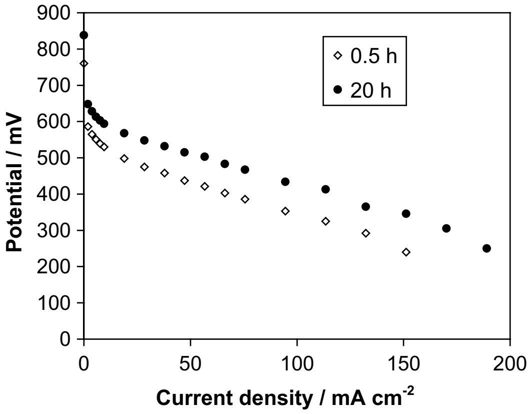

Fig. 3. Polarization curves at different times for a DMFC with an MEA that was not pressed (MEA c). The cell was operated for 2–4 h each day, with MeOH(aq) left in the anode compartment at ambient temperature when the cell was not operating.

3.4. *Recycling of Nafion® membranes*

Nafion® is expensive and hazardous as a waste material. It will have to be recycled when fuel cells reach widespread commercialization. Membranes coated with catalyst during manufacturing and membranes from hot pressed MEAs will be very difficult to recycle because it will be very difficult to remove the old catalyst. They will probably have to be dissolved and recast, which will be

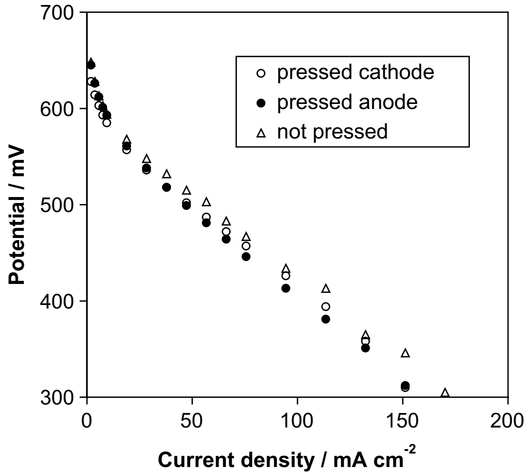

Fig. 4. Polarization curves for DMFCs with MEAs containing a hot pressed (3 min at 130 °C and 155 kg cm^{-2}) cathode and unpressed anode (○), a hot pressed anode and unpressed cathode (●), and with an unpressed MEA (△).

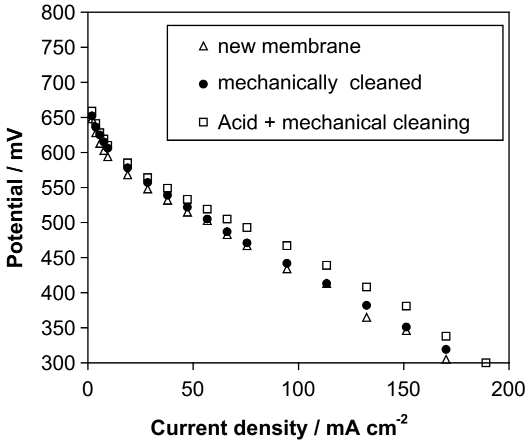

Fig. 5. Polarization curves for DMFCs with new (△) and recycled (●, □) membranes. MEAs were not pressed.

expensive and environmentally unfriendly, as well as likely to result in an inferior recycled product.

MEAs prepared from catalyst coated electrodes that are not hot pressed onto the membrane offer better potential for recycling. The re-use of such membranes is demonstrated in Figure 5, which shows the performance of the two MEAs (not pressed) containing recycled Nafion® membranes. One was re-used following removal of adherent catalyst by gently scraping with a scalpel; the other was treated with boiling acid (see experimental section) before mechanical cleaning in this way.

The performance of the recycled membranes was slightly better than for a new membrane, although the differences are perhaps not statistically significant. The acid washed membrane gave a particularly good performance. The resistances of the recycled membranes were similar to those of new membranes (Table 1). Methanol crossover currents were slightly high, but appear to be within the range obtained with new membranes (Table 1). The activation of MEAs containing recycled membranes (not pressed) was similar in rate and character to that of similar MEAs containing new membranes.

4. Discussion

The results presented in Figures 1–4 and Table 1 clearly show that pressing of electrodes onto Nafion® membranes has a detrimental effect upon their performance. Part of this effect is recoverable, and results only in increased activation times (e.g., Figure 2) while part is often permanent. Hot pressing degrades the performance of the anode more than that of the cathode, at least over the first few days of cell operation.

The resistance and crossover results presented in Table 1 do not reveal any differences that are large enough to explain the observed differences in cell performance. This rules out significant effects due to changes in the membrane, and leaves ion transport in the catalyst layers and mass transport as the only possible explanations. Since compression of the electrodes would be expected to reduce pore volume, their ionic conductivity would be expected to increase while their mass transport rates would decrease. Compression of the carbon paper would also be expected to decrease its porosity and mass transport rates. Since the diffusion of methanol in water is much slower than that of oxygen in air, these reductions in porosity would influence the anode more than the cathode, consistent with the experimental results. Theoretically, restricted mass transport in the anode catalyst layer would lead to an increased slope in the polarization curve [15], and this is what is observed experimentally (Figures 1 and 2). In contrast, restricted mass transport in the carbon paper backing would produce a limiting current, which is not observed. The much higher porosity of the carbon paper relative to the catalyst layer also makes a significant effect due to restricted mass transport in the carbon paper unlikely.

The final points that need to be addressed are the effects of activation of the MEA and some apparent inconsistencies in the results for pressed MEAs. In particular, why did the MEA pressed at 43 kg cm^{-2} (4.3 MPa) exhibit slow activation (Figure 2), but eventually reached the same performance as an MEA that had not been pressed (Figure 1)? Why was the performance degradation observed for the MEA hot presssed at 155 kg cm^{-2} (15.4 MPa) (Figure 1) so much larger than the degradation observed for either of the half-pressed MEAs (Figure 4)?

The conditioning or activation of methanol and other fuel cells has been discussed by several authors [16, 17]. Dinh et al. [16] activated the anode catalyst by operating the fuel cell with H_2/air before running with methanol. This causes the reduction of Ru and Pt oxides in the catalyst layer [16], resulting in better alloying and better activity for methanol oxidation. It has been suggested that similar processes occur during operation of a DMFC [16] and this would explain the activation of unpressed MEAs (e.g., Figure 3), which primarily involves an increase in catalyst activity.

Ha et al. [17] reported the activation of formic acid cells by conditioning with methanol. Although the reasons are not clear, they appear to be related to changes in the pore structure of the anode due to the flow of current and the formation of CO_2 bubbles. It is likely that similar changes occur within the anodes used in this work, and this would explain the activation behavior of the pressed MEAs, which presumably have less porous anodes than unpressed MEAs. Anodes pressed at 155 kg cm^{-2} (15.5 MPa) appear to be too compressed to recover sufficient porosity for optimum DMFC operation, while those pressed at 43 kg cm^{-2} (4.3 MPa) can recover sufficiently.

The rate and effectiveness of anode activation will depend on the current and anode potential during conditioning. Poor cathode performance can limit the current, and/or raise the anode potential, both of which may limit anode activation. This may explain why hot pressing of both the anode and the cathode has a much greater effect than hot pressing just one electrode. The very poor initial performance of the cell does not allow it to activate effectively. It may also result in irreversible damage due to excessive heat generation and dehydration of the cathode catalyst layer.

5. Conclusions

The most important finding of this work is that catalyst coated carbon fibre electrodes do not need to be hot pressed onto Nafion® membranes to achieve optimum performance in a DMFC. This simplifies the manufacturing of membrane and electrode assemblies and makes recycling of membranes and catalysts more feasible.

It has also been observed that pressing of electrodes onto Nafion® membranes generally decreases their performance, particularly at start-up. Elevated temperature (130 °C) and higher pressures (155 kg cm^{-2} vs 43 kg cm^{-2}) exacerbate these performance losses, which appear to be due mainly to the collapsing of pores within the catalyst layers. The lower diffusion coefficient of methanol in water relative to that of oxygen in air means that performance losses are greater for the anode than the cathode.

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