Contents lists available at ScienceDirect

## Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Nafion<sup>®</sup> nanofibers and their effect on polymer electrolyte membrane fuel cell performance

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#### ARTICLE INFO

Article history: Received 9 September 2008 Received in revised form 7 October 2008 Accepted 8 October 2008 Available online 21 October 2008

*Keywords:* Fuel cells Nanofibers Catalyst layer Triple phase boundary

1. Introduction

#### ABSTRACT

Current fuel cell research is focused on reducing manufacturing costs by reducing platinum catalyst loading without sacrificing performance. Although improvements have been demonstrated by using platinum supported on porous carbon nanoparticles, significant losses in "active" platinum surface area within the catalyst layer (CL) still occur. Optimizing the reactant gas/Nafion<sup>®</sup>/platinum triple phase boundary (TPB) in the CL (i.e., CL morphology) will result in increased "active" catalyst area and overall fuel cell performance. In this study, the effect of temperature on the formation of Nafion<sup>®</sup> nanofibers in the CL during fuel cell operation and its subsequent improvement on fuel cell performance was clearly characterized. *Post mortem* scanning electron micrographs clearly show that Nafion<sup>®</sup> nanofibers improve the TPB, where Nafion<sup>®</sup> nanofibers act as a more efficient proton transport route from the catalyst particles to the polymer electrolyte membrane reducing ohmic and mass transport resistance.

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Research on both the applications and optimization of proton exchange membrane fuel cells (PEMFC) has received exponentially increasing interest in recent years. The potential for fuel cells to provide portable, high density, and emissions free power make them attractive. However, at present, the cost of fuel cell systems limits their commercial production. A significant portion of the cost can be attributed to the anode and cathode catalyst. The first high power density fuel cells incorporated electrodes containing large platinum (Pt) loadings approaching 4 mg<sub>Pt</sub> cm<sup>-2</sup>. The initial breakthrough leading to a 10-fold decrease in Pt loading with no loss in performance was achieved by impregnating the catalyst layer with Nafion<sup>®</sup> ionomer; effectively increasing the contact between the catalyst and proton conducting medium [1]. Low loading was achieved through this technique due to enhancement of the triple phase boundary (TPB) contact. The TPB is the point at which the catalytic and electron conducting sites, reactant gases, and proton conducting polymer meet and it is the optimization of the TPB that allows efficient utilization of a larger percentage of the Pt present in the catalyst layer (CL). Further decreases in required Pt loading were achieved through the dispersion of Pt nanoparticles on high surface area carbon supports (Pt/C), which is still the state-of-theart catalyst/support structure used today [2]. By using a Nafion<sup>®</sup>

ionomer/suspended Pt/C solution in a water/2-propanol solvent, thin-film CLs were fabricated with enhanced TPB contact enabling loadings as low as 0.13 mg<sub>Pt</sub> cm<sup>-2</sup> to be used [3]. The use of Nafion<sup>®</sup> as a binder in the catalyst layer not only enhances proton transport from the catalyst particles to the PEM, but also enhances adhesion between the CL and the PEM, minimizing interfacial resistance. The importance of the TPB is exemplified by the delicate balance that must be attained between ionomer content and catalyst/support within the CL. At low ionomer loading, reactant gas diffusion is sufficient, but catalyst utilization is low due to poor ionic conduction from lack of ionomer/catalyst contact. At high ionomer loading, gas diffusion to reactant sites is limited, and Pt/C particles are separated to a degree which limits the electrical conductivity of the CL. Optimization of the CL morphology through adjustment of the Nafion<sup>®</sup> content has resulted in significant performance enhancements alluding to the role played by CL morphology and the TPB in PEMFC operation [4-8].

Enhancements in catalyst utilization, as well as, specific and mass activity can also be achieved through optimization of the dispersion of Pt on the porous carbon catalyst support. Specifically, decreasing the Pt nanoparticle size will increase active surface area with a lower overall mass of catalyst leading to lower loadings in the PEMFC [9]. There are, however, limitations to the performance enhancements achieved by decreasing Pt particle size as a method for increasing the active Pt surface area. The oxygen reduction reaction (ORR) on Pt decorated carbon particles has been given significant attention, and the general consensus is that specific activity for the ORR decreases with decreasing particle size





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beginning at particle diameters of approximately 5 nm [10-12]. The origin of the specific activity loss with decreasing particle size, however, is still under debate. Watanabe et al. have proposed that the ORR activity does not necessarily depend on the size of the crystallites, but on the intercrystallite distance, the ideal distance being approximately 20 nm [13]. The Pt particle size effect has also been attributed to geometric factors associated with the distribution of crystal facets on the particle surface. ORR studies of Pt surfaces in H<sub>2</sub>SO<sub>4</sub> have determined the general activity trend for Pt crystal faces to be (110)>(100)>(111)[14]. Modeling and experimental studies have shown that the fraction of the Pt particle surface in the (111) orientation grows rapidly as the particle size decreases below 5 nm [11]. Eventually the surface becomes saturated with the least active crystallographic face resulting in a decrease in ORR activity with decreasing Pt particle size. Liquid electrolyte studies have shown that the surface oxidation potential of Pt shifts to lower potentials with decreasing particle size. The reason being that smaller particles have a higher proportion of lower coordinated sites allowing more facile adsorption of OH<sup>-</sup> species, which can act to block adsorption of oxygen, decreasing the activity of the surface for ORR [12]. The interaction of Pt with oxygen can also be changed due to an increase in the binding energy of Pt with oxygen as the particle size decreases, limiting the rate of oxygen radical desorption and consequently the overall ORR rate [10].

Aside from the limitations associated with ORR activity loss with decreasing Pt particle size, the Pt/C catalysts are also susceptible to active area loss through both coalescence of Pt nanoparticles on the surface of the supports and agglomeration of the Pt/C particles themselves into clusters ranging in size from several hundred nanometers to several microns. Due to the acidic environment of the PEMFC CL and the relatively weak physisorption of Pt nanoparticles on the carbon support, there exists a high diffusion coefficient for the Pt particles, which increases with decreasing particle size [15]. This enhanced rate of diffusion leads to coalescence or agglomeration of Pt nanoparticles resulting in an overall decrease in the surface area of catalytically active Pt. A source of greater active area loss is the physical agglomeration of Pt/C catalyst particles in the PEMFC CL, which significantly lowers the Pt utilization percentage. The agglomeration of particles results in a distribution of pores sizes that can be categorized as one of two types: primary pores, which include the space between the aggregated catalyst particles and secondary pores, which are the larger pores between the aggregates [16]. Transport of both gas to the Pt surface within the primary pores and protons from the primary pores to the PEM is severely limited effectively rendering the Pt within the aggregates inactive. Thin-film CLs created using a dispersion of Pt/C in a Nafion<sup>®</sup>/2-propanol/water solution are susceptible to catalyst agglomeration, where Pt usage percentages as low as 45% have been experimentally measured [5]. That is more than half of the Pt in the CL that is unavailable and will not participate in the hydrogen oxidation and oxygen reduction reactions. By reducing Pt/C particle agglomeration, one could potentially obtain much higher Pt usage percentages.

While there is currently a concerted effort to decrease the Pt loading required to reach a desired power density in PEMFCs, there is only limited research focused on reducing catalyst particle agglomeration through optimization of the CL morphology, specifically the TPB [6,7]. CL morphology is sensitive to many steps in the membrane electrode assembly (MEA) fabrication process, including catalyst ink composition and dispersion, thin-film formation and method of CL transfer. Aside from the catalyst enhancements gained by decreasing Pt/C particle agglomeration, optimization of the CL morphology can lead to a decrease in transport resistances, which will directly result in an increase in PEMFC performance. More intimate contact between Nafion<sup>®</sup> and Pt/C will make proton transport from Pt to the PEM more efficient, increasing the conductivity of the catalyst layer [17]. A better distribution of porosity will limit reactant gas diffusion resistances and ensure that a large percentage of Pt can make contact with the reactant gases. An optimized dispersion of Pt/C particles will also decrease the electrical resistance of the CL allowing better transport of electrons from the Pt to the electrodes and vice versa. Limiting transport resistances will result in a direct performance improvement by decreasing of overpotential for both the cathodic and anodic reactions.

The research presented in this work provides evidence of the performance enhancements that can be gained through optimization of the CL morphology allowing improved transport of reactant gases, protons and electrons. Hronec [18] revealed through post mortem SEM and EDAX that during operation of a PEMFC, Nafion® nanofibers formed within the CL initiating a morphology change which had a direct impact on fuel cell performance. In this study, using an experimental approach, we propose a mechanism for the formation of these nanofibers and show that while the main driving force is temperature, pressure and temperature have a combinatorial effect leading to high numbers of small diameter nanofibers. Through MEA pretreatment experiments, we identify the onset temperature at which these fibers begin to form and demonstrate the significant increase in current density in the mass transport dominated region of the polarization curve caused by the formation of these fibers.

#### 2. Experimental

#### 2.1. Materials

De-ionized water, 2-propanol 99.5% (Aldrich, CAS: 67-63-0), 5 wt.% Nafion<sup>®</sup> in water/2-propanol solution (Ion Power), and 20 wt.% Pt on carbon catalyst (Vulcan XC-72, ETEK) were used to formulate the catalyst ink. Prior to construction of the MEA, the Nafion<sup>®</sup> 117 membrane (Dupont; Aldrich, CAS: 31175-20-9), 0.178 mm in thickness, was purified with hydrogen peroxide 3% (Aldrich, CAS: 7722-84-1), de-ionized water with a resistivity of 18 M $\Omega$ -cm, and sulfuric acid 99.999% (Aldrich, CAS: 7664-93-9). Teflon<sup>®</sup>-coated decals (CS Hyde) were used to transfer the CL to the Nafion<sup>®</sup> membrane. ELAT gas diffusion layers (ETEK), singlesided (A-6 ELAT/SS/NC/V2.1 ELAT (R) V2.1) and double-sided (A-7 ELAT/DS/NC/V2.1 ELAT (R) V2.1) woven carbon cloth, with a microporous coating and a 0.381 mm (15 mil) thick virgin PTFE Teflon<sup>®</sup> (McMaster Carr) gasket were also used in the MEA.

#### 2.2. Membrane electrode assembly (MEA)

Membrane electrode assemblies (MEAs) were fabricated through a decal/hot press technique. Each MEA was composed of a Nafion<sup>®</sup> 117 membrane, a catalyst layer composed of platinum supported on carbon (Pt/C) particles in a Nafion<sup>®</sup> polymer network, and single and double-sided gas diffusion layers (GDLs). The CL was formed from a catalyst ink composed of three components: Pt/C particles, 5 wt.% Nafion® ionomer solution, and a water/2-propanol solvent. Preparation of the ink begins by mixing a specified amount of a 3:1 (v/v ratio) 2-propanol and water solution. This solvent was then mixed with Pt/C particles to make a 5 wt.% particle solution. The catalyst particles were dispersed in the solution using an ultrasonicator (sonicating bath; Cole-Parmer 8890) for 20 min at 30 °C. The next step was the addition of Nafion<sup>®</sup> ionomer. Studies have shown that optimal fuel cell performance was obtained with a CL containing 33 wt.% by solid weight Nafion® [19]. Nafion® ionomer solution was added to the mixture of Pt/C and water/2-propanol

1.20

1.00

in a 3:1 (w/w ratio) of Pt/C and Nafion<sup>®</sup>. The dispersion was again mixed by ultrasonication for 20 min at 30 °C.

Teflon<sup>®</sup>-coated fiberglass decals were cut to a size equal to that of the desired MEA active area, which is the area that will participate in the oxidation and reduction reactions; 5 cm<sup>2</sup> was used for all of the tests conducted within this study. The catalyst ink was then hand painted onto the decals, allowing each individual layer to dry before applying the subsequent layer. This process was repeated until the desired catalyst loading of 0.5  $\mathrm{mg}_{\mathrm{Pt}}\,\mathrm{cm}^{-2}$  was achieved.

The Nafion<sup>®</sup> 117 membranes were purified after they were received. Membrane purification consisted of a three step process in which Nafion® was refluxed in 3 wt.% hydrogen peroxide, deionized water, and 1 M sulfuric acid. Each step was 1 h in duration, followed by washing with de-ionized water before the next reflux stage. The purified membranes were dried at ambient conditions before preparation of the membrane electrode assembly.

Both the anode and cathode catalyst layers were transferred to the Nafion<sup>®</sup> 117 membrane from the Teflon<sup>®</sup>-coated decals via hot pressing (heat press, Carver). The membrane was sandwiched between two catalyst-coated decals; catalyst side of the decal was in contact with the membrane. Two pieces of 0.76 mm thick Teflon<sup>®</sup> were placed on either side of the assembly to prevent contamination from the heat press. The MEA was pressed for 30s at 31 MPa and 150 °C. The Teflon<sup>®</sup>-coated decals were removed after the heat-pressed assembly was allowed to cool to room temperature resulting in transfer of the CL from the decals to each side of the membrane. Completion of the MEA fabrication was finalized by the addition of the single and double-sided GDL during the construction of the fuel cell stack. Single-sided GDL was placed, microporous layer side contacting CL, on the cathode side of the MEA and the double-sided GDL was placed, microporous layer side contacting CL, on the anode side of the MEA.

#### 2.3. Fuel cell construction and testing

Each MEA was tested in a  $5 \text{ cm}^2$  fuel cell assembly supplied by Scribner Associates Inc. The MEA was placed between two serpentine flow field graphite plates separated by a 0.381 mm thick Teflon<sup>®</sup> gasket. The setup, including flow plates, MEA, and gasket, was placed between two copper electrodes followed by two endplates. The entire setup was held together by tie rods (bolts) connecting the two endplates; these tie rods were tightened at 100 in lbs (11.3 mN) of torque.

Fuel cell performance of each MEA was characterized by polarization curves (voltage vs. current density), which were plotted from data recorded by an 850 C Fuel Cell Testing Station (Scribner Associates Inc.). The test station was configured to run with industrial hydrogen (nominal 10 ppm CO) and air with a nitrogen purge. Fuel cell tests were conducted at 25 psi backpressure on both the anode and cathode, 1.0 and  $0.5 \, \text{Lmin}^{-1}$  flow rates for the cathode and anode respectively, and variable humidification and stack temperatures. Polarization curves were run from open circuit voltage (system voltage in the absence of a load) to a terminal voltage of 0.2 V at increments of 0.01 V every 10 s. Five polarization curves were collected in succession for each MEA in order to ensure an equilibrium performance.

#### 3. Results and discussion

#### 3.1. Fuel cell performance

Fuel cell performance is strongly influenced by operating temperature. Fig. 1 demonstrates this temperature effect, where the fuel cell performance for Nafion<sup>®</sup> 117 MEAs is shown at 25, 40, 60,



perature; polarization curves (open), power density curves (filled) at 25 (◊,♦), 40  $(\Box, \blacksquare)$ , 60 ( $\triangle, \blacktriangle$ ), and 80 ( $\bigcirc, \bullet$ )°C. Anode/cathode temperature matches stack temperature, 25 psi backpressure,  $H_2/air$  flow rates of 0.5/1.0 L min<sup>-1</sup>. The polarization curves shown here represent the equilibrium performance of four different MEAs.

and 80 °C. Each polarization curve in Fig. 1 corresponds to a different MEA. For each experiment, five polarization curves were taken in succession, the first starting immediately after the fuel cell stack and fuel lines reached the desired temperature. The polarization curves in Fig. 1 represent the fuel cell performance after equilibrium was reached, or when there was no longer a change in performance with time. In other words, the last of the five polarization curves. The dependence of fuel cell performance on temperature is clearly shown, where the voltage increases approximately more than 2fold at any given current density and the profile extends almost 3-fold in current density from 25 to 80°C. Performance increase can also be quantified by the change in power density. Fig. 1 shows an increase in maximum power density of 215 mW cm<sup>-2</sup> from 25 to 80°C.

Note that the absolute fuel cell performance in Fig. 1 has not been optimized to the current state-of-the-art performance:  $\sim$ 0.65 mW cm<sup>-2</sup> at 1 A cm<sup>-2</sup> [20]. Usually, thinner membranes, different catalysts, different catalyst loadings, MEA fabrication techniques, and operating conditions will result in higher PEMFC performances [20]. Also, the use of air rather than pure oxygen and industrial hydrogen with nominal 10 ppm CO has been shown to significantly limit PEMFC performance [21]. In this study, the absolute performance is not the focus, but rather comparing fuel cell performance at different pretreatment conditions to ascertain the effect of CL morphology on fuel cell performance.

For the oxidation and reduction reactions, an energy barrier must be surpassed in order for the reaction to occur. The reaction rates, specifically the oxygen reduction reaction (ORR), which is the rate limiting reaction in the fuel cell, can be affected by three parameters: catalyst type, available catalyst reaction area, and temperature. Catalysts with higher reactivity will lower the activation energy and therefore increase reaction rate. Typically, rate constants follow an Arrhenius model in relation to temperature (i.e., rate constant increases exponentially with increasing temperature). This dependency explains why temperature can increase reaction rate and therefore the steady-state fuel cell performance shown in Fig. 1. In addition to catalyst type and temperature, the available reaction area is specific to fuel cells. Fuel cell performance can be improved if the available active area of the catalyst that is in contact with both the PEM and electrode can be increased. Varying any of these three parameters can lead to a change in fuel cell performance [22].

350

300

As stated previously, temperature affects the reaction rate empirically through the rate constant. Temperature not only affects the reaction rate, but also diffusion within a fuel cell. Higher temperatures can increase the diffusivity of reactant gases and product water; however, this does not have a significant affect on performance. Another form of diffusion in a fuel cell is the diffusion of protons through the PEM. This diffusion is characterized by the conductivity of the Nafion<sup>®</sup> membrane. Conductivity also has an Arrhenius relationship with temperature. As temperature increases, the conductivity increases exponentially. Diffusion of protons is assisted by a higher rate of molecular motion at higher temperatures [23]. Therefore, the steady-state enhancement with increasing temperature can be attributed to higher reaction rate constants (ORR) and high proton conductivity in the PEM.

After accounting for all of these factors, while conducting the fuel cell experiments as a function of temperature, a shift in performance with time was observed (i.e., steady-state performance was only reached after a certain amount of time). The transient behavior in fuel cell performance is shown in Fig. 2. For the 80 °C test, the current density at 0.2 V increased by 61.8 mA cm<sup>-2</sup> over the course of the testing, while the maximum power density increased by 37.8 mW cm<sup>-2</sup>. Others [24] have observed transient fuel cell performance in the start-up phase and attribute this to a number of factors, including temperature and hydration equilibration. Based on work by Hronec [18] and Middleman [25], this change may also result from the change in CL morphology, which can affect gas diffusion (porosity), proton conductivity (ionomer arrangement), and reaction kinetics (available catalyst area). The results shown in Fig. 2 shows that most of the change in the polarization curve occurs in the range of mid to high current densities. This suggests that the change in transient behavior is due to changes in ohmic and mass transfer resistance. In other words, the change in Nafion® arrangement (ohmic) and porosity (mass transfer) in the CL appear to dominate over any affect a change in available catalyst area has on the ORR.

To explore this transient fuel cell performance and its relationship with the CL morphology in more depth, a pretreatment study was conducted. In other words, the fuel cell performance was explored as a function of time to decouple the temperature effect. The fuel cell tests in Fig. 1 were repeated at all four temperatures; only this time each MEA was subjected to flowing humidified nitrogen at 80 °C in the fuel cell stack for 3 h and then cooled to the desired temperature at which point polarization curves were collected. Figs. 3–6 include the polarization curves of this pre-



**Fig. 2.** Transient behavior of 80 °C cell (stack) temperature unpretreated test; polarization curves (open), power density curves (filled). 80 °C anode/cathode temperature, 25 psi backpressure,  $H_2$ /air flow rates of 0.5/1.0 L min<sup>-1</sup>.



**Fig. 3.** Transient ( $\diamond$ ) and pretreated ( $\blacklozenge$ ) fuel cell performance of Nafion<sup>®</sup> 117 MEAs at 25 °C cell (stack) temperature. 25 °C anode/cathode temperature, 25 psi backpressure, H<sub>2</sub>/air flow rates of 0.5/1.0 L min<sup>-1</sup>.



**Fig. 4.** Transient ( $\square$ ) and pretreated ( $\blacksquare$ ) fuel cell performance of Nafion<sup>®</sup> 117 MEAs at 40 °C cell (stack) temperature. 40 °C anode/cathode temperature, 25 psi backpressure, H<sub>2</sub>/air flow rates of 0.5/1.0 L min<sup>-1</sup>.

treatment study. Each graph includes the transient curves from the unpretreated temperature study and the curve from the pretreated study. For the 25 and 40 °C tests, there was no significant increase in performance with time. However, both the 60 and 80 °C unpretreated temperature tests show a measurable increase and



**Fig. 5.** Transient ( $\triangle$ ) and pretreated ( $\blacktriangle$ ) fuel cell performance of Nafion<sup>®</sup> 117 MEAs at 60 °C cell (stack) temperature. 60 °C anode/cathode temperature, 25 psi backpressure, H<sub>2</sub>/air flow rates of 0.5/1.0 L min<sup>-1</sup>.



**Fig. 6.** Transient ( $\bigcirc$ ) and pretreated ( $\bullet$ ) fuel cell performance of Nafion<sup>®</sup> 117 MEAs at 80 °C cell (stack) temperature. 80 °C anode/cathode temperature, 25 psi backpressure, H<sub>2</sub>/air flow rates of 0.5/1.0 L min<sup>-1</sup>.

the final steady-state performance is nearly identical to that of the pretreatment tests at 60 and  $80 \,^{\circ}$ C.

The transient fuel cell performance presented in Figs. 3-6 suggests that other factors besides the change in reaction rate constant and proton conductivity in the PEM affect the performance. Temperature is the main driving force for this change throughout the pretreatment study. Pretreating the MEAs at 80°C for 3 h causes a significant increase in performance when compared to the first polarization curve taken during the unpretreated temperature study. Fig. 7 shows transient fuel cell performance of each MEA after pretreatment, where there is no significant change in performance with time. This suggests that the application of temperature during pretreatment, along with pressure [18], results in a change to the CL morphology, which impacts the overall fuel cell performance. Figs. 5 and 6 show that the steady-state polarization curves on the unpretreated temperature tests match the performance of the pretreated MEAs for the 60 and 80 °C tests. However, this was not the case for the 25 and 40°C tests. This suggests that other factors (e.g., morphology) aside from equilibration contribute to the difference between steady-state and pretreated MEA performance and that temperatures around 60 °C are required to initiate the morphological change within the CL.



**Fig. 7.** Polarization curves for pretreatment tests. Includes all five successive polarization curves taken at 25 ( $\Diamond$ ), 40 ( $\Box$ ), 60 ( $\Delta$ ), and 80 ( $\bigcirc$ )°C. Anode/cathode temperature matches cell temperature, 25 psi backpressure, H<sub>2</sub>/air flow rates of 0.5/1.0 L min<sup>-1</sup>.



Fig. 8. Post mortem SEM image of the cross-section of an MEA tested in the fuel cell.

#### 3.2. SEM analysis

Fig. 8 contains a post mortem SEM image of the cross-section of a MEA tested in a fuel cell. At this magnification, there is no apparent difference among any of the MEAs that would provide insight into the transient fuel cell performance data previously described. However, high magnification of the post mortem SEM images shown in Fig. 9 show that morphological changes have occurred within the CLs that were pretreated at 80 °C for 3 h in the fuel cell and the CLs that were exposed to temperatures above 60 °C in the fuel cell. SEM images of the MEAs tested in the fuel cell without pretreatment at 80°C are in the left column of each figure, while those pretreated in the fuel cell at 80 °C are in the right column. Noticeable differences occur between the non-pretreated and pretreated MEAs at 25 and 40 °C, while there is no significant difference in morphology of the CLs tested at 60 and 80 °C. Particularly, there is a formation of Nafion<sup>®</sup> nanofibers in the CL for unpretreated MEAs operated at 60 and 80 °C and all MEAs pretreated at 80 °C. This suggests that temperatures near 60 °C are required to initiate the formation of fibers.

Hronec [18] also observed the formation of Nafion<sup>®</sup> nanofibers in the CL after fuel cell operation at 80 °C. Moore and coworkers [26] performed dynamic mechanical analysis (DMA) on Nafion<sup>®</sup> and observed an onset of loss in elastic modulus at ~60–75 °C. This work along with the findings presented in the SEM images suggest that at 60 °C under the pressure of the fuel cell assembly the bulk structure of Nafion<sup>®</sup> can undergo changes. The images in this study clearly demonstrate the formation of nanofibers at 60 °C and above and that this change in CL morphology contributes to the transient fuel cell performance. Furthermore, pretreating MEAs at temperatures at or above 60 °C will alter the CL morphology and can improve the fuel cell performance at lower temperatures as shown in Figs. 3 and 4.

In addition to temperature, pressure also contributes to nanofiber formation in the CL. Hronec [18] compared the CL after being exposed to  $80 \,^{\circ}$ C for 3 h both inside and outside of a fuel cell. Under the pressure of the fuel cell assembly, the nanofibers in the CL became oriented and reduced in average diameter from  $\sim 300$  to  $\sim 50$  nm. In a fuel cell assembly, 100 in-lbs of torque was applied to each bolt in the assembly, which applies pressure to the MEA. Therefore, in this study, temperature and pressure combine to result in nanofiber formation in the CL within a fuel cell stack that leads to increased performance.



Fig. 9. Post mortem SEM micrographs of CL from fuel cell tests: unpretreated (left) and pretreated (right) at (a) 25 °C, (b) 40 °C, (c) 60 °C, (d) 80 °C.

The size and distribution of catalyst particles and Nafion<sup>®</sup> nanofibers from the SEM images in Fig. 9 were evaluated using ImageJ software and the results are shown in Fig. 10. For the unpretreated temperature study, no fibers were formed in the CL during the 25 and 40 °C tests, which is in agreement with the theory previously presented. Particle sizes for both the unpretreated and pretreated tests have an average diameter of approximately 100 nm

(see Table 1). Table 1 shows the average fiber size for each CL is  $\sim$ 30–50 nm. The fiber size distribution is broader in the 60 °C test compared to 80 °C. This suggests that the fibers are beginning to form around 60 °C; the Nafion<sup>®</sup> continues to undergo morphological changes leading to smaller diameter fibers at higher temperature, 80 °C, as well as a narrower size distribution. The pretreatment at 80 °C for 3 h created nearly identical CL morpholo-



**Fig. 10.** Nanofiber and particle size diameter distributions for the unpretreated (open bars) and the pretreated (solid bars) temperature study. (a) 25 °C particles, (b) 25 °C fibers, (c) 40 °C particles, (d) 40 °C fibers, (e) 60 °C particles, (f) 60 °C fibers, (g) 80 °C particles, (h) 80 °C fibers.

#### Table 1

Average Nafion® nanofiber and Pt/C agglomerate particle sizes in CL.

Temperature (°C)	Avg. particle diameter (nm)		Avg. fiber diameter (nm)	
	No pretreatment	Pretreated at 80 °C	No pretreatment	Pretreated at 80°C
25	100 ± 36	80 ± 27	NA	42 ± 16
40	91 ± 32	$127 \pm 43$	NA	38 ± 13
60	$110 \pm 52$	$105 \pm 40$	$54\pm22$	$42 \pm 16$
80	$114\pm49$	$118 \pm 41$	$44\pm17$	$43\pm20$

#### Table 2

Void fraction in CL.

Temperature (°C)	Void fraction		
	No pretreatment	Pretreated at 80 °C	
25	0.45	0.47	
40	0.57	0.57	
60	0.41	0.49	
80	0.54	0.54	

gies at all four of the tested temperatures. This further proves that temperature plays a significant role in the formation of Nafion<sup>®</sup> nanofibers within the CL. In addition to particle size and fiber size, the void fraction or porosity of the CL was determined and is listed in Table 2.

#### 4. Conclusions

In this study, the effect of Nafion<sup>®</sup> nanofibers on fuel cell performance was characterized with fuel cell performance and high magnification *post mortem* electron microscopy. Fuel cell tests conducted at 60 and 80 °C showed an increase in performance with time until a steady-state was reached. It was hypothesized that this increase in performance with time was due to the formation of Nafion<sup>®</sup> nanofibers based on prior work by Hronec [18]. The nanofibers may optimize the morphology of the CL and act as a proton transport bridge from the catalyst particles to the PEM.

Identification of temperature as the main driving force for the fiber formation was demonstrated through pretreatment of the MEAs prior to fuel cell testing. Each MEA was exposed to humidified nitrogen at 80 °C for 3 h in a fuel cell prior to testing at the desired temperature. It was found that pretreatment caused the fuel cell performance to be stable and nearly identical to the steady-state performance of the unpretreated MEAs at 60 and 80 °C. It is clear from these results that temperature is the main driving force for the formation of Nafion<sup>®</sup> nanofibers in the CL and temperatures

of approximately 60 °C and above are required to initiate the fiber formation. The results of this study emphasize the importance of transport issues within the PEMFC and demonstrate that enhancement of TPB through CL morphology optimization may be a unique and fruitful approach to designing state-of-the-art PEMFC CLs.

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