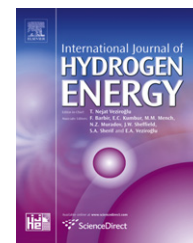Available online at www.sciencedirect.com

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Ultra-low Pt loading for proton exchange membrane fuel cells by catalyst coating technique with ultrasonic spray coating machine

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ABSTRACT

This paper reports use of an ultrasonic spray for producing ultra-low Pt load membrane electrode assemblies (MEAs) with the catalyst coated membrane (CCM) fabrication technique. Anode Pt loading optimization and rough cathode Pt loading were investigated in the first stage of this research. Accurate cathode Pt coating with catalyst ink using the ultrasonic spray method was investigated in the second stage. It was found that 0.272 mg_{Pt}/cm^2 showed the best observed performance for a 33 wt% Nafion CCM when it was ultrasonically spray coated with SGL 24BC, a Sigracet manufactured gas diffusion layer (GDL). Two different loadings (0.232 and 0.155 mg_{Pt}/cm^2) exposed to 600 mA/cm^2 showed cathode power mass densities of 1.69 and 2.36 W/mg_{Pt}, respectively. This paper presents impressive cathode mass power density and high fuel cell performance using air as the oxidant and operated at ambient pressure.

1. Introduction

Due to the high power density, high efficiency, zero emissions, high-quality power, scalability, and fast start-up, proton exchange membrane fuel cells (PEMFCs) are a promising future power source [1]. Membrane electrode assemblies (MEAs) play an important role in performance. A MEA is a composite of a GDL, catalyst layer (CL), and proton exchange membrane (PEM). The electrochemical reaction occurs at the CL. The electrochemical reaction needs a three-phase boundary (TPB) where the catalytic electrode, electrolyte, and gas are all in physical contact. The amount of TPB strongly affects the fuel cell performance. The formula of the catalyst ink dominates not only the fuel cell performance but also the cost. For mass production, the catalyst ink cost is approximately 34% of the total stack cost [2].

Typically, catalyst ink includes catalyst support, ionomer, solvent, and additive (PTFE, pore former, etc.). Generally, a MEA can be prepared by the three following methods: (i) Catalyst coated membrane (CCM), which is coating CL onto a membrane directly, (ii) Decal transfer CCM, which is coating CL on a substrate and then transferring the CL onto a membrane, and (iii) Catalyst coated substrate (CCS), which is coating CL on GDL (a GDL with CL is called a gas diffusion electrode (GDE)). A MEA is fabricated by sandwiching a CCM between two GDLs, or sandwiching a PEM between two GDEs. MEAs fabricated by CCM offered better performance than CCS. The CCM delivers lower resistance than CCS due to improved CL-membrane ionic contact, regardless of if the CCM is spray [3] or electrospray [4] coated. The CCM also showed better durability than CCS [3]. Millington et al. [5] investigated four different solvents for producing catalyst

inks; the solvents were tetrahydrofuran (THF), iso-propanol (IPA), ethylene glycol (EG) and glycerol. Due to its low dielectric constant, THF showed better performance than IPA as the solvent in the catalyst inks, while EG and glycerol led to poor performance [5]. Song et al. [6] investigated the effect of PTFE content in the CL; results indicated that adding certain PTFEs could improve the concentration polarization of the CL. The optimal PTFE content was 5 wt%, which did not affect the charge transfer resistance but improved the internal mass diffusion of the CL [6]. Pore former can modify the pore volume. The optimal pore former content is 30 wt%, but it led to lower durability [7].

There are many coating techniques for fabricating a CL, such as sputter deposition [8−10], ion-beam assisted deposition [11−14], doctor blade [15], screen printing [16], inkjet printing [17−19], spraying [20], electrospraying [4,21−27], and ultrasonic spraying [28]. Chaparro et al. [25] reported that for an electrospraying process, the optimum Pt loading (cathode) and Nafion content ratio were 0.17 mg/cm^2 and 17 wt%, respectively. The electrospray process homogeneously covered the ionomer film with the Pt/C agglomerate, forming a highly porous material with lower resistivity [26]. Sasikumar et al. [29] and Martin et al. [21] investigated the optimum Nafion content ratio at various Pt loadings. The results indicated that the optimum Nafion content ratio decreases with increasing Pt loading with CLs coated by either brush [29] or electrospray [21]. The optimum values are significantly different depending on the coating method used. Millington et al. [28] indicated the main problem with the electrospraying technique is that the peak power density value is too low to be used in practical applications. A MEA fabricated by ultrasonic spray demonstrated high performance at low Pt loading [28]. However, Millington et al. fabricated the MEA using the CCS technique and tested with oxygen as the oxidant and under high back pressure (2 bar). In this paper, the CCM technique was used and investigated with air oxidant and at ambient pressure; this approach is more consistent with real applications. In addition, it is the first study to use ultrasonic spray for investigating Pt loading using the CCM technique.

2. Experimental

2.1. MEA fabrication

Catalyst inks consisted of supported catalyst (40 wt% Pt/C, Johnson Matthey HiSpecTM 4000), aqueous Nafion® solution (5 wt%), DI water, and ethanol. All the contents were added to a glass vial and mixed using an ultrasonic bath. The ratio of the supported catalyst to Nafion® was 2:1. The catalyst inks were ultrasonically sprayed onto the Nafion®212 membrane directly. Run paths were created using the Sono-Tek 'Exactacoat' ultrasonic spray instrument operating at 48 kHz and an ink flow rate 0.125 ml/min; the Pt loading was controlled by the number of passes using a given run path. The CCMs were flat and uniform (see Fig. 1), and our CCMs were without wrinkles, which was comparable to the Sono-Tek example [28]. The CL active area was about 5 cm^2 (23 mm × 23 mm), and the GDL was 25 mm × 25 mm. Each CCM was sandwiched
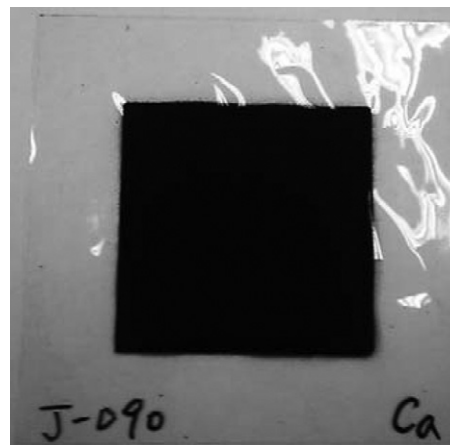

Fig. 1 − The photo of homemade ultrasonic spray CCM.

between two GDLs and assembled in a single cell without hot press for fuel cell performance tests.

2.2. Performance test

In this study, a homemade cell was utilized. The cell was made up of three components: insulating glass fiber end plates, gold-coated brass collecting plates, and graphite flow field plates. The channel depth, channel width, and rib width of the serpentine flow field plate were all 1 mm. Measurements for polarization tests were performed using the Fuel cell test system 850C (Scribner Associates Incorporated, USA). The operating conditions during polarization measurement were 65 °C, relative humidity (RH) of 100%, 100 sccm hydrogen flow rate, and 250 sccm air flow rate. No back pressure was used during experiments.

3. Results and discussion

3.1. Pt loading test with SGL 10BC

Sigracet GDLs (SGL group) are widely used in fuel cells. Sigracet GDL 10 series is their first-generation baseline material. Therefore, Sigracet SGL 10BC GDL was chosen for the first stage Pt loading test. Since the RH is always high in Taiwan, the Nafion from the ionomer or membrane could absorb water from the environment. Before experiments started, the Pt loading was precisely calibrated. The catalyst ink was sprayed on several plastic substrates with various run paths and dried at 80 °C overnight. Fig. 2 demonstrates the Pt loading was well controlled; each run path increased loading by 0.0387 mg$_{Pt}$/cm^2. Fig. 3 shows the current density at 0.6 V and peak power density with various Pt loadings. Fig. 3(a) shows the anode Pt loading while the cathode Pt loading was about 0.465 mg$_{Pt}$/cm^2 (12 run path times). Fig. 3(b) shows the cathode Pt loading while the anode Pt loading was about 0.232 mg$_{Pt}$/cm^2 (6 run path times). For this specific ink formula and operating conditions, the optimum run paths for anode and cathode are 2−3 and 6−8, respectively. Therefore, the optimum Pt loading for anode and cathode are 0.077−0.116 and 0.232−0.310 mg$_{Pt}$/cm^2, respectively.
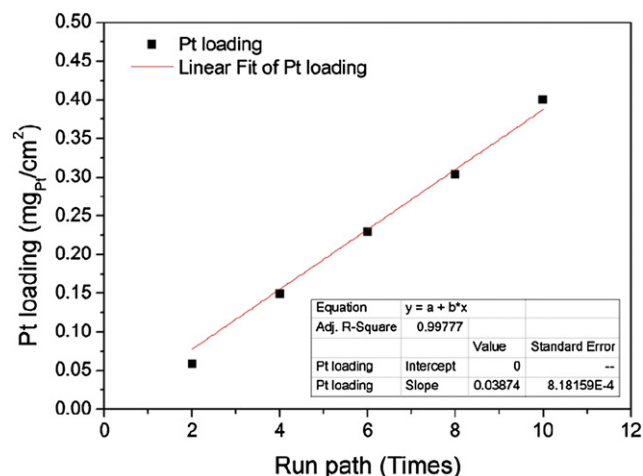
Fig. 2 – The calibration line of Pt loading versus run paths.

3.2.   Cathode Pt loading test with SGL 24BC

SGL 24BC GDL is suggested for use at low RH conditions. For that case, the target operating conditions were 90 °C with a RH of 50% (High temperature (HT)–low RH). Under these conditions, the second stage of this work measured the Pt loading using SGL 24BC GDL. According to the rough Pt loading optimization from the first stage effort, the optimum number of run paths were 2–3 and 6–8 for the anode and cathode, respectively. Fig. 4(a) shows the cathode mass polarization and cathode mass power density curves at various cathode Pt loadings with the anode run paths fixed at 3. The results

Fig. 3 – The optimization of (a) anode and, (b) cathode Pt loading.

Fig. 4 – The (a) cathode mass polarization and cathode mass power density curve, (b) polarization and power density curve, and (c) specific voltage variation with various Pt loading.

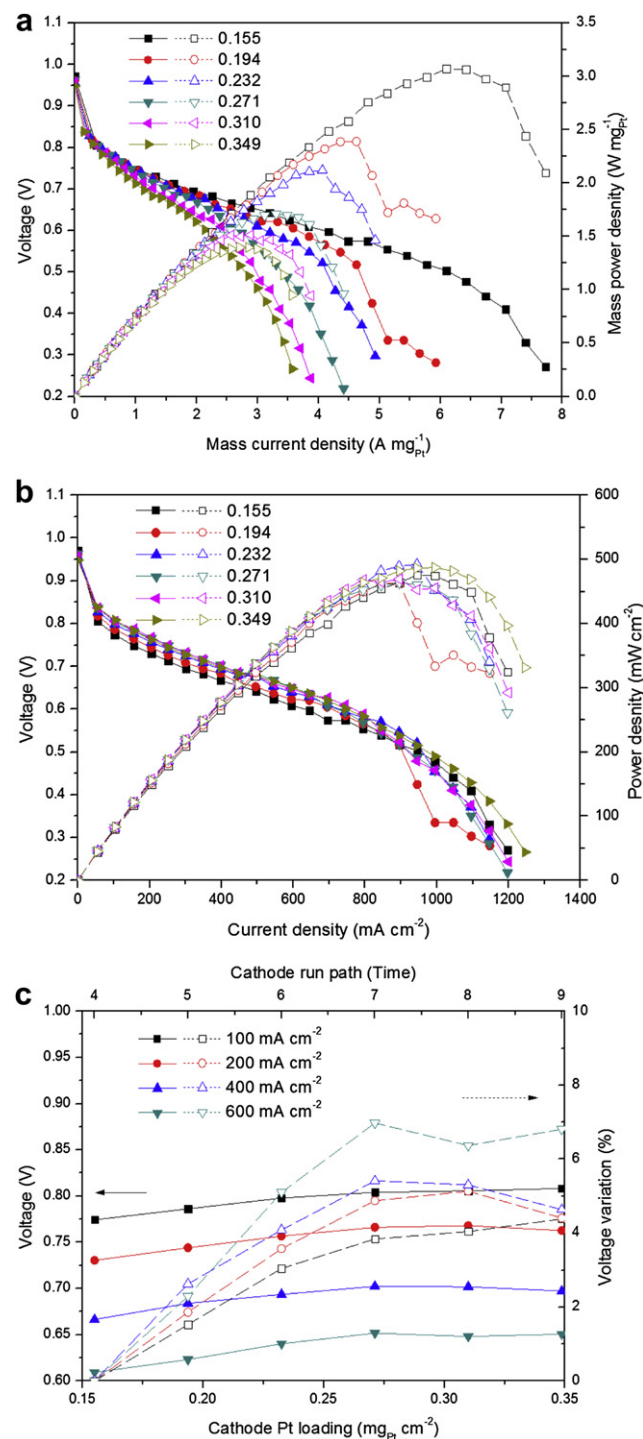clearly demonstrate that lower Pt loading leads to higher cathode mass power density, which means higher Pt utilization. Not only ultrasonic spray coating method shows that Pt loading decreases as mass power density increases, but also other methods do. And this will be discussed in Section 3.4 and Table 1. Fig. 4(b) shows the polarization and power density curves for various cathode Pt loadings. Due to water flooding and drainage issues, it was difficult to analyze the fuel cell performance under high current loads, but a slight increase in performance was observed when Pt loading was increased. For high mass power density purpose, the Pt loading indicated in Fig. 4(a) should be as low as possible. But for high power density (high performance) purpose, the Pt loading should be further investigated. Because the higher Pt loading would increase the total volume of TPB which is benefit on performance. In the other hand, higher Pt loading increases the thickness of catalyst layer and leads higher resistance causing lower performance. Therefore, for high performance purpose, the Pt loading should be optimized. Based on Fig. 4(b), the best cathode Pt loading for high performance purpose seems to be 0.232–0.271 mg_{Pt}/cm^2, because the performance of Pt loading higher than 0.232–0.271 mg_{Pt}/cm^2 is almost the same. Fig. 4(c) shows the specific voltage and voltage variation with various cathode Pt loadings for different current loads. For a small current load, increasing cathode Pt loading can improve performance. However, the best Pt loading depends on the current load. For current load 100 mA/cm^2, the best Pt loading is 0.349 mg_{Pt}/cm^2 (9 run path times). For current load 200 mA/cm^2, the best Pt loading is 0.310 mg_{Pt}/cm^2 (8 run path times). For current load 400–600 mA/cm^2, the best Pt loading is 0.271 mg_{Pt}/cm^2 (7 run path times). For the peak power density, the best Pt loading is 0.232 mg_{Pt}/cm^2 (7 run path times) and the current load is about 900–1000 mA/cm^2. So, the best Pt loading depends on the goal of operation condition. So far, either in the low current or peak power, the performance increased lower than 10% (0.155 mg_{Pt}/cm^2 as the base line) in this study. But the cathode Pt loading is increased from 25% to 125% (0.155 mg_{Pt}/cm^2 as the base line). So, from the information above, the most economic cathode Pt loading is 0.155 mg_{Pt}/cm^2, and it could be more economic when cathode Pt loading decrease more.

3.3. Cathode Nafion content ratio test

Fig. 5 shows the polarization and power density curve with various cathode Nafion content ratios, when the cathode Pt loading is fixed at 0.232 mg/cm^2. The 20 wt% Nafion content ratio shows the better mass transport than the 33 wt% sample. However, when the operating voltage was higher than 0.6 V, it was comparable to the 20 and 33 wt% samples. The 40 wt% Nafion showed poor performance due to larger activation polarization and decreased mass transfer.

The Nafion content ratio of the catalyst layer form 20 wt% to 33 wt% performed a very slight decrease for current loads lower than 1000 mA/cm^2. And the slight changes on performance may be due to a very slight increase on electronic resistance which is effected by the increased Nafion content ratio and its poor electronic conductivity. The most important thing is the mass transfer part, 33 wt% Nafion of catalyst layer shows higher mass transfer resistance than the 20 wt% one.

The increase of mass transfer resistance could be caused by the following reasons : the increasing catalyst layer thickness, the increasing water capture ability (for high RH condition) and the decreasing pore volume of catalyst layer. But once the Nafion content ratio is up to 40 wt%, the performance decreased dramatically on either low or high current load. This result indicates that too much Nafion content ratio of catalyst layer would decrease the performance seriously, which because too much Nafion content ratio of catalyst layer lead to thicker catalyst layer, lower electronic conductivity and poor pore volume of catalyst layer. For the activation polarization region under the low current load, thicker catalyst layer and poor pore volume lead to fuel/oxidant having difficulty in diffusing to catalyst surface. The more difficult for fuel/oxidant diffusing to catalyst surface, the smaller volume of TPB would be. And the decreasing total volume of TPB is the main reason for activation polarization increased. But there are not only the activation polarization, but also the mass transfer polarization region that would negatively affected by too much Nafion content ratio of catalyst layer. And it would also cause the pore volume decrease and water capture ability increase (for high RH condition). Therefore, too much Nafion content ratio would cause serious water flooding phenomenon. And that is why the mass transport region was found at 500 mA/cm^2, and this result occurred much earlier than other cases. Since the whole experiments are used the same type of membrane, the differences of ohmic polarization region is only varied from the ink formula (Nafion content ratio). In that case, it could be implied that the main reason for the increasing ohmic polarization is the increasing Nafion content ratio which caused a thicker catalyst layer and lower electronic conductivity.

Fig. 6 shows the cell voltage at 600 mA/cm^2 cathode mass power density operating under various cathode Nafion contents and Pt loadings. The 33 wt% Nafion displayed a consistent performance from low to high Pt loadings. For the cathode Pt loading lower than 0.232 mg_{Pt}/cm^2, 20 wt% Nafion content displayed better performance than 33 wt%. Once cathode Pt loading is higher than 0.310 mg_{Pt}/cm^2, the 33 wt% performed better than 20 wt%. But the 40 wt% Nafion exhibited poor performance at all Pt loadings examined. Therefore, when using ultrasonic spraying, the Nafion content should be lower than 40 wt%, and at low Pt loading, a low Nafion content is preferred.

3.4. Recent ultra-low loading MEAs

Ultrasonic spray coating technique is replacing air spray coating technique in a wide range of industrial and R&D applications, such as photo resistor coating, solar cell industry and fuel cell industry. Ultrasonic spray coating is a technology that is more precise, more controllable, and tighter of drop distribution. Tight drop distribution and non-clogging ultrasonic create very uniform thin films, therefore, ultrasonic spray coating technique is very suitable for fabricate ultra-low Pt loading MEAs. But, the cost of ultrasonic spray system is higher than air spray coating system or screen printing coating system. The high cost of system is the main disadvantage of ultrasonic spray coating in the fuel cell industry. The other disadvantage of ultrasonic spray coating is that the

Table 1 – The current state of ultra-low Pt loading for the various coating technique.

Coating technique	MEA fabrication method	An. Pt loading (mg$_{Pt}$/cm^2)	Ca. Pt loading (mg$_{Pt}$/cm^2)	Ca. Nafion content ratio (%)	Voltage @ 600 mA cm^{-2} (V)	Peak power W/cm^2	T$_{cell}$	RH. A/C (%)	Gas type A/C	Pressure A/C (bar)	Supported catalyst	GDL type	Ca. mass power density @ 600 mA cm^{-2} (W/mg$_{Pt}$)	Ca. mass power density @ peak power (W/mg$_{Pt}$)	Ref.
Ultrasonic spray (48 kHz)	CCM	0.116	0.155	20	0.609	0.454	65	100/100	H$_2$/air	Ambient	HiSpec 4000 (40 wt%)	SGL 24BC	2.36	2.93	**This work**
Ultrasonic spray (48 kHz)	CCM	0.116	0.232	20	0.652	0.500	65	100/100	H$_2$/air	Ambient	HiSpec 4000 (40 wt%)	SGL 24BC	1.69	2.16	**This work**
Ultrasonic spray (120 kHz)	CCS	0.4	0.15	33	0.700	0.650	70	50/50	H$_2$/O$_2$	2/2	HiSpec (20 wt%)	SGL 10BC	2.80	4.33	[28]
Ultrasonic spray (120 kHz)	CCS	0.05	0.15	33	0.689	0.584	70	50/50	H$_2$/O$_2$	2/2	HiSpec (20 wt%)	SGL 10BC	2.76	3.89	[28]
Electrospray	CCM	0.25 (E-Tek commercial GDE)	0.21	15	0.665	0.750	80	100/100	H$_2$/O$_2$	2.02/2.02	E-TEK (20 wt%)	E-TEK LT1200W	1.90	3.57	[4]
Electrospray	CCS	0.25 (E-Tek commercial GDE)	0.21	15	0.639	0.585	80	100/100	H$_2$/O$_2$	2.02/2.02	E-TEK (20 wt%)	E-TEK LT1200W	1.83	2.79	[4]
Electrospray	CCS	1	0.012	40	0.183	0.125	40	Dry	H$_2$/O$_2$	Ambient	10 wt% on Vulcan XC-72R	Toray TGP-H-060	9.15	10.42	[27]
Electrospray	CCS	1	0.012	30	0.401	0.243	70	Dry	H$_2$/O$_2$	3.4/3.4	10 wt% on Vulcan XC-72R	Toray TGP-H-060	20.05	20.25	[27]
Electrospray	CCS	1	0.1	30	0.241	0.160	40	Dry	H$_2$/O$_2$	Ambient	10 wt% on Vulcan XC-72R	Toray TGP-H-060	1.45	1.60	[21]
Electrospray	CCS	0.25 (E-Tek commercial GDE)	0.2	40	0.575	0.341	80	100/100	H$_2$/O$_2$	2.02/2.02	E-TEK (20 wt%)	E-TEK LT1200W	1.73	1.71	[25]
Dual ion-beam	CCS	0.04	0.04	–	0.468	0.281	80	100/100	H$_2$/air	4.46/5.15	–	E-TEK LT1400	7.02	7.03	[11]
Dual ion-beam	CCS	0.08	0.08	–	0.509	0.305	80	100/100	H$_2$/air	4.46/5.15	–	E-TEK LT1400	3.82	3.81	[11]
Dual ion-beam	CCS	0.12	0.12	–	0.577	0.352	80	100/100	H$_2$/air	4.46/5.15	–	E-TEK LT1400	2.89	2.93	[11]
Dual ion-beam	CCS	0.08	0.08	–	0.774	0.825	80	100/100	H$_2$/O$_2$	4.46/5.15	–	E-TEK LT1400	5.81	10.31	[14]
	CCM		0.08	25	0.444	0.266	60		H$_2$/air	1.35/1.35		Toray	3.33	3.33	[18]

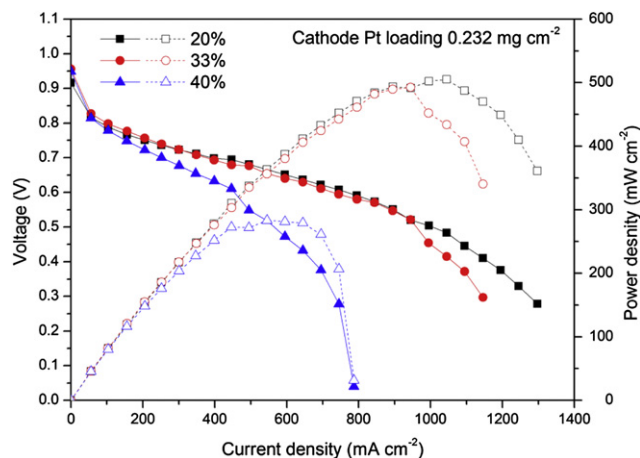| Piezo-electric Printer	Plasma Sputter	Plasma Sputter
	CCS	CCS
Ion-power commercial half CCM	0.01	0.16
	0.01	0.16
	–	–
	0.557	0.726
	0.394	0.652
	80	80
100/100	100/16	100/16
	H_2/O_2 3.1/3.8	H_2/O_2 3.1/3.8
E-TEK (20 wt%)	–	–
	E-TEK	E-TEK
	33.42	2.72
	39.40	4.08
	[8]	[8]

Fig. 5 – The polarization and power density curve with various cathode Nafion content ratios and cathode Pt loading fixed at 0.232 mg/cm^2.

machine is not suitable for high viscosity ink, which means the ink cannot be too thick. However, the thicker ink can reduce the time of coating process. Since the target is fabricating ultra-low Pt loading MEAs, this disadvantage could be neglected.

There are many coating techniques reported in the literature for the fabrication of ultra-low Pt loaded MEAs. Table 1 lists literature data available on current methods of ultra-low Pt loaded MEAs. The performances of five key coating techniques (ultrasonic spray, electrospray, dual ion-beam, piezo-electric printer, and plasma sputter) are compared. These coating methods have been included, as they have shown the most promising results for ultra-low Pt loaded MEAs. Electrospray and plasma sputter demonstrate extremely high cathode mass power density when Pt loading was one order of magnitude lower than other methods. When the Pt loading increases, the cathode mass power density decreases regardless of the coating technique used. It would be expected that ultrasonic coating would achieve
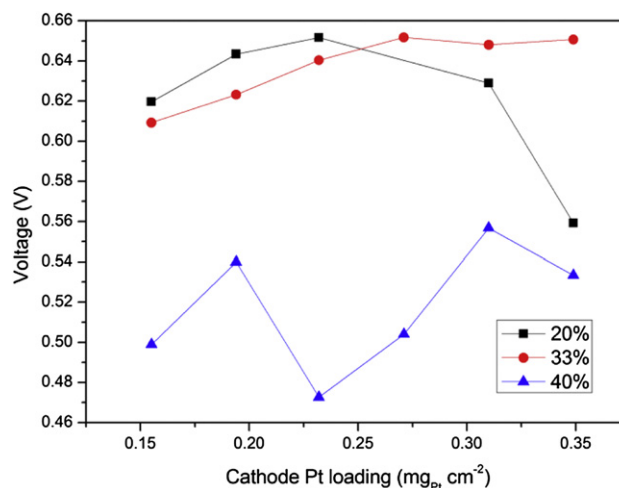

Fig. 6 – Shows the cell voltage at 600 mA cm^{-2} operating at various cathode Nafion contents and Pt loading.

comparably high cathode mass power density if the Pt loading was decreased one order of magnitude. However, the performance would decrease more than 20% when the Pt loading was one order of magnitude lower. While this would reduce the cost of catalyst, it would also have negative impacts on the cost of other components of the fuel cell stack, and the volume (weight) of the fuel cell stack would need to be increased to achieve the same power output. Notice that there are only four results (one presented in this work) in Table 1 that Pt loading was higher than 0.1 mg$_{Pt}$/cm^2 and the performances are higher than 2 W/mg$_{Pt}$ at 600 mA/cm^2 load. For the other three literature results, the conditions of the tests are using oxygen as the oxidant and/or high back pressure. The result from this research is the only one which showed higher than 2 W/mg$_{Pt}$ at a load of 600 mA/cm^2 with air oxidant and ambient pressure. Typically, oxygen oxidant performs about 1.5–3.0 times performance which depends on the chosen cell voltage than air oxidant. And using the back pressure has the similar effect. Therefore, the cathode mass power density at 600 mA/cm^2 in this work is similar with others literature results (for Pt loading higher than 0.1 mg$_{Pt}$/cm^2), even those using oxygen oxidant or back pressure. But the cathode mass power density at peak power density is not that good, since the performance of oxygen oxidant or back pressure should be divided to compare with air oxidant, which implies that the cathode power mass density in this work is higher than other literature results, if the measurements are under the same operation conditions. This paper demonstrated that the ultrasonic spray technique can be delivered high cathode mass power density and fuel cell performance using the described laboratory MEA fabrication technique.

4. Conclusion

This paper discusses the use of an ultrasonic spray for the fabrication ultra-low Pt loading MEAs with the CCM technique. Cathode Pt loading coated with catalyst ink by the ultrasonic spray method was investigated. It was determined that 0.272 mg$_{Pt}$/cm^2 showed the best performance for 33 wt% Nafion content in a CCM when it was ultrasonically spray coated with SGL 24BC GDL. The various cathode Pt loading and Nafion content ratio had been tested in this work. It was found that lower Pt loading favor lower Nafion content ratio. It was also found that at Pt loadings of 0.232 and 0.155 mg$_{Pt}$/cm^2, the cathode mass power density performance for a 20 wt% Nafion at 600 mA/cm^2 current density is 1.69 and 2.36 W/mg$_{Pt}$, respectively. And at Pt loadings 0.232 and 0.155 mg$_{Pt}$/cm^2, the cathode mass power density performance for 20 wt% Nafion cathode at peak power is 2.16 and 2.93 W/mg$_{Pt}$, respectively. In other literature, the cathode mass power density is higher than this work when Pt loading is lower than 0.1 mg$_{Pt}$/cm^2. Although these cases reduced the cost of catalyst (about 20%), increasing the total cost. And the total cost increasing means the other components in fuel cells (membrane, GDL and bipolar plate) is increasing due to lower performance need more cells to keep the same power output. This work performed similar cathode mass power density with other literature, even those tested under oxygen oxidant or back pressure for Pt loading higher than 0.1 mg$_{Pt}$/cm^2. And these

results implied that the cathode power mass density under the same operation conditions is higher than other literature results in this work. The higher cathode mass power density could contribute to the optimization of Nafion content ratio and CCM technique in this paper.

Further improvement in the cathode mass power density may be achieved by either decreasing the cathode Pt loading or ink formula. This study presents the first results demonstrating high cathode mass power density and fuel cell performance with air oxidant and ambient pressure. Further study (e.g., HT-low RH, conditions, AC impedance tests) will be reported in the future.

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