



A novel method for preparing proton exchange membrane fuel cell electrodes by the ultrasonic-spray technique

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ABSTRACT

A novel ultrasonic-spray method for preparing gas diffusion electrodes (GDEs) for proton exchange membrane fuel cell (PEMFC) is described. Platinum (Pt) loaded on Nafion[®]-bonded GDEs were prepared by the ultrasonic-spray method on various commercial woven and non-woven gas diffusion layers (GDLs) at several Pt loadings in the range of 0.40–0.05 mg cm⁻². The ultrasonic-sprayed GDEs were tested and compared to commercial and *hand*-painted GDEs. It was found that the GDEs prepared by the ultrasonic-spray method exhibited better performances compared to those prepared by the *hand*-painting technique, especially at low Pt loadings. GDEs fabricated by the ultrasonic-spray method with a platinum loading of 0.05 mg cm⁻² exhibited a peak power rating of 10.9 W mg⁻¹ compared to 9.8 W mg⁻¹ for *hand*-painted GDEs. For all experiments using various GDLs, Sigracet SGL 10BC exhibited the best performance with a peak power of 0.695 W cm⁻².

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1. Introduction

The main scope for the development and successful market deployment of low-temperature (LT) and high-temperature (HT) proton exchange membrane fuel cells (PEMFC) is to reduce the Pt catalyst loading of both anode and cathode electrodes together with the associated cost without compromising on the PEMFC performance [1,2]. For example, in the automotive sector, the major issue to PEMFC commercialisation is the high intrinsic cost of Pt (\$61 g⁻¹ as of 18/03/11 [3]). Current state-of-the-technology Membrane Electrode Assemblies (MEAs) have a total Pt loading of about 0.40 mg Pt cm⁻² amounting to (i) ca. 0.05 and 0.35 mg Pt cm⁻² of Pt catalyst used on the anode for the fast hydrogen oxidation reaction (HOR) and the cathode for the sluggish four-electron oxygen reduction reaction (ORR) respectively and (ii) ca. ~30g Pt per 100 kW PEMFC stack.

In order to achieve this challenging goal (up to 10-fold decrease in Pt loading in PEMFC stacks), it is necessary to either (i) lower the Pt loading by alloying Pt (either as binary or ternary [4]), (ii) replace Pt by a non-precious electrocatalyst (inorganic or organic [5]) or/and (iii) maximising the effective surface area of the Pt cat-

alyst, in other words, the surface contact between the electrode catalyst layers (CL), the carbonaceous electronic conductor (gas diffusion layer, GDL), the polymer electrolyte membrane (Nafion[®], PEM) and the reactants (hydrogen and oxygen). Since the electrochemical reactions occur in this active part of the electrodes (also known as the ‘three-phase reaction zone’ or the triple phase boundary – TPB), the PEMFC performance depends greatly on the kinetics of interfacial phenomena [1,2].

PEMFC electrodes are usually constituted of carbon black powder (C) acting as a catalyst support mixed with solid polymer electrolyte, e.g. Nafion[®] [1]. In this case, to increase the performance of the PEMFC electrodes (in other words, the ‘true’ catalyst surface area), either (i) an increase in CL thickness, for a given Pt catalyst loading or (ii) an increase in the amount of Pt catalyst in the CL is required. However, increasing the thickness of the catalyst layer leads to a decrease in reactants diffusion rate towards active Pt catalytic sites, whereas increasing the electrocatalyst loading generally leads to an increase in particle size, thus a decrease in PEMFC efficiency [1,2].

There are numerous well-documented methods describing the application of catalyst ink to the substrate (GDL) and the membrane electrolyte (PEM) leading to GDEs and CCMs (catalyst coated membranes) respectively. For example, Litster and McLean [1] and Wee et al. [2] give excellent overviews of PEMFC electrode fabrication methods. The catalyst ink is commonly constituted of carbon supported on Pt agglomerates (Pt/C) mixed with a solubilised polymer

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electrolyte (e.g. Nafion[®] ionomer) and a solvent (e.g. IPA or THF). The most common techniques used for the fabrication of PEMFC electrodes are by the decal, blade process, screen-printing, painting, spraying or electrospraying methods. However, the main drawback for some of these methods is that (i) heating, i.e. oxidative treatment is required in order to 'clean' the Pt particles from preparative chemical contamination, (ii) these treatments can greatly affect the surface structure/morphology of the Pt particles and (iii) the presence of inactive Pt sites for electrochemical reactions at the *TPB* is often observed [1,2].

One of the many approaches to reduce chemical contaminations and inactive Pt in the *TPB* is to employ efficient stirring or forced convection in the form of ultrasound. Recently, Pollet reviewed [6] and reported [7,8] that ultrasound can be used for fabricating noble metals and catalysts and preparing fuel cell materials. Pollet [6] showed in his comprehensive review that the ultrasonic, sonochemical and sonoelectrochemical methods for the preparation of efficient *mono-* and *bi-*metallic nanoparticles, carbon-supported electrocatalysts, fuel cell electrodes and membranes have an advantage over many other methods due to the unusual experimental conditions caused by cavitation, water sonolysis and enhanced mass transport phenomenon [6–8].

In this paper, it is reported that ultrasound (120 kHz) can be successfully used for the fabrication of GDEs with low-catalyst loadings whereby MEA performances are compared to *in-house* GDEs where the catalyst ink is directly painted onto the GDLs.

2. Experimental

2.1. Materials

All materials were used as-received without any further treatments. All solvents of analytical purity were purchased from Fischer. Five types of commercial GDLs (Table 1) were used in this study: *Freudenberg* H2315 C2 (*Freudenberg* – FCCT, Germany), *ELAT[®] LT 1200-W* (*E-TEK*, USA) and *Sigracet* SGL 10BC, 24BC and 34BC (*Sigracet*, Germany). 20 wt% Pt/C *Johnson Matthey* HiSpec[™] catalyst ink was used (*Alfa Aesar*). *Dupont* Nafion[®] 212 membranes were purchased from fuelcellstore.com and were used as received.

2.2. MEA fabrication and testing

The catalyst ink preparation was carried out using the method suggested by Lee et al. [9]. Catalyst inks were prepared by thoroughly mixing ultrasonically (Langford 40 kHz ultrasonic bath, ultrasonic power = 2 W, irradiation time = 30 min) the supported catalyst (20 wt% Pt/C, *Johnson Matthey* HiSpec[™]), aqueous Nafion[®] solution (10 wt%) and an appropriate amount of tetrahydrofuran (THF). The ratio of the supported catalyst to Nafion[®] was typically 2:1 by weight. The catalyst inks were ultrasonic-sprayed onto the commercial GDLs at various catalyst loadings of 0.40, 0.15 and 0.05 mg Pt cm⁻² using the Sono-Tek 'Exacta-coat' ultrasonic spray instrument operating at 120 kHz (Fig. 1(a)). The catalyst inks (14.5 ml) were first inserted in a sonicated (60 kHz) syringe (Fig. 1(b)) prior to atomisation in the nozzle (*Accumist*) (Fig. 1(c)) and sprayed at a flow rate up to 2.4 ml min⁻¹. Various passes (up to 25 in total) were performed in views of obtaining the appropriate loading. The fabricated GDEs were then dried at 50 °C for 15 min and then tested. Here, the Sono-Tek 'Exacta-coat' ultrasonic spray incorporate an ultrasonic atomizing nozzle, vibrating at high frequency ultrasound (120 kHz) created by piezoelectric transducers inside the nozzles's titanium housing (Fig. 1(b)). The catalyst inks were pumped through the nozzle and were atomized into a fine mist at the nozzle tip (Fig. 1(c)) to produce highly repeatable

thin films of micron-sized droplets, with coating thicknesses from 200 nm to 50 μm (Fig. 1(d)).

For comparison purposes, commercial GDEs were used: *Johnson Matthey* Fuel Cells GDEs (GDL: SGL 34BC) of 0.40 mg Pt cm⁻² catalyst loading were used as anodes. The active area of all MEAs was 16 cm².

A thin layer of Nafion[®] solution (Nafion[®] dry weight of 0.6 mg cm⁻²) was applied to all GDE surfaces. All GDEs were placed on either side of untreated Nafion[®] 212 membranes. The MEAs were prepared by hot-pressing at 393 K for 60 s under a pressure of 500 lb. The fuel cell tests were performed using a Bio-logic FCT-50S PEMFC test stand with EIS capabilities. All measurements were performed at 343 K at 50% relative humidity with pressures of 2 bar on the anode and cathode sides in H₂ and O₂ (1.3/2.2 stoics) respectively. The polarization curves were recorded at a scan rate of 1 mV s⁻¹.

Physical morphology of the surface and cross-section of *home-made* and commercial GDEs was performed by using a scanning electron microscopy (SEM) Joel 6060.

3. Results and discussion

In this study, various commercial GDLs were coated using the ultrasonic spray and the *hand*-painting methods at several platinum loadings. The ultrasonic-sprayed GDEs were then compared to *hand*-painted GDEs at three different loadings: 0.40, 0.15 and 0.05 mg cm⁻² on a *Sigracet* 10BC GDL.

Here, the loadings of 0.15 and 0.05 mg cm⁻² were chosen as they conform with the US Department of Energy's (DoE) goal to reduce the total platinum loading in an MEA to a total of 0.2 mg cm⁻² (0.05 mg cm⁻² on the anode and 0.15 mg cm⁻² on the cathode) by 2015 [10].

3.1. Comparison of GDLs for the ultrasonic-spray technique

Five different types of commercial GDLs were ultrasonically sprayed with the catalyst inks and tested for their performances. The five GDLs used were as follows: *Freudenberg* H2315 C2; *E-TEK* Elat LT 1200W and *Sigracet* SGL 34BC, 24BC, 10BC. Fig. 2 shows the polarisation (a) and power density (b) curves for MEAs using several cathode GDEs (anode: JMFC 0.40 mg Pt cm⁻²) fabricated by the ultrasonic-spray method for the five commercial GDLs. It can be observed from the figure that the SGL 10BC exhibits the best performance with a peak power density of 0.695 W cm⁻². This is then followed by *E-TEK* Elat LT 1200W (0.669 W cm⁻²), *Freudenberg* H2315 C2 and SGL 34 BC (0.627 W cm⁻²) and SGL 24BC (0.597 W cm⁻²).

It was recently reported by Millington et al. [11] in this journal that SGL 10BC provided the best performance when the catalyst was applied by *hand*-painting, which is in good agreement with our findings. There is no evident difference in performance between the *hand*-painted *Freudenberg* H2315 and the *E-TEK* Elat LT 1200W [11], however, the ultrasonic-sprayed *E-TEK* Elat LT 1200W provides a better performance.

Compared to the *Sigracet* SGL 24BC and 34BC, the 10BC exhibits a better performance due to its 3D non-woven structure compared to the 2D paper structure of the SGL 24BC and SGL 34BC. For that reason, the 10BC has an open pore structure leading to higher air permeability (Table 1), and is also more compressible and resilient. In our conditions, it can also be observed that the SGL 34BC suffers from mass transport issues observed by the drop on the polarisation curve at higher current densities. According to *Sigracet*, SGL 34BC is not appropriate for use at high current densities due to its high mass transport resistance as it has a 2D paper structure and is much thicker than the 24BC which leads to more 'resistance' through the

Table 1
Five GDL types and their properties used in this study.

Properties	GDL materials				
Trademark	Freudenberg H2315 C1	E-Tel Elat LT-1200W	Sigracet 10BC	Sigracet 24BC	Sigracet 34BC
Type	Paper	Woven cloth	3D-non-woven	2D-paper	2D-paper
Thickness/ μm	252	275	420	235	315
Area weight/ g m^{-2}	132	200	135	100	140
Through-plane resistance/ $\text{m}\Omega \text{cm}^{-2}$	12	410	<16	<12	<14
Air permeability/ $\text{cm}^3 \text{cm}^{-2} \text{s}^{-2}$	–	>8	1.45	0.6	0.35

GDL. Thus, in this study, it was decided to use *Sigracet* 10BC GDL throughout.

3.2. Platinum loading comparison

The performance of GDEs of various loadings was investigated on a *Sigracet* 10BC GDL, as the *Sigracet* 10BC exhibited the best performance at $0.40 \text{ mg Pt cm}^{-2}$ [11]. Fig. 3(a) shows a comparison of polarisation and power curves for various loadings of 0.40, 0.15 and $0.05 \text{ mg Pt cm}^{-2}$ using the *Sigracet* SGL 10BC GDL (cathode) and the ultrasonic-spray method. The performance of the MEAs predictably decreases when the platinum loading is lowered. It can be

noted however that there is not much difference in performances with loadings of 0.40 and $0.15 \text{ mg Pt cm}^{-2}$. The peak power densities for the 0.40 , 0.15 , and 0.05 mg cm^{-2} loadings are 0.695 , 0.677 and 0.544 W cm^{-2} , respectively as stated earlier.

Fig. 3(a) also shows that at a loading of 0.40 mg cm^{-2} , there is a mass transport issue compared to the 0.15 mg cm^{-2} loading in the region above 1.5 A cm^{-2} . This is most likely to be due to the fact that the thickness at a loading of 0.40 mg cm^{-2} is much higher in turns leading to a higher mass transport resistance. This is highlighted in the Nyquist plots in Fig. 3(b). The figure shows that the GDE with a loading of 0.40 mg cm^{-2} has a higher impedance, indicated by the broad width of the plot, of $0.0425 \Omega \text{ cm}^2$, compared to Pt loadings of

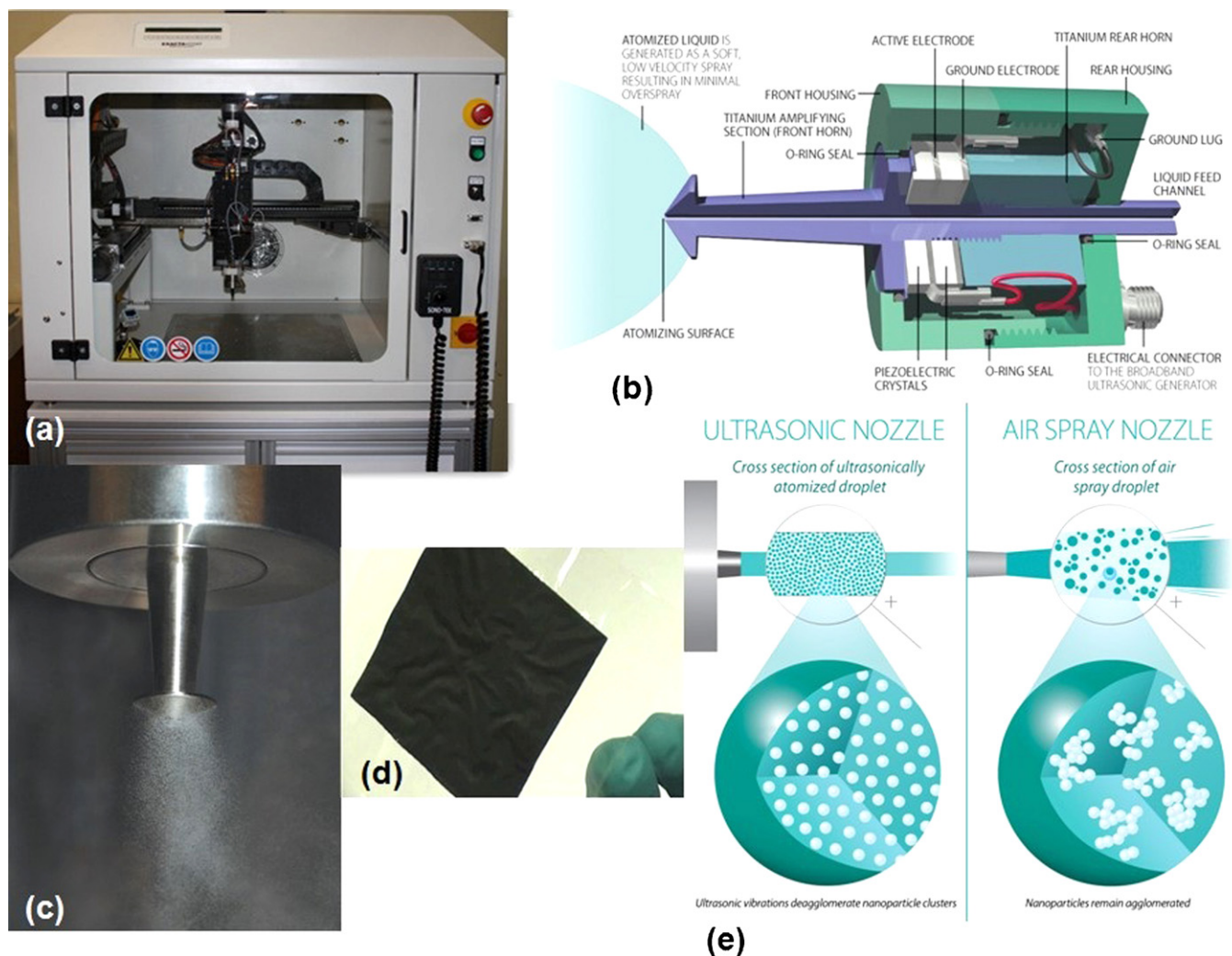


Fig. 1. (a) Sono-Tek Ultrasonic Spray system – ‘ExactaCoat’. (b) Schematic of the vibrating nozzle cross-section. (c) Picture showing mist formation of the liquid. (d) Catalyst coated membrane (CCM) for PEMFC and DMFC fabricated by the Sono-Tek method. (e) Schematic of deagglomeration of nanoparticles by the ultrasonic-spray method compared with the air spray method.

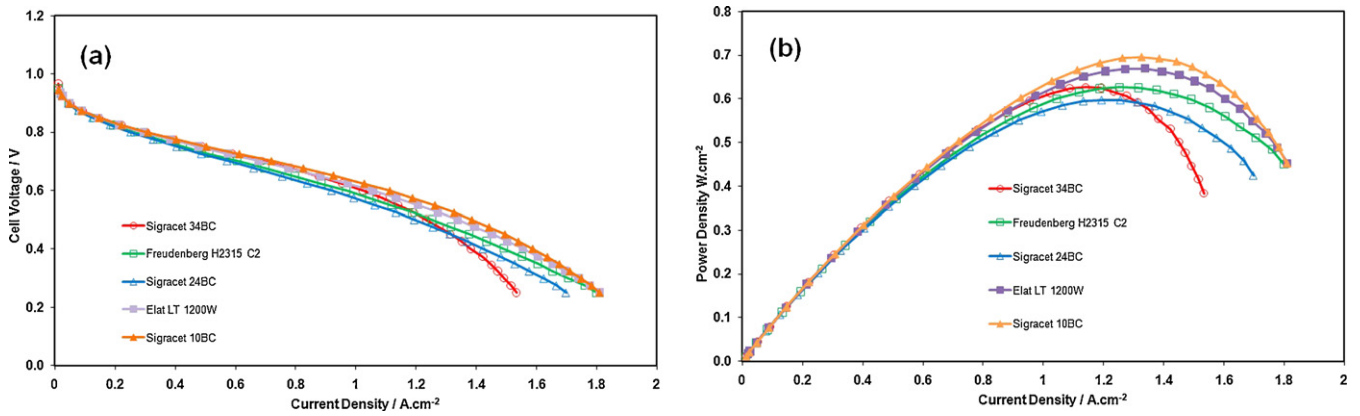


Fig. 2. (a) Polarisation curves; ultrasonic-sprayed GDEs (*Sigracet SGL 10BC, Sigracet SGL 24BC, Sigracet SGL 34BC, Freudenberg H2315 C2; E-TEK Elat LT 1200W GDLs*) of cathode loadings of 0.40 mg cm^{-2} at A = 50%; C = 50%. (b) Power density curves. The anode loading for all experiments was 0.40 mg cm^{-2} (JMFC).

0.015 mg cm^{-2} ($0.0375 \Omega \text{ cm}^2$) and 0.05 mg cm^{-2} ($0.0355 \Omega \text{ cm}^2$), in the region of 0.40 V , which indicates a higher mass transport resistance.

Fig. 3(c) shows the polarisation and power curves *per mg* of platinum for the various loadings of $0.40, 0.15$ and $0.05 \text{ mg Pt cm}^{-2}$ on the *Sigracet SGL 10BC GDL* using the ultrasonic-spray technique. The figure clearly shows that lower platinum loadings lead to higher platinum utilisation. Here, the peak power rating with a platinum loading of 0.05 mg cm^{-2} is 10.9 W mg^{-1} , of 0.15 mg cm^{-2} is 4.5 W mg^{-1} and of 0.40 mg cm^{-2} is 1.7 W mg^{-1} .

3.3. Hand-painted GDEs at various platinum loadings

Fig. 4(a) shows the polarisation and power density curves for the different loadings of $0.40, 0.15$ and $0.05 \text{ mg Pt cm}^{-2}$ on the *Sigracet*

SGL 10BC GDL for *hand-painted GDEs*. Similarly to the ultrasonic-sprayed GDEs, it can be observed that predictably the performance of the MEA decreases as the platinum loading is lowered. However, with the *hand-painted GDEs*, a direct relationship between the decrease in MEA performance and the loading compared to the ultrasonic-sprayed GDEs [Fig. 3(a)] is observed. For example, the peak power densities for the $0.40, 0.15$, and 0.05 mg cm^{-2} loadings are $0.667, 0.530$ and 0.490 W cm^{-2} , respectively.

Fig. 4(b) shows the polarisation and power curves *per mg* of platinum for the various loadings of $0.40, 0.15$ and $0.05 \text{ mg Pt cm}^{-2}$ on the *Sigracet SGL 10BC GDL* for *hand-painted GDEs*. The figure evidently shows that as the loading of platinum is lowered, higher Pt utilisation is obtained. The peak power rating with a platinum loading of 0.05 mg cm^{-2} is 9.8 W mg^{-1} , of 0.15 mg cm^{-2} is 3.5 W mg^{-1} and of 0.40 mg cm^{-2} is 1.7 W mg^{-1} .

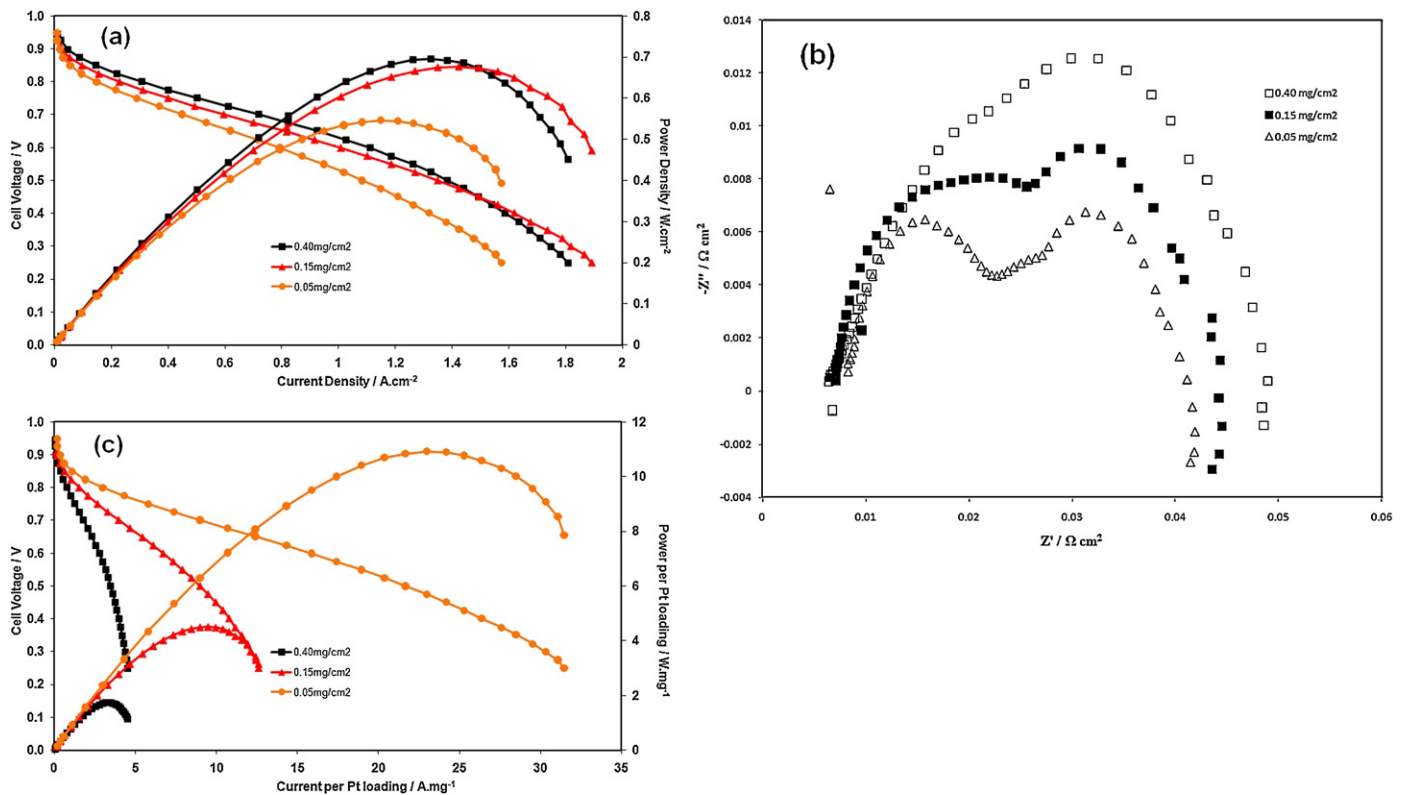


Fig. 3. (a) Polarisation and power density curves, (b) Nyquist plots at 0.40 V for all Pt loadings and (c) polarisation and power density curves *per mg Pt* for ultrasonic-sprayed *Sigracet SGL 10BC GDLs*: $0.40 \text{ mg cm}^{-2}, 0.15 \text{ mg cm}^{-2}, 0.05 \text{ mg cm}^{-2}$ at C = 50%, A = 50%. The anode loading for all experiments was 0.40 mg cm^{-2} (JMFC).

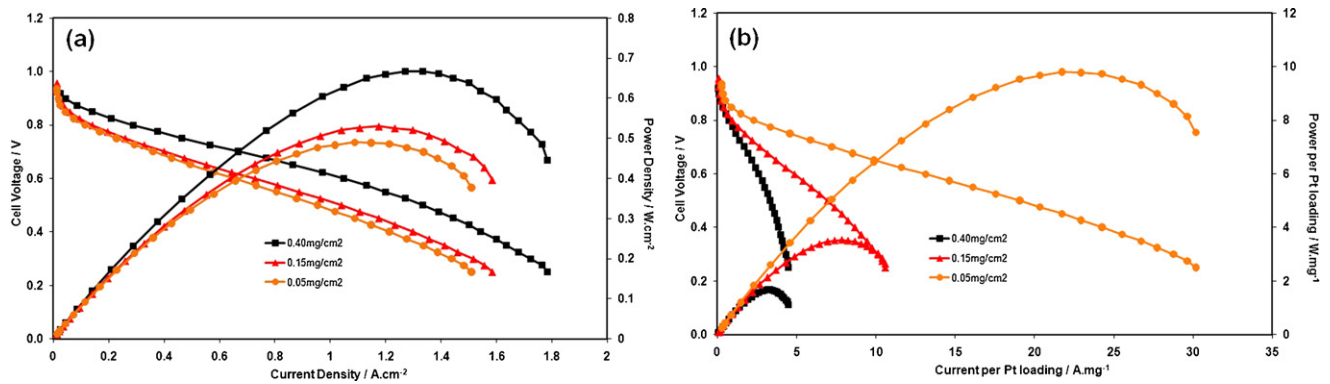


Fig. 4. (a) Polarisation and power density curves and (b) polarisation and power curves *per mg Pt*, for *hand-painted* SGL 10BC GDLs: 0.40 mg cm⁻², 0.15 mg cm⁻², 0.05 mg cm⁻² at A = 50%; C = 50%. The anode loading for all experiments was 0.40 mg cm⁻² (JMFC).

Fig. 5(a)–(c) show the polarisation and power density curves of the *hand-painted* and ultrasonic-sprayed GDEs at various Pt loadings of 0.40, 0.15, and 0.05 mg cm⁻², respectively. It can be noted that with a loading of 0.40 mg cm⁻² the difference between the two methods is negligible in terms of performance compared to Pt loadings of 0.15 and 0.05 mg cm⁻². The average increases in performance for the ultrasonic-sprayed GDEs over the *hand-painted* GDEs are 4% at a loading of 0.40 mg cm⁻², 28% at a loading of 0.15 mg cm⁻² and 11% at a loading of 0.05 mg cm⁻². This is also shown in Fig. 6(a) and (b), as column histograms indicating the peak power densities and power *per Pt* loading for both methods employed at various Pt loadings.

Fig. 7 shows polarisation and power density curves between ultrasonic-sprayed and *hand-painted* GDEs with lower Pt loading anodes as well as cathodes. The platinum loading for the ultrasonic-sprayed GDE was 0.05 mg cm⁻² for the anode and 0.15 mg cm⁻²

for the cathode, and for the *hand-painted* GDE was 0.09 mg cm⁻² for the anode and 0.18 mg cm⁻² for the cathode. The peak power densities for the MEAs fabricated using the ultrasonic spray and *hand-painting* methods are 0.584 and 0.386 W cm⁻², respectively. This observation is interesting as a ca. 50% increase in performance with the MEAs fabricated with lower Pt loading anode GDEs for the ultrasonic-spray technique over the *hand-painted* technique, compared to a 28% increase with the commercial GDEs as the anode at a cathode Pt loading of 0.15 mg cm⁻² is obtained. This is to be expected as both the anode and cathode would provide a better performance with the MEAs using the commercial GDEs as anodes. Here, only the difference in the cathode performance is shown (both have the same anode), whereas where the ultrasonic-sprayed and *hand-painted* GDEs are used on both the anode and cathode would provide a better performance leading to a higher overall increase in performance.

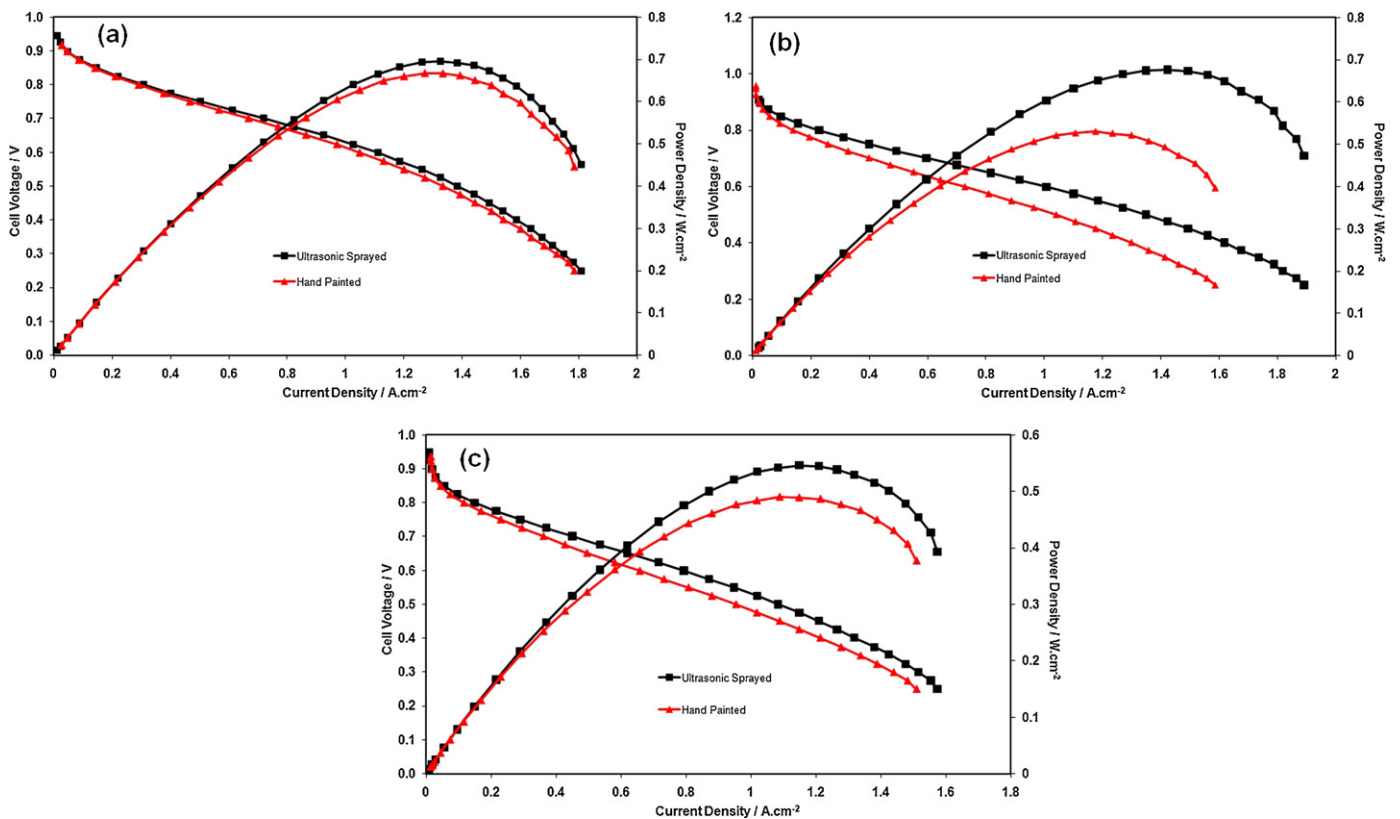


Fig. 5. Polarisation and power density curves comparing ultrasonic-sprayed and *hand-painted* SGL 10BC GDLs: (a) 0.40 mg cm⁻², (b) 0.15 mg cm⁻², and (c) 0.05 mg cm⁻². A = 50%; C = 50%. The anode loading for all experiments was 0.40 mg cm⁻² (JMFC).

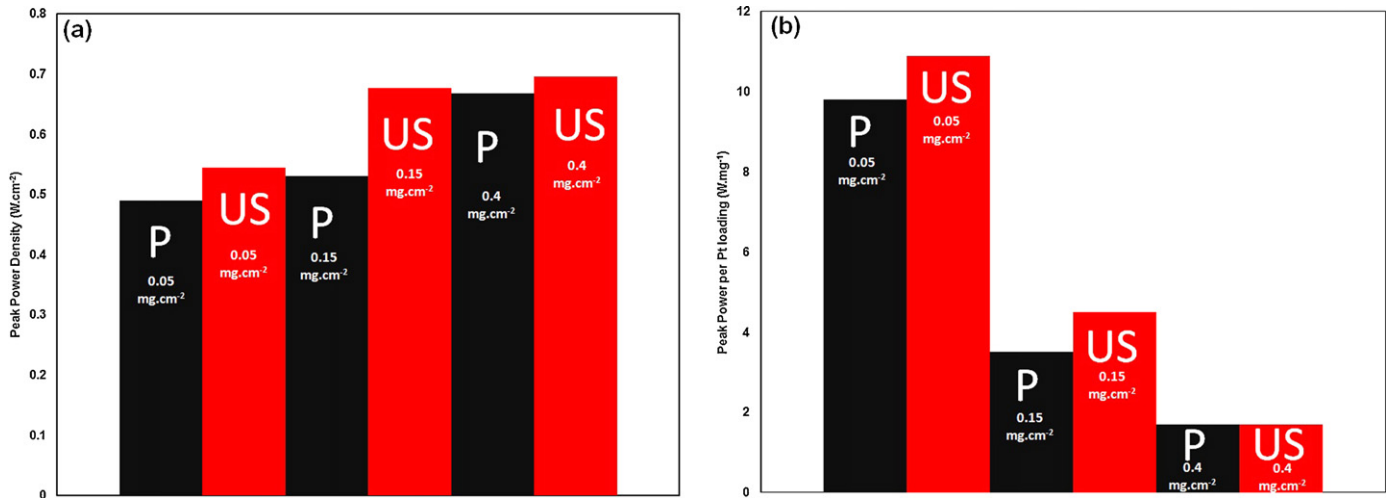


Fig. 6. Column histograms comparing (a) peak power densities and (b) peak power per Pt loading for both *hand-painted* (P) and ultrasonic-sprayed (US) SGL 10BC GDLs: 0.40 mg cm⁻², 0.15 mg cm⁻², 0.05 mg cm⁻².

It can be observed that the ultrasonic-spray method provides better performances compared to the *hand-painted* method especially at low loadings of platinum. However, at higher Pt loadings (0.40 mg Pt cm⁻²), the two methods lead to similar performances. A possible explanation to our findings is due to the fact that ultrasonic spraying leads to better distribution of the catalyst ink onto the GDL giving better platinum utilisation. This is mainly caused by ‘cavitation’ phenomena [6–8] aiding the de-agglomeration of the catalyst ink. Furthermore, the authors have found that ultrasonic spray system offer many advantages as follows: (i) minimal bounce-back and overspray of the liquid onto the substrate, (ii) non-clogging issues at the nozzle tip and (iii) de-agglomeration of the nanoparticles in solution due to the nozzle’s high frequency vibration (Fig. 1(e)). Other benefits are high transfer efficiency, the ability to precisely control thickness of deposition and drop size (by varying the nozzle ultrasonic frequency), and tight drop distribution that results in highly uniform deposition. The soft and low velocity ultrasonic spray provides an excellent adherence to substrates of any geometry [6].

3.4. SEM images of GDEs

Fig. 8(a)–(f) are SEM images of ultrasonic-sprayed GDEs for the three different loadings of 0.40, 0.15, and 0.05 mg cm⁻². The appearance of the surface of the catalyst layers with 0.05 and 0.15 mg cm⁻² platinum loading are very similar, however, there is a difference in the appearance compared to the 0.40 mg cm⁻² catalyst loading layer. At the higher loading of 0.40 mg cm⁻² the surface of the GDE appears to possess more ‘cracks’ which are more distinct than the cracks on the surface of the lower loaded GDEs.

Cross-sectional images of the ultrasonic-sprayed GDEs appear to be of consistent thicknesses across the substrates, compared to the *hand-painted* GDEs shown in Fig. 8(g) and (h) where it is clear that the surface thickness is not uniform. It can also be observed that at higher Pt loading, thicker catalyst layers are observed, which is to be expected. The total thicknesses of the ultrasonic-sprayed GDEs at various loadings are: ~413 μm (0.05 mg cm⁻²), ~427 μm (0.15 mg cm⁻²) and ~454 μm (0.40 mg cm⁻²). Note that these thicknesses are only approximates as it is difficult to obtain

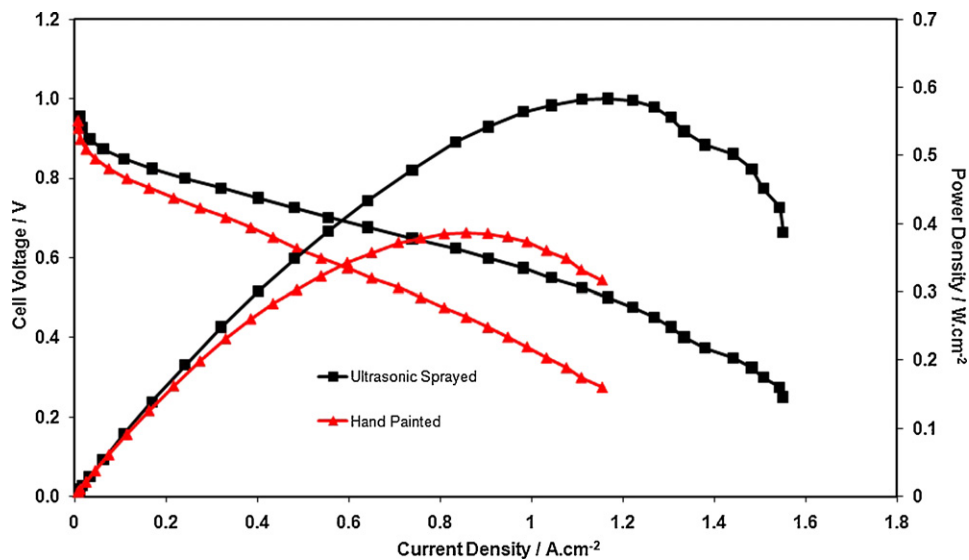


Fig. 7. Polarisation and power density curves comparing ultrasonic-sprayed and *hand-painted* SGL 10BC GDLs. A = 50%; C = 50%. The loadings for the MEAs were; ultrasonic-sprayed: A = 0.05 mg cm⁻², C = 0.15 mg cm⁻² and *hand-painted*: A = 0.09 mg cm⁻², C = 0.18 mg cm⁻².

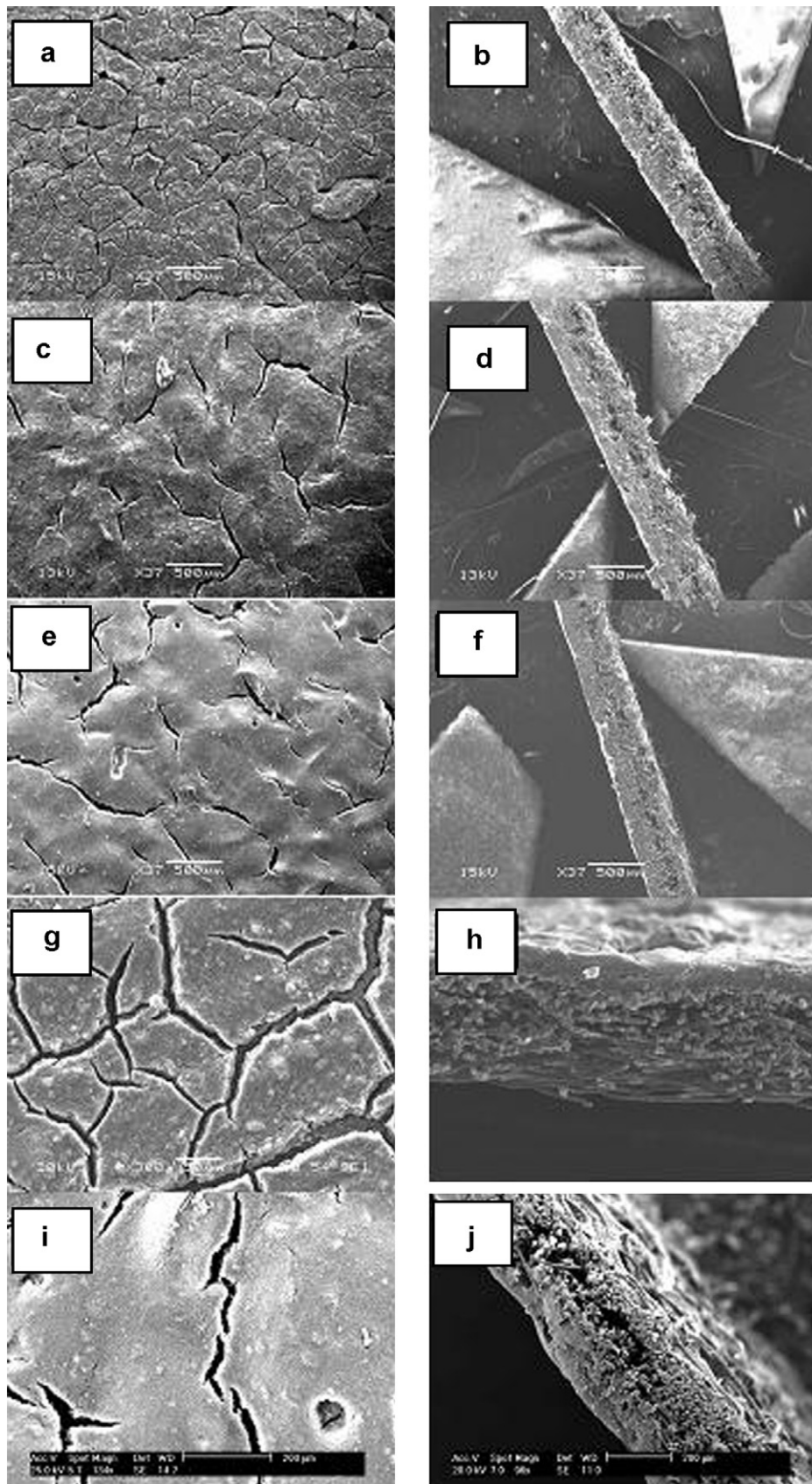


Fig. 8. SEM images: (a) top view and (b) cross-section of the catalyst layer prepared by the ultrasonic-spray method. The platinum loading is 0.40 mg cm^{-2} on Sigracet 10BC GDL, (c) top view and (d) cross-section of catalyst layer prepared by the ultrasonic-spray technique. The platinum loading is 0.15 mg cm^{-2} on Sigracet 10BC GDL, (e) top view and (f) cross-section of catalyst layer prepared by ultrasonic-spray. The platinum loading is 0.05 mg cm^{-2} on Sigracet 10BC GDL, (g) top view and (h) cross-section of catalyst layer prepared by *hand-painting*. Platinum loading: 0.40 mg cm^{-2} on Sigracet 34BC GDL, (i) Top view and (j) cross-section of Sigracet 10BC GDL with microporous layer (MPL) with no catalyst layer.

Table 2
Performance values at various anode and cathode platinum loadings using several GDLs and 'deposition' methods: ultrasonic-spray, electro-spray, double catalyst layer (spray), sputtering and hand-paint.

Technique	Pt cathode loading/mg cm ⁻²	Peak power density/W cm ⁻²	Current density @ 0.6 V/A cm ⁻²	Operating conditions		Pt	Commercial catalyst	GDL type	Cathode peak Power per Pt load-ing/W mg ⁻¹	Total Peak Power per Pt load-ing/W mg ⁻¹	Ref.
				Temperature/°C	Pressure/bar						
Ultrasonic spray	0.05	0.544	0.79	70	2	50	HiSpec	SGL 10BC	10.9	1.2	Our work
Ultrasonic spray	0.15	0.677	1	70	2	50	HiSpec	SGL 10BC	4.5	1.2	Our work
Ultrasonic spray	0.40	0.695	1.10	70	2	50	HiSpec	SGL 10BC	1.7	0.87	Our work
Ultrasonic spray	0.15	0.584	0.90	70	2	50	HiSpec	SGL 10BC	3.9	2.9	Our work
Electrospray	0.012	0.243	0.25	70	3.4	Dry H ₂ /O ₂	^a	Toray	20	0.24	[12]
Electrospray	0.10	0.07	0.06	80	Ambient	100	Electrochem	^a TGP-H-060	0.7	0.35	[13]
Double catalyst layer (spray)	0.12	0.66	0.90	65	1.4	100	HiSpec	Toray	5.5	4.1	[14,15]
Sputtering	0.01	0.40	0.50	80	3.1–3.8	100	^a	TGP-H-060	40	20	[16]
Sputtering	0.16	0.70	1	80	3.1–3.8	100	^a	E-Tek	4.4	2.2	[16]
Hand-paint	0.18	0.386	0.54	70	2	50	HiSpec	SGL 10BC	2.1	1.4	Our work

^a Not specified.

accurate values. Fig. 8(i) and (j) show SEM images of the Sigracet SGL 10BC GDL whereby the micro porous layer (MPL) can be seen on top of the GDL. Here, the appearance of the MPL is very similar to the catalyst layer, making it hard to distinguish between the two.

3.5. Other methods of fabrication for low loading GDEs

For completeness, the authors have performed a literature search on current methods leading to low/ultra-low Pt loading for PEMFC electrodes. There are many techniques reported in the literature for the fabrication of PEMFC electrodes. Table 2 shows the performance of several MEAs fabricated by the various methods (including the authors' data on the ultrasonic-spray method): electro-spraying [12,13], the double catalyst layer technique [14,15] and sputtering [16]. These methods have been included as they show most promising results for low to ultra-low loading PEMFC electrodes.

The table also shows that the sputter deposition technique offers better performances in terms of peak power per mg of platinum, with a total peak power of 20 W mg⁻¹ at a loading of 0.01 mg Pt cm⁻². However, it should be emphasized that the conditions of testing are not similar to those used for the other methods highlighted in the table. For example, the temperature, pressure and humidity used for the sputtering technique are higher than those used in our and other studies, which would lead to better performances. It can also be noted that even though the peak power per mg of platinum is high, the peak power density of 0.40 W cm⁻² is still fairly low and would not be sufficient for practical use. Interestingly, Table 2 shows that the performance between sputtering and ultrasonic-spray methods are very comparable, e.g. at a loading of 0.15 mg cm⁻² for ultrasonic-sprayed GDEs and 0.16 mg cm⁻² for sputtered GDEs, the performance values are very similar. The electro-spray method also shows promising results with a cathodic peak power of 20 W mg⁻¹ at a low loading of 0.012 mg cm⁻². However, the main problem with the electro-spray technique is that the peak power density value of 0.243 W cm⁻² is too low to be used in practical applications (here, the anode loading used in the testing was 1.0 mg cm⁻², which is quite high). The double catalyst layer is a spray technique, whereby the catalyst layer is made up of two different layers of different platinum loadings [14,15]. This technique gives a cathodic peak power of 5.5 W mg⁻¹ at a loading of 0.12 mg cm⁻². Overall, Table 2 shows that the ultrasonic spray technique is a very promising method compared to other techniques.

4. Conclusions

This paper reports for the first time, the use of ultrasonic-spray for the fabrication of PEMFC electrodes (GDEs). Five types of GDL were coated with catalyst ink by the ultrasonic-spray method and their performances were compared. It was found that SGL 10BC showed the best performance in an MEA when the GDL was ultrasonically spray coated. Mass transport issues were highlighted with the SGL 34BC. This paper also shows that the ultrasonic-spray method provides better performances compared to the hand-painted method especially at low loadings of platinum. Peak power ratings were found at loadings of 0.40, 0.15, and 0.05 mg cm⁻² to be 1.7, 4.5 and 10.9 W mg⁻¹, respectively, for the ultrasonic-spray method, and 1.7, 3.5 and 9.8 W mg⁻¹, respectively, for the hand-paint method. It was found that the ultrasonic-spray method distribute the catalyst ink more evenly leading to better platinum utilisation compared to the hand-painted method and this is further evident at lower platinum loadings.

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