



Short communication

The effect of materials on proton exchange membrane fuel cell electrode performance

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ABSTRACT

This paper describes the optimisation in the fabrication materials and techniques used in proton exchange membrane fuel cell (PEMFC) electrodes. The effect on the performance of membrane electrode assemblies (MEAs) from the solvents used in producing catalyst inks is reported. Comparison in MEA performances between various gas diffusion layers (GDLs) and the importance of microporous layers (MPLs) in gas diffusion electrodes (GDEs) are also shown. It was found that the best performances were achieved for GDEs using tetrahydrofuran (THF) as the solvent in the catalyst ink formulation and Sigracet 10BC as the GDL. The results also showed that our *in-house* painted GDEs were comparable to commercial ones (using Johnson Matthey HiSpec™ and E-TEK catalysts).

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1. Introduction

The main scope for the development and successful market deployment of proton exchange membrane fuel cells (PEMFCs) is to reduce the Pt catalyst loading on both anode and cathode electrodes together with the associated cost without compromising on the PEMFC performance [1,2]. In order to achieve this challenging goal, it is necessary to increase the effective surface area of the Pt catalyst, in other words, the triple phase boundary (TPB) between the catalyst, electrolyte (Nafion®, PEM) and the reactants (hydrogen and oxygen where the electrochemical reactions occur) in the catalyst layer (CL). Since maximising and optimising the TPB is of great importance, the PEMFC performance depends greatly on the kinetics of interfacial phenomena [1,2].

Gas diffusion electrodes (GDEs) mainly consist of two or three layers: the GDL and the CL as well as the microporous layer (MPL) 'sandwiched' between the GDL and the CL. The MPL consists of a carbon powder mixed with a hydrophobic agent which is applied onto the GDL surface. Its main role is to (i) prevent flooding in the CL (water management) and (ii) act as a good electrical conductor between the GDL and the CL, as well as improving reactant gas distribution [3].

PEMFC electrodes are usually constituted of Pt nanoparticles on carbon black acting as support (Pt/C) mixed with polymer electrolyte ionomer solution e.g. Nafion® to form the CL [1]. In this case, to improve the performance of 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 catalysts in the CL is required. However, increasing the thickness of the catalyst layer leads to a high diffusion resistance for reactants towards active Pt catalytic sites, whereas high electrocatalyst loadings generally result in an increase in particle size, thus in poor PEMFC efficiencies [1,2]. Therefore, optimisation on fabricated techniques is required to obtain good PEMFC performances.

There are numerous well-documented methods describing the loading of electrocatalysts onto the GDL and the electrolyte membrane. For example, Litster and McLean [1] and Wee et al. [2] give excellent overviews of PEMFC electrode fabrication methods. The most common method for the fabrication of CLs is to mix catalyst black Pt/C (Pt supported on porous carbon particles) by the colloidal route, with a solubilised electrolyte ionomer solution (e.g. Nafion®) and other solvents, followed by applying the 'paste' onto the support by either decal, blade process, screen-printing, hand-spray, electrospray, electrodeposition or sonoelectrodeposition methods [4–8]. The main drawback of these methods is that heating i.e. oxidative treatment is required in order to 'clean' the Pt particles from the preparative chemical contamination. These treatments can greatly affect the surface structure/morphology of the Pt parti-

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Table 1
Three types of GDLs and their properties used in this study.

	GDL material		
	Freudenberg	E-Tek	Sigracet
Product	H2315 C2	ELAT [®] LT 1200-W	10BC
Type	Paper	Woven Cloth	Paper
Thickness (μm)	252	275	415
Area weight (g m^{-2})	132	200	135

cles and result in inactive Pt sites for electrochemical reactions at the 'three-phase reaction zone' [1,2].

In this paper, we report the effect of catalyst ink solvents on GDEs and the influence of GDLs and MPLs on MEA performances. All our data are compared to commercial GDEs and catalyst inks (*E-TEK* and *Johnson Matthey HiSpecTM*). Our *in-house* GDEs were also compared to commercial GDEs to validate and benchmark our findings.

2. Experimental

2.1. Materials

All materials were used as received without any further treatments. All solvents of analytical purity were purchased from Fischer. Three types of GDLs (as shown in Table 1) were used in this study: Freudenberg H2315 C2 (*Freudenberg* – FCCT, Germany), ELAT[®] LT 1200-W (*E-TEK*, USA) and Sigracet SGL 10BC (*Sigracet*, Germany). Two types of 20 wt% Pt/C catalyst black were used: *E-TEK* (Fuelcellstore) and *Johnson Matthey (JM) HiSpecTM* (Ionpower). DuPont Nafion[®] 212 membrane and commercial *E-TEK* ELAT[®] GDE LT 120E-W (used as the cathode, Pt loading of 0.5 mg cm^{-2}) were purchased from Fuelcellstore.

2.2. MEA fabrication and fuel cell testing

The MEA fabrication was carried out using the method suggested by Kim et al. [6]. Catalyst inks were prepared by thoroughly mixing the supported catalyst (20 wt% Pt/C, *E-TEK* or *JM*), Nafion[®] aqueous solution (10 wt%) and an appropriate amount of solvent [e.g. tetrahydrofuran (THF)] ultrasonically (Langford 40 kHz ultrasonic bath, ultrasonic power = 8 W). The ratio of the supported catalyst to Nafion[®] was typically 2:1 by weight. The 'sonicated' ink was painted onto GDLs with a catalyst loading of $0.4 \text{ mg Pt cm}^{-2}$. The active area of all MEAs was 16 cm^2 .

A thin layer of Nafion[®] solution (Nafion[®] dry weight of 0.6 mg cm^{-2}) was applied to the commercial *E-TEK* GDE surface. The commercial anodes and the painted cathodes were placed on either side of untreated Nafion[®] 212 membranes. The MEAs were prepared by hot-pressing at 120°C for 60 s under a pressure of 500 psi. For comparison purposes, an MEA was fabricated using the commercial GDE on both the anode and cathode sides. The MEA tests were performed using a Bio-logic FCT-50S PEM Fuel Cell test stand with EIS capabilities. All measurements were performed at 70°C with a gas relative humidity of 50% and back pressure of 2 bar at the anode and cathode sides in H_2 and air (1.2/2.2 stoics) respectively.

Physical morphology of the surface and cross-section of *in-house* and commercial GDEs was performed using a scanning electron microscopy (SEM) Philips XL-30.

3. Results and discussion

3.1. Effect of catalyst ink solvents

The solvent used in the catalyst ink can have a dramatic effect on the performance of MEAs. Indeed, the di-electric constant of the

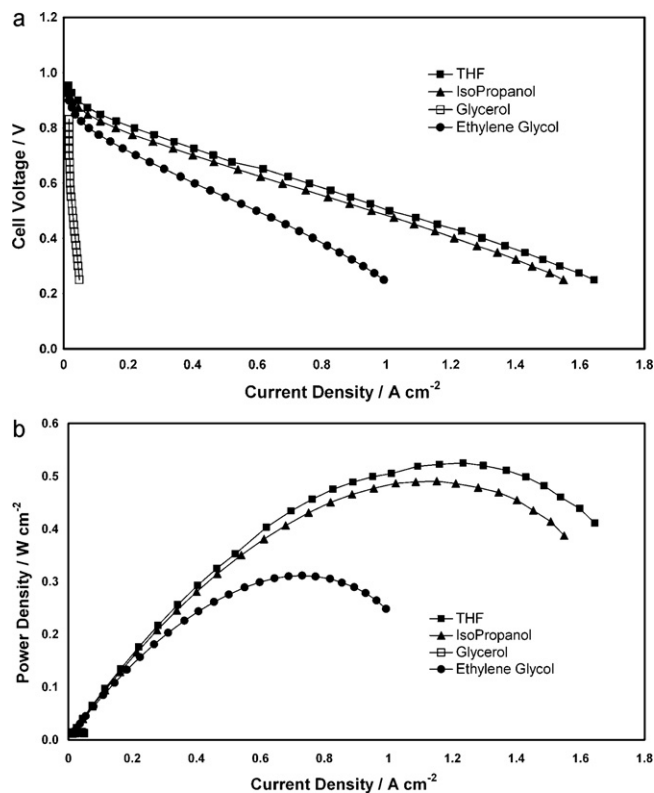


Fig. 1. Comparison between MEAs fabricated using different solvents in the catalyst ink: (a) voltage-currents and (b) power density curves.

solvent determines the form that the electrolyte Nafion[®] ionomer takes within the catalyst ink. Nafion[®] ionomer forms either a solution or a colloidal dispersion in solvents with di-electric constants higher than 10 and in the range [5–10] respectively [9,10]. It has been shown that the nature of the solvent has an impact on the morphology of the resulting catalyst layer and the catalyst inks containing Nafion[®] ionomer as a colloidal dispersion produce better performances than those where Nafion[®] ionomer is fully solvated [10]. This is due to a more 'effective' distribution of Nafion[®] ionomer within the catalyst layer as well as enhanced porosity [9,10]. In a solution ink, the Nafion[®] ionomer covers the carbon surface blocking the conduction of electrons and thus decreasing catalyst utilisation. Also in the colloidal ink, the porosity of the catalyst layer increases due to the Pt/C being adsorbed, leading to an increase in the size of the agglomerates [9–13].

In this study, we have investigated four different solvents in producing catalyst inks, namely: tetrahydrofuran (THF), iso-propanol (IPA), ethylene glycol (EG) and glycerol (G). Fig. 1 shows the polarization and power density curves for MEAs using GDEs fabricated with various catalyst ink solvents. The figure shows that the GDE using THF in the catalyst ink produces the best performance (0.52 W cm^{-2}) followed by IPA (0.49 W cm^{-2}), EG (0.31 W cm^{-2}) and a very poor performance from glycerol (0.01 W cm^{-2}). The difference in performances is mainly due to a variation in solvent di-electric constants. For example, THF has a di-electric constant of 7 [14] and therefore produces a 'colloidal' ink. The other three solvents have di-electric constants above 10 and therefore produce 'solvent' inks. This observation supports our earlier findings that colloidal inks produce better performances.

Another possible explanation from our observations could be due to the way that GDEs were treated after the ink had been painted onto the GDL surface. For example, THF and IPA dry very rapidly at room temperature, however, EG and glycerol need much higher temperatures to evaporate from the catalyst layer and it is

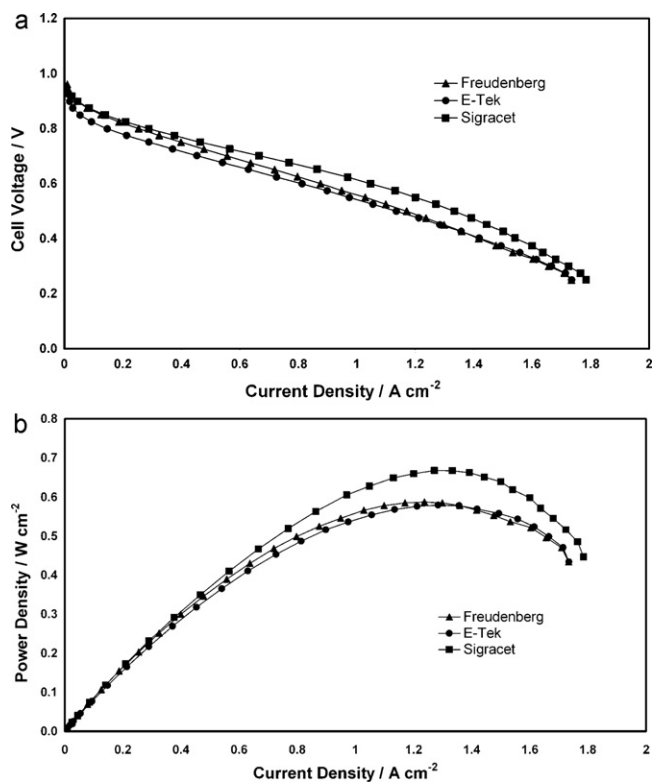


Fig. 2. Effect of GDL on MEA performance: (a) current–voltage and (b) power density curves.

therefore impossible to ‘eliminate’ all the solvent from the layer as the GDEs were dried at 120 °C (NB: glycerol has a boiling point of 180 °C). At 120 °C, the GDEs take a considerable amount of time to completely dry. Therefore, it is possible that some of the solvent remains when the GDEs were hot-pressed against the membrane. The remaining solvent in the catalyst layer could reduce the ‘effectiveness’ of the TPB in turn leading to poor performances. In this case, THF is more adequate to use as catalyst ink solvent, as it evaporates from the CL much faster than the other solvents and eliminates the need to use an oven for solvent evaporation.

3.2. Effect of gas diffusion layers

Three different types of GDL were painted with the catalyst ink and tested for their performances, namely Freudenberg H2315 C2, E-TEK ELAT[®] LT 1200W and Sigracet 10BC. Here, the E-TEK GDL is a woven carbon cloth and the Freudenberg and Sigracet GDLs are both carbon papers. Table 1 lists the relevant properties of the three GDLs. The thickness of the Freudenberg and the E-TEK GDLs are very similar, however, the Sigracet GDL is much thicker (with a low area weight indicating high porosity). It should also be noted that the two carbon papers have similar area weights (ca. 130 g m⁻²) and the E-TEK carbon cloth has a higher area weight (200 g m⁻²).

Fig. 2 shows the performances of the MEAs fabricated using the three types of GDL. The figure also shows that the MEA fabricated with the Sigracet GDL exhibits a better performance than both the Freudenberg and E-TEK types which show similar performances. It is shown that the peak power densities for the Sigracet GDL and the E-TEK/Freudenberg GDLs are 0.68 W cm⁻² and 0.59 W cm⁻² respectively. It can also be observed that the performance of MEAs fabricated with the Sigracet 10BC GDL drops much faster than the two others, especially in the high current density region. This indicates a high mass transport ‘resistance’ possibly due to the large thickness of the Sigracet 10BC. Fig. 3 shows Nyquist plots for the

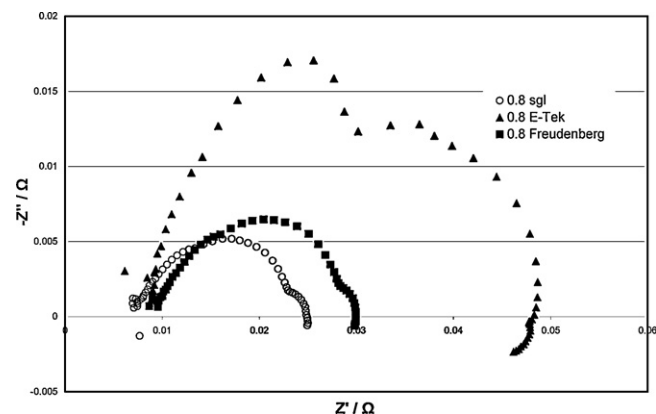


Fig. 3. Nyquist plots of MEAs fabricated using various GDLs.

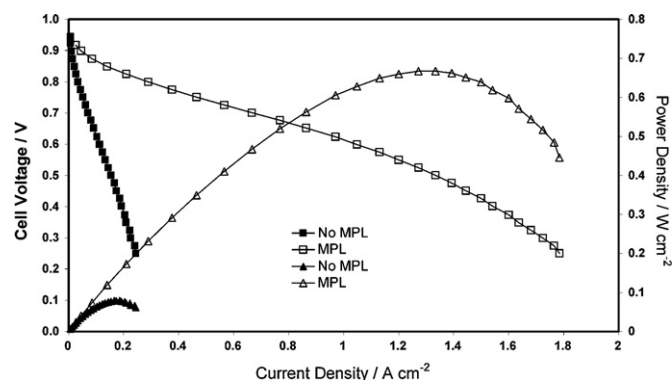


Fig. 4. Effect of MPL on GDE performance.

three GDLs recorded at a cell voltage of 0.8 V. It can be seen that the Sigracet 10BC shows a smaller impedance response compared to the two other GDLs, with the E-TEK GDL exhibiting a much larger impedance.

These results indicate that a high porosity is required to achieve a better performance for a GDL. The Sigracet GDL leads to a smaller impedance and a larger power density, with the E-TEK GDL exhibiting a larger impedance and a relatively poor performance. This is possibly due to a higher porosity acting towards a better ‘water management’.

3.3. Effect of microporous layer

In this study, two GDEs were fabricated: one with a microporous layer (MPL) and one without. Fig. 4 shows the performance of the

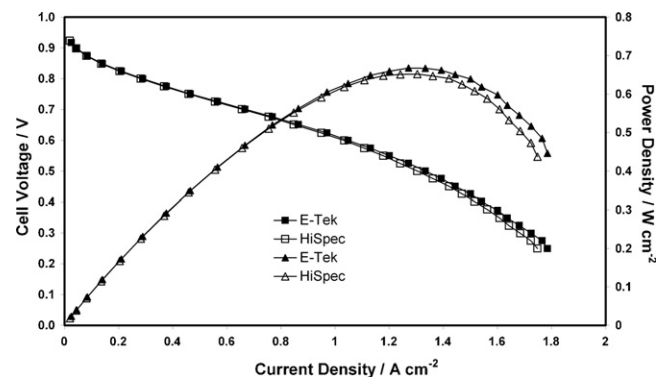


Fig. 5. Current–voltage and power density curves comparing Pt/C from E-TEK and JMFC HiSpec[™] catalysts.

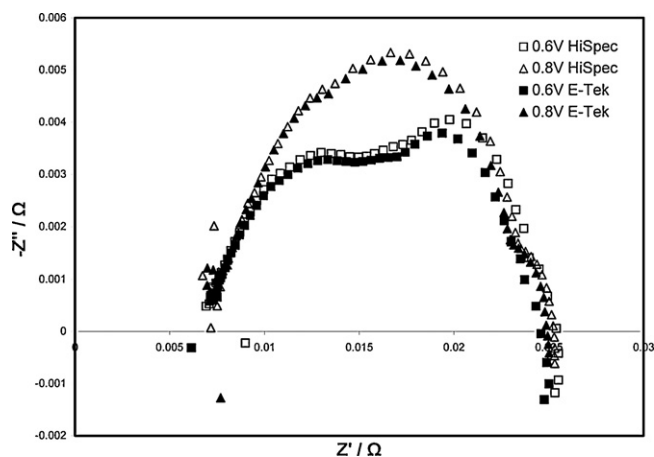


Fig. 6. Nyquist plots for MEAs fabricated using *E-TEK* and JMFC HiSpec™ catalysts.

two MEAs. It can be clearly observed from the polarization curves that the performance of the MEA without the MPL is very poor i.e. a peak power density below 0.1 W cm^{-2} was obtained, demonstrating the importance of the MPL in GDLs. Indeed, the MPL consists of carbon spheres mixed with the hydrophobic agent PTFE whereby its main function is to improve (i) contact between the catalyst layer and the GDL and (ii) the distribution of reactant gases as well as water removal from the CL.

3.4. Commercial catalyst benchmarking

All *in-house* GDEs were fabricated using the same *E-TEK* 20 wt% Pt/C catalyst batch. Recent studies [15] have shown the unreliability of the *E-TEK* catalyst which was also observed electrochemically (using a 3-electrode set-up by cyclic voltammetry and rotating disc

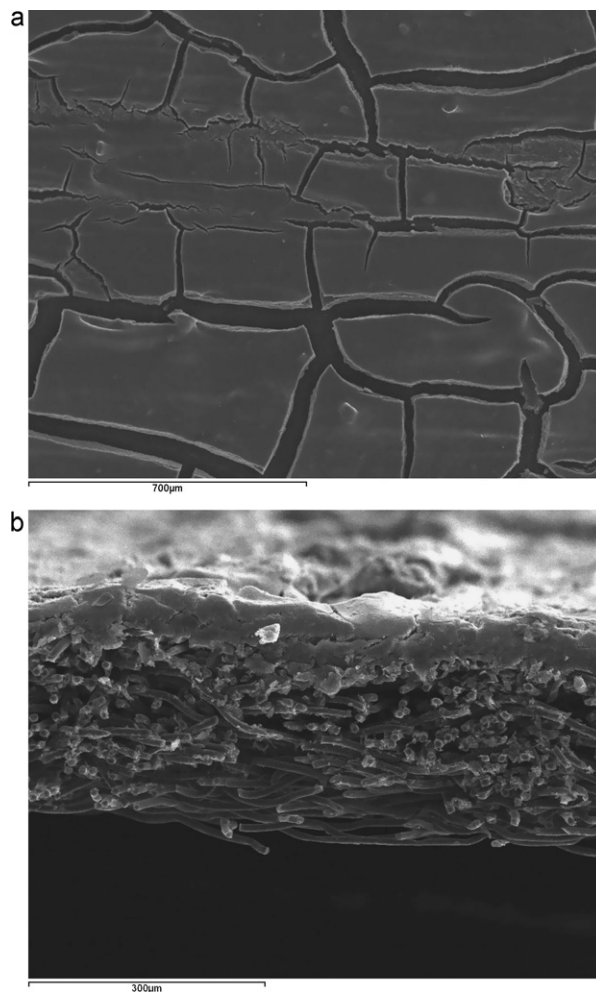


Fig. 8. Surface and cross sectional SEM images of hand-painted GDEs.

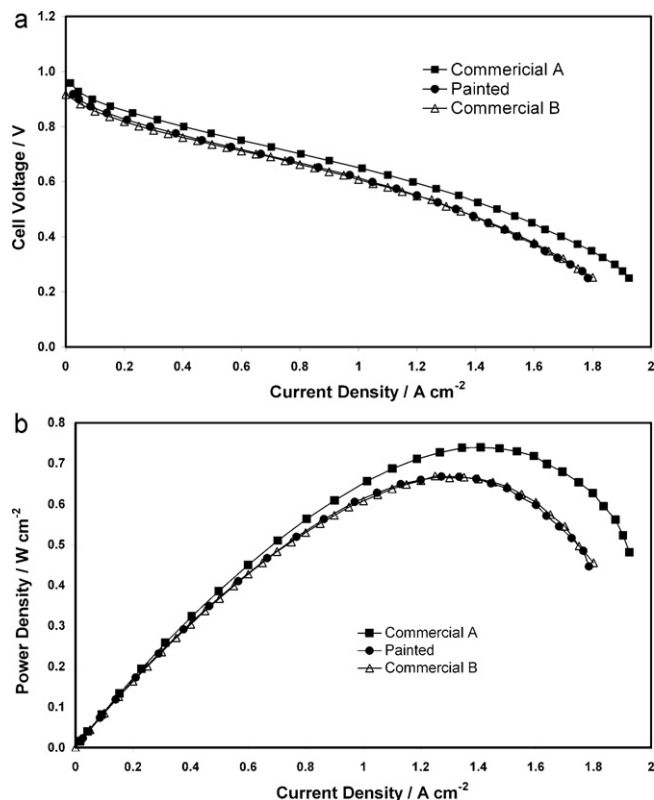


Fig. 7. Commercial MEAs: (a) current–voltage and (b) power density curves.

electrode thin-film experiments) in our laboratory. To validate our results and verify the reliability of the *E-TEK* catalyst, an MEA was fabricated with a GDE using HiSpec™ Pt/C 20 wt% catalyst from *Johnson-Matthey*.

Fig. 5 shows the polarization and power density curves of two MEAs using *E-TEK* and *Johnson Matthey* HiSpec™ catalysts. It is clear from the figure that the performances of both MEAs are very comparable, and show no obvious differences. Fig. 6 shows Nyquist plots of the two MEAs and indicates that there is no difference between the two in terms of electrochemical impedance. These results confirm that the batch of *E-TEK* catalyst used in this study is reliable and consistent.

3.5. Commercial GDEs

To provide a basis for this study, commercial GDEs were compared to our *in-house* GDEs. MEAs were produced using commercially manufactured GDEs, from *Johnson Matthey* (*JM*) and *E-TEK*, where the technique used for preparing catalyst layers onto the GDLs is screen-printing. Here, the *JM* and *E-TEK* GDEs have a Pt loading of 0.4 mg cm^{-2} and 0.5 mg cm^{-2} respectively. Fig. 7 shows the performance of the commercial GDEs compared to our *in-house* painted GDE. It can be observed that our *in-house* painted GDE showed a very comparable performance to the *E-TEK* (peak power density of 0.68 W cm^{-2}), with the *JM* GDE showing a slightly better performance (peak power density of 0.75 W cm^{-2}). These results demonstrate that our hand-painting process produces good per-

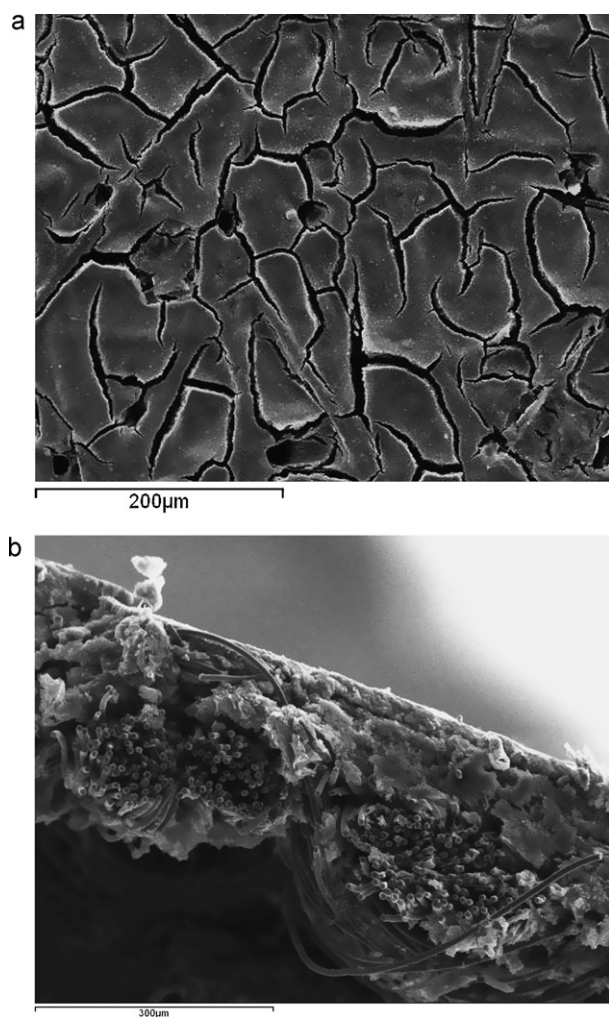


Fig. 9. Surface and cross sectional SEM images of two commercial GDEs.

formances (and comparable to screen-printed commercial GDEs). However, the main problem with the hand-painting method is the poor reproducibility (especially from different operators) and scalability of the process.

Figs. 8 and 9 show both the GDE surfaces and cross-sectional SEM images of the painted and commercial GDEs. From the top view, the appearance of the catalyst layers is similar on both the hand-painted and commercial GDEs. The catalyst layers in both GDEs show obvious uniform ‘cracks’ providing ‘lands’ of 50–100 μm for screen-printed GDEs and 700 μm for painted GDEs. Furthermore, the gaps between the cracks for the painted GDEs can be as large as 100 μm compared to a few micrometers for commercial GDEs. The main differences in catalyst layer surfaces, especially for painted GDEs, may lead to poor contact with the electrolyte membrane and result in poor performances. From the cross-sectional views, it can also be observed that the thickness of the catalyst layers varies along the cloth for the painted GDE i.e. between approximately 30 and 100 μm , whereas the thickness of the catalyst layer is consistent throughout the commercial GDE i.e. approximately 40 μm . Furthermore, the catalyst layer is much porous in the commercial GDE. The hand-painting method

might not be a good and viable technique to ensure reproducibility and accuracy compared to commercial screen-printing technology, however, in our conditions, the painted GDE exhibited a comparable performance to screen-printed commercial GDEs.

4. Conclusions

In this study, the effect of the catalyst ink solvent and GDL material on MEA performances was investigated. Due to a low dielectric constant, THF showed a better performance than IPA as solvent in the catalyst inks, while EG and glycerol led to poor performances. Three types of GDLs were compared and it was shown that Sigracet SGL 10BC exhibited the best GDE performance when compared to two other commercial GDLs (*E-TEK* GDL 1200W and *Freudenberg* H2315 C2), due to the high porosity of Sigracet 10BC. It was also shown that the presence of MPL on the GDL surface improves dramatically MEA performances. Two types of commercial catalyst inks (*E-TEK* and *JM*) were compared and the results showed very similar performances. Furthermore, our *in-house* painted GDEs exhibited comparable performances to commercial screen-printed GDEs with peak power densities of 0.68–0.75 W cm^{-2} . However, SEM top and cross-sectional images of our *in-house* GDEs showed the presence of larger ‘cracks’ and ‘lands’ areas (up to 700 μm) and non-uniform thicknesses along the GDE (30–100 μm) compared to commercial GDEs exhibiting uniform smaller layer thicknesses (ca. 40 μm) and ‘lands’ areas below 100 μm . Overall, our results showed that GDEs produced with the catalyst ink made from THF painted onto Sigracet SGL 10BC GDL led to good performances which were comparable to commercial GDEs at similar Pt loadings.

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