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ARTICLE *in* JOURNAL OF POWER SOURCES · JULY 2014

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Fabrication of gas diffusion electrodes *via* electrophoretic deposition for high temperature polymer electrolyte membrane fuel cells



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HIGHLIGHTS

- EPD was adapted for the fabrication of GDEs for high temperature PEMFCs operating at 160 °C.
- EPD GDEs showed higher porosity and more uniform particle size distribution compared to ultrasonically sprayed GDEs.
- Heat treatment of GDEs negatively affected MEA performance.
- EPD MEA showed ~12% peak power increase over ultrasonically sprayed MEA at ~4% lower Pt loading.
- PTFE was shown to be more suitable than Nafion® ionomer for MEAs in HT-PEMFCs.

ARTICLE INFO

Article history:

Received 2 October 2013

Received in revised form

6 January 2014

Accepted 8 February 2014

Available online 20 February 2014

Keywords:

Electrophoretic deposition
High temperature polymer electrolyte
membrane fuel cell
Gas diffusion electrode
Membrane electrode assembly
Zeta potential

ABSTRACT

The Electrophoretic Deposition (EPD) method was adapted to fabricate Gas Diffusion Electrodes (GDEs) for Membrane Electrode Assemblies (MEA) for High Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFC) operating at 160 °C. Suspensions containing the Pt/C catalyst, polytetrafluoroethylene (PTFE) and NaCl were studied. Stable catalyst suspensions were observed when the NaCl concentrations were ≤ 0.1 mM. Mercury intrusion porosity analysis showed that the GDEs obtained *via* the EPD method had higher porosity ($30.5 \text{ m}^2 \text{ g}^{-1}$) than the GDEs fabricated by the ultrasonic spray method ($25.2 \text{ m}^2 \text{ g}^{-1}$). Compared to the ultrasonically sprayed MEA, the EPD MEA showed ~12% increase in peak power at a slightly lower (~4 wt %) Pt loading. Electrochemical Impedance Spectroscopy (EIS) analysis showed a lower charge transfer resistance for the EPD MEA compared to the ultrasonically sprayed MEA while Cyclic Voltammetry (CV) analysis showed ~16% higher Electrochemical Surface Area (ECSA) for the EPD MEA compared to the ultrasonically sprayed MEA. These observations were attributed to the higher porosity and better catalyst particle size distribution of the EPD GDEs. A comparison between PTFE and Nafion® ionomer in the Catalyst Layers (CL) of two EPD MEAs revealed that PTFE yielded MEAs with better performance and is therefore more suitable in HT-PEMFCs.

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1. Introduction

Electrophoretic Deposition (EPD) is an electrochemical method attracting increasing interest as a material processing technique. The EPD method is highly efficient and is most commonly employed in the processing of ceramics, coatings and composite materials from colloidal suspensions [1]. During EPD, charged particles dispersed in a suitable liquid are deposited onto a target substrate under the force of an externally applied electric field. EPD has already been demonstrated for the deposition of Catalyst

Layers (CL) in Membrane Electrode Assemblies (MEA) where deposition was achieved on electron-conducting substrates (like Gas Diffusion Layers, GDLs) which simultaneously served as one of the electrodes as well as ion-conducting substrates (like proton exchange membranes) where the membrane was placed between two external electrodes [2–6]. Munakata et al. [4] used the EPD method to deposit the catalyst particles directly onto a Nafion® membrane to form a catalyst coated membrane. They observed that the CLs attached well onto the membrane and their EPD MEAs showed better performance than the hot-pressed MEAs which was mainly attributed to improved Pt utilisation. Morikawa et al. [6] showed that the EPD process has selectivity for particle size since they only observed fine carbon particles in the deposited CL. Selectivity for particle size would produce deposits of high

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uniformity and increase Pt utilisation. The same researchers applied the EPD method to fabricate MEAs for Low Temperature Polymer Electrolyte Membrane Fuel Cell (LT-PEMFC) applications. Due to the limitations associated with LT-PEMFCs, such as a need for high purity hydrogen and a sophisticated water management system, many researchers have given attention to HT-PEMFCs that operate at temperatures between 100 and 200 °C. At these temperatures important advantages over low temperature operation exist i.e. faster electrode kinetics, higher CO tolerance of the Pt catalyst, use of lower purity hydrogen, no requirements for humidification, and a simpler cooling system [7,8]. In LT-PEMFCs, Nafion® ionomer is incorporated into both anode and cathode CLs to increase the formation of the triple phase boundaries and to improve proton conduction. The addition of the Nafion® ionomer to the catalyst inks also produces stable suspensions due to the steric repulsive forces generated by the negatively charged sulfonic acid end groups. In our previous work [9], we demonstrated that the Pt/C particles coated with Nafion® ionomer, readily deposited when subjected to an externally applied electric field. The fabricated EPD MEAs showed a significant improvement (~73%) in peak power performance in comparison to the conventional hand-sprayed MEAs and were stable at 160 °C HT-PEMFC operation conditions. However the Nafion® ionomer is not commonly incorporated into the CLs for HT-PEMFC because it operates at temperatures above the glass transition temperature (T_g) of the Nafion® ionomer. Above the glass transition temperature of the Nafion® ionomer, decomposition of Nafion® occurs where sulphur oxide from the sulfonic acid side chains is lost [10]. The decomposition of the Nafion® ionomer could have a negative impact on the overall MEA performance. Polytetrafluoroethylene (PTFE) is a polymer that is hydrophobic and is commonly incorporated in the micro porous layer of the Gas Diffusion Electrode (GDE) to maintain the integrity of carbon particles and to improve water management [11]. PTFE forms porous catalyst structures [12] and allow both reactant gases and liquid acid to access the active catalyst sites [12,13]. PTFE also facilitates the formation of triple phase boundaries [13]. For these reasons, PTFE are commonly incorporated into the CL structure of HT-PEMFC electrodes [8,14]. The main drawback of HT-PEMFCs is that it requires significantly higher Pt loadings (0.6–1.2 mg cm⁻² Pt on each side; total ~2.4 mg cm⁻² Pt) than LT-PEMFCs [13,15]. Therefore, alternative MEA fabrication methods are needed to improve the Polymer Electrolyte Membrane Fuel Cell (PEMFC) efficiency and reduce the Pt loading, hence the investigation into the EPD method for the fabrication of GDEs in HT-PEMFCs. An ultrasonic spray method was previously demonstrated [16,17] and proved very useful for the fabrication of ultra-low Pt loadings in MEAs for LT-PEMFCs. Thus MEAs were fabricated *via* the ultrasonic spray method and used as a comparison in this study. A comparison between EPD MEAs containing PTFE and Nafion® ionomer in the CL structure is also presented.

2. Experimental section

2.1. Materials

HiSpec 4000, 40 wt% Pt/C (Johnson Matthey, United Kingdom) was used as received as catalyst material for all experiments. PTFE solution 60 wt% (Electrochem, USA) was diluted with ultra pure water ($R = 18.3 \text{ M}\Omega$) to obtain a 20 wt% solution. Nafion® solution, 5 wt% (Johnson Matthey, United Kingdom) was used as received. Isopropyl alcohol (Kimix, South Africa) was used as the dispersing medium. NaCl (Kimix, South Africa) was added to adjust the conductivity of the catalyst suspension. A commercially available GDL (Freudenberg H2315 CX196, Germany) was used as received. A

commercially available poly-(2,5-benzimidazole) also known as ABPBI (Fumatech, Germany) was doped in phosphoric acid (PA) (Kimix, South Africa) for 24 h at 130 °C prior to use.

2.2. Zeta potential and particle size

The zeta potential and size of the Pt/C particles in isopropyl alcohol were obtained using the Zetasizer Nano ZS (Malvern Instrument Ltd., United Kingdom). The catalyst inks were obtained *via* ultrasonic mixing (20 kHz) of the Pt/C, PTFE solution and isopropyl alcohol for 5 min using a Biologics 3000 ultrasonic homogenizer (Biologics, Inc., USA). Catalyst suspensions with NaCl concentrations between 0 and 0.5 mM were studied. A syringe was used to fill a semi-disposable capillary cell with the sample which was then immersed into a temperature controlled block holder to avoid thermal gradients in the absence of the applied electric field [18]. Electrophoretic mobility was measured by applying a fixed voltage of 100 V. The instrument calculated the zeta potential from electrophoretic mobility using the *Smoluchowski* equation (Eq. (1)) [9].

$$u = \frac{\epsilon\epsilon_0\zeta E}{\eta} \quad (1)$$

where ζ is the zeta potential, E is the electric field strength and $\epsilon\epsilon_0$ and η are the dielectric constant and the viscosity of dispersion medium, respectively. All measurements were performed at 25 °C.

2.3. Fabrication of MEAs by EPD

Catalyst inks were obtained *via* ultrasonic mixing of the Pt/C, PTFE or Nafion® ionomer solution and isopropyl alcohol for 30 min. The ionic strength of the suspension was adjusted by adding NaCl. An *in-house* EPD cell [9] was used to fabricate the GDEs. A microelectrophoresis power supply (Consort, Belgium) was used to deposit the catalyst particles onto the GDLs. The obtained GDEs were placed in a vacuum oven (Binder GmbH, Germany) at room temperature and heated to 50 °C ($\sim 1.5 \text{ }^\circ\text{C min}^{-1}$) to dry the CL. Heat treatment of GDEs were carried out at 340 °C under Ar atmosphere to remove the surfactant from the PTFE binder and to increase the porosity of the GDE. GDEs and MEAs fabricated *via* the EPD method are termed EPD GDEs and EPDs MEA respectively. Heat treatment of the GDEs was performed by heating the furnace to 340 °C within ~1 h followed by maintaining 340 °C for 30 min and then cooling the furnace to room temperature without artificial cooling. GDE/MEAs that received heat treatment are termed “340 °C HT” while GDE/MEAs that received no heat treatment is termed “no HT”. The MEAs were obtained by sandwiching the anode and cathode GDEs and the acid doped membrane together inside a high temperature cell. No prior hot pressing step was performed on the MEAs.

2.4. Fabrication of MEAs by Sonotek

Catalyst inks were obtained *via* ultrasonic mixing of Pt/C, PTFE solution, ultra pure water and ethanol for 30 min. The well-mixed catalyst ink was loaded into the Sonotek ultrasonic sprayer (Sono-tek Corporation, USA) then sprayed onto the GDLs. The ultrasonic nozzle operated at 120 kHz and an ultrasonic power of 3 W. The heat treatment procedures of the GDEs were the same as for the EPD GDEs. MEAs were obtained by the same procedures as for the EPD MEAs. GDEs and MEAs fabricated *via* the ultrasonic spray method are termed Sonotek GDEs and Sonotek MEAs respectively.

2.5. Electrochemical characterisation of MEAs

An *in-house* HT-PEMFC test bench was used to study the electrochemical properties of the MEAs. The *in-house* HT-PEMFC test bench consisted of a PC loaded with Labview software to control the electronic load (Höcherl&Hackl GmbH, Germany) and mass flow controllers (Bronkhorst, The Netherlands). A cell compression unit (Pragma Industries, France) controlled the cell pressure and temperature. All measurements were carried out at 160 °C and a cell compression pressure of 20 bar while supplying dry air (1 slpm) at the cathode and dry hydrogen (0.5 slpm) at the anode. MEAs were activated for 3 h at +0.55 V followed by measuring the polarisation curve between Open Circuit Voltage (OCV) and +0.2 V. The Autolab PGSTAT302N (The Netherlands) was used for EIS analysis at a cell voltage of 0.6 V in a frequency range of 0.1 Hz–50,000 Hz and an amplitude of 5 mV. The Autolab PGSTAT302N was also used for CV analysis by cycling the potential between 20 mV and 800 mV at a scan rate of 50 mV s⁻¹.

2.6. Physical characterization of GDEs

Morphology of the GDEs were characterised by High Resolution Scanning Electron Microscopy (HR-SEM) using the Carl Zeiss Auriga HRFEG SEM working at 5 kV. Porosity of the GDEs were obtained via mercury intrusion porosimetry analysis using the Autopore IV 9510 (Micromeritics, USA) mercury porosimeter applying pressures between 0.0145 and 4136.85 bar.

3. Results and discussion

3.1. Catalyst ink characterisation

The first step in EPD is to prepare a stable suspension of independent particles [19]. Suspension stability is characterised by the particle settling rate and the tendency for particles to undergo or avoid flocculation [20,21]. To prepare stable suspensions suitable for EPD the following four conditions should be met: (i) the particles in solution need to be charged otherwise the particles will not migrate with the externally applied electric field, (ii) the particles should be well dispersed and stable over the EPD duration to form homogeneous deposits, (iii) ions other than the charged particles should be kept to a minimum as these lower the transport number of the particles. Compression of the electrical double layer occurs at high ionic concentration which reduces the stability of the suspension, and (iv) the particles should strongly adhere to the target substrate which may be improved by the addition of polymer binders. Measuring the particle zeta potential is useful to understand the stability of the suspension. For stable suspensions, zeta potential values more positive than +30 mV or more negative than -30 mV, depending on the sign is recommended. For some systems, stable suspensions with particles having high zeta potentials are obtained by simply dispersing the particles in the solution. However in general, particles can be positively or negatively charged by adding the appropriate amount of acid, base or polyelectrolytes having functional groups such as carboxylic acid groups or amino groups on the side chains, to the suspension. Particle surfaces modified by polyelectrolytes have charges corresponding to the functional groups. The addition of excess acid or base is disadvantageous as the un-adsorbed ions compress the electrical double layer and affects the suspension stability. Furthermore, free ions become the majority of charge carriers during EPD and the transport number of the charged particles drops which affects the deposition rate of the particles resulting in thin deposited layers [22]. In this study, we added a charger salt (NaCl) to adjust the ionic concentration and conductivity of the

catalyst suspension. For the case of Carbon Nanotubes (CNT), it was observed that the addition of charger salts can increase the suspension stability by associating a charge with the CNT surface in the solvent and improve the adhesion and deposition of the CNTs to the target substrate [1]. Fig. 1a and b shows the zeta potential and average sizes of the Pt/C particles mixed with various PTFE contents in solutions with various NaCl concentrations, respectively. Fig. 1a shows that the catalyst particles were negatively charged in all suspensions and would therefore deposit onto the positively charged electrode. When no NaCl is added to the solution, the catalyst particles show the highest zeta potentials ranging between -44 mV and -52 mV with average particle sizes ranging between ~248 nm and ~263 nm. These suspensions were stable since no significant change in particle size was observed which is indicative of very slow coagulation. These types of suspensions are commonly prepared when using other coating techniques such as spraying where the conductivity of the suspension is not crucial. For these suspensions, the highest zeta potential (-52 mV) and smallest particle size (~248 nm) were observed when 20 wt% PTFE was added while the lowest zeta potential (-44 mV) and largest particle size (~263 nm) were observed when no PTFE was added. These suspensions however are not suitable for EPD as there is insufficient conductivity due to the low dielectric constant

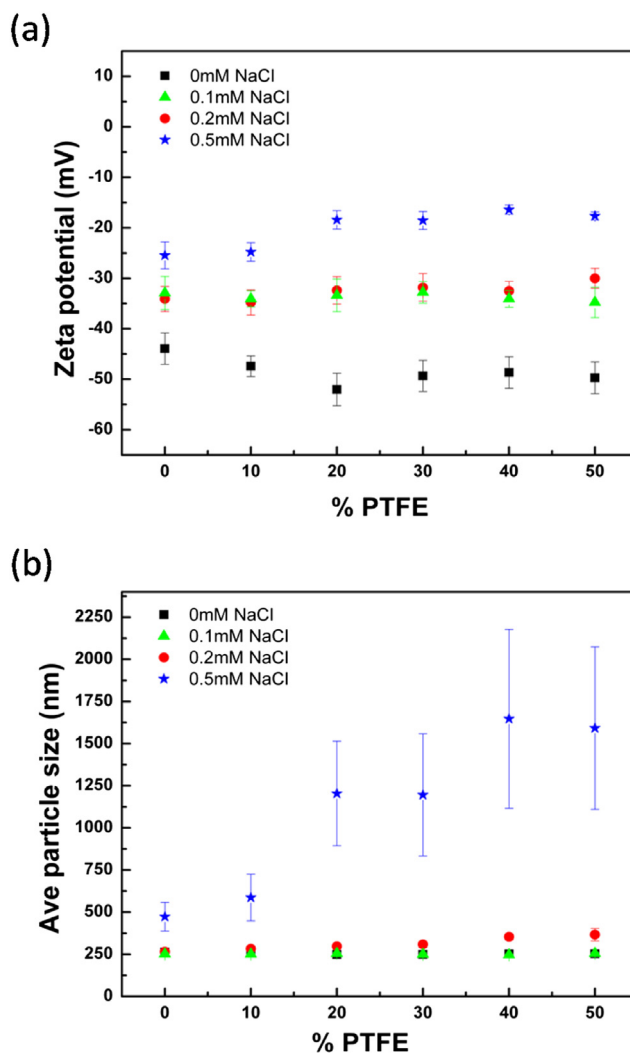


Fig. 1. (a) Zeta potential and (b) average particle size of Pt/C in isopropyl alcohol with various PTFE compositions and NaCl concentrations.

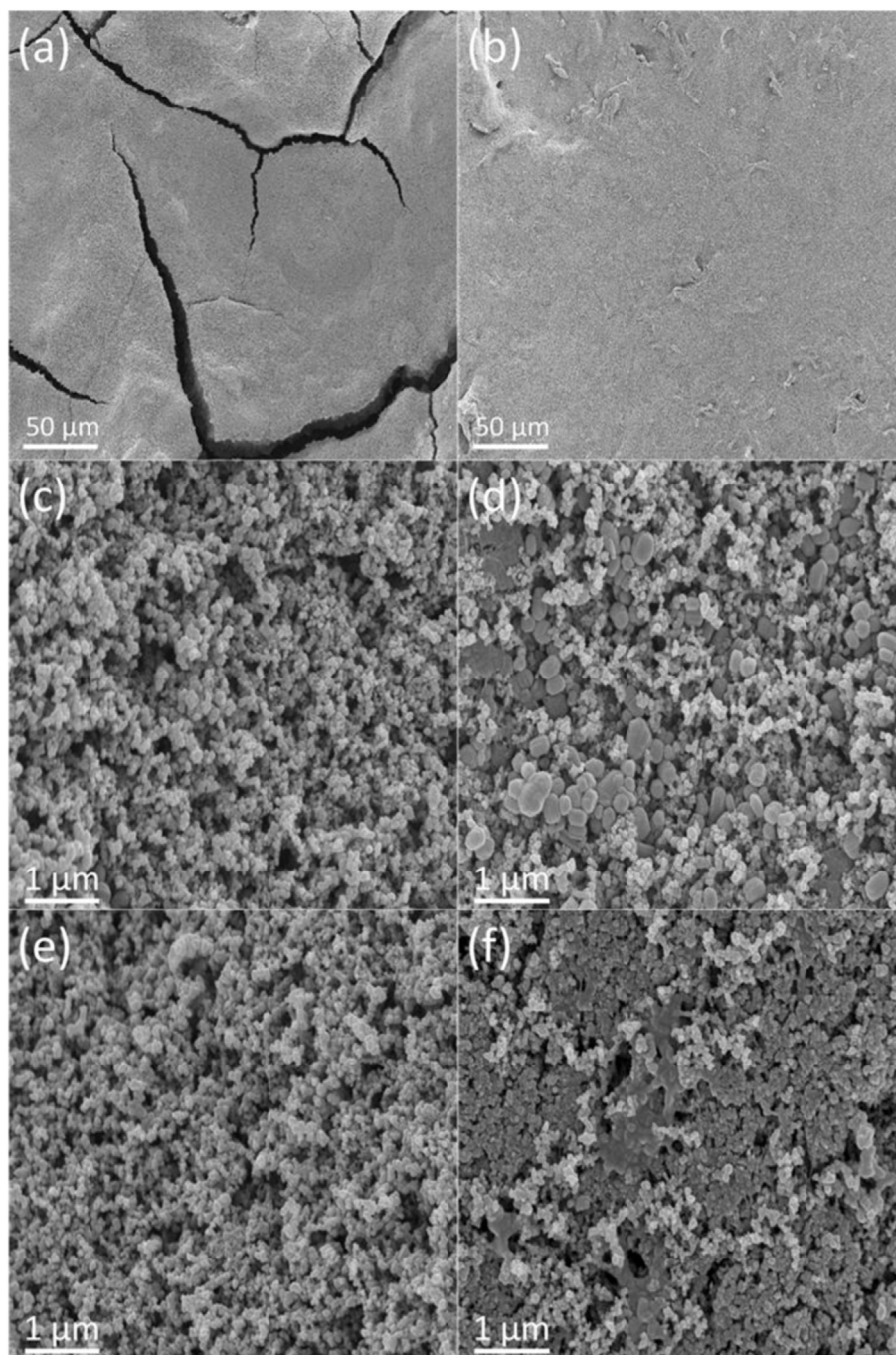


Fig. 2. HR-SEM images of (a) EPD GDE (no HT) at 1,000 \times magnification, (b) Sonotek GDE (no HT) at 1,000 \times magnification, (c) EPD GDE (no HT) at 50,000 \times magnification, (d) Sonotek GDE (no HT) at 50,000 \times magnification, (e) EPD GDE (340 $^{\circ}$ C HT) at 50,000 \times magnification and (f) Sonotek GDE (340 $^{\circ}$ C HT) at 50,000 \times magnification.

($\epsilon_r \approx 18.23$) of isopropyl alcohol and the particles would not deposit under the force of the externally applied electric field. For the suspensions containing 0.1 mM NaCl concentration, the zeta potentials ranged between -33 mV and -35 mV. The zeta potentials were noticeably smaller in magnitude however the particle sizes were not affected. The particle sizes ranged between ~ 246 nm and ~ 255 nm. For suspensions containing 0.2 mM NaCl concentration, the zeta potentials ranged between -30 mV and -34 mV. For suspensions containing 0.5 mM NaCl concentration, the particle zeta potentials became less negative than -30 mV and the particle sizes was significantly affected. The zeta potentials decreased from -25 mV for 0 wt% PTFE to ~ -17 mV for 40 and 50 wt% PTFE.

The average particle sizes ranged from ~ 472 nm for 0 wt% PTFE, to ~ 1600 nm for 40 and 50 wt% PTFE. This signified significant coagulation and unstable suspensions. At high ionic concentrations where electrical double layer compression occurs, PTFE had a significant influence on the stability of the suspension. From the Fig. 1 it was clear that to obtain stable catalyst suspensions for EPD, the NaCl concentration should be ≤ 0.1 mM.

3.2. GDE fabrication and physical characterisation

A NaCl concentration of 0.01 mM was selected for all catalyst suspensions to minimise the NaCl concentration deposited in the

CLs and to avoid the formation of unstable suspensions. Ali et al. [23] observed that the chloride impurity can drastically decrease the performance and durability of the PBI based MEAs. It was proposed that Pt chloro-complexes such as hexachloroplatinate (PtCl_6^{2-}) or tetrachloroplatinate (PtCl_4^{2-}) were formed in the presence of chloride impurities. A NaCl concentration of 0.01 mM yielded a stable electric field during EPD whereas at lower NaCl concentrations the electric field was not maintained and deposition ceased. At higher NaCl concentrations, the excess free ions became the major charge carriers resulting in high currents and joule heating significantly affecting the morphology of the deposited CL. The EPD GDEs had a 0.48 mg cm^{-2} Pt loading while the Sonotek GDEs had a 0.5 mg cm^{-2} Pt loading. The PTFE content was 40 wt% for all GDEs. Fig. 2a and b shows the HR-SEM images of the EPD GDE (no HT) and the Sonotek GDE (no HT) at $1,000\times$ magnification, respectively. The EPD GDE was covered in cracks which is the result of drying of a relatively thick ($\sim 25 \mu\text{m}$) CL in a single step. The Sonotek GDE has relatively smooth and uniform morphology. The Sonotek ultrasonic sprayer is capable of spraying a very fine mist of the catalyst particles which is continuously dried *via* a hot plate operating at 80°C during the spraying process. Fig. 2c and d shows the HR-SEM images of the EPD GDE (no HT) and the Sonotek GDE (no HT) at $50,000\times$ magnification, respectively. The EPD GDE forms a uniform network of porous structures while the Sonotek GDE morphology is notably different. The Sonotek GDE morphology exhibits catalyst particles that are smaller than that of the EPD GDE but also contains larger particles ($>300 \text{ nm}$). Energy Dispersive X-Ray (EDX) analysis showed that these larger particles had higher ($\sim 60\%$) PTFE contents than the smaller catalyst particles. The PTFE resulted in the agglomeration of the catalyst particles in the CL of the Sonotek GDE. Fig. 2e and f shows the HR-SEM images of the EPD GDE (340°C HT) and the Sonotek GDE (340°C HT) at $50,000\times$ magnification, respectively. The EPD GDE showed no notable change in morphology after the heat treatment process. The Sonotek GDE, however, showed significant agglomeration of the catalyst particles due to the melting of PTFE whereas no agglomeration of the catalyst particles was noted for the EPD GDE. This suggested that for EPD, the Pt/C particles are uniformly coated with PTFE probably due to the formation of stable suspensions. Furthermore it suggested that only fine catalyst particles deposit during EPD which is consistent to that reported in the literature [4,6]. Fig. 3a and b shows the HR-SEM images of the EPD GDE (no HT) with PTFE in the CL and the EPD GDE (no HT) with Nafion[®] ionomer in the CL at $50,000\times$ magnification, respectively. The EPD GDE containing the Nafion[®] ionomer in the CL shows slightly larger catalyst particle structures and larger pore sizes. Fig. 4a shows the

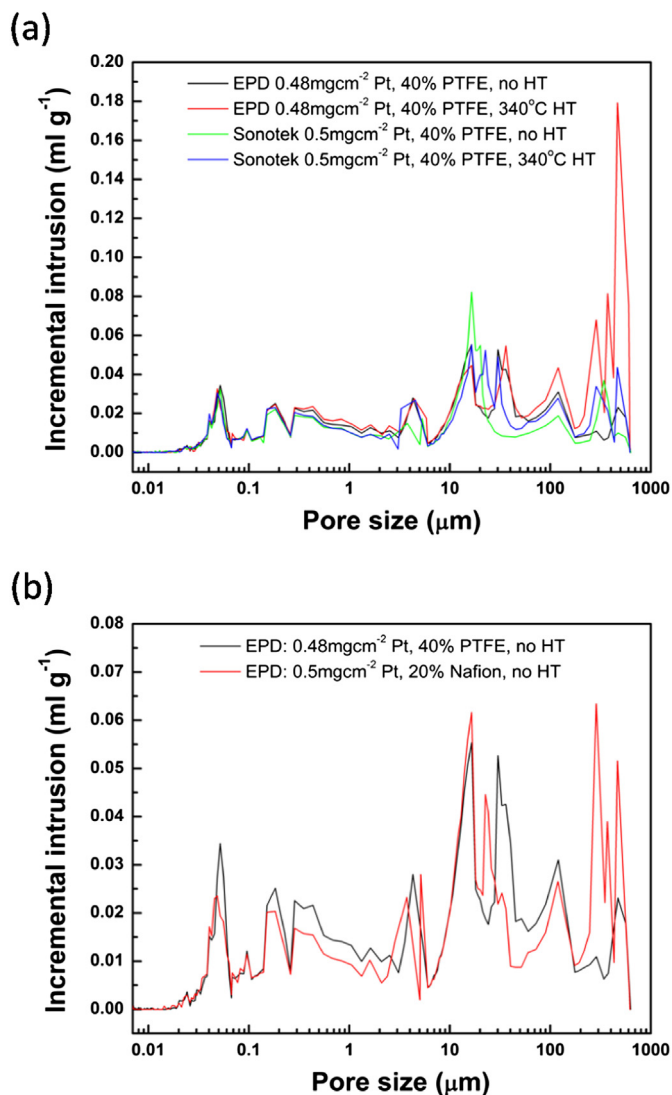


Fig. 4. Mercury intrusion porosity analysis of (a) EPD and Sonotek GDEs with PTFE in CLs and (b) EPD GDEs with PTFE and Nafion[®] ionomer in CLs.

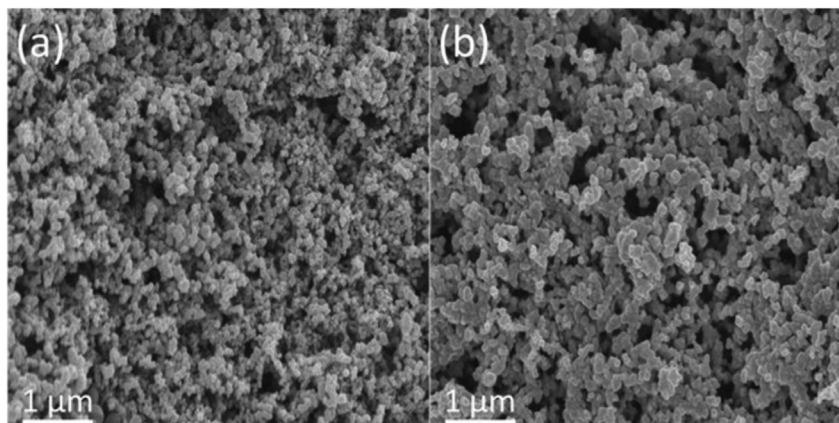


Fig. 3. HR-SEM images of (a) EPD GDE (no HT) with PTFE in CL at $50,000\times$ magnification and (b) EPD GDE (no HT) with Nafion[®] ionomer at $50,000\times$ magnification.

mercury intrusion porosity analysis of the EPD and Sonotek GDEs with PTFE in the CLs, heat treated and non heat treated. The EPD GDE (no HT) shows a higher porosity ($30.5 \text{ m}^2 \text{ g}^{-1}$) than the Sonotek GDE (no HT) which had a total pore area of $25.2 \text{ m}^2 \text{ g}^{-1}$. Heat treatment of the GDEs yielded an increase in porosity for both GDE types which were expected due to the presence of the PTFE binder [24]. However the increase in porosity was mainly a result of a significant increase in macro pores. Fig. 4b shows the mercury intrusion analysis of the EPD GDEs containing PTFE and Nafion® ionomer in the CLs. The EPD GDE with Nafion® ionomer in the CL had a slightly lower total pore area of $27.4 \text{ m}^2 \text{ g}^{-1}$. The figure shows significantly more macro pores for the EPD GDE with Nafion® ionomer in the CL which is consistent to that observed from HR-SEM (Fig. 3b).

3.3. Single cell test

Fig. 5 shows the polarisation and power density curves of the EPD and Sonotek MEAs. The EPD MEA (no HT) shows the highest MEA performance with ~12% increase in peak power compared to the Sonotek MEA (no HT). Heat treatment of the GDEs resulted in a slight lowering in performance of the EPD MEA while significantly lowering the performance of the Sonotek MEA. CV analysis of the EPD and Sonotek MEAs are shown in Fig. 6. The ECSA of each MEA was calculated using Eq. (2) [25].

$$\text{ECSA} = \frac{10^5 \times A_d}{C \times m \times v} \quad (2)$$

where A_d is the integral area of the hydrogen adsorption peak (AV), C is the coefficient of hydrogen adsorbed by Pt (0.21 mC cm^{-2}), m is the mass of Pt at the cathode (mg cm^{-2}) and v is the potential scan rate (mV s^{-1}). Fig. 6a shows that the ECSAs decreased by ~3% and ~51% after heat treatment for EPD and Sonotek MEAs, respectively. The reduction in ECSA implies that the available surface Pt sites are reduced which affects MEA performance. The increase in porosity of the GDEs usually results in improved MEA performance due to improved access of both the reactant gases and the liquid acid to the active catalyst sites [12,13]. On the contrary however, the increase in porosity (due to macro pores) may allow easier covering of the active Pt sites by PTFE and PA. The PO_4^{3-} ions in PA strongly

adsorbs onto the active Pt sites causing it to be inaccessible for electrochemical reactions. The significant lowering in the performance of the Sonotek MEA (340°C HT) can be explained using the HR-SEM image (Fig. 2f) where the melting of PTFE clearly resulted in the agglomeration of the catalyst particles and covering of the active Pt sites. Fig. 7 shows the EIS analysis of the EPD and Sonotek MEAs and revealed highest charge transfer resistance (observed from the larger diameter of the arc) for the Sonotek MEA (340°C HT). This is an indication that the Sonotek GDE (340°C HT) had less active Pt sites which was the result of being covered by PTFE and becoming inaccessible to the reactant gases for electrochemical reactions. The EPD MEA (no HT) showed the lowest charge transfer resistance indicative of better electrode kinetics which resulted in better MEA performance. Fig. 7 shows differences in the membrane resistances of the MEAs therefore IR free polarisation curves, where internal cell resistances were corrected based on the high frequency resistances of the EIS analysis, are provided in Fig. 8. The EPD MEA (no HT) clearly exhibits better electrode kinetics which resulted in the better MEA performance. The IR free curves shows that the Sonotek (no HT) and EPD (340°C) had comparable

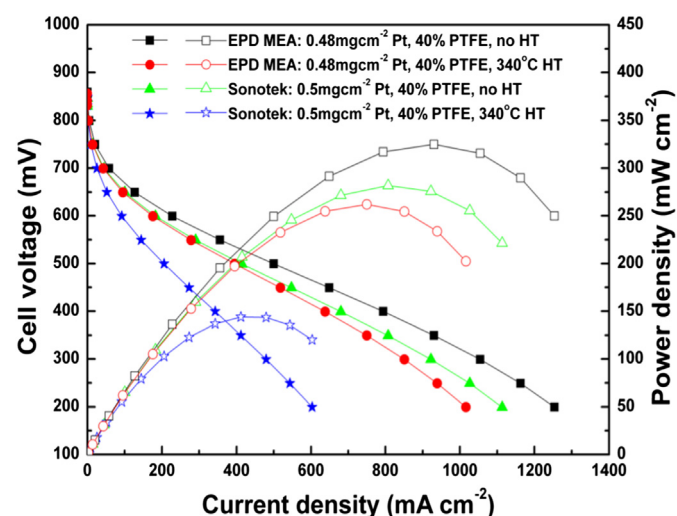


Fig. 5. Polarisation and power density curves of EPD and Sonotek MEAs with PTFE in CLs.

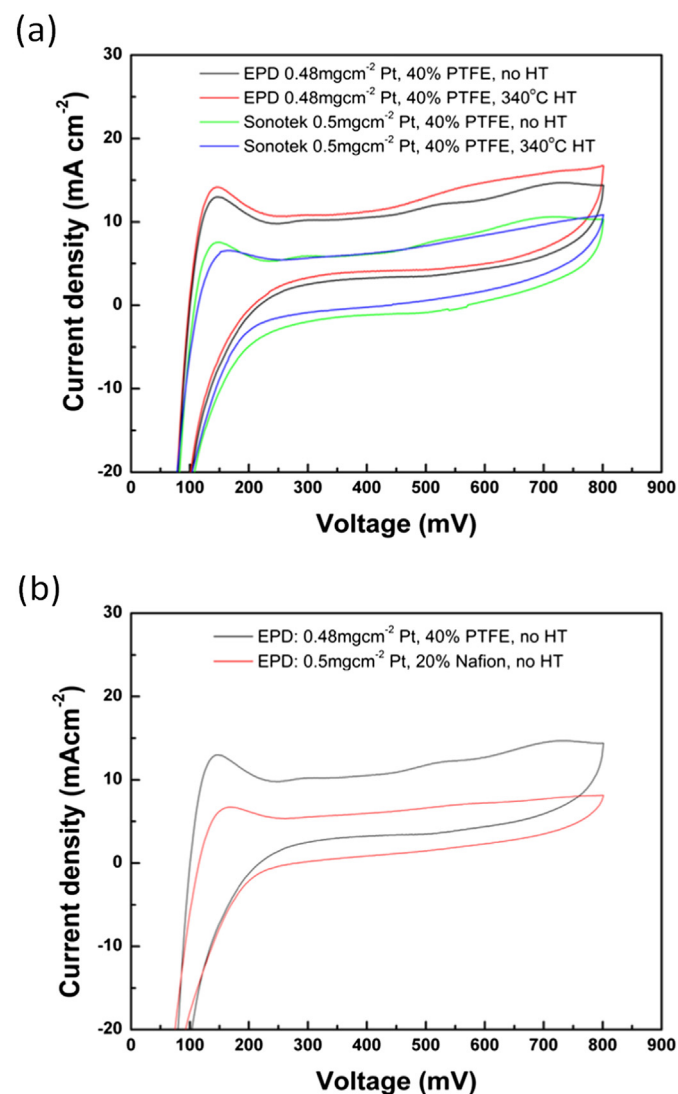


Fig. 6. Cyclic voltammetry analysis of (a) EPD and Sonotek MEAs with PTFE in CLs and (b) EPD MEAs with PTFE and Nafion® ionomer in CLs.

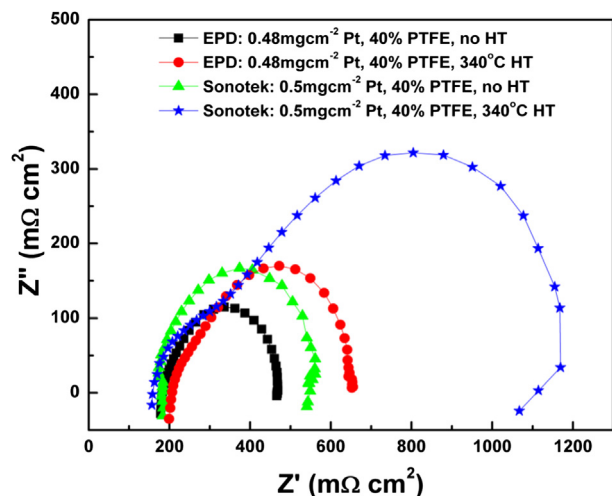


Fig. 7. EIS analysis of EPD and Sonotek MEAs with PTFE in CLs at 0.6 V.

performances however the Sonotek (no HT) showed slightly better performance under high current conditions.

Fig. 9 shows the polarisation and power density curves of the EPD MEAs (no HT) containing PTFE and Nafion® ionomer in the CLs. The EPD MEA containing PTFE in the CLs exhibited better MEA performance than the EPD MEA containing the Nafion® ionomer in the CLs. The tests were performed at 160 °C which is above the glass transition temperature of the Nafion® ionomer which may negatively affect the CL structure. Above the glass transition temperature, the polymer chain may rearrange which can lead to structural changes. The structural changes may have a negative effect on the stability and performance of the Nafion® ionomer [26]. Fig. 6b shows the CV analysis of the EPD MEAs (no HT) with PTFE and the Nafion® ionomer in the CLs. The EPD MEA (no HT) with PTFE in the CL shows ~53% higher ECSA than the EPD MEA (no HT) with the Nafion® ionomer in the CL. The HR-SEM image (Fig. 3b) revealed larger catalyst structures when the Nafion® ionomer was incorporated into the CLs which are associated with a reduction in the ECSA. Both GDEs showed porous morphologies however the CLs containing the Nafion® ionomer consisted of significantly more macro pores which may lead to easier poisoning of the Pt sites by

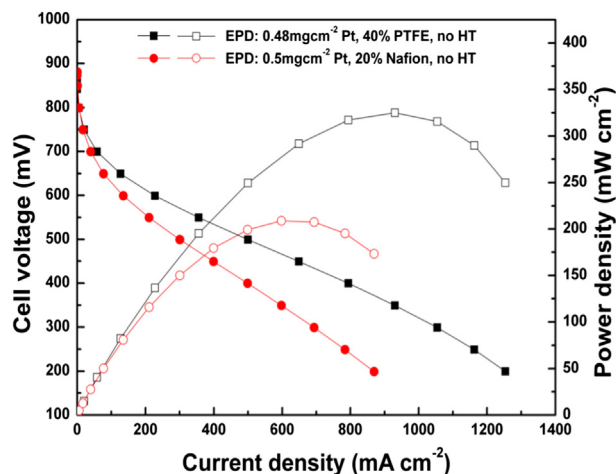


Fig. 9. Polarisation and power density curves of EPD MEAs with PTFE and Nafion® ionomer in CLs.

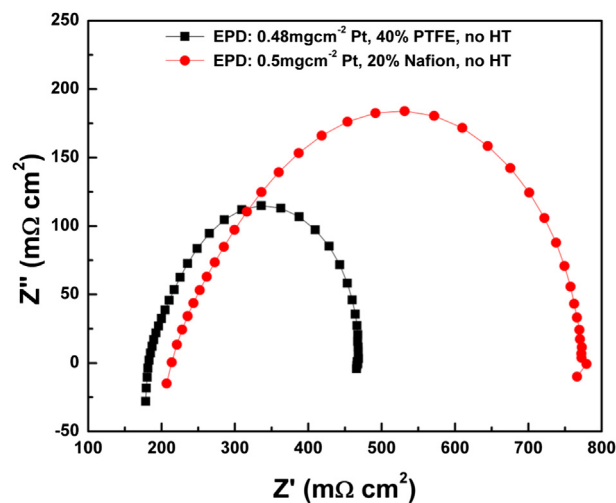


Fig. 10. EIS analysis of EPD MEAs with PTFE and Nafion® ionomer in CLs at 0.6 V.

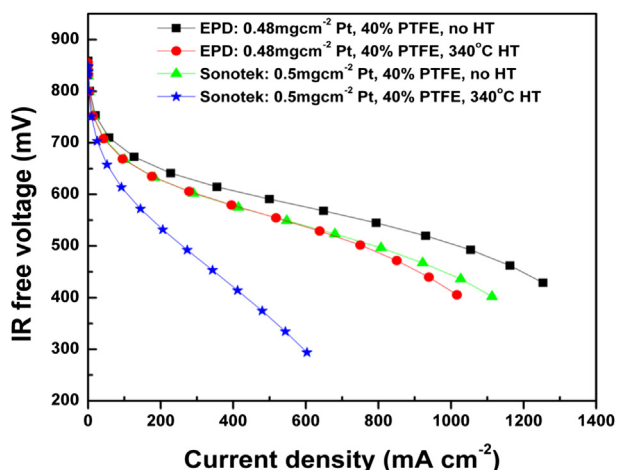


Fig. 8. IR free polarisation curves of EPD and Sonotek MEAs with PTFE in CLs.

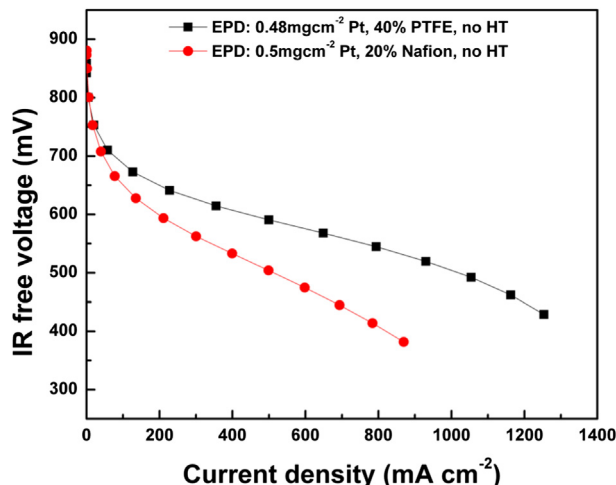


Fig. 11. IR free polarisation curves of EPD MEAs with PTFE and Nafion® ionomer in CLs.

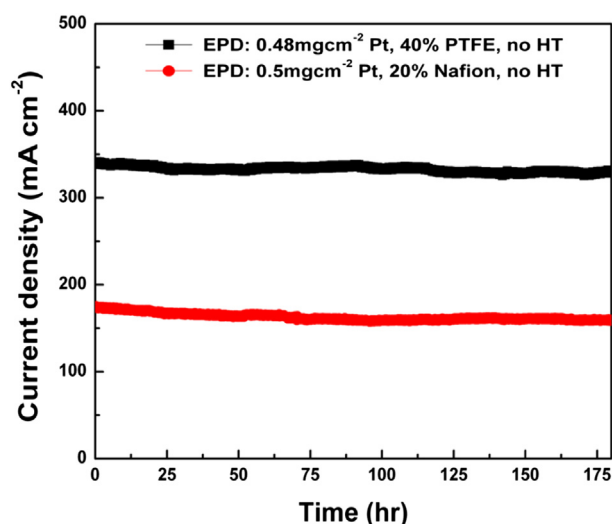


Fig. 12. Stability of EPD MEAs with PTFE and Nafion® ionomer in the CLs at 0.55 V.

PA. Fig. 10 shows the EIS analysis of the EPD MEAs (no HT) containing PTFE and Nafion® ionomer in the CLs. Significantly higher charge transfer resistance is noted when the Nafion® ionomer was present in the CLs. Fig. 11 shows the IR free polarisation curves of the EPD MEAs containing PTFE and Nafion® ionomer in the CLs and also revealed that PTFE resulted in higher MEA performance under high temperature (160 °C) operation. Fig. 12 shows the stability behaviour of the EPD MEAs with PTFE and the Nafion® ionomer in the CLs. The tests were performed at 160 °C at a constant voltage of +0.55 V. Both MEAs showed stable behaviour over the duration of the test (i.e. 180 h). The EPD MEA with PTFE in the CL showed double the current density (i.e. $\sim 340 \text{ mA cm}^{-2}$) compared to the EPD MEA with the Nafion® ionomer in the CL (i.e. $\sim 170 \text{ mA cm}^{-2}$).

4. Conclusions

MEAs for HT-PEMFCs were fabricated via the EPD method. Suspension conditions were studied and suspensions having low NaCl concentrations ($<0.1 \text{ mM}$) should be considered for the fabrication of the GDEs. For comparison purposes, MEAs fabricated using the Sonotek ultrasonic sprayer were tested and characterised under similar conditions. HR-SEM images revealed cracked but uniform morphologies for the EPD GDEs while the Sonotek GDEs exhibited morphology consisting of small, fine particle structures and larger particle structures that contained higher PTFE contents. Heat treatment of both GDE types resulted in higher porosity but a lowering in MEA performance. For the Sonotek GDE, the melting of the PTFE resulted in the covering of the active Pt sites which significantly affected the electrochemical performance of the MEA. Under the test conditions the EPD MEA (no HT) performed better than the EPD MEA (340 °C HT) and Sonotek MEAs as revealed by the polarisation measurements. EPD MEAs containing PTFE in the CLs yielded better MEA performance compared to the EPD MEA containing the Nafion® ionomer in the CLs under high temperature (160 °C) operation. Future work will focus on the long term durability of the fabricated EPD MEAs.

Acknowledgements

This work was supported by the Hydrogen and Fuel Cell Technologies RDI Programme (HySA) funded by the Department of Science and Technology (DST) in South Africa (Project KP1-S01).

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List of abbreviations

EPD: Electrophoretic Deposition
 GDE: Gas Diffusion Electrode
 GDL: Gas Diffusion Layer
 PEMFC: Polymer Electrolyte Membrane Fuel Cell
 HT-PEMFC: High Temperature Polymer Electrolyte Membrane Fuel Cell
 LT-PEMFC: Low Temperature Polymer Electrolyte Membrane Fuel Cell
 MEA: Membrane Electrode Assembly
 PTFE: Polytetrafluoroethylene
 EIS: Electrochemical Impedance Spectroscopy
 CV: Cyclic Voltammetry
 ECSA: Electrochemical Surface Area
 CL: Catalyst Layer

Nomenclature

μ : electrophoretic mobility
 ϵ : permittivity
 ϵ_0 : permittivity of vacuum
 ζ : zeta potential
 E : electric field strength
 η : viscosity
 A_d : integral area of the hydrogen adsorption peak
 C : hydrogen adsorption coefficient
 m : mass
 v : potential scan rate