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A high-performance membrane electrode assembly for polymer electrolyte membrane fuel cell with poly(arylene ether sulfone) nanofibers as effective membrane reinforcements



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Novel membrane electrode assembly is prepared by direct membrane deposition method.
- It has high internal shorting resistance because of the reinforcements.
- The highest power density of the fuel cell could be 2.85W/cm².



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ABSTRACT

Direct membrane deposition was recently introduced as a novel polymer electrolyte membrane fabrication method. This method is extended to fabricate a high-performance membrane electrode assembly for polymer electrolyte membrane fuel cell with poly(arylene ether sulfone) nanofibers as effective membrane reinforcements. The nanofibers are directly electrospun onto gas diffusion electrodes. By spray-coating ionomer dispersion into the pore space of nanofiber mats, composite membranes of 15 µm thickness are fabricated. The introduction of the electrically and ionically insulating nanofibers do not hamper the cell performance. At 80 °C and 75% relative humidity, the power density of the fuel cell employing direct membrane deposition, 2.85 W cm⁻², is about 1.36 times higher than that of the reference fuel cell (2.09 W cm⁻²) with Nafion® 211 membrane and identical catalyst. Its cell resistance ($28 \text{ m}\Omega \text{ cm}^2$) is much lower than that of the membrane electrode assembly fabricated by the catalyst coating membrane method ($46 \text{ m}\Omega \text{ cm}^2$). The performance differences between two fabrication methods are systematically analyzed by electrochemical impedance spectroscopy. Most notably, even though the thickness of the polymer electrolyte is much lower than that of Nafion® 211

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 $(25\,\mu\text{m})$, it shows much higher internal short resistance and better durability because of the existence of reinforcement.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been regarded as one of the most promising alternative power sources for use in stationary and automotive applications due to their high energy conversion efficiency, high power density, and low air pollutant emissions. The most critical component of PEMFC is the membrane electrode assembly (MEA), where the electrochemical reaction occurs, and the electricity is produced. It is comprised of a cathode gas diffusion layer (GDL), cathode catalyst layer, polymer electrolyte membrane, anode catalyst layer, and anode gas diffusion layer, in sequence [1]. Currently, the gas diffusion electrode (GDE) method [2,3] and catalyst coated membrane (CCM) method [4,5] are used to prepare MEAs. In the CCM technique, the catalyst is directly applied to both sides of the polymer electrolyte, and it is reported that the CCM-based MEA technique yields better cell performance than the GDE-based MEA due to its higher catalyst utilization efficiency and reduced catalyst/membrane interface resistance [6]. Nevertheless, with the growing commercial interest in and more widespread application of PEMFCs, MEAs with high power density and low cost are sought. A more straightforward and practical method to increase the power density and to reduce cost of a fuel cell stack is to simply reduce the polymer electrolyte thickness, thereby minimizing ohmic losses and saving the raw material [7]. However, a polymer electrolyte membrane must possess sufficient mechanical integrity to be assembled into a fuel cell. Using extremely thin membranes may affect the mechanical stability and thereby increase the difficulty of the MEA fabrication [8]. To solve this concern, research on improving the manufacturing technique of MEAs is needed for next generation fuel cells.

Recently, direct membrane deposition (DMD) has been utilized as a novel alternative MEA manufacturing approach [9-12]. This method replaces the conventional membrane foil by two Nafion® layers deposited directly on top of the anode and cathode GDEs. The fuel cell is assembled with the GDEs facing each other. In this process, the thickness of the polymer electrolyte is controlled by the deposited amount of perfluorosulfonic ionomer. As a result, it is convenient to fabricate the MEA with extremely thin polymer electrolyte. Klingele et al. [9] first introduced DMD to fabricate directly deposited membranes (8-25 µm thickness) for PEMFCs with extremely low ionic and charge transfer resistances. The fuel cell showed power densities up to 4 W cm⁻² with hydrogen/oxygen feed gas. Through the extensive testing and analysis, Vierrath et al. [13] concluded that the low membrane resistance, low ionic contact resistance at the membrane|catalyst layer interface, and small mass transport resistance were the major reasons for the increased power density of the DMD fuel cell compared to a CCM reference fuel cell.

More significantly, DMD technique provided a new method to prepare MEAs with reinforced polymer electrolyte [14–16]. Thin layers of PVDF-HFP nanofibers [14] or sulfonated poly(ether ketone) nanofibers [15] were electrospun directly onto both the anode and cathode gas diffusion electrodes. Subsequently, an ionomer dispersion was printed into the pore space of the nanofiber mesh. This simple method avoided the required post-processing steps of conventional reinforcement membrane, such as annealing, acidic-boiling, and hot-pressing. As summarized by the above researchers, DMD-based MEA with dimensionally stable and insulating reinforcement materials exhibited much higher internal short resistance and lower hydrogen crossover current than those of DMD-based MEAs with pure ionomer. The resulting extremely thin membranes enabled construction of MEAs with improved open circuit voltage, cell performance, and chemical stability.

Uncharged fluoropolymers (PTFE [17], PVDF [18], PVDF-HFP [19])

and sulfonated aromatic polymers (SPPO [20], SPAES [21], SPEEK [22]) were the commonly used nanofiber materials for reinforcing perfluorosulfonic ionomer. In this study, poly(arylene ether sulfone) (PAES) was chosen as the reinforcement material for a DMD-based MEA. The uncharged and hydrophobic PAES which surrounds perfluorosulfonic resin would restrict ionomer swelling in water and provide mechanical strength to the polymer electrolyte. Compared with uncharged fluoropolymers, PAES possesses excellent thermal stability, a simple synthesis technique, and low cost [23]. Compared with sulfonated aromatic polymers, it provides excellent dimensional stability and chemical stability, especially at high temperature and high humidity [24]. However, because the reinforcing PAES nanofibers are not proton-conductive, the integration of such materials into polymer electrolyte would impede proton conduction. Hence, we chose Aquivion® D79-25BS as the ionomer, with an equivalent weight (EW = 790 g/mol) much higher than that of a commercial ionomer. Compared to Nafion® ionomer, Aquivion ionomer possesses shorter side chains which lead to higher polymer crystallinity. Aquivion has a higher glass transition temperature of 140 °C–160 °C and enhanced water uptake, leading to improved proton conductivity, especially at low relative humidity and high operating temperatures. In brief, the non-conductive PAES reinforcement provides additional mechanical strength, and its pores are filled with the conductive Aquivion ionomer to enable a continuous transport pathway through the polymer electrolyte.

2. Experimental

2.1. Materials

4,4'-difluoro-diphenyl sulfone (DFDPS), 2,2-bis(3-methyl-4-hydroxyphenyl) propane (BPC), and bisphenol A (BPA) were purchased from J&K Scientific Chemical Company. Potassium carbonate (K_2CO_3), toluene, dichloroethane (DCE), 1-methyl-2-pyrrolidinone (NMP), methanol, isopropyl alcohol, dimethylformamide (DMF), and ethanol were purchased from Beijing Reagent Company. HCP 120 (Shanghai Hesen Co., Ltd.) was chosen as the gas diffusion layer. Pt/C (60%, Johnson Matthey), Nafion® 211 (Shanghai Hesen Co., Ltd.), Nafion® D520 ionomer were used for MEA fabrication. Aquivion® dispersion (D79-25BS) was purchased from Sigma-Aldrich. Sigracet gas diffusion layer (SGL 25BC) was purchased from Fuel Cell Store. All reagents were used as received, without further purification. Deionized water made in the laboratory was used for all the experiments.

2.2. Synthesis of poly(arylene ether sulfone) (PAES)

A typical procedure was as follows. A 250 ml three-neck flask equipped with a mechanical stirrer, Dean-Stark trap, and an argon gas inlet was sequentially filled with DFDPS (10.27 g, 40 mmol), BPA (6.46 g, 28 mmol), BPC (3.11 g, 12 mmol), NMP (72 ml), and toluene (36 ml). To obtain a homogeneous solution without oxygen, the mixture was stirred for 2 h while purging with argon at room temperature. Then the solution was further stirred for 1 h after K₂CO₃ (6.91 g, 50 mmol) was added. The reaction mixture was heated to 145 °C and held for 4 h. After dehydration and removal of toluene for several hours, the reaction temperature was increased to about 180 $^\circ C$ and held for 12 h. After that, the reaction mixture was cooled to 60 $^\circ\text{C},$ diluted with the addition of 90 ml NMP, and poured into a large excess of deionized water with vigorous stirring. The resulting fibrous copolymer (PAES) was washed thoroughly with water and methanol alternately and dried under vacuum at 100 °C for 24 h. Yield, 94.13%; Mn, 78949; Mw, 128787; Mp, 120834; PDI, 1.63.

2.3. Preparation of the MEA

As a GDL substrate, HCP 120 was employed. For the ultrasonic spraycoating of the catalyst layer and membrane layer, a commercially available ultrasonic spray coating system (Siansonic Technology Co., Ltd.) was used. The catalyst ink comprised 0.1 wt% solids content in 1:10H₂O: ethanol. The Pt loading of cathode and anode were 0.4 mg cm⁻² and 0.2 mg cm⁻², respectively. The Nafion® D520 ionomer content was 30 wt % in the catalyst layer in both electrodes. During the spraying process, the temperature of the baseplate in the spray coating system was set to 85 °C, and the spraying speed was set to 1 ml/min.

A homogeneous solution of 15 wt% PAES in DMF and CH₂Cl₂ (4:6 vol ratio) was prepared and stirred for 12 h at room temperature. For electrospinning, a commercial nanofiber electrospinning unit from Kato Tech Co. Ltd. with a plane collector was used. The GDE was placed on the plane collector of the electrospinning device. The nanofibers were fabricated by applying 10.6 kV voltage, a tip-collector distance of 15 cm and a syringe x-y speed of 30 cm min⁻¹. The nanofiber deposition continued for 2 min, resulting in a mass of 0.2 ± 0.03 mg cm⁻² of PAES fibers on each GDE.

For the membrane coating, we used the commercially available Aquivion® D79-25BS ionomer dispersion, diluted with isopropyl alcohol, ethanol and deionized water. According to the mass ratio, the diluted solution was comprised of 3.5% ionomer, 10.5% deionized water, 36% isopropyl alcohol and 50% ethanol. To create a spray-coated membrane layer with a total thickness of ca. $15 \,\mu\text{m}$, $1.8 \,\text{mg resin} \cdot \text{cm}^{-2}$ was sprayed onto the nanofiber coated GDEs. During the spraying process, the temperature of the baseplate in the spray coating system was also set to 85 °C, and the spraying speed was set to 0.75 ml/min. After that, the sample would stay on the baseplate for a short time to make sure all the solvent had been evaporated. Two 5 cm² samples with nanofibers and ionomer were assembled by facing each other, and separated by open square sub-gaskets (12.5 µm thickness, FEP foil, DuPont) with 3 cm² active area. Common silicone rubber with a nominal thickness of 200 μ m and an opening dimension of 5 cm² was used as the main-gaskets. The fuel cell fixture with graphite serpentine flow channels was assembled with a torque of 4 N m.

For comparison, the recognized Nafion $^{\circ}$ 211 membrane (25 μ m) was used to fabricate MEA using the CCM method. Equally, the HCP 120 was employed for the gas diffusion layer, and the Pt loading of cathode and anode were 0.4 mg cm $^{-2}$ and 0.2 mg cm $^{-2}$, respectively. The ionomer content was 30 wt % in the catalyst layer in both electrodes. The sealing and assembly process of the single cell with CCM-based MEA were also same as for the DMD-based MEA.

Fuel cell polarization data was measured at different temperatures and relative humidities in a dedicated fuel cell test station (Scribner Associates, Inc., Model 850e). Prior to the measurements, the fuel cells underwent a break-in procedure consisting in constant voltage (0.55 V) at 80 °C and 100% RH until stable fuel cell performance was achieved (approx. 8 h). Polarization curves measurement, electrochemical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV) were used to analyze the cell's performance. To ensure enough stabilization time during the measurement, the polarization data was acquired with 2 min hold time at each point in the kinetic region $(0-0.1 \text{ A cm}^{-2})$, and 3 min over the rest of the polarization curve (>0.1 A $\rm cm^{-2}$). The cell resistance (high frequency resistance, HFR) was measured by in-situ EIS at a frequency of 3 kHz. The EIS data was investigated and fitted using an equivalent circuit (Scheme 1) [25] with the program ZSim Demo®. Rohm is ohmic resistance (high frequency resistance), as discussed above. Rct is charge transfer resistance, associated with the energy barrier that must be overcome for the electrochemical reactions to take place. R_{ct} is generally dominated by the kinetic losses at the cathode. R_{mass} is the mass transfer resistance, associated with the reactant transport resistance to the catalyst layer active sites, and is typically related to liquid water flooding occurring in the catalyst layer, GDL and gas channels. Constant phase element (CPE) that accounts for the storage of charges at



Scheme 1. Equivalent circuit of PEMFC.

electrode-electrolyte interface considering the porous nature of PEM fuel cell electrodes [25]. In order to determine the hydrogen crossover current as well as the electrical resistance of the MEAs, LSV was performed with anode $0.21 \text{ min}^{-1} \text{ H}_2$ and cathode $0.21 \text{ min}^{-1} \text{ N}_2$ gas flow by sweeping the cell voltage with a potentiostat from open circuit voltage to 0.6 V. To study the membrane durability and stability under chemical degradation by free radicals, the fuel cell was held at open circuit voltage for 100 h, at 90 °C, 30% RH, 250 kPa ab and at gas flows equivalent to stoichiometric flows of $10/10H_2/\text{air}$ at 0.2 A/cm². To examine membrane degradation, the OCV was logged during the time of the accelerated stress test (AST) [15]. For measuring polarization curve after AST, the fuel cells should also undergo a constant voltage (0.55 V) for 2 h at 80 °C and 100% RH.

For the microscopic investigations, a scanning electron microscope (SEM) (Phenom Pro) was used at an electron acceleration voltage of 10 kV. Proper cross-sections were prepared by cooling the operated MEA in liquid nitrogen and subsequently fracturing.

3. Results and discussion

3.1. Synthesis and characterization of monomer and copolymers

The PAES copolymer used here is ready-made in the lab. We also used the PAES copolymer with similar structures used for other application and obtained the appropriate performance [26]. Here, the PAES polymer with high molecular weight was prepared by polycondensation of three monomers according to the typical procedure reported in the literature [27].The corresponding ¹H NMR spectrum is shown in the Fig. S1 for structure validation. The assignment of the peaks confirms the successful synthesis of the copolymer. Additionally, the Mn, Mw, and PDI from GPC were 78.9k, 128.8k, and 1.63, respectively. Its molecular weight, which was higher than that of commercial PAES polymer, would be more suitable for the formation of the nanofibers [28].

3.2. Preparation of the DMD-based MEA

Scheme 2 shows the production process flow and the corresponding SEM morphologies of the DMD-based MEA. The first step was to choose a suitable GDL substrate, because its surface quality was directly related to electrical shorts as well as gas crossover [7,29]. Herein, HCP 120 was selected because of its crack-free and smooth surface, as shown in Scheme 2 (1). In comparison, the surface morphology of commercial SGL 25BC, shown in the Fig. S2, was severely cracked and not suitable for DMD. The second step was to spray the catalyst ink, comprised of 70 wt% Pt/C and 30 wt % ionomer, on the surface of the GDL to fabricate the GDE. It was characterized by SEM as crack-free, even, and homogeneous. Then, the PAES fiber network was directly electrospun on the GDE with fiber diameters in the range of 600-900 nm. The introduction of the PAES nanofiber network not only effectively restricted the swelling of the polymer, but also improved the mechanical property of the composite electrolyte. Finally, the ionomer solution was sprayed on top of the nanofiber, forming a homogeneous surface distribution, as observed by SEM, shown in Scheme 2 (4). More information about the homogeneity and thickness of the polymer electrolyte could be found in Fig. S3 of the supplementary material. It showed a clear SEM image of



Scheme 2. The production steps and corresponding SEM morphologies of the DMD-based MEA.

the fabricated MEA cross-section and indicated that the ultrasonic spraying used in catalyst ink and ionomer deposition process was a repeatable and effective method for every sample. Finally, the total electrolyte thickness is about $15 \pm 1.5 \,\mu$ m, which is significantly thinner than that of most commercially available membranes such as Nafion® 211 ($25 \,\mu$ m) or Nafion® HP ($20 \,\mu$ m). The thinner membrane would impose less resistance to proton transport and provide better hydration due to faster water osmosis from the cathode to anode [30].

3.3. Electrochemical characterization and analysis

The fuel cell experiments detailed in this section demonstrate the effect of different operating conditions on the fuel cell performance. The DMD-based MEA and the reference MEA (CCM-based MEA) were characterized and analyzed by polarization curve measurement, EIS, and LSV. Among these, the polarization curve measurement yielded insights into operation at different temperatures, and relative humidities. EIS was used to analyze and compare the performance of two fuel cells, and the LSV was used to evaluate the hydrogen crossover and internal short resistance.

Polarization curve and power density data for the DMD fuel cell and CCM reference are shown in Fig. 1. Obviously, the introduction of the ionically insulating PAES did not reduce the performance of the MEA; rather, it enhanced the fuel cell performance. At the same relative humidity (75%), a current density of 2.8 A cm^{-2} at 0.7 V was obtained for the DMD-based MEA, which was 1.65 times higher than that of CCM-based MEA (2.1 A cm⁻² @ 0.7 V). At lower humidity (32%), a more obvious distinction was observed: at 0.7 V, the current densities of DMD and CCM were 2.1 A/cm² and 1.1 A cm⁻², respectively. The highest power density of 2.85 W cm⁻² was reached at 75% relative humidity.

Under identical operation conditions, the CCM-based MEA showed a peak power density of $2.09 \,\mathrm{W \, cm^{-2}}$, which was 73.3% of the power density of the DMD-based MEA.

The HFR data for both MEAs were collected under different relative humidities. The HFR included the protonic resistance of the membrane and membrane catalyst layer interface, and the electrical resistance of the catalyst layer, the GDL, and their layer interface [31]. Among these, the protonic resistance of the membrane dominated the high frequency resistance; thus, the HFR changed with the relative humidity and membrane thickness. The HFR data indicated the resistance of DMD-based MEA was lower than that of the CCM-based MEA for the same relative humidity, which contributed to better fuel cell performance. The main reasons were believed to be the relatively thinner polymer electrolyte, and a strongly decreased contact resistance of for membrane-electrode interface in the DMD-based MEA. Furthermore, relative humidity had a remarkable effect on HFR at low current density (less than $0.75 \,\mathrm{A \, cm^{-2}}$) when little water was generated from the electrochemical reaction and the membrane was hydrated mainly by the water in the humidified inlet gas. When the current density was higher than $1.5 \,\mathrm{A}\,\mathrm{cm}^{-2}$, the water generated by the fuel cell would be enough to humidify the membrane and keep it well hydrated, leading to relatively constant HFR. For the CCM-based MEA, at higher current densities, the HFR increased slightly due to drying-out of the membrane on the anode side. Membrane drying-out within fuel cells is a common phenomenon at high current densities and occurs because water molecules associated with proton migration are dragged from the anode to the cathode at a higher rate than back diffusion from the cathode (where water is produced) to the anode [32]. This phenomenon is more clearly seen with thicker membranes, such as the Nafion® 211 in the CCM, than with thinner polymer electrolyte such as the one deposited in the DMD.



Fig. 1. a) Cell voltage and HFR as a function of current density; b) Power density as a function of current density. Operating gases are H_2 and O_2 . Anode stoichiometry is 1.5; cathode stoichiometry is 2.0. Cell temperature is 80 °C; relative humidities are 32% (blue) and 75% (green). Both anode and cathode backpressures are 300 kPa ab. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 2 shows the H_2/O_2 cell performance of the DMD and CCM fuel cells under ambient pressure with different humidification. The DMDbased MEA consistently exhibited superior performance under low relative humidity (less than 32%) even with the introduction of the ionically insulating PAES. Notably, at 12% RH, the power density of the DMD-based MEA (1.31 W cm^{-2}) was close to its power density $(1.50 \,\mathrm{W \, cm^{-2}})$ at 32% RH and 2.85 times higher than that of CCM-based MEA (0.46 W cm⁻²@12% RH). The relatively thinner polymer electrolyte used in the DMD-based MEA required less water to be hydrated, and back diffusion from the cathode to anode was much easier because the diffusion distance was much shorter. Specifically, the enhanced selfhumidification capacity provided by the thinner membrane of the DMD-based MEA enabled relatively better cell performance than that of the CCM-based MEA (25 µm membrane thickness) under low humidity (less than 32% RH). Fig. 2 d) shows the HFRs of both MEAs at different humidification values. When the current density was lower than 0.8 A/ cm², the water in the reaction gas was not enough to hydrate the membrane, leading to relatively high HFRs for all the MEAs. However, the DMD-based MEA with a thin electrolyte later exhibited lower HFR, and no obvious difference was observed under different RH when the current density was increased to $1.2 \,\mathrm{A}\,\mathrm{cm}^{-2}$ or higher. At a current density of 2 A cm⁻², the HFRs of DMD at 12% RH, 22% RH, and 32 %RH were 0.054, 0.049, and 0.044 Ω cm², respectively. Conversely, the HFR of CCM-based MEA, with relatively thick Nafion® 211 membrane, strongly dependened on the relative humidity. At the same current density, the HFRs of the CCM at 12% RH, 22% RH, and 32% RH were 0.151, 0.115, and 0.090 Ω cm², respectively. Consequently, the difference in the HFR directly leads to the different fuel cell performance.

The semi-log plot of iR-free voltage as a function of current density was used to analyze the effect of the activation polarization of these two kinds of MEAs on the fuel cell performance. Because the activation polarization due to electrode kinetic limitations was dominant at very low current densities $(10-100 \text{ mA cm}^{-2})$ [33,34]. The fitting slopes of the DMD-based MEA at 12% RH, 22% RH, and 32% RH were 118.9 mV·dec⁻¹, 102.1 mV·dec⁻¹, and 95.8 mV·dec⁻¹, respectively. The same trend was also observed for the CCM-based MEA. The apparent

resistance to the oxygen reduction reaction increased significantly at low humidity levels, as indicated by the large Tafel slope. However, the measured Tafel slope was much higher than calculated Tafel slope from 2.303 RT/F ($72 \text{ mV} \cdot \text{dec}^{-1}$) partially because of the uncorrected ionic resistance at the cathode [30]. The iR-free voltage was corrected only for ohmic resistance, which was measured by the current-interrupt technique. It did not include the ionic resistance at the cathode [28]. The kinetic effect of relative humidity on the oxygen reduction reaction is below, using data from EIS.

EIS was performed to further elucidate the reasons for the higher performance of the DMD fuel cell compared with CCM fuel cell. The equivalent circuit used to analyze EIS data was shown in Scheme 1. The close agreement between the experimental data and fitting data shows that the selected equivalent circuit is suitable for the fuel cells. Fig. 3 shows the effects of RH (at a constant current density of $1 \,\mathrm{A \, cm^{-2}}$) and current density (at a constant relative humidity of 32% RH) on fuel cell resistance. Compared with the CCM-based MEA at the same relative humidity or current density, Rohm was significantly lower for the DMDbased MEA, due to relatively thin polymer electrolyte layer and strongly decreased contact resistance of the membrane-electrode interface. When the relative humidity was 12% at current density of 1 A cm⁻², the R_{ohm} values of the DMD and CCM were $0.081 \,\Omega \,\mathrm{cm}^2$ and $0.198 \,\Omega \,\mathrm{cm}^2$, respectively; and when the humidity level increase to 32% RH, the Rohm of DMD and CCM were $0.055 \,\Omega \,\mathrm{cm}^2$ and $0.111 \,\Omega \,\mathrm{cm}^2$, respectively. At a constant current density (a-c in Fig. 3), the relative humidity appeared to significantly affect the R_{mass} of the CCM-based MEA, because the mass transfer resistances were $0.139 \,\Omega \,\mathrm{cm}^2$, $0.046 \,\Omega \,\mathrm{cm}^2$, and $0.014 \,\Omega \,\mathrm{cm}^2$ at 12% RH, 22% RH, and 32% RH, respectively. Conversely, the relative humidity had little influence on the mass transfer resistance of the DMDbased MEA. Because the mass transfer resistance was mainly comprised of gas-phase diffusion resistance and oxygen transport resistance through the thin film at the surface of Pt [32,35]. These studies also showed that oxygen permeability through the ionomer layer on the cathode catalyst decreased with decreasing relative humidity and increased with increasing temperature. One explanation could be that the thinner polymer electrolyte layer in the DMD-based MEA needed less



Fig. 2. a) Cell voltage as a function of current density; b) Power density as a function of current density; c) Semi-log plot of iR-free voltage as a function of current density $(10-100 \text{ mA/cm}^2)$; d) HFR as a function of current density. Operating gases were H₂ and O₂. Anode stoichiometry is 1.5; cathode stoichiometry is 2.0. Cell temperature is 80 °C; relative humidities are 12% (blue), 22% (red), and 32% (green). Both anode and cathode backpressures are ambient pressure. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 3. EIS for a H_2/O_2 PEM fuel cell at different humidify conditions (a-c, current density: 1 A cm^{-2}); EIS for a H_2/O_2 PEM fuel cell under different current densities (d-f, relative humidity: 32% RH).

water to be hydrated than the Nafion® 211 membrane. In that case, much more water was used to hydrate the ionomer in the cathode catalyst layer at relatively low RH. As a result, in the DMD-based MEA, the oxygen moleculars easily permeate through the ionomer layer covering the Pt nanoparticles.

Herein, we also found that the relative humidity had a distinct effect on R_{ct} values for both MEAs. The actual values for the DMD and CCM were 0.131 vs. $0.189\,\Omega\,cm^2$ (12% RH), 0.120 vs. $0.146\,\Omega\,cm^2$ (22% RH), and 0.101 vs. $0.124\,\Omega\,cm^2$ (32% RH), respectively. The increased relative humidity reduced the kinetic loss of the fuel cell which was not confirmed in the above discussion of the Tafel slope due to the existence of protonic resistance in cathode catalyst layer.

The effect of current density on the resistance was also investigated under constant relative humidity (d-f in Fig. 3). The HFR slightly decreased with an increase in the current density, e.g., $0.055 \,\Omega \,\mathrm{cm}^2$ at $1 \,\mathrm{A \, cm}^{-2}$, $0.038 \,\Omega \,\mathrm{cm}^2$ at $2 \,\mathrm{A \, cm}^{-2}$, and $0.034 \,\Omega \,\mathrm{cm}^2$ at $3 \,\mathrm{A \, cm}^{-2}$, respectively. The reason was that much more water would be generated at high current density so that the membrane would be better hydrated. For both MEAs, the mass transfer resistance increased with current density because of the starvation of oxygen in the catalyst layer. From the result of the polarization in Fig. 2 (a), the DMD-based MEA possessed a higher limiting current density than the CCM-based MEA. Accordingly, for identical current densities, the mass transfer resistance of the DMD ($0.023 \,\Omega \,\mathrm{cm}^2$) was much lower than that of CCM ($0.099 \,\Omega \,\mathrm{cm}^2$), based on the calculation of mass transfer resistance [32] at $3 \,\mathrm{A \, cm}^{-2}$.

Hydrogen crossover from anode to cathode by permeation through the electrolyte degrades the performance and durability of the cell [36, 37]. Fig. 4 shows LSV measurements for all samples at 80 °C at different relative humidities. The current density was extracted from the platform at about 0.3 V. Compared to that of the Nafion® 211-based MEA, the hydrogen crossover current density of the DMD-based MEA showed a slight upward trend due to its thinner polymer electrolyte. It exhibited crossover current densities of 1.89 mA cm^{-2} , 2.13 mA cm^{-2} and 2.39 mA cm⁻² at 12% RH, 22% RH and 32% RH, respectively. Meanwhile, the crossover current density of the Nafion® 211-based MEA was around 1.75 mA cm^{-2} . Direct conduction of electrons between the electrodes through the electrolyte was also a source of performance loss within a fuel cell. Although the polymer electrolyte was designed to be electrically insulating and ionically conducting, a finite amount of electron conduction could also occur, especially if small portions of the individual electrode contacted one another due to electrolyte thinning.



Fig. 4. Linear sweep voltammetry for both MEAs at different relative humidities.

The internal shorting resistance was extracted from a linear fit of the LSV data between 0.4 V and 0.6 V. The value for the Nafion® 211-based MEA was in the range of 897–991 $\Omega\,cm^2$ in these conditions, while that of DMD-based MEA was in the range of 1659–1937 $\Omega\,cm^2$. Obviously, even though the polymer electrolyte became thinner in the DMD, the electrical shorting resistance was improved by the introduction of the dimensionally stable and insulating PAES nanofibers.

The comparative performance of the DMD and CCM fuel cells operated with H_2/O_2 were analyzed by a series of electrochemical methods. Most intuitively, the DMD-based MEA achieved better performance than CCM-based MEA, especially under low relative humidity conditions. However, considering the practical application of fuel cells for transportation, it is also important to evaluate of the H_2/Air fuel cell performance. The polarization curves are also discussed under different relative humidities and the EIS was also used to analyze the different resistance in the air condition.

The H₂/Air fuel cell performance of both MEAs are shown in Fig. 5. In order to improve the back diffusion of the generated water in the cathode, a pressure gradient was applied across the cell (anode, 250 kPa ab; cathode, 300 kPa ab). At a current density of 1 A cm^{-2} , the



Fig. 5. a) Cell voltage and high frequency resistance as a function of current density; b) Power density as a function of current density. Operating gases were H_2 and Air. Anode stoichiometry is 1.5; cathode stoichiometry is 5.0. Cell temperature is 80 °C; and relative humidity is 75%. Anode backpressure is 250 kPa ab; and cathode backpressure is 300 kPa ab.

cell voltages of DMD and CCM were about 0.72V and 0.69V, respectively. The power densities of the DMD and CCM were 0.99 W cm⁻² (@ 1.70 A cm^{-2}) and 0.82 W cm⁻² (@ 1.40 A cm^{-2}), respectively. The reasons for the higher performance of the DMD fuel cell are discussed below. In addition, the DMD-based MEA exhibited a lower HFR (0.032 $\Omega \text{ cm}^2$ @ 1.0 A cm^{-2}) than the CCM-based MEA (0.050 $\Omega \text{ cm}^2$ @ 1.0 A cm^{-2}). Notably, as described in the literature, at larger current densities, the ohmic resistance increased slightly due to drying-out of the membrane on the anode side [38]. However, under these conditions, when the fuel cell was operating at high current density (>1.5 A cm⁻²), the HFRs always remained constant and did not show an upward tendency. This constantly illustrated that the existence of the pressure gradient indeed improved the back diffusion of the generated water to enhance the membrane water content.

To further elucidate the reasons for the higher performance of the DMD fuel cell, EIS analysis was performed, which was shown in Fig. 6. The equivalent circuit model of the PEMFC was shown in Scheme 1. The parameters of the electric equivalent circuit considered were described in detail above, and there was a good consistency between the experimental result and the fitting data. EIS data was collected to compare the resistances of both MEAs at different current densities. Obviously, as with the H_2/O_2 fuel cell, a significant reduction of R_{ohm} was obtained in the DMD-based MEAs due to their thinner polymer electrolyte and effective membrane-electrode interface. For example, when the current density was $0.5\,A\,cm^{-2}\!,$ the R_{ohm} of the DMD and CCM were $0.047\,\Omega\,\text{cm}^2$ and $0.057\,\Omega\,\text{cm}^2$, respectively. The same trends were also found at $0.1 \,\mathrm{A \, cm^{-2}}$ and $1.0 \,\mathrm{A \, cm^{-2}}$. At low current density $(0.1 \,\mathrm{A}\,\mathrm{cm}^{-2})$, the spectrum consisted of a single semicircle, with a high frequency intercept value for Rohm and a diameter of Rct, indicating the near-absence of diffusion-related resistance. Under this condition, the majority of the total cell resistance is due to the resistance of the charge transfer reaction. The similar R_{ct} values of DMD and CCM at 0.1 A cm⁻² were 0.480 and $0.474 \,\Omega \,\mathrm{cm}^2$, respectively. As the current density increased (0.5 A cm⁻²), the R_{ct} of DMD and CCM reduced to 0.134 and $0.156 \,\Omega \,\text{cm}^2$, respectively. The diameter of the high frequency arc decreased, reflecting the increasing driving force for the oxygen reduction reaction. In addition, a very small low-frequency loop was observed for both MEAs at $0.5\,\mathrm{A\,cm^{-2}}$, indicating a modest resistance due to transport of cathode reactant in this condition. The similar R_{mass} values of the DMD and CCM were 0.020 and 0.021 Ω cm², respectively. Accordingly, when the current density was less than $0.5 \,\mathrm{A \, cm^{-2}}$, only a tiny difference existed in their polarization, as shown in Fig. 5. With a further increase the current density $(1.0 \,\mathrm{A \, cm^{-2}})$, the R_{ct} of DMD and CCM decreased to 0.084 and $0.125 \,\Omega \,\text{cm}^2$, respectively, which was a direct cause of their polarization difference. Moreover, the lowfrequency loops consistently increased in size with current density for both MEAs, as seen the spectra acquired at current densities of $0.5 \,\mathrm{A}\,\mathrm{cm}^{-2}$ and $1.0 \,\mathrm{A}\,\mathrm{cm}^{-2}$. Their values were $0.053 \,\Omega\,\mathrm{cm}^2$ and $0.070 \,\Omega \,\mathrm{cm}^2$ for the DMD and CCM, respectively. This behavior indicated that the limitations on mass transfer are exacerbated at high reaction rates because of the reduced oxygen concentration in the catalyst layer, which was explained in Vierrathan's research work [13]. The back diffusion of generated water, would be enhanced through the thin directly deposited membrane layer and thicker conventional membrane, would cause significant amount of water accumulation in the cathode catalyst layer [39]. Consequently, the DMD fuel cell would accumulate less water in the pore space of the cathode, facilitating oxygen diffusivity inside the cathode catalyst layer.

The Fig. 7 a) shows the accelerated stress test comparison of DMDbased and CCM-based MEAs. It is worth noting that the backpressure (250 kPa ab) used here is much more serious than that of DOE requirement (150 kPa abs) in order to reduce the test time. The OCV decrease of the DMD-based MEA was less than 18%, which was in good agreement of measured decay rates for the MEA in Ref. [14]. For the Nafion® 211-based MEA without reinforcement layer, it was difficult to accomplish the whole test process. The breakdown of OCV was occurred around 50 h. This may be linked to degradation of the membrane ionomer itself and/or a deterioration of the interface between catalyst layer and membrane by delamination or crack formation. In addition, the polarization curves were also compared before and after AST for the DMD-based MEA, which was shown in Fig. 7 b). After AST, the OCV was still higher than 0.9V due to the existence of PAES reinforcement; and



Fig. 6. EIS for the H₂/Air PEM fuel cell under different current density conditions.



Fig. 7. a) The AST comparison of DMD-based and CCM-based MEAs; b) the polarization curves of DMD-based MEA before and after AST (b).

the power density after AST was reduced to 1.23 W/cm^2 (from 1.50 W/cm^2), which was higher than the original performance of Nafion® 211-based MEA under the same conditions. Future work on the analysis of degradation mechanism and improvement of durability is in process.4. Conclusions.

Direct membrane deposition was introduced as a novel polymer electrolyte membrane fabrication method. Herein, this approach is extended to fabricate a high-performance MEA for polymer electrolyte membrane fuel cells with poly(arylene ether sulfone) nanofibers as effective membrane reinforcements. PAES nanofibers were directly electrospun onto gas diffusion electrodes. By spray-coating an ionomer dispersion into the pore space of PAES nanofiber mats, composite membranes of 15 μ m thickness were fabricated. The introduction of the electrically and ionically insulating PAES did not reduce the performance of the MEA. At 80 $^\circ\text{C}$ and 75% relative humidity, the power density of the DMD fuel cell (2.85 W cm^{-2}) was about 1.36 times higher than that of the reference fuel cell $(2.09 \,\mathrm{W \, cm^{-2}})$ with a Nafion® 211 membrane and identical catalyst. The cell resistance $(28 \text{ m}\Omega \text{ cm}^2)$ was well below that of the CCM-based MEA (46 m Ω cm²). The reasons for the differences between the DMD and CCM were systematically analyzed by EIS. Most notably, even though the polymer electrolyte (15 µm) was much thinner than Nafion® 211 (25 µm), it showed much higher shorting resistance and better durability because of the reinforcement by PAES nanofibers. After the accelerated stress test, the fuel cell performance was still acceptable. Further research should emphatically focus on improving the mass transfer of the DMD-based MEA and lower the Pt loading so that the performance can be even better, and cost shall decrease.

Author contributions

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Appendix A. Supplementary data

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