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Development of gas diffusion layer using water based carbon slurry for proton exchange membrane fuel cells

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ABSTRACT

The micro-porous layer of gas diffusion layers (GDLs) was fabricated with the carbon slurry dispersed in water containing sodium dodecyl sulfate (SDS), by wire rod coating process. The aqueous carbon slurry with micelle-encapsulation was highly consistent and stable without losing any homogeneity even after adding polytetrafluoroethylene (PTFE) binder for hundreds of hours. The surface morphology, contact angle and pore size distribution of the GDLs were examined using SEM, Goniometer and Hg Porosimeter, respectively. GDLs fabricated with various SDS concentrations were assembled into MEAs and evaluated in a single cell PEMFC under diverse operating relative humidity (RH) conditions using H_2/O_2 and H_2/air as reactants. The peak power density of the single cell using the GDLs with optimum SDS concentration was 1400 and 500 mW cm^{-2} with H_2/O_2 and H_2/air at 90% RH, respectively. GDLs were also fabricated with isopropyl alcohol (IPA) based carbon slurry for fuel cell performance comparison. It was found that the composition of the carbon slurry, specifically SDS concentration played a critical role in controlling the pore diameter as well as the corresponding pore volumes of the GDLs.

1. Introduction

Gas diffusion layers (GDLs) perform the significant functions in the proton exchange membrane fuel cells (PEMFCs), such as maintaining the water balance in the membrane electrode assembly (MEA) by allowing appropriate amount of water to move in and out from the reaction zone, providing the mechanical support for the MEA and electrical contact between the electrodes and the current collectors [1–3]. The key characteristics of GDLs include structural design, porosity, hydrophobicity, hydrophilicity, gas permeability/transport properties, water management and surface morphology. The GDLs consist of a micro-porous layer made of teflonized carbon black on the top of macro-porous carbon paper or cloth substrate. The effects of macro-porous carbon substrate on the GDL performance have been reported in our previous study [4]. Alcohol based solvents are widely used for preparing homogenous dispersion of teflonized carbon slurries for GDL fabrication of micro-porous layers [4–6]. However, the alcohols pose environmental and health safety issues when used in larger volume for any commercial manufacturing. To our knowledge, there is no literature describing carbon slurry preparation using water as a medium.

Sodium dodecyl sulfate (SDS) has been reported as an effective dispersing agent for hydrophobic materials [7–9]. For example, Moshammer et al. has used SDS aqueous solution as dispersing agent for carbon nanotubes (CNTs) and gotten the long time suspended slurry [10]. It has been reported that the formation of micelles occurs above the SDS critical micelle concentration (CMC: ~8 mM) at 25 °C [11].

In our present study, Pureblack carbon powder along with vapor grown carbon fiber (VGCF) was well dispersed with SDS aqueous solution instead of alcohol based solvent. It was found that the PEM fuel cell performance (such as power output, cell water management at high current density range) of GDLs fabricated with SDS aqueous solution is better than that of GDLs fabricated with alcohol based solution at 80 °C with H_2/O_2 and H_2/air, various relative humidities (RH).

2. Experimental

2.1. Gas diffusion layer

Teflonized non-woven carbon substrate (GD12012T) was developed and supplied by Hollingsworth & Vose Company. Teflon dispersion (TE-3859) from DuPont Fluoroproducts, Nano-chain Pureblack (grade 205-110) carbon from Superior Graphite Co., VGCF from Showa Denko America Inc. and SDS ($C_{12}H_{25}SO_4Na$) from Fisher Scientific were used for slurry preparation.

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Table 1
GDLs fabrication parameters and performance characteristics at 90% RH.

Sample number	SDS amount (mg)	SDS concentration (mM)	Dispersion medium	Wetting angle (°)	Fuel cell peak power density (mW cm^{-2})	
					H_2/O_2	H_2/air
1	60	25	DI water	137	1255	510
2	120	50	DI water	135	1415	505
3	240	100	DI water	133	1060	435
4	–	–	IPA	136	935	410

0.5 g of carbon powder (75 wt% Pureblack carbon powder and 25 wt% VGCF) was dispersed in 8 ml DI water containing various amounts of SDS (25, 50 and 100 mM, labeled as sample #s 1, 2 and 3 in Table 1) by sonicating for 10 min. PTFE (25 wt%) dispersion was added into the mixture and followed with the magnetic stirring for 5 min. The carbon slurry was coated onto the non-woven carbon paper substrates using Easycoater equipment (EC26, Coatema) with the velocity of 3 m min^{-1} as depicted by Kannan et al. [12]. The carbon loading on the micro-porous layer was about 3 mg cm^{-2}, controlled by the wire thickness on the wire rod. After coating the micro-porous layer, the GDL samples were dried at room temperature overnight and then sintered at 350 °C for 30 min in air. One set of GDL samples was washed to remove the SDS impurities by immersing them in warm DI water for 30 min. For fuel cell performance comparison purposes, a GDL (sample # 4 in Table 1) was also prepared with IPA based carbon slurry [4,12].

The surface morphology of the GDL samples was examined by JEOL JSM-5900LV Scanning Electron Microscope (SEM). The pore diameter, pore size distribution and pore volume/porosity of various GDL samples were measured by Hg porosimeter (PoreMaster-60 GT, Quantachrome Instruments, Boynton Beach, FL). The pore size distributions were calculated from the mercury intrusion data by applying the Washburn equation. The wetting characteristics (contact angle) of the GDL samples were analyzed

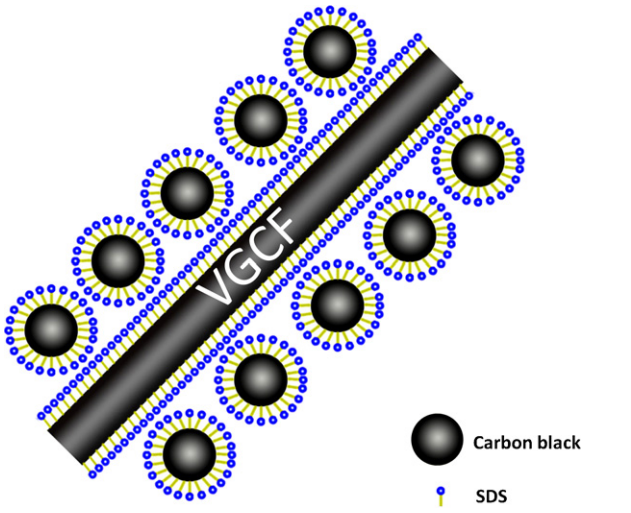

Fig. 1. Schematic representation of micelle-encapsulated Pureblack and VGCF carbons.

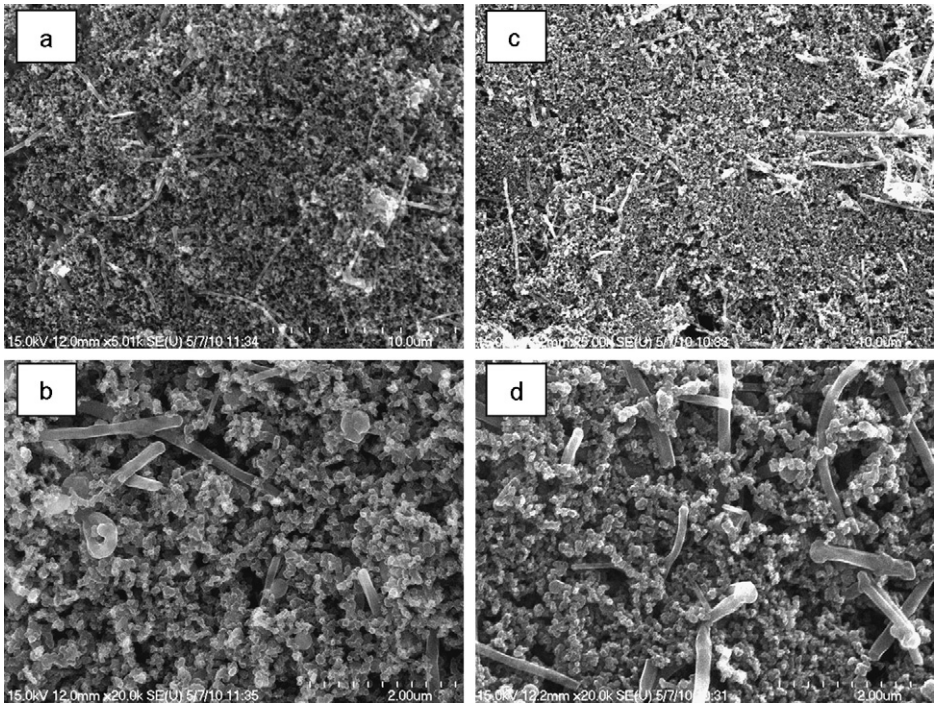

Fig. 2. SEM of GDL samples 2 ((a) and (b)) and 4 ((c) and (d)) at two different magnifications.

by the Ramehart Advanced Automated Goniometer using water drop.

2.2. Membrane electrode assembly and fuel cell performance

Fabrication of membrane electrode assembly (MEA) consisting of commercial catalyst (Pt/C) coated on both anode and cathode sides of the Nafion-212 membrane (Ion Power Inc., New Castle, DE, USA) was reported elsewhere [12]. Briefly, catalyst ink was prepared by adding IPA (20 ml for 1 g of electrocatalyst) after purging the Pt/C catalyst powder (TKK, Japan) in flowing nitrogen gas for about 30 min to avoid any flame/ignition. In order to extend the reaction zone of the catalyst layer, 5 wt% Nafion® (Ion Power Inc., New Castle, DE, USA) dispersion (10 ml for 1 g of electrocatalyst) was added to the catalyst slurry. Catalyst layer on the Nafion membrane with 5 cm^2 active area was fabricated on both sides by spraying the catalyst ink using the micro-spray method. The catalyst loadings on the anode and cathode were about 0.1 and 0.2 mg Pt cm^{-2}, respectively. The MEA was vacuum dried at 70 °C for 15 min before assembling them in the single cell test cell.

The MEA was assembled by sandwiching inside a single test cell (Fuel Cell Technologies Inc, Albuquerque, NM, USA) along with the GDLs (with and without washing in water) on both sides. Gas sealing was achieved using silicone coated fabric gasket (Product # CF1007, Saint-Gobain Performance Plastics, USA) and with a uniform torque of 0.45 N m. The single cell fuel cell performance was evaluated at 80 °C, various RH conditions and ambient pressure with H_2/O_2 and H_2/air by using Greenlight Test Station (G50 Fuel Cell System, Hydrogenics, Vancouver, Canada) with fixed flow rates

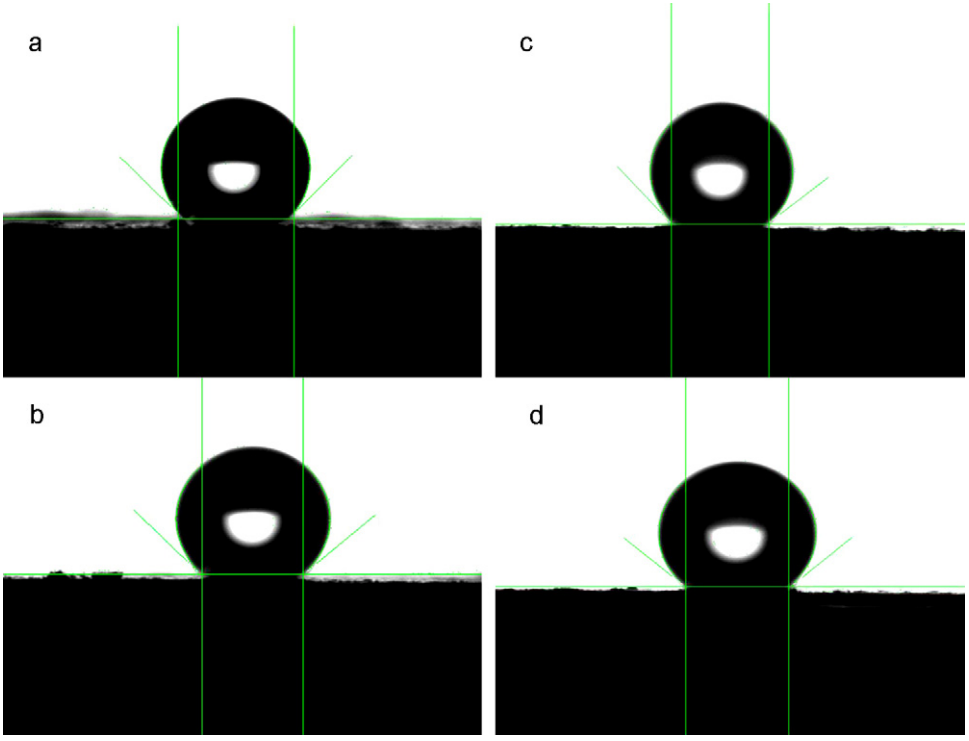

Fig. 3. Wetting angle images of various GDL samples (a) 1, (b) 2, (c) 3 and (d) 4.

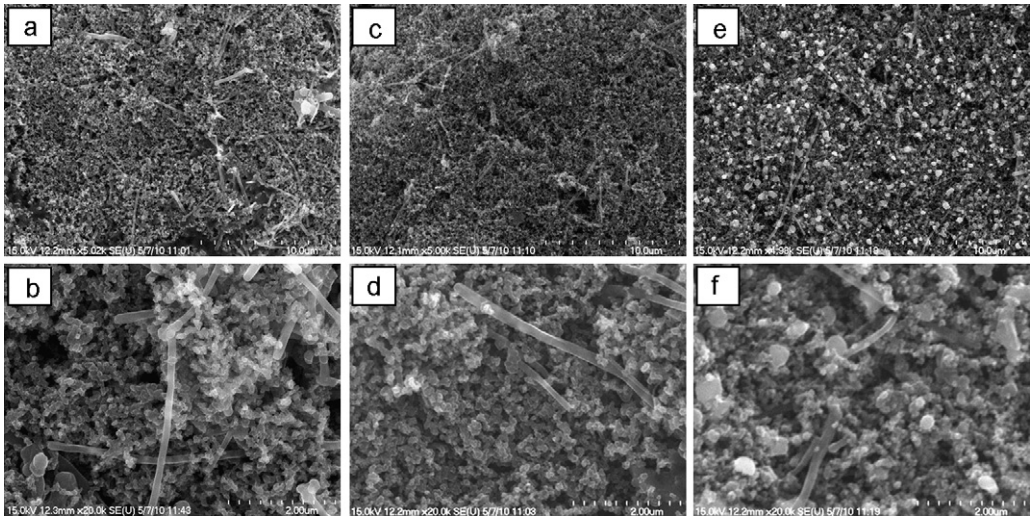

Fig. 4. SEM images of GDL samples 1 ((a) and (b)), 2 ((c) and (d)) and 3 ((e) and (f)) at two different magnifications.

of 200 sccm on anode side (H_2) and 400 sccm on cathode side (O_2 or air). The flow tracking modes were not used.

3. Result and discussion

Based on many experiments, the minimum SDS concentration was found to be about 24 mM for the formation of homogenous and stable carbon slurry. The SDS molecules are chemically adsorbed on the surface of the carbon particles, forming micelle-encapsulation [13]. Fig. 1 schematically illustrates micelle-encapsulated carbon particles and carbon fibers. The SDS, anionic surfactant is attached to the surface of carbon particle/fiber facilitating homogenous dispersion of the slurry in water medium. The surface morphology of the GDL samples was examined by SEM at different magnifications and is shown in Fig. 2. It is observed that the GDLs fabricated with SDS (Fig. 2(a) and (b) for sample 2) have less micro-cracks/holes than the one fabricated with IPA based slurry (Fig. 2(c) and (d) for sample 4). It is worth noting that the IPA solvent can evaporate much faster compared to water in the micro-porous layer leading to relatively more cracks/holes in sample 4.

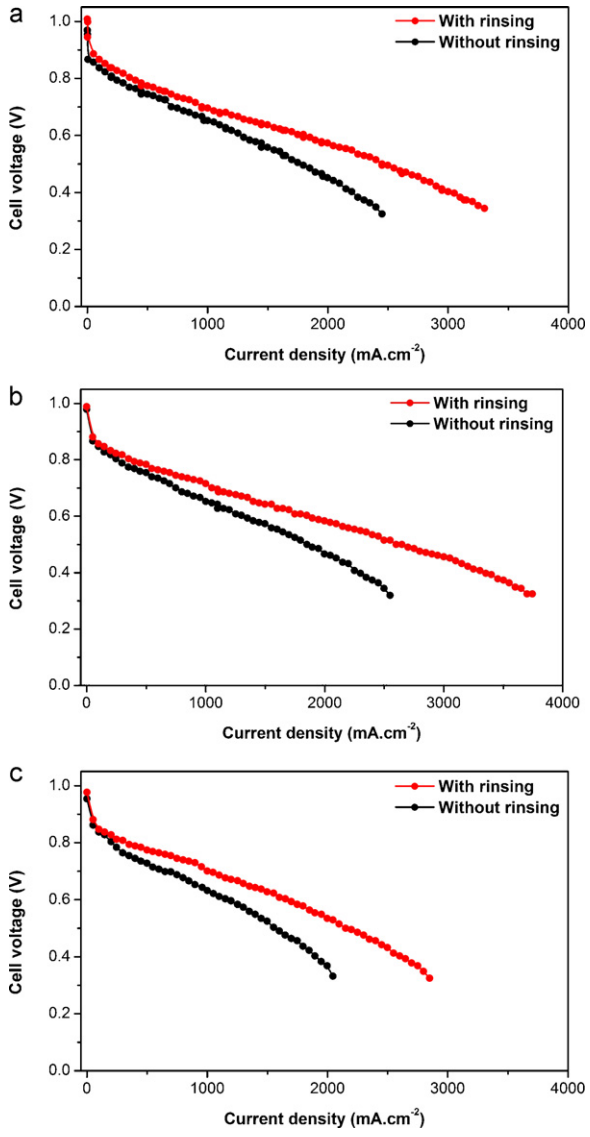

Fig. 5. PEMFC performance comparisons of various GDL samples (a) 1, (b) 2 and (c) 3 with and without rinsing in water, at 80 °C with H_2/O_2, 100% RH.

Fig. 3 shows the wetting angle images of the GDL samples 1–4 with water–alcohol droplet. As seen from the images, the wetting angle values for all the samples (Table 1) are almost similar ($135 \pm 2°$), as the Teflon content is 25 wt.% in the slurries. From the wetting angle values, it is clear that the surface property of the micro-porous layer does not change due to water or IPA medium.

GDL samples with various SDS concentrations were also examined by SEM to observe the surface morphology. Fig. 4 shows SEM images of GDL samples 1–3 at two different magnifications. Clearly, these images show less holes/non-uniformity compared to sample 4 (Fig. 2c and d) indicating the function of SDS in improving the dispersion. In fact, when the carbon slurry was prepared with SDS, it was found to be highly stable without any settling. Even though higher concentration of SDS enhances the dispersion of carbon particle/fiber (Fig. 4(e) and (f)) as compared to that of lower concentration (Fig. 4(a) and (b)), it brings in more impurities as observed as white spots in Fig. 4(e, f). Hence the GDL samples were subjected to washing in warm water to remove the excess SDS before evaluating them in PEMFCs.

Fig. 5(a–c) compares the PEM fuel cell performance of MEAs using H_2/O_2, at 80 °C and 100% RH with the GDL samples 1 and 2 and 3 before and after rinsing them in warm water. As seen from Fig. 5(a–c), all the MEAs with washed GDL samples showed relatively higher performance compared to that with un-washed GDLs. In addition, the open circuit voltage values of the MEAs with washed GDLs were also relatively higher compared to that of the un-washed GDLs. It has been reported that sodium ion will contaminate the MEA and dramatically decrease the ion conductivity of the Nafion membrane [14]. GDL samples were immersed and washed in warm (about 50 °C) DI water to dissolve the remaining SDS to overcome the issue of contamination.

The GDL samples after washing in water were also evaluated in the PEMFCs at various operating RH conditions using H_2/air and H_2/O_2 at 80 °C and ambient pressure to analyze the water management. Fig. 6(a–d) compares the fuel cell performance with H_2/air at various RH conditions. Similarly Fig. 7(a–d) compares the fuel cell performance with H_2/O_2 at various RH conditions. Table 1 consolidates the peak power density values of the MEAs with various GDL samples using H_2/O_2 and H_2/air at 90% RH. It is observed that the MEAs with GDL sample 1 maintained stable and good performance with various RH conditions using H_2/air (Fig. 6(a)) as well as H_2/O_2 (Fig. 7(a)). It is evident that the MEAs with GDL sample 2 exhibited the best fuel cell performance with peak power density values of 1415 and 505 mW cm^{-2} with H_2/O_2 and H_2/air (Figs. 6(b) and 7(b)), respectively whereas the cell with GDLs fabricated with IPA just showed 935 and 410 mW cm^{-2} at the similar operating conditions, as seen in Figs. 6(d) and 7(d) as well as in Table 1. It is interesting to note that the MEAs with GDL sample 3 showed very poor fuel cell performance compared to that of samples 1 and 2.

As reported by Lee et al. [15], the pore size distribution is one of the most critical parameters responsible for different modes of gas and water transport across the GDLs in the PEMFCs. The pore size distribution data for GDL samples are shown in Fig. 8. It is observed that the GDLs fabricated with water based and IPA based slurries have majority of the pores in the region of ~40 μm. However, the IPA based GDL sample showed relatively less volume of macro-pore size distribution (between 0.1 and 1 mm) which may due to the carbon slurry permeating into macro-porous layer and blocking the macro-hole of the carbon paper substrate. High concentration of SDS dispersion agent helps to form large volume of micro-pore (30–60 μm), as shown in Fig. 8, yet it is believed the thickness of micelle layer on the encapsulated carbon powder/fiber was also larger at high SDS concentration (sample 3) than that at low SDS concentration (samples 1 and 2), so sample 3 has formed more macro-pores (size ranged from 0.1 to 1 mm) on the GDL which

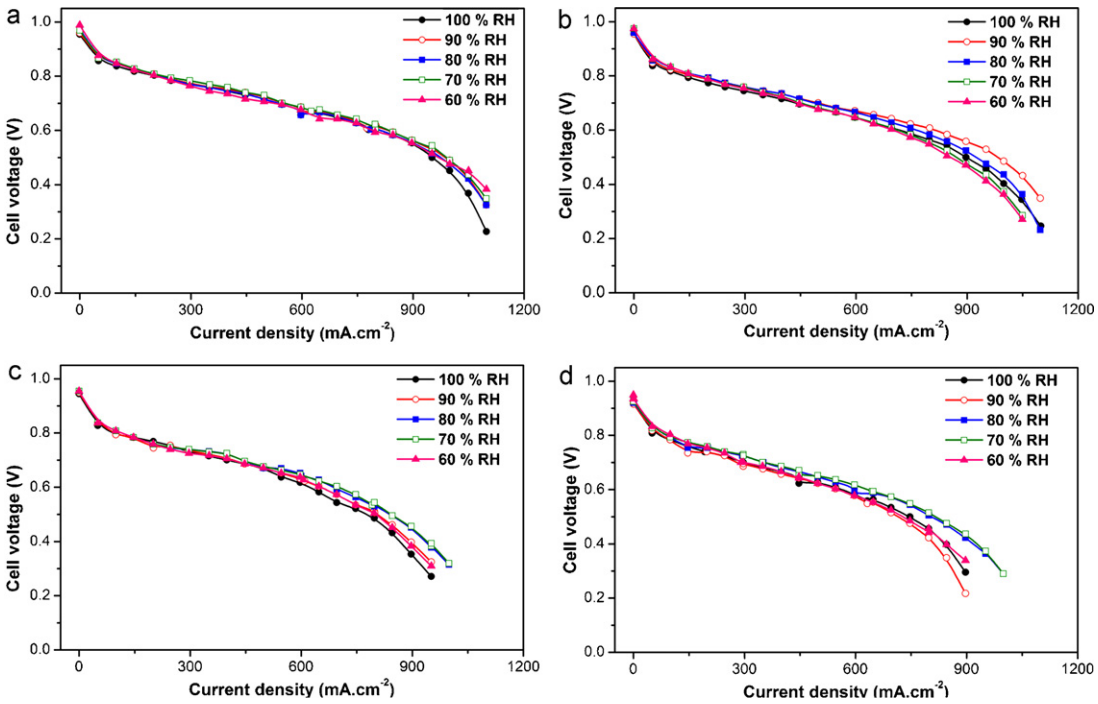

Fig. 6. PEMFC performances of various GDL samples (a) 1, (b) 2, (c) 3 and (d) 4 at 80 °C with H_2/air at different RH conditions.

render the cell more easy to trigger the water flood and decrease the cell performance.

In order for optimum gas and water transport of the GDLs, carbon slurry permeating into the macro-porous carbon paper has to be prevented. Since the SEM cross-sections were not very clear, gas transport study was carried out at various pressures. Fig. 9 compares the gas transport of the GDLs (samples 2–4). Fig. 9 shows that high SDS concentration of GDL (sample 3) possesses many macro-holes and it enables more gas to transport through the GDL as pressure increase, compared to low SDS concentration GDL (sample 2) does. As mentioned before the GDLs fabricated using IPA based slurry tends to permeate through the macro-porous layer and block the holes of carbon substrate, it is also believed that micro-cracks or even macro-cracks were formed during the GDL sintering procedure leading to higher gas flow rate for sample 4 than that of sample 2. The carbon slurry permeation into the macro-porous layer is extremely low for the water based slurry due to its hydrophobic characteristics.

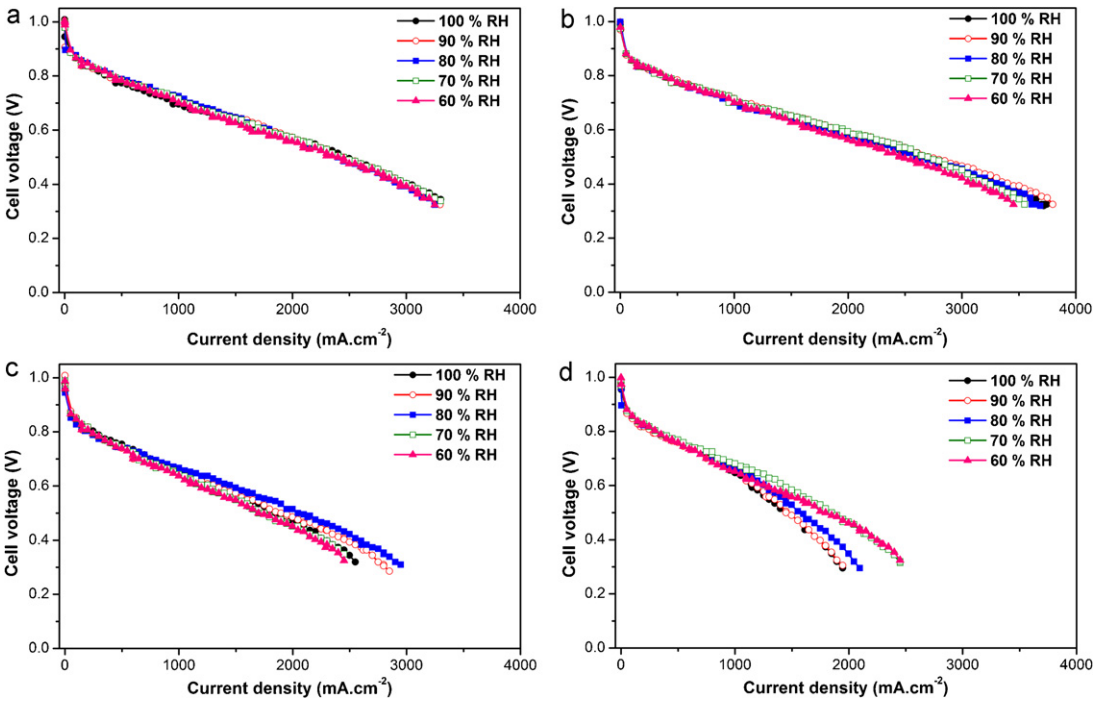

Fig. 7. PEMFC performances of various GDL samples (a) 1, (b) 2, (c) 3 and (d) 4 at 80 °C with H_2/O_2 at different RH conditions.

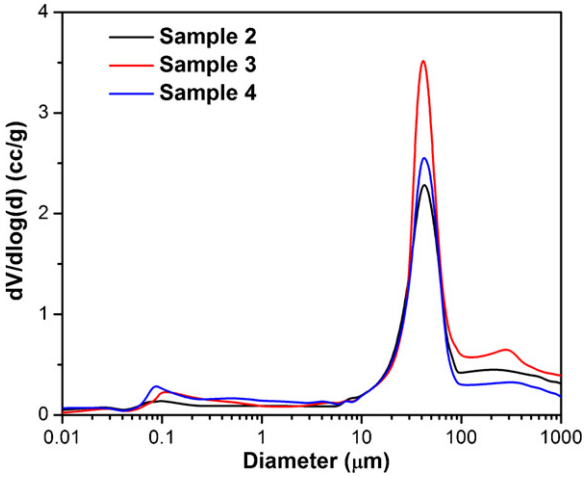

Fig. 8. Pore size distribution with Hg porosimetry for various GDL samples 2–4.

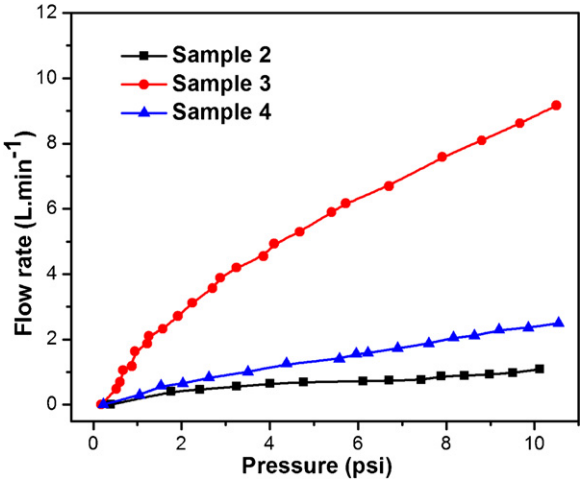

Fig. 9. Pressure-flow rate data with N_2 gas for various GDL samples 2–4.

4. Conclusion

The micro-porous layer of GDLs was fabricated with the carbon slurry dispersed in SDS aqueous solvent by wire rod coating process. The aqueous carbon slurry with micelle-encapsulation was highly consistent and stable without losing any homogeneity even after adding PTFE binder for hundreds of hours. As seen from the SEM images, the surface morphology of the GDL samples fabricated with water based slurry do not show any micro-cracks. The peak power density of the single cell using the GDLs with optimum SDS concentration was 1400 and 500 mW cm^{-2} with H_2/O_2 and H_2/air at 90% RH, respectively. The major advantage of the water based carbon slurry is environmental friendliness of the fabrication process compared to any alcohol medium based slurries.

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