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Influence of Cathode Catalyst Layer with SiO₂-Coated Pt/Ketjen Black Catalysts on Performance for Polymer Electrolyte Fuel Cells

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Abstract: In this study, we investigated the effect of silica (SiO₂) layer included in a cathode catalyst layer (CL) on the performance for polymer electrolyte fuel cells (PEFCs). Porous carbons such as Ketjen black (KB) have been widely used as a support for Pt catalysts in PEFCs. Such KB-supported Pt catalyst (Pt/KB) was used as a cathode CL with low ionomer content (a condition of low proton conductivity). The Pt/KB was then coated with SiO₂. In addition, the Pt/KB and SiO₂-coated Pt/KB (SiO₂-Pt/KB) were measured and analyzed under relative humidity (RH) conditions (100% and 20%). The catalyst ink of SiO₂-Pt/KB showed higher stability and dispersion compared to Pt/KB, due to the hydrophilic surface characteristics of SiO₂, which act as a binder-like ionomer. The performance of the SiO₂-Pt/KB at 100% RH, was significantly lower than that of Pt/KB, whereas the performance of the Pt/KB at 20% RH, was significantly improved by SiO₂ coating. This is due to an increase in the proton conductivity, which can be attributed to the hydrophilic properties of SiO₂. Based on these results, the effect of SiO₂ coating on performance, depending on carbon supports of SiO₂-coated Pt/Carbon catalysts, could be evaluated.

Keywords: silica-coated Pt catalyst; porous carbon; catalyst layer; silica coating; polymer electrolyte fuel cell

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted much attention as efficient power sources for fuel cell vehicles (FCVs), due to advantages such as their high energy efficiency, a low operating temperature (20–100 °C), no emission of CO, CO₂, and NO_x, as well as their simplicity [1]. However, the use of expensive Pt metals used as electrode catalysts, especially at the cathode, where a significant amount of Pt metal is wasted by slow kinetics of oxygen reduction reaction (ORR), is a major drawback of PEFCs. The cell performance and durability are not adequate for the further popularization of PEFCs. In an effort to reduce the usage of Pt, cathode catalysts, such as low-Pt and non-precious metal catalysts, have been developed as potential materials for replacing Pt, and have improved Pt utilization [2–4]. Despite all these efforts, the overpotential which occurs during the reaction, and mass transport with proton and oxygen in cathode catalyst layers (CLs), hinders the maintenance of a high performance. Thus, the design of an optimal structure of cathode CLs, is required, to reduce the overpotential.

For the cathode CLs, the ionomer, which acts as a path of proton conduction, can affect proton conductivity and oxygen transport around Pt particle [5]. Depending on and ionomer distribution such as an inside or surface of CLs, cell performance was different [6]. An increase in the ionomer content improved the proton conductivity, but decreased

the oxygen diffusivity [7,8]. High content of Nafion ionomer, generally used in the CLs, thickens the carbon surface, preventing the movement of electrons because of its property as an electric insulator. Therefore, a reduction in the ionomer content in the CLs of PEFC has been required. However, if the ionomer content is too low, the place for proton paths will decrease, resulting in an increase in proton transport resistance. In our previous study [9], we developed cathode CLs with low ionomer content, and SiO₂-coated Pt/carbon catalysts were used to enhance the proton conductivity. For these catalysts, developed by Takenaka et al., SiO₂ coating has the advantages of high durability, minimization of Pt particle agglomeration and diffusion of Pt cations in the catalyst, and flexible control of surface characteristics like hydrophobicity or hydrophilicity [10–12]. This SiO₂ coating was applied to Pt/Vulcan XC-72 (known as non-porous carbon) catalysts (denoted as SiO₂-Pt/VB), and then the SiO₂-Pt/VB was used for fabrication of cathode CLs with ratio of ionomer to carbon (I/C) of 0.25, for reducing the oxygen diffusion resistances using an inkjet printing method. As a result, the CLs, including SiO₂-Pt/VB with the low ionomer content, showed higher cell performance at 0.6 V than Pt/VB under conditions of all the relative humidity (RH). Notably, the SiO₂-Pt/VB showed significantly enhanced performance compared with Pt/VB under low humidity, such as the condition of 20% RH. This result suggests that the hydrophilic groups included in SiO₂ layers contribute to enhancement of proton conductivity, resulting in enhanced cell performance [9].

Although the CLs with SiO₂-Pt/VB showed superior cell performance, it was investigated to only non-porous carbon like Vulcan XC-72. Recently, porous carbons such as Ketjen black, porous carbon nanofiber, and high surface carbon have been widely used and investigated as a support of Pt catalysts because of their high surface area and inside pores. It can be lead to high Pt dispersion on the carbon supports, resulting in improved ORR activity and durability [13–17]. In this study, we investigated the influence of SiO₂-coated Pt catalysts on cell performance when Ketjen black, known as one of the porous carbons, was used as a support for cathode catalysts. CLs with SiO₂-coated Pt catalysts were evaluated by electrochemical measurements under various humidity conditions. In addition, we examined how SiO₂ coating affects the catalyst ink, the morphology of CLs, cell performance, and considered the differences in the influence of SiO₂ coating on performance, depending on different carbon support.

2. Results and Discussion

In this study, it will not mention the information about analysis results for SiO₂-Pt/KB catalysts because we focused on the catalyst layer containing SiO₂-Pt/KB. The information about SiO₂-Pt/KB can be found in Takenaka group's papers [10,12,18]. For SiO₂-Pt/KB catalyst used in this study, it was confirmed that the SiO₂ layer was coated on the surface of catalysts by TEM images.

2.1. Particle Size Distribution of the Catalyst Ink

Figure 1 exhibits the particle size distribution of the catalyst ink with I/C = 0.25. The composition of the Pt catalysts with or without SiO₂ is shown in Table 1. For Pt/KB ink, particles formed large agglomerates within 1 day, whether or not ultrasonication was performed, because the ionomer content was not sufficient to cover a specific large surface area of approximately 875 m² g^{−1} [17]. In contrast, SiO₂-Pt/KB ink maintained good dispersion for 3 days, and the range of these particle size in diameter (0.1–3 µm) were smaller than that of the Pt/KB (0.1–100 µm). These results suggest that the SiO₂ contributes to improved dispersion of the SiO₂-Pt/KB ink due to the hydrophilic surface characteristics of SiO₂ surface characteristics like hydrophilicity, which act as a binder- like ionomer.

The zeta-potential (ζ-potential) of catalyst ink was evaluated at 25 °C, in order to examine the stability of the ink. The values of the ζ-potential mean the degree of electrostatic repulsion between charged particles in the ink and the basic equation of repulsive potential energy is as shown below [9]:

$$V_R = \frac{\zeta^2 \varepsilon_0 \varepsilon_r a_p^2}{L + 2a_p} \exp(-kL) \quad (1)$$

$$V_R = \frac{\zeta^2 \varepsilon_0 \varepsilon_r a_p^2}{L + 2a_p} \quad (2)$$

where ζ is the zeta-potential, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of carbon, a_p is the particle radius, L is the inter-particle distance, and k is the reciprocal of the “Debye length”. The reciprocal of the Debye length can be approximated as zero due to without using the ionomer. Thus, Equation (1) changed Equation (2) because $\exp(-kL)$ becomes 1. As shown in Equation (2), the high ζ -potential has high ink stability due to repelling effect between the particles. On the other hand, the low ζ -potential is easy to aggregate between particles because of attracting effect each other. As shown in Figure 2, in the case of fresh which is measured right after the ink slurry was prepared, ζ -potential of Pt/KB was higher than that of SiO₂-Pt/KB. A week later, the Pt/KB showed a lower ζ -potential than SiO₂-Pt/KB, which means lower stability. With time, the ink of Pt/KB and SiO₂-Pt/KB showed low ζ -potential. However, compared to Pt/KB, the ink of SiO₂-Pt/KB had a relatively small reduction in ζ -potential, which is attributed to the addition of Si-OH groups (i.e., an increase in ink stability) because the Si-OH group on the surface of the SiO₂ layer become ionized, and the particles tend to become a more negative charge [4]. This result is consistent with the results of the particle size distribution in process of time, described in Figure 1. On the basis of these results, the morphology of cathode CLs might be dissimilarly formed depending on whether the catalyst ink was with or without SiO₂, affecting different dispersion and particle size distribution.

Figure 1. Particle size distribution of Pt/KB (a) and SiO₂-Pt/KB (b) with I/C = 0.25.

Table 1. Composition of MEA cathode samples.

Catalysts	Composition (Unit: Mass%)		
	SiO ₂	Pt	C
Pt/KB	-	46.5	53.5
SiO ₂ -Pt/KB	14.4	39.8	45.8

2.2. Morphology of Cathode CLs

The morphology of cathode CLs was measured by FIB-SEM. Figure 3 exhibits FIB-SEM cross-sectional images for cathode CLs with Pt/KB and SiO₂-Pt/KB. The CL with SiO₂-Pt/KB showed slightly larger pores than that of Pt/KB (see Figure 3a–d). Information on histograms of the length and diameter of pores can be seen in Figure 3e–h. The pore size distribution of the SiO₂-Pt/KB possessed larger pores (maximum length, equivalent diameter) than that of the Pt/KB. However, for two catalysts, the cross-sectional images were partial in Figure 3a,b, and the overall pore size distribution was identical considering

histogram results. The Pt/KB (approximately 0.33) showed lower porosity compared with SiO₂-Pt/KB (approximately 0.37). However, this porosity of two CLs was the smaller than our previous values of 0.4–0.6 because the results were obtained by 2D cross-sectional image processing. Thus, it is difficult to directly compare to those of previous results. In addition, it is difficult to accurately measure the thickness by the FIB-SEM equipment we used even if we know the angle of SEM and ion beam. Therefore, we considered the thickness measured using a micrometer. The thickness of Pt/KB was 7 µm and SiO₂-Pt/KB was 8 µm by micrometer measurement. This result can be considered to reflect that the porosity of SiO₂-Pt/KB is slightly larger compared to that of Pt/KB mentioned above Figure 3. In addition, the difference in thickness between the two CLs indicates that the morphology of CLs was changed after SiO₂ coating.

Figure 2. Zeta potential of Pt/KB and SiO₂-Pt/KB.

2.3. Electrochemical Analysis of Pt Catalysts

Figure 4 shows the i-V curves, current densities at 0.8 V and 0.2 V, and limiting current curves at 80 °C and 100% RH. When the Pt/KB was coated by SiO₂, the coverage of SiO₂ layers led to a significant drop in performance throughout all the current density regions, as shown in Figure 4a. In the high potential region (0.8 V) where ORR is predominant, the performance of the Pt/KB declined by 2.5 times after SiO₂ coating. This result indicates that the active surface area of Pt particles decreased by SiO₂ layers. In the low potential region (0.2 V), related to mass transport like oxygen, the performance of the Pt/KB also slightly decreased after SiO₂ coating, meaning that the coverage of catalyst with SiO₂ layers increases oxygen diffusion resistance. In addition, the limiting current density for CLs with both catalysts showed low values because only 1% O₂ was supplied to the cathode. The limiting current density for the CLs showed the same trend as the above results. These results indicate that SiO₂-Pt/ KB has overall losses came from activation loss or mass transport loss at 100% RH condition. Cell performance of the CLs with Pt catalysts was also examined at 80 °C under 20% RH. As seen in Figure 5, Pt/KB exhibited poor performance due to insufficient proton conductivity, which is attributed to low humidity conditions. In contrast, the performance of CLs with Pt/KB was improved after SiO₂ coating, as opposed to that of high humidity conditions.

In the high potential region (0.8 V), Pt/KB showed considerably enhanced performance after SiO₂ coating; i.e., the performance SiO₂-Pt/KB was 11 times higher compared with that of Pt/KB. In the case of too low RH, mass transfer is dominant as a whole, so even high potential regions related to ORR kinetics can be affected by mass transfer. These results can be attributed to the improved proton conductivity as a result of the hydrophilic SiO₂ layers. Moreover, CLs with Pt/KB at 0.2 V (low potential region) exhibited the same tendency to improved performance by SiO₂ coating, as shown in Figure 5b. In case of low humidity, SiO₂-Pt/Vulcan also had superior performance compared to Pt/Vulcan [9]. Therefore, it is

noted that the SiO₂ coating of Pt catalysts significantly improves performance, regardless of carbon support, at low humidity condition that is severely low proton conductivity.

Figure 3. FIB-SEM cross-sectional images (a–d), histograms of maximum length pore size (e,f) and equivalent diameter pore size (g,h) of the CLs with Pt/KB (left side), SiO₂-Pt/KB (right side).

Figure 4. i-V curves (a), change in the activity at 0.8 V (b) and 0.2 V (c), and limiting current curves (c) of Pt/KB and SiO₂-Pt/KB at 100% RH and 80 °C.

Figure 5. i-V curves (a) and change in the activity at 0.8 V and 0.2 V (b) of Pt/KB and SiO₂-Pt/KB at 20% RH and 80 °C.

ECSA of each sample was calculated using the Q value [mC/m^2] of adsorbed H₂. In the case of 100% RH, ECSA of Pt/KB was $193 \text{ m}^2 \text{ g}^{-1}$, SiO₂-Pt/KB was $165 \text{ m}^2 \text{ g}^{-1}$, and ECSA decreased by about 15% after SiO₂ coating. On the other hand, for 20% RH, ECSA of Pt/KB increased by about 5% from $107 \text{ m}^2 \text{ g}^{-1}$ to $113 \text{ m}^2 \text{ g}^{-1}$ after SiO₂ coating. This change in active surface area on the Pt before and after SiO₂ coating can support the result of changing the cell performance between CLs with Pt/KB and SiO₂-Pt/KB according to RH conditions.

EIS was evaluated to investigate the resistance of the CLs with Pt catalysts. Figure 6 shows the impedance spectra at 0.8 V of the Pt catalysts under 100% RH and 20% RH. In the case of 100% RH, Pt/KB exhibited the lowest charge transfer resistance at $0.97 \Omega \text{ cm}^{-2}$, while SiO₂-Pt/KB had the higher resistance at $2.27 \Omega \text{ cm}^{-2}$. In contrast, the charge transfer resistance of Pt/KB at 20% RH was reduced from 41 to $6 \Omega \text{ cm}^{-2}$ after SiO₂ coating. Particularly, the shape of semicircle is not general compared to SiO₂-Pt/KB. It is difficult to measure the EIS of general Pt/C at low RH, especially 20% RH because the proton conductivity was overwhelmingly low at 20% RH, resulting in sensitivity changes. Few measurements of such 20% RH conditions have been made in papers presented by other researchers. Herein, it is a noteworthy fact that SiO₂-Pt/C could be clearly measured differently from Pt/KB. That is, a stable reaction state inside the CLs could be maintained even at low RH. Therefore, the impedance spectra of Pt/KB was used for comparison with SiO₂-Pt/KB. In addition, for 20% RH, enhanced performance could be explained by a decrease in charge transfer resistance at 0.8 V; ORR region. Therefore, these results were consistent with the performance of CLs, as shown in Figures 4 and 5.

Figure 6. Impedance spectra at 0.8 V of Pt/KB and SiO₂-Pt/KB at (a) 100% RH and (b) 20% RH at 80 °C.

With regard to the SiO₂ coating of Pt/KB, the performance at 100% RH of SiO₂-Pt/KB decreased throughout all the current density areas despite having favorable morphology for mass transport including larger pore size and higher porosity. Here, we considered how the SiO₂ coating of Pt catalysts with different carbon supports, affects the performance.

In order to consider the effects of SiO_2 coatings on CLs with Ketjen black supports as well as the effects on various carbon supports, the results of previously studied Pt/Vulcan and SiO_2 -Pt/Vulcan [9] were discussed simultaneously. As shown in Figure 7a, Pt particles of the Pt/VB can be uniformly contacted by ionomer as proton conductor because most Pt particles are located on the surface of Vulcan support. When Pt/VB is covered by SiO_2 layers, the proton conductivity can be improved due to hydrophilic groups of SiO_2 acting as proton conductor in company with ionomer. This can result in higher performance. This explanation can be applied to Vulcan-based Pt catalysts regardless of humidity conditions. On the other hand, Ketjen-based Pt catalysts can be explained as distinct from Vulcan-based Pt catalysts. As shown in Figure 7b, Pt particles are located on the surface and in the pores <20 nm inside Ketjen support. The Pt particles deposited on the surface can be easily contacted by ionomers, whereas the Pt particles inside pores cannot directly obtain the proton from ionomer. It was reported that pore space inside Ketjen support was filled with water due to the capillary condensation of water. As a result, Pt particles located in the inside pores can absorb water, thus act as proton conductors [19]. Accordingly, the Pt particles of the Pt/KB can gain protons regardless of the location of Pt particles. When the Pt/KB is covered by SiO_2 layers, Pt particles located inside pores cannot obtain the protons because SiO_2 layers block water which penetrates into inside Pt particles. In order to support this assumption, the experimental results of Takenaka et al. were considered [18]. They examined the adsorption isotherms of water vapor on Pt/KB, SiO_2 -Pt/KB with hydrophilic SiO_2 groups, and CH_3 - SiO_2 /Pt/KB with hydrophobic SiO_2 groups, at 298 K. Adsorbed amount of water rose with the increase in water vapor pressure for all catalysts. Also, the amount of water adsorbed increased in the order of CH_3 - SiO_2 /Pt/KB < Pt/KB < SiO_2 -Pt/KB. It was found that when the SiO_2 -Pt/KB examined in this paper, is applied to the graph by Takenaka et al., relative pressure (p/p_0) is approximately 0.47, the amount of water adsorbed on the SiO_2 -Pt/KB was twice than that of the Pt/KB. In view of these results, for the SiO_2 -Pt/KB, water cannot penetrate into pores of Ketjen support because water is adsorbed on SiO_2 layers. Consequentially, Pt particles located inside pores are unreacted; i.e., only exterior Pt particles are only reacted with reactants such as oxygen and protons, resulting in the lower performance. This explanation can be applied to 100% RH condition. In the case of 20% RH, the improved performance after SiO_2 coating is attributed to increasing the water content, leading to higher proton conductivity by contact between Pt particles on surface of Ketjen support and ionomer at severe conditions with low proton conductivity. In conclusion, effects of SiO_2 coating of Pt catalysts on performance highly depend on carbon supports and humidity conditions. Although SiO_2 -Pt/KB performance was reduced than Pt/KB at 100% RH, considering poorly performance generally observed at low humidity, it is noteworthy important to note that the performance improves after SiO_2 coating at 20% RH. However, the addition of SiO_2 layer may affect the interaction between ionomer-carbon support. The proton conductivity is primarily functioned by the ionomer, which could be aided by the hydrophilic SiO_2 layer. The ionomer will align its hydrophilic side-chains to the support, resulting in hydrophobic backbone surrounding the agglomerate-therefore making it more stable. Thus, we will investigate and find out the effect of the addition of the SiO_2 layer on the interface between support and ionomer using the simulation applying the SiO_2 layer later. Based on these results and considerations, the next step will be to perform numerical analysis on the mass transfer phenomenon inside the cathode CLs using the 3D catalyst layer simulation developed in our research group in order to improve the cell performance. In order to understand the effect of nano and mesoscale structure of Pt/Carbon catalyst layer on cell performance and internal phenomena, various simulation models which included the effect of the structure of carbon aggregate, ionomer coverage, and formation of agglomerate have already been developed with some experimental knowledge, such as FIB-SEM observation, the actual pore size distribution of CLs, relative oxygen diffusion coefficient, agglomerate size distribution measurement in CL ink [20–24]. These simulation technologies are useful to the analysis of CLs with SiO_2 -coated Pt catalysts.

Figure 7. Schematic illustration of the effects of silica coating of (a) SiO₂-Pt/VB and (b) SiO₂-Pt/KB on cell performance.

3. Materials and Methods

3.1. Preparation of SiO₂-Coated Pt Catalyst

Ketjen black-supported Pt catalyst (TEC10E50E, 46.5 mass% Pt) was purchased from Tanaka Kikinzoku Kogyo, and denoted as Pt/Ketjen Black. SiO₂-coated Pt/Ketjen black was prepared by hydrolysis and polycondensation of SiO₂ sources such as tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) in the same way as the SiO₂ coating method used in Takenaka group's paper [18]. First, Pt/KB/distilled water mixture was sonicated and then NH₃ was added to adjust the pH value up to 10. APTES was added to the mixture, followed by TEOS. Next, the mixture was stirred for 2 h, at 333 K, and then centrifuged for the complete removal of unreacted reagents. After drying at 333 K, the obtained samples were treated for 2 h, at 623 K, under H₂ and Ar gas. The SiO₂-coated Pt/KB is denoted as SiO₂-Pt/KB [18].

3.2. Fabrication of the MEA

A membrane electrode assembly (MEA) was fabricated using a purchased anode CL (Pt loading of 0.2 mg_{Pt} cm⁻²) and a fabricated cathode CL. The anode CL was hot-pressed at 413 K (6 MPa, 4 min) to the Nafion film (NR-211 from DuPont, Wilmington, DE, USA)

before the cathode CL had been set. The cathode CLs including Pt/KB or SiO₂-Pt/KB, were fabricated by the inkjet printing method [9,16,25]. For the preparation of catalyst ink of cathode CLs, Pt/KB or SiO₂-Pt/KB was mixed with distilled water, followed by 1-propanol (NPA) and the ionomer (20 mass% Nafion solution from Sigma-Aldrich, St. Louis, MO, USA) using an ultrasonic homogenizer for 25 min. The obtained ink was then printed onto Nafion film (NR-211 from DuPont) with an inkjet printer resulting in Pt loading of 0.15 mg_{Pt} cm⁻².

3.3. Characterization of Catalysts, Ink, CLs

Thermogravimetric analysis (Thermo Gravimetry TG-60, Shimadzu Corporation, Kyoto, Japan) was carried out to get the composition data of the obtained samples. TGA of the Pt/KB was performed in air (flow rate: 50 mL/min) at temperatures up to 65 °C at the heating rate of 5 °C/min. After burning the carbons, Pt content was evaluated from the residual sample weight. TGA of SiO₂-Pt/KB was also conducted under the same conditions and procedures as the Pt/KB.

Measurement of the particle size distribution of the catalyst ink and the catalyst ink containing the solid content (catalyst + Nafion) of 2 wt% was performed using a laser diffraction particle size analyzer (SALD-2300 from SHIMADZU). A zeta potential analyzer (ELSZ-2000 from Otsuka electronics) was used for the measurement of zeta potential (ζ -potential) with 2 wt% ink, including NPA and distilled water.

CL morphology was examined by evaluating each porosity by a cross-sectional image of the CLs with FIB-SEM (Helios NanoLab 600i from Thermo Fisher Scientific). A more accurate evaluation of the porosity would require 3D reconstruction from cross-sectional images captured every few nanometers [12,25–27].

3.4. Electrochemical Measurements

Electrochemical measurements were carried out using a single cell (JARI, Active area 10 × 10 mm²). During the aging process, the cell potential was cycled at an open circuit voltage (OCV) and 0.3 V for every 30 s (1 cycle) with humidified H₂/N₂ gas (anode) and O₂/N₂ gas (cathode), respectively, until the current at 0.3 V remained constant. Polarization curves (i-V curves) were measured in a potential range of 0.9–0.2 V with each 0.1 V change in current, where each potential was maintained for 5 min. In addition, limiting current curves at 80 °C and 95% RH were obtained by cycling between 0.9 V and 0.1 V, using air gas containing 1% O₂ at the cathode with H₂ and N₂ gases at the anode. Electrochemical impedance spectroscopy (EIS) was also conducted in a frequency range of 100 kHz to 1 Hz. i-V curves and EIS were measured at 80 °C and RH conditions (20% and 100%, respectively). In addition, cyclic voltammetry (CV) was measured by changing the voltage between 0.02 V and 0.9 V at a rate of 50 mV/s under the conditions of hydrogen gas only in anode to calculate electrochemically surface area (ECSA).

4. Conclusions

In order to investigate the influence of SiO₂ coating of Pt/KB on performance, the performance of SiO₂-Pt/KB including porous carbon in cathode CLs with I/C = 0.25 was examined by electrochemical measurement, at 80 °C under RH conditions (100% and 20%). In the case of catalyst ink for the fabrication of CLs, Pt/KB maintained good dispersion for 3 days after SiO₂ coating due to SiO₂ of surface characteristics like hydrophilicity. For the morphology of CLs for both catalysts measured by FIB-SEM, the SiO₂-Pt/KB had a larger pore size (length and diameter) and higher porosity than Pt/KB. These results indicate that catalyst ink conditions are reflected to CL morphology.

Electrochemical performance of all the Pt catalysts was estimated by a single cell. In the case of 100% RH, the SiO₂-Pt/KB showed lower performance than that of Pt/KB. This is attributed to SiO₂ layers that block pores (<20 nm) inside Ketjen support, leading to inactive Pt particles located inside the pores. In contrast, in the case of 20% RH, the performance of Pt/KB was significantly enhanced by SiO₂ coating.

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