



Preparation of a self-assembled organosilane coating on carbon black as a catalyst support in polymer electrolyte membrane fuel cells



Woong Hee Lee ^a, Jungmok Seo ^b, Taeyoon Lee ^{b, **, 1}, Hansung Kim ^{a, *, 1}

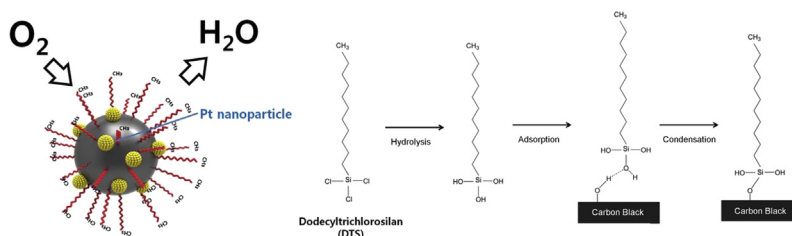
^a Dept. of Chemical and Biomolecular Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-gu, Seoul 120-749, Republic of Korea

^b Nanobio Device Laboratory, School of Electrical and Electronic Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-gu, Seoul 120-749, Republic of Korea

HIGHLIGHTS

- DTS coated carbon blacks were used as catalyst supports for PEM fuel cells.
- DTS coating converts carbon black surface from hydrophilic to hydrophobic.
- DTS coating does not have a detrimental effect on fuel cell performance.
- DTS coating improves the mass transfer rate of reactant gas in the electrode.
- DTS coating improves the electrochemical carbon corrosion resistance of carbon black.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method is developed to increase the resistance to electrochemical carbon corrosion using a self-assembled organosilane coating of dodecyltrichlorosilane (DTS) on carbon black (CB). This process successfully creates a hydrophobic coating on the hydrophilic surface of carbon black without poisoning Pt nanoparticles. The hydrophobic DTS coating improves the performance of CB in fuel cells by enhancing the mass transfer rate. Following carbon corrosion tests, on-line mass spectrometry shows that this DTS coating improves the electrochemical carbon corrosion resistance of CB by increasing the contact resistance of water, which is necessary for electrochemical carbon corrosion. Thus, this DTS coating is a very effective means to improve the performance and durability of fuel cells.

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1. Introduction

Electrochemical corrosion of carbon support in the catalyst layer is considered as a major obstacle for commercialization of polymer electrolyte membrane (PEM) fuel cells because carbon corrosion is considered to be one of the major factors to degrade performance during fuel cell operation [1–4]. Based on the mechanism of

* Corresponding author.

** Corresponding author.

E-mail addresses: taeyoon.lee@yonsei.ac.kr (T. Lee), elchem@yonsei.ac.kr (H. Kim).

¹ These authors equally contributed to this work.

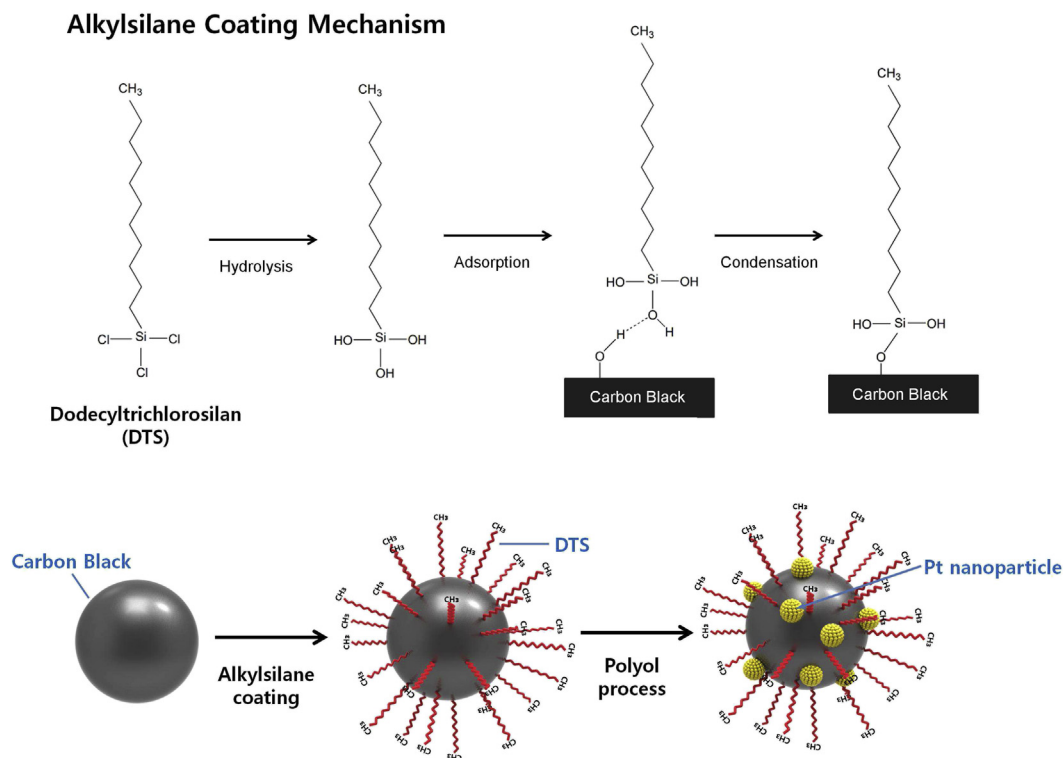
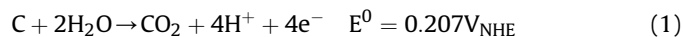


Fig. 1. Schematic diagrams of processes to form a DTS coating on carbon black and to prepare Pt supported on DTS coated carbon black.

electrochemical carbon corrosion, carbon reacts with water and oxidized to CO_2 , as shown in the following reaction [5,6].



Although carbon is unstable thermodynamically within normal PEM fuel cell operating voltage range, the rate of carbon corrosion could be ignored due to its slow electrochemical kinetics. However, under abnormal operational conditions, such as repetitive start-up/shut-down processes or fuel starvation, severe carbon corrosion occurs because the potential of electrode rises higher than the open circuit voltage [7–10]. Such a high potential increases overpotential for the oxidation of carbon, resulting in a poor durability of fuel cell.

Various carbon materials have been evaluated as supports for catalyst of fuel cell. Generally, carbon black (CB) which has advantages such as high surface area, low cost and high electrical conductivity is widely used as a catalyst support in fuel cell. However, carbon black is prone to suffer from electrochemical corrosion due to a high amorphous carbon content and oxygen functional groups on the surface [11–14]. In an effort to reduce carbon corrosion, extensive researches have been done on the development of corrosion resistant carbon support which are carbon nanofibers [15–18], carbon nanotubes [19–24], carbon nanocage [25,26]. These corrosion-resistant carbons possess high degree of graphitization and hydrophobicity. Our previous studies demonstrated that the hydrophobic characterization is a critical factor to reduce electrochemical carbon corrosion because hydrophobic surface of carbon makes it difficult to contact with water which is a reactant of electrochemical carbon corrosion [27,28]. However, there are several issues associated with these hydrophobic graphitized carbons. In general, hydrophobic carbons are relatively expensive because they are prepared by high temperature heat-treatment to eliminate oxygen functional groups. High temperature treatment also causes higher degree of graphitization

so that the surface area of carbon is reduced, which leads to an increase in the particle size of catalyst loaded on carbon supports.

To solve this problem, new approach of self-assembled monolayer (SAM) coating on the surface of CB was suggested to decrease the electrochemical carbon corrosion. The SAM coatings are ideal for forming an organized surface and changing surface properties by exposing specific functionality of the molecules especially [29–35]. Especially, silane modification of carbon surface with various functional groups have been introduced to increase performance of fuel cell and reduce the amount of Nafion content in

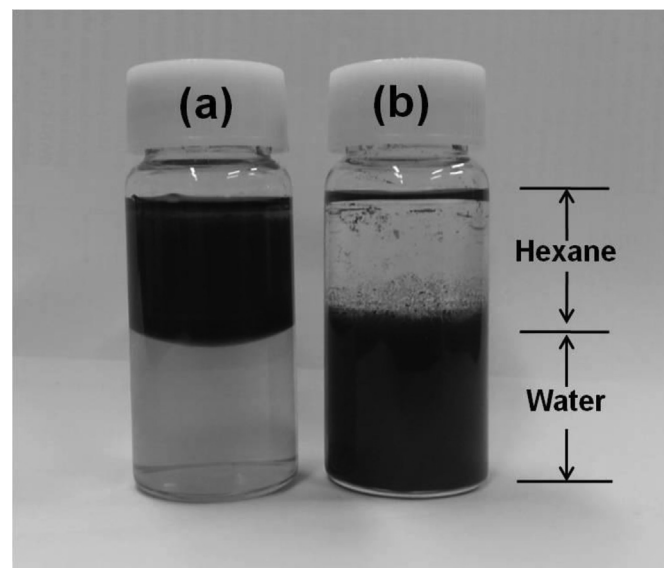


Fig. 2. The dispersion of carbon supports in a water/hexane mixture: (a) DTS coated CB and (b) raw CB.

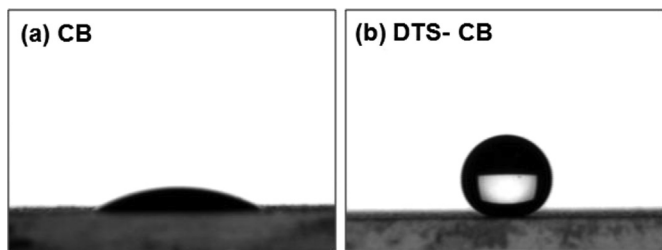


Fig. 3. Photographs of a water droplet on (a) CB coated surface and (b) DTS-CB coated surface.

the catalyst layer [36,37] In this study, dodecyltrichlorosilane (DTS) was used to form SAM coating which is covalently bound to hydrophilic hydroxyl groups on the surface of CB. The alkyl chain in the DTS transforms hydrophilic surface of CB to hydrophobic surface. This strategy is expected to decrease electrochemical carbon corrosion of CB without poisoning Pt catalyst. The effect of DTS coating on the electrochemical carbon corrosion was evaluated by various techniques including the measurement of CO_2 using on-line mass spectrometry, which is the final product of carbon corrosion [38].

2. Experimental

2.1. DTS coating of carbon black

The surface of CB powder (Vulcan XC-72) was modified with dodecyltrichlorosilane (DTS) by immersing the CB powder in a 3 mM solution of DTS dissolved in toluene for 30 min at room temperature. Then, the DTS-coated CB powder suspension was vacuum-filtrated using a membrane with 200 nm pores. The powder was cleaned with ethanol several times to remove residual reactants and the membrane with DTS coated CB powder was baked at 150 °C for 1 h to obtain a dense DTS layer on the CB powder. The content of coated DTS was 2 wt% of CB.

2.2. Preparation of catalysts

Pt catalysts were loaded onto the DTS coated CB using the modified polyol process, which was previously reported [39]. The DTS coated CBs were mixed with an appropriate amount of PtCl_4 and NaOH in ethylene glycol to prepare a 40 wt% Pt content. This mixture was refluxed at 160 °C for 3 h while stirring vigorously.

Next, the mixture was allowed to cool to room temperature, and it was adjusted to pH 3 using 0.1 M H_2SO_4 . Then the mixture was stirred for 12 h. The catalyst was collected from the solution by filtration, washed several times with de-ionized water and dried in an oven for 30 min at 160 °C.

2.3. Preparation of the MEA

Membrane electrode assemblies (MEAs) were fabricated from a commercial Pt/C catalyst (46 wt.% Pt from Tanaka Kikinzoku Kogyo Co Ltd., TTK) as anodes and catalysts prepared in this study as cathodes. Catalyst ink was made by ultrasonically mixing catalyst powder (30 mg) with 5 wt% Nafion ionomer solution (257 mg) in isopropanol (1.8 ml) for 15 min. The Nafion content in the electrode was 30 wt%. This catalyst ink was sprayed directly on Nafion 212 membranes as received without further pre-treatment. The geometric area of an MEA was a 5 cm² (2.23 cm × 2.23 cm), and the amount of Pt loaded was 0.4 mg cm⁻² for both the anode and cathode electrodes. The catalyst coated membrane was hot-pressed at 140 °C for 3 min at an assembling torque of 3 Nm to form a membrane-electrode assembly. For a gas diffusion layer, GDL-10BC (GSL group) was used.

2.4. Electrochemical and physical characterization

Prior to carbon corrosion tests, polarization curves were obtained at 75 °C under 1atm using relative humidity (RH) 100% O_2 and H_2 . When using the air instead of O_2 , H_2 and air were supplied to the anode and cathode at a stoic of 1.5 and 2, respectively. Impedance analysis (Biologic, VSP) was performed at 0.8 V to determine membrane and charge-transfer resistances of MEA. A carbon corrosion experiment was performed by applying 1.3 V at cell temperature and humidity of 90 °C and 100%, respectively, for 30 min. The flow rate was 30 cm³ min⁻¹. The CO_2 produced during the corrosion test was measured by on-line mass spectrometry (Hiden HPR-20QIC). The detailed procedure for this measurement was described in our previous study [38]. High resolution transmission electron microscopy (HR-TEM, JEM-30100 model) was conducted to examine the distribution of Pt on the carbon support. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo scientific, iCAP 6000 DUO) was used to measure the Pt content of the catalyst. X-ray photoelectron spectroscopy (XPS, Sigma probe UK) was performed to investigate the surface characteristics of Pt nanoparticles.

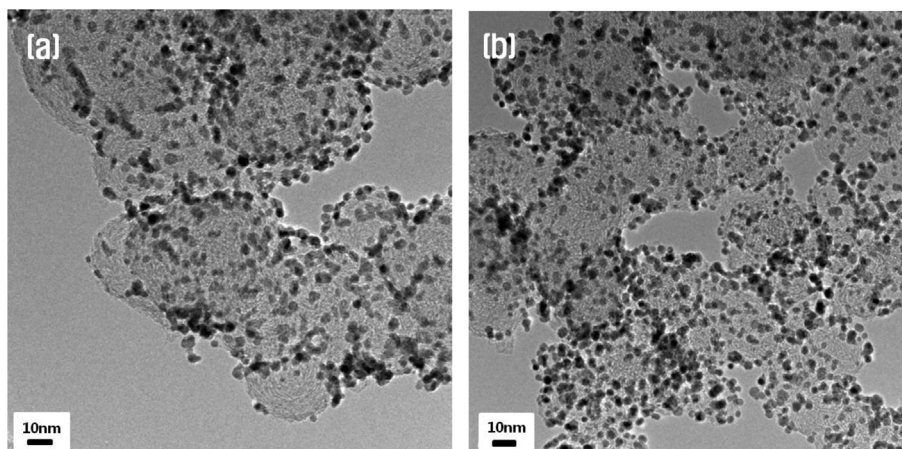


Fig. 4. HR-TEM images of Pt nanoparticles supported on (a) raw CB and (b) DTS-coated CB.

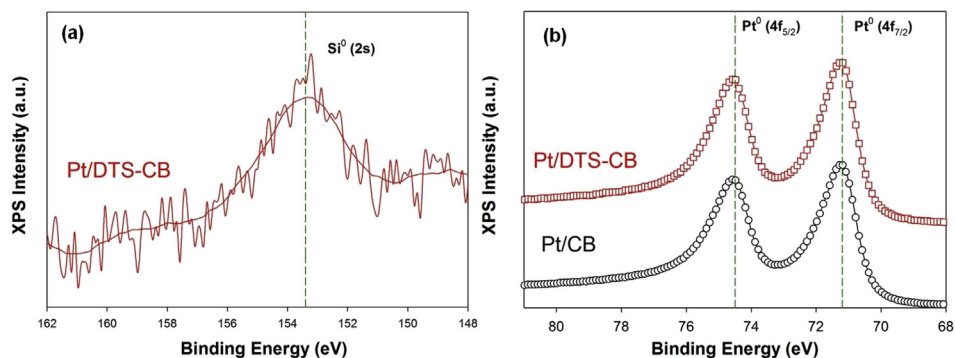


Fig. 5. X-ray photoelectron spectra of the (a) Si 2s binding energies for Pt/DTS-CB (b) Pt 4f binding energies for Pt/DTS-CB and Pt/CB.

3. Result and discussion

The raw CB powder is hydrophilic due to the presence of oxygen functional groups such as hydroxyl groups on the surface. The surface of CB could be modified chemically with a simple dip coating in DTS solution. The DTS coating mechanism and deposition of Pt on a DTS coated CB (Pt/DTS-CB) is proposed in Fig. 1. As shown in Fig. 1, the DTS consists of chlorosilane groups and alkyl chains. Because chlorosilane is easily hydrolyzed, water adsorbed on CB hydrolyzes chlorosilane groups in DTS during the coating process. Hydrolyzed DTS is adsorbed on CB and covalently anchored to its surface by intermolecular hydrogen bonding and condensation between OH groups on the CB surface and hydrolyzed DTS [40]. Water produced from this condensation reaction could be used to hydrolyze DTS. Thus, CB is decollated with long alkyl chains resulting in exhibiting hydrophobic property due to the lowered surface energy. After DTS coating was applied, Pt nanoparticles were deposited onto DTS-CB using the polyol process. These Pt nanoparticles are deposited on CB sites that are not coated with DTS, which ensures the direct passage of electrons to Pt nanoparticles through CB. Modification of CB with DTS could be demonstrated by examining the surface hydrophobicity. The hydrophobicity was determined simply by observing the dispersion of CB and DTS-CB in a water/hexane (1:1) mixture. One milligram of each carbon support was wetted with 10 mL of water and dispersed in a sonication bath for 1 min. Next, an equal volume of hexane was added. Mixtures were agitated quickly by hand, and a change was observed. As shown in Fig. 2, CB was located in the water phase due to their hydrophilic nature, whereas DTS-CB rose to the hexane phase, indicating the successful formation of a hydrophobic DTS coating on CB. To investigate the effect of DTS coating on the wettability change of carbon surface further, the water contact angle values were measured as shown in Fig. 3. The water droplet was spread on the surface of CB coated electrode and the contact angle was measured to be 22° . However, by modifying the CB with the self-assembled organosilane coating of dodecyltrichlorosilane (DTS), the wetting behavior changed remarkably. The contact angle increased to 153° suggesting that the DTS coating can lead to the formation of hydrophobic surface.

These Pt nanoparticles were deposited on CB and DTS-CB using the polyol process described in the experimental section, and their HR-TEM images are shown in Fig. 4. In the case of Pt supported on raw CB (Fig. 4-a), Pt nanoparticles approximately 3 nm in diameter were dispersed homogeneously on raw CB. As confirmed in Fig. 4-b, Pt and dispersion with similar particle sizes were also observed for Pt supported on DTS-CB, implying that Pt deposition is not affected by the presence of DTS on the surface of CB and that interactions between Pt nanoparticles and DTS are not present. For the Pt

content in the Pt/CB and Pt/DTS-CB measured using ICP-AES, both of them showed the target ratio of 40 wt%.

To examine catalyst surface characteristics in more detail, XPS analysis was performed on Pt/DTS-CB catalyst, and results are represented in Fig. 5-a and b. In Fig. 5-a, a Si peak was observed due to the silane group in DTS. Fig. 5-b shows the Pt 4f peak of Pt/DTS-CB and compares it with the Pt 4f peak of uncoated Pt/CB. The Pt 4f peak position is constant in the presence and absence of DTS

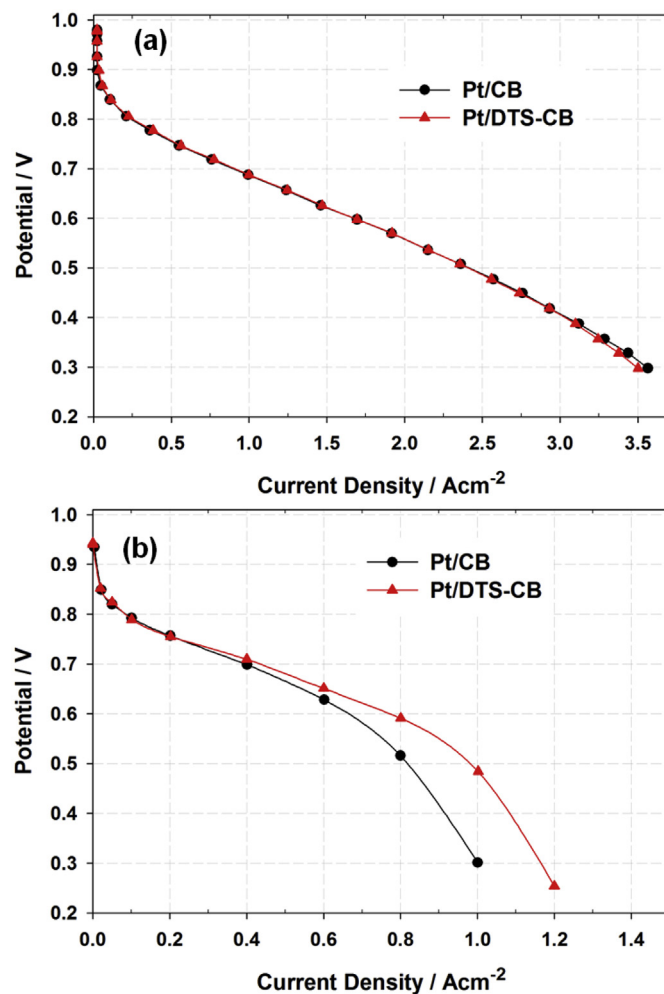


Fig. 6. Comparison of MEA performances for Pt/DTS-CB and Pt/CB using (a) anode gas: H_2 ($150 \text{ cm}^3 \text{ min}^{-1}$), cathode gas: O_2 ($150 \text{ cm}^3 \text{ min}^{-1}$) and (b) anode gas: H_2 (1.5 stoic), cathode gas: air (2 stoic). Cell temperature: 75°C ; Pressure: 1 atm.

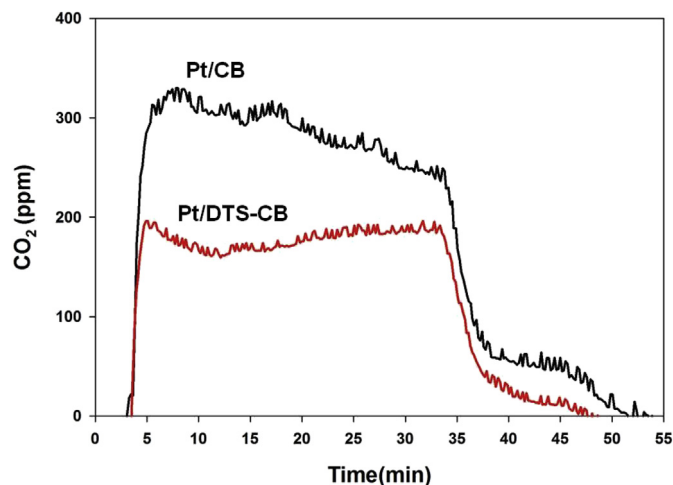


Fig. 7. CO₂ mass-spectrographic profiles of MEAs for Pt/CB and Pt/DTS-CB. The potential was fixed at 1.3 V for 30 min. Anode gas: H₂ (20 cm³ min⁻¹); cathode gas: N₂ (30 cm³ min⁻¹); cell temperature: 90 °C; relative humidity: 100%; pressure: 1 atm.

coating, indicating no interactions between DTS and Pt catalysts. In our previous report, certain functional groups, such as thiol and amine, were added to carbon surfaces, and they interacted with Pt and acted as poisons by decreasing the active surface area of Pt catalysts. In this case, the Pt 4f peak was shifted to a higher binding energy [41]. Thus, it is expected that this DTS coating will not have a detrimental effect on fuel cell performance.

These results were confirmed by measurements of fuel cell performance. As shown in Fig. 6-a, fuel cells with Pt/DTS-CB and Pt/CB had almost identical polarization curves when oxygen was used as the reactant gas in the cathode. This result implies that this DTS coating does not poison Pt catalysts. However, this DTS coating is advantageous, especially when air is used as a reactant gas instead of oxygen. From a practical point of view, fuel cell performance with air is more important because most fuel cell applications, such as automobiles, use air as a reactant gas. When using air instead of oxygen, however, the mass transfer rate of reactant gas in the electrode plays an important role in fuel cell performance. According to the polarization curves for fuel cells using air as a reactant gas in the cathode, Fig. 6-b, fuel cell performance is better with Pt/DTS-CB than Pt/CB at high currents where the mass transfer overpotential dominates. This result contributes to the improvement of the mass transfer rate of reactant gas in the catalyst layer containing the DTS coating. As confirmed in Fig. 2, the DTS coated CB is strongly hydrophobic and efficiently repels water, improving the diffusion of air in the electrode. This result is in accordance with the previous report. It has been reported that chemically linked hydrophobic 2,3,4,5,6-pentafluorophenyl groups (-C₆F₅) onto carbon catalyst support showed higher performance due to its increased ability to prevent local flooding [42].

The motivation to coat CB with DTS is to decrease carbon corrosion. Thus, it is necessary to examine the electrochemical

carbon corrosion of Pt/DTS-CB catalyst in a fuel cell. A carbon corrosion experiment was performed by applying constant potential of 1.3 V for 30 min and the CO₂ produced during the corrosion test was measured by on-line mass spectrometry [36]. This potential is high enough for the rate of carbon corrosion to be accelerated. As shown in Equation (1) for the mechanism of electrochemical carbon corrosion, CO₂ generation is direct evidence of electrochemical carbon corrosion. Thus, the degree of electrochemical carbon corrosion was determined by measuring the CO₂ concentration. Fig. 7 shows a mass spectrogram for CO₂ production from Pt/DTS-CB and Pt/CB catalysts during corrosion experiments. For the Pt/CB catalyst, the concentration of emitted CO₂ increased to 330 ppm as a potential of 1.3 V was applied to the cell and then decreased to zero after the corrosion test was concluded. The total amount of emitted CO₂ is 291 μL. In contrast, the Pt/DTS-CB catalyst produced much less CO₂, 177 μL total. This result demonstrates clearly that the electrochemical corrosion resistance was greater for Pt/DTS-CB than Pt/CB. This result could be explained by the hydrophobicity provided by the DTS coating on CB. According to our previous study, it was revealed that hydrophobicity could be a critical factor enhancing corrosion-resistance of carbon supports because the hydrophobicity increases the contact resistance with water which is indispensable for electrochemical carbon corrosion [27,28].

Several electrochemical analyses were conducted before and after corrosion tests to examine the effect of this DTS coating, and the results are summarized in Table 1. Polarization curves of MEA before and after corrosion tests are shown in Fig. 8. The performance of Pt/CB decreased considerably, approximately 59% at 0.6 V, whereas the performance of Pt/DTS-CB decreased slightly by 17% after corrosion testing. These results are in agreement with the mass spectrometry data in Fig. 6.

Impedance analyses were performed to examine the effect of carbon corrosion on resistance changes in fuel cells. These experiments were performed at 0.8 V in the frequency range between 0.1 and 1 kHz, and the results were shown in Fig. 9. The charge transfer resistance of Pt/CB increased significantly after the carbon corrosion test due to the carbon corrosion in the catalyst layer. In contrast, the charge transfer resistance for the Pt/DTS-CB catalyst underwent little change because the DTS coating impeded carbon corrosion. Thus, the DTS coating is an effective way to decrease the electrochemical carbon corrosion of CB by converting its surface from hydrophilic to hydrophobic without any having any negative effects on the Pt catalyst.

4. Conclusion

Hydrophilic carbon blacks (CBs) were functionalized with self-assembled coatings of dodecyltrichlorosilane (DTS) and used as catalyst supports for PEM fuel cells. Chlorosilane groups in DTS reacted with OH groups on the surface of CB. As a result, DTS was coated successfully on CB and converted CB surfaces from hydrophilic to hydrophobic. Pt nanoparticles were distributed homogeneously on DTS coated CB, and DTS did not poison the Pt catalyst.

Table 1
Summary of changes before and after corrosion test for Pt/CB and Pt/DTS-CB.

Condition	MEA performance at 0.6 V (A cm ⁻²)		Membrane resistance (Ω)		Charge transfer resistance (Ω)		CO ₂ production (μL) 30 min @1.3V
	Before	After	Before	After	Before	After	
Pt/CB	1.69	0.69	0.013	0.0131	0.0424	0.1301	291
	-59%		+1%		+207%		
Pt/DTS-CB	1.69	1.4	0.0129	0.0130	0.0421	0.0519	177
	-17%		+1%		+23%		

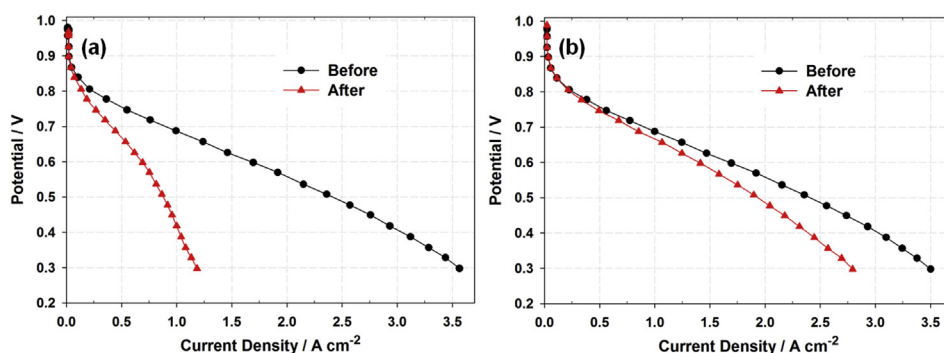


Fig. 8. Polarization curves of the MEAs before and after the corrosion test: (a) Pt/CB and (b) Pt/DTS-CB. Anode gas: H_2 ($150 \text{ cm}^3 \text{ min}^{-1}$); cathode gas: O_2 ($150 \text{ cm}^3 \text{ min}^{-1}$); cell temperature: 75°C ; pressure: 1 atm.

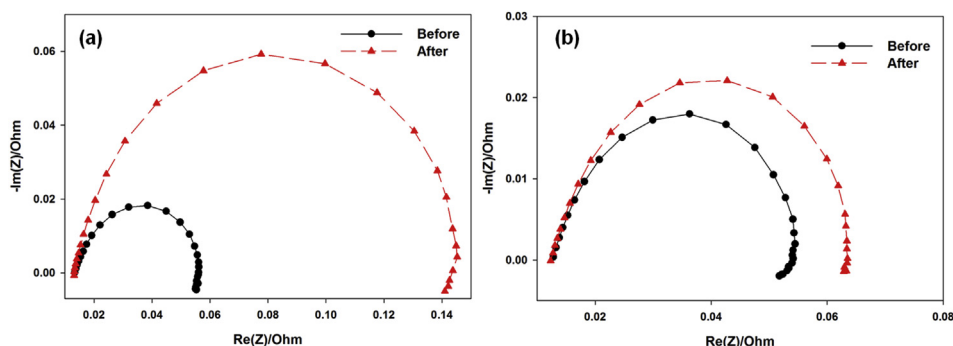


Fig. 9. Nyquist plots of MEAs at 0.8 V before and after corrosion tests: (a) Pt/CB and (b) Pt/DTS-CB.

The hydrophobicity of DTS-CB improves the mass transfer rate of reactant gas in the catalyst layer, and better fuel cell performance was measured at high current region when using air in the cathode. After corrosion tests, on-line mass spectrometry showed that the resistance to electrochemical carbon corrosion is greater for Pt/DTS-CB than Pt/CB due to the hydrophobic modification of CB by DTS. Thus, this DTS coating on CB is a promising cost-effective method to develop corrosion resistant, stable carbon supports for PEM fuel cells.

Acknowledgments

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