Novel hydrophobic coating process for gas diffusion layer in PEMFCs

Gug-Ho Yoon · Sung Bum Park · Eun Hyung Kim · Myung-Hoon Oh · Kyeong-Sik Cho · Soon Wook Jeong · Sungjin Kim · Yong-il Park

Abstract The behavior of water and gas distribution in the gas diffusion layers (GDLs) of proton exchange membrane fuel cells (PEMFCs) were investigated analytically. In order to prevent the flooding phenomenon of the electrodes by the product water, gas diffusion layer is usually hydrophobed. Formerly, gas diffusion layer was partially coated with PTFE (polytetrafluroethylene) suspension but flaking-off of PTFE particles were observed. In this study, gas diffusion layer is coated with HTTS ((hepradecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane)-derived layers having hydrophobic functional group. The influence of the HTTS coating on gas permeability and hydrophobicity of gas diffusion layer are analyzed and discussed.

Keywords Proton exchange membrane fuel cell · Gas diffusion layer · (Hepradecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane

1 Introduction

The proton exchange membrane fuel cells (PEMFCs) have a high energy density and their operation is simple. Because of these characteristics, the PEMFC expands its application fields including power units of the chemical free vehicles, space ship, mobile and military services [1–7]. General fuel cell operation is based on electrochemical reaction between hydrogen and oxygen [8]. At the anode, hydrogen is

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oxidized and created an electron and a proton. Created electrons are moved to the other way through the exterior circle and produce an electronic energy. Created proton is moved to the other way through the membrane. At the cathode, oxygen is reduced with the moved electron and proton and, as a result of this reduction, water is produced. When oxidation and reduction are occurred faster and larger amount, the fuel cell improves its performance. There are many ways to increase the speed of reactions. One of the methods to increase the reaction is increasing the catalyst. However, this method is inefficient because of high cost. Another method to increase the reaction is the uniform movement of reactive gases to electrode which results in the increase of reaction amounts. This method can improve performance by using gas diffusion layer (GDL).

In general, GDLs are used with the catalyst layer of the membrane electrode assembly (MEA). GDLs in PEMFCs are made of carbon papers or carbon cloths because of their high porosity and good electrical conductivity [9–15]. Several essential properties which should be considered for manufacturing the GDLs are as follows [16]: (a) reaction gas pathway to the catalyst layer, (b) pathway of by-produced water to the outside of the catalyst layer, (c) heat transfer during cell operation, (d) mechanical strength enough to hold MEA from extension caused by water absorbance. High porosity over 70%, large pore size around 20~40 μm, enough hydrophobicity, low electrical resistance and high mechanical strength are needed to achieve the desirable properties of GDL [17].

In the past years, almost all the studies on GDLs were performed on the hydrophobic material which was partially coated with polytetrafluroethylene (PTFE) particles of several micrometers having size. For example, Neergat and Shukla [18] and Jordan et al. [19] investigated the morphology and hydrophobicity of the micro-porous layer

(MPL) on the performance of both PEMFC and DMFC. Bevers et al. [20] studied the properties of carbon paper with different PTFE contents, including through-plane conductivity, gas permeability and hydrophobicity. Lim and Wang [21] studied the effect of hydrophobic polymer (i.e., fluorinated ethylene propylene, FEP) content in the cathode diffusion layer on the cell performance of H_2-fed PEMFC. Liu et al. [22] studied a sintered stainless steel fiber worked as GDLs in air-breathing direct methanol fuel cell (DMFC) instead of a carbon paper and a carbon cloth.

In this study, we developed new GDL coating process using (Hepradecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (HTTS)-derived 'functional silicate layers' having strong hydrophobic ligands as well as siloxane bonds. The influence of the uniform HTTS coating on gas permeability and hydrophobicity of the developed HTTS-coated GDLs were systematically studied. It was found that the developed GDL can solve the physical adhesion problem of PTFE particles, and also it provides a wide pore size and more safety in long term operation.

2 Experimental

In this study, all the used carbon papers were prepared by Toray Corporation (Model No.: TGP-H-090, Thickness: 280 μm). As raw material for the silicate layers having hydrophobic functional groups, HTTS ((hepradecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane, Gelest. Inc.) was used.

In order to make hydrophobic coating layer, 3 cm ×3 cm square pieces of the carbon paper were cut out and allowed to dip in acetone for 1 h in order to ensure that the carbon papers were clean and dust free. After dipping, the carbon papers were allowed to dry at 90°C for 20 min, and their immersed into the HTTS solution for 5 min to coat HTTS onto the carbon papers. The speed of immersion of carbon papers into HTTS solution was about 10 mm/s. After dipping, the carbon papers were dried for 6 h at room temperature in air. After drying, it was dipped into the 0.1 M H_2SO_4 aqueous solution for 10 min to complete the poly-condensation reaction of HTTS. This sample was dried for one day at room temperature in air and it was heat treated at 200°C for 30 min (heating rate, 5°C/min). HTTS wt% in the fabricated GDL was calculated using the follows equation;

$$\frac{m_{\text{coated}} - m_{\text{uncoated}}}{m_{\text{uncoated}}} \times 100 \tag{1}$$

Where m_{uncoated} is the weight before coating and m_{coated} is the weight after coating.

In order to compare the properties of the carbon paper coated with HTTS, carbon paper coated with commercial

PTFE emulsion was also prepared and heat treated at 350°C in air during 30 min [23].

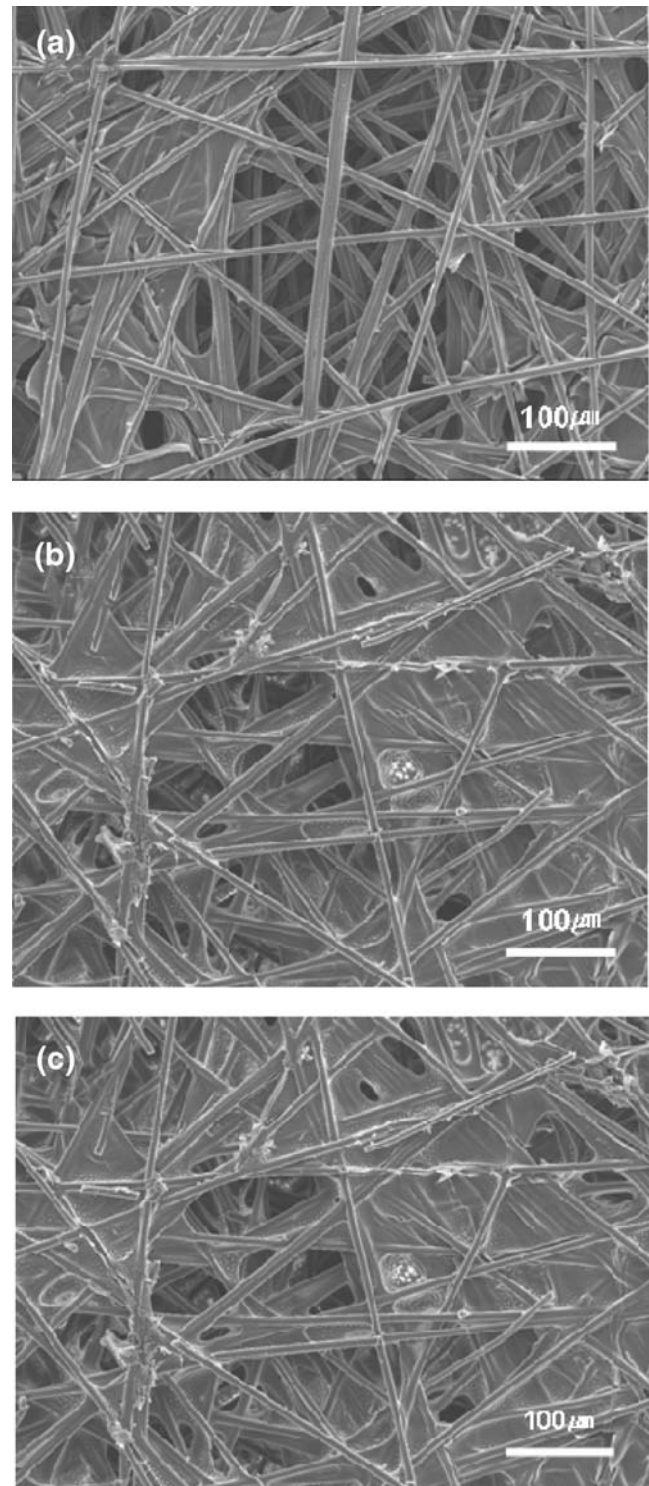The surface and the cross-section of the samples were observed with scanning electron microscopy (SEM, HITA-

Fig. 1 Scanning electrode microscopy (*SEM*) images of (**a**) uncoated carbon paper, (**b**) PTFE-coated carbon paper and (**c**) HTTS-coated carbon paper

CHI, JP/S-2400). The bonding type of the HTTS molecular structure was analyzed with Fourier transform infrared spectrometer (FT-IR, Vertex-70, Eruker Optics). Hydrophobicity was measured by both water uptake and contact angle measurements. The water uptake was measured by dipping samples in distilled water under atmospheric pressure and comparing sample weights taken both before and after immersion in water. Adhesion test of PTFE and HTTS was performed using ultrasonic vibration during 100 h. The carbon papers were fixed with polymer adhesives on the end of silicone tubes connected to the oxygen cylinder, and then immersed in water to measure the gas permeability. The used oxygen pressure (ΔP) for the test was 0.05 MPa [24]. The surface electronic resistance was measured using four-point probe (Chang Min Tech., CMT-SR100N). The resistance was measured five times per sample, and the average value was used.

3 Results and discussion

Figure 1 shows the morphologies of the carbon papers with PTFE and HTTS content obtained by using scanning electron micrographs (SEM). In the case of uncoated carbon paper, as shown in Fig. 1(a), the open pores are uniformly distributed, and carbonized resin connecting component carbon fibers films are observed [25]. The carbonized resin films are from carbonizable thermoset phenolic resin that allows the paper to be subsequently molded to the desired thickness and density [25]. Phenolic resins are usually used due to their carbon yield (50% of initial weight) and binders of the carbon fibers. Fig. 1(b, c) shows the carbon papers coated with PTFE emulsion and HTTS solution. The average surface pore size of the PTFE-coated and the HTTS-coated carbon papers decrease
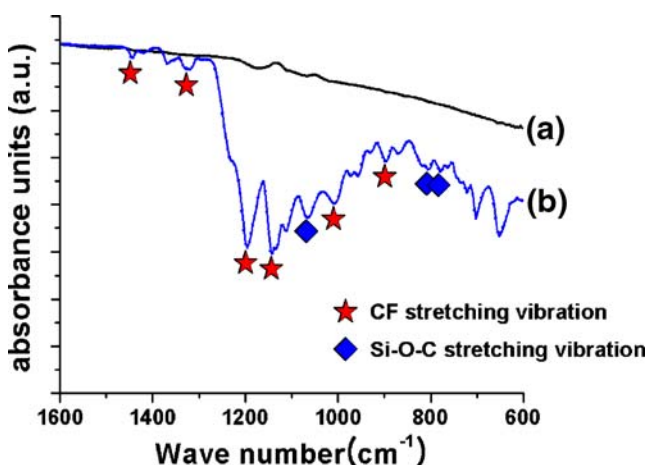

Fig. 2 FT-IR spectra of (a) uncoated carbon paper and (b) HTTS-coated carbon paper
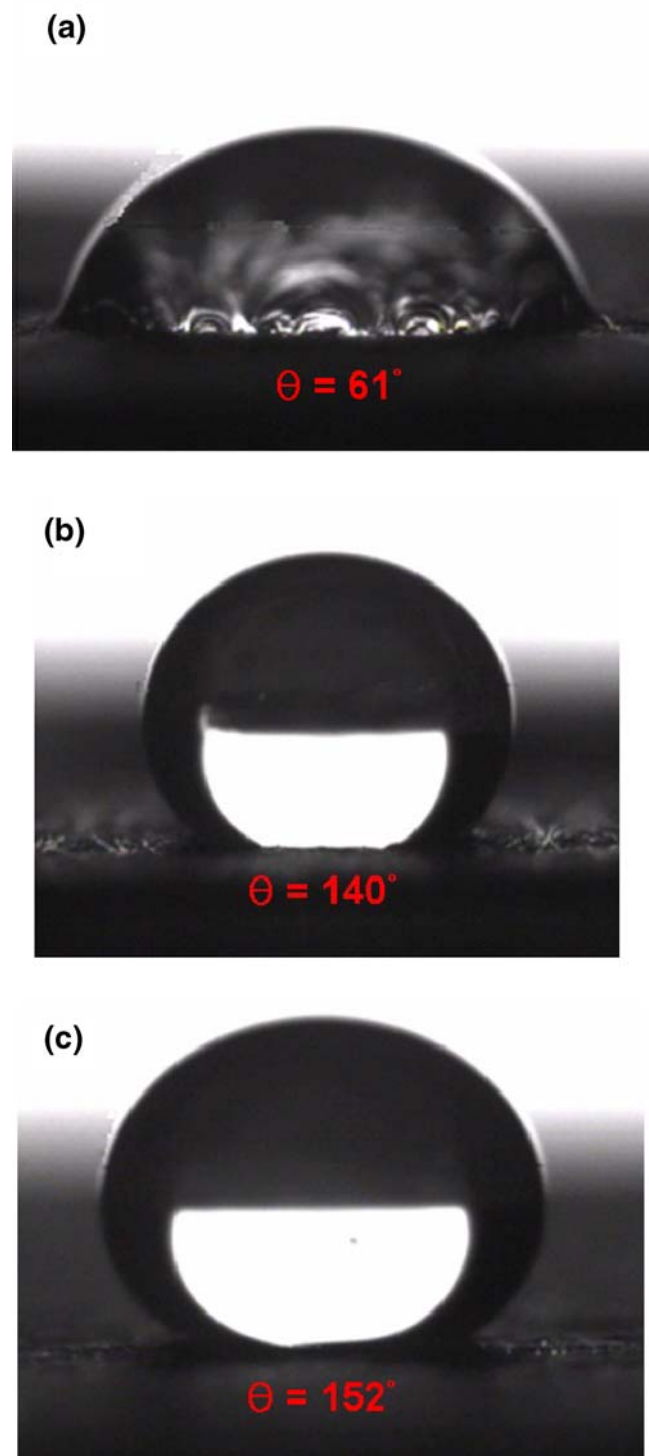

Fig. 3 Photographs of water drops on carbon paper: (a) uncoated carbon paper, (b) PTFE-coated carbon paper and (c) HTTS-coated carbon paper

compared to the uncoated carbon paper. But the HTTS-coated carbon paper shows extremely thin and uniform coating layers compared to the PTFE-coated one. And the HTTS-derived hydrophobic silicate layers are firmly formed on the carbon fibers without any flaking-offs.
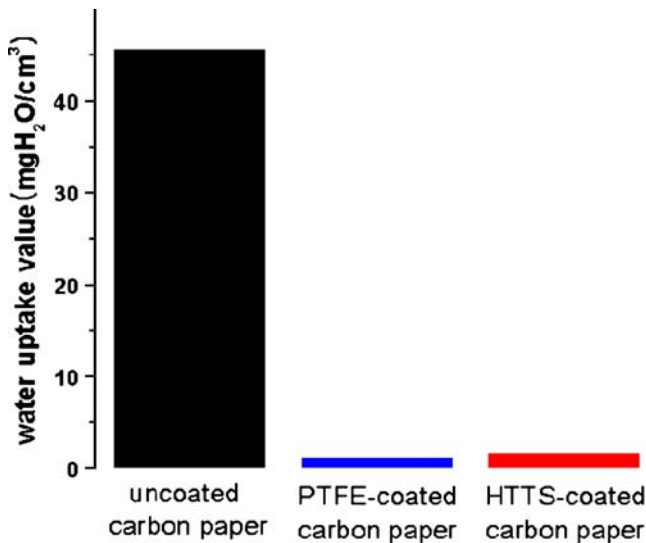
Fig. 4 Water uptake weight values of uncoated carbon paper, PTFE-coated carbon paper and HTTS-coated carbon paper
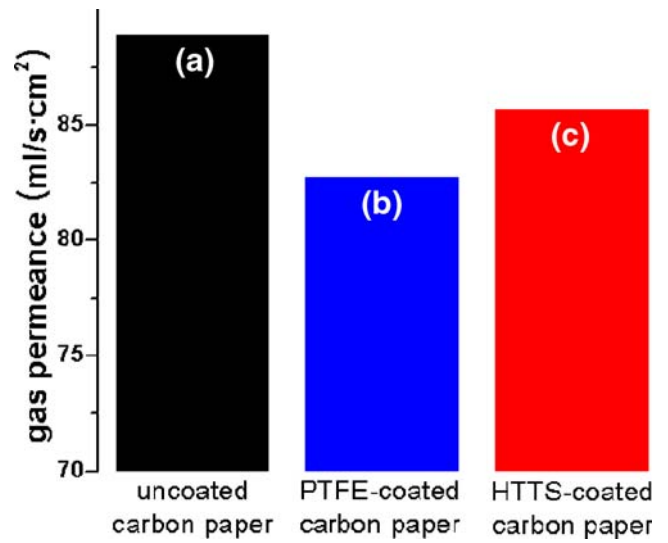

Fig. 6 Gas permeance of the samples: *a* uncoated carbon paper, *b* PTFE-coated carbon paper and *c* HTTS-coated carbon paper
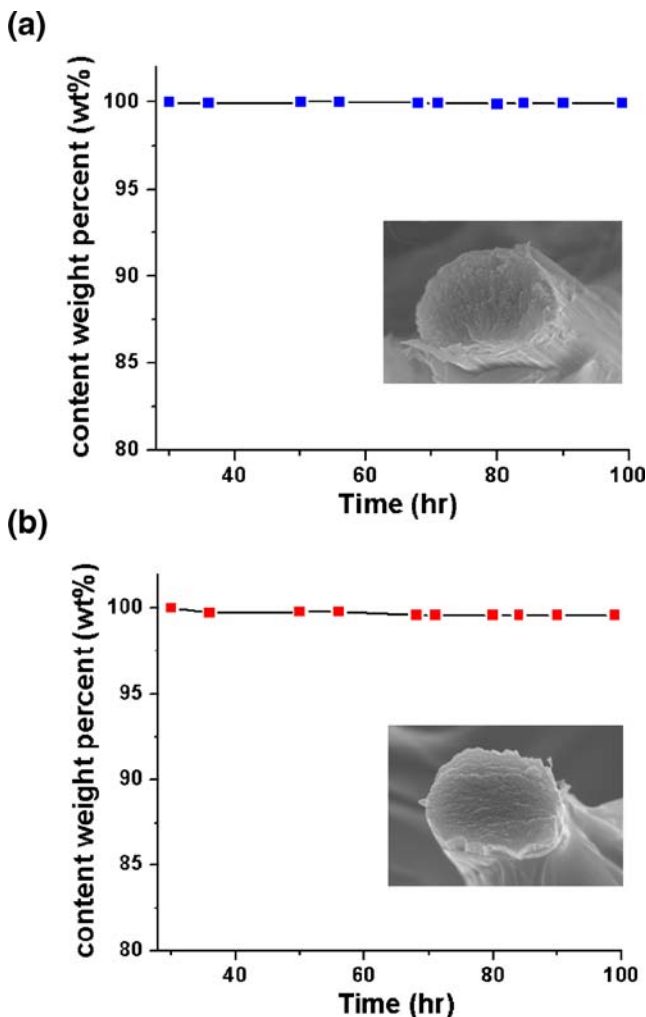

Fig. 5 Hydrophobic content weight loss of (**a**) PTFE-coated carbon paper and (**b**) HTTS-coated carbon paper

Otherwise, the PTFE-coated sample shows rough surface and partial flaking-offs.

In order to check bonding types of the HTTS molecular structure, FT-IR measurement of the HTTS-coated carbon paper are made and the obtained spectrum is shown in Fig. 2. Bands due to the C–F stretching vibration in the –CF_2– and –CF_3– groups which are formed by the hydrolysis and poly-condensation reaction of HTTS are detected at 1010, 1114, 1145, 1200, 1326 and 1373 cm^{-1} [26]. The –CF_2– and –CF_3– groups are hydrophobic functional groups which give hydrophobic characteristic to the carbon paper. Another bands due to the Si–O–C stretching vibration are detected at 780, 810 and 1072 cm^{-1}. These bands reveal a chemical bond of carbon fibers and binders through the hydrolysis and poly-condensation reaction. Consequently, HTTS was firmly
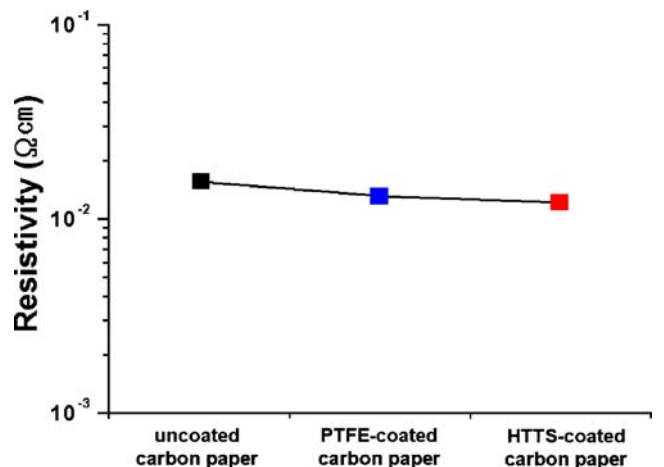

Fig. 7 The surface electronic resistances of uncoated carbon paper, PTFE-coated carbon paper and HTTS-coated carbon paper

and uniformly coated on the carbon surface forming chemical bonds unlike of PTFE.

The contact angle images of the water droplet on each carbon paper (uncoated, PTFE-coated and HTTS-coated) are given in Fig. 3. In general, contact angle is represented as follows [27];

$$\theta_c < 90° \ (i.e., \text{hydrophilic})$$

$$\theta_c > 90° \ (i.e., \text{hydrophobic})$$

where θ_c is the contact angle. For the uncoated carbon paper, as shown in Fig. 3(a), contact angle is 61° which means that this carbon paper has a hydrophilic property. However, as shown in Fig. 3(b, c), the contact angles of PTFE- and HTTS-coated carbon papers changes to 140 and 152°, respectively. The contact angle of HTTS-coated carbon paper is even larger than that of PTFE-coated carbon paper. Therefore, it could be supposed that the HTTS-coated carbon paper show stronger hydrophobic characteristic than PTFE-coated carbon paper.

The hydrophobic characteristic can also be measured by water uptake. Water uptake measurement is based on the measuring of water absorption amount. Hydrophilic material absorbs water resulting in an increase of water uptake quantity. Conversely, hydrophobic material does not absorb water. As shown in Fig. 4, weight values of water uptake are 45.63 mg for uncoated carbon paper, 1.13 mg for PTFE-coated carbon paper and 1.59 mg for HTTS-coated carbon paper. Since uncoated carbon paper is basically hydrophilic material, its absorbs much water. However, PTFE- and HTTS-coated carbon papers absorb very little amount of water due to the strong hydrophobicity of coated layer. The observed water uptake weight value of HTTS-coated carbon paper is similar to that of the PTFE-coated carbon paper.

After pre-treatment during 30 hours in the ultrasonic bath, weight loss of the PTFE- and the HTTS-coated carbon papers set in the ultrasonic bath was measured at every set time. As can be seen in Fig. 5, both PTFE- and HTTS-coated carbon paper shows almost no change in the content weight during long term ultrasonic vibration test. However, some flaking-off of PTFE particles from carbon fibers was observed after the test, as shown in SEM images in Fig. 5(a).

Figure 6 shows the results of gas permeability measurement for the uncoated, PTFE-coated and HTTS-coated carbon papers at the operating oxygen pressure of 0.05 MPa. As shown in Fig. 6, the observed gas permeability values are 88.87 ml/s·cm^2 for uncoated carbon paper, 82.75 ml/s·cm^2 for PTFE-coated carbon paper and 85.66 ml/s·cm^2 for HTTS-coated carbon paper. Compared to the uncoated paper [Fig. 6(a)], the value of gas permeability for HTTS-coated carbon paper [Fig. 6(b)] is

slightly decreased. The lowered pore size of the HTTS-coated sample in responsible for the reduced permeability, and Fig. 1 supports this assumption. In contrast, PTFE-coated carbon paper [Fig. 1(c)] had even lower value than HTTS-coated carbon paper. As shown in Fig. 1(b), the number of open pores in the PTFE-coated sample is smaller than HTTS-coated sample, and the pore-blocking effect seems to be more serious in the PTFE-coated carbon paper.

Figure 7 shows the measured surface electronic resistances of the coated carbon papers. As a result, the measured surface electronic resistances of the uncoated, PTFE-coated and HTTS-coated carbon papers are similar. That is, the measured surface electronic resistances showed very litter change. The slight decrease of resistance values of PTFE- and HTTS-coated samples seem to be due to the PTFE particles and HTTS-derived silicate layers on the surface of carbon fibers.

4 Conclusion

In this study, new hydrophobic coating process for GDLs using HTTS ((hepradecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane)-derived 'functional silicate layers' was developed. Several property test including water uptake, hydrophobicity, long-term vibration test and surface electronic resistances showed that HTTS-coated carbon paper has higher quality than PTFE-coated carbon paper. Furthermore, the obtained experimental results show that the average surface pore size of HTTS-coated carbon paper is larger than that of the PTFE-coated carbon paper. Moreover, the HTTS-derived silicate layer is extremely thin and uniform, resulting in bigger pore size, better gas permeability values and surface electronic resistances than that of the PTFE-coated carbon paper decreasing permeability.

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