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Hydrophilicity and hydrophobicity study of catalyst layers in proton exchange membrane fuel cells

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Abstract

The catalyst layer is one of the key components of PEMFCs. As the electrochemical reaction occurs at the three-phase interface of the catalyst layer, it is necessary to investigate the hydrophobicity and/or hydrophilicity properties of catalyst layers, which have a large impact on the water transport and even on the performance of the PEMFC. In this paper, time dependent contact angle measurements and porosity analyses have been performed to characterize the catalyst-coated membranes. For the first time, environmental scanning electron microscopy (ESEM) has been used to measure the hydrophilicity and hydrophobicity in the catalyst layer microstructure. The micro-contact angle distribution is given based on the microstructure. It shows a micro-scale hydrophobicity and hydrophilicity study, especially for an inhomogenous material. By means of conventional time-dependent contact angle measurements, porosity measurements and micro-contact angle measurements by ESEM, the hydrophobicity and hydrophilicity of catalyst-coated membranes have been investigated. Useful information has been gained to assist the understanding of catalyst layers from catalyst-coated membranes.

Keywords: Hydrophobicity; Hydrophilicity; Contact angle; Microstructure; Membrane electrode assembly

1. Introduction

Due to their environmentally friendly characteristics and high energy conversion efficiency, proton exchange membrane fuel cells (PEMFCs) are promising energy converters for stationary and portable applications as well as for applications in automobiles in the hydrogen era, that is the 21st century. The durability and the cost of PEMFCs must meet the requirements for market commercialization. Therefore, the improvement of the key materials of PEMFCs is an ongoing process.

In a PEMFC, the chemical energy of fuel is converted directly to electricity. Generally, the fuel is a hydrogen-rich gas, and the oxidant is air or oxygen. Water is the main chemical byproduct of this electrochemical process. Protons are also transported through the polymer electrolyte when the humidification of the polymer is high enough. Electrically conductive material, i.e. carbon, is necessary for electron transport. As the catalyst layer is one of the key components of PEMFCs, the investigation on improving the performance of the catalyst layer is regarded as a very important topic in PEMFC research field.

To date, there are two commercialized catalyst layers in PEMFCs: catalyst coated membrane (CCM) and catalyzed gas diffusion layer. The catalyst-coated membrane is a membrane attached by catalyst layers, first proposed by Wilson and Gottesfeld [1,2]. It is made of a proton exchange resin and a Pt/C electrocatalyst to form a thin film. The film is attached to a polymer membrane electrolyte. The thickness of the catalyst layer is about 5–10 μm. The catalyzed gas diffusion layer is prepared by brushing or spraying catalyst on the gas diffusion layer. In this case, the catalyst layer is a hydrophobic electrode made of PTFE and Pt/C with 20–50 μm thickness. When the membrane electrode assembly MEA is prepared, the ionomer is also imbibed to extend the three-phase zone in

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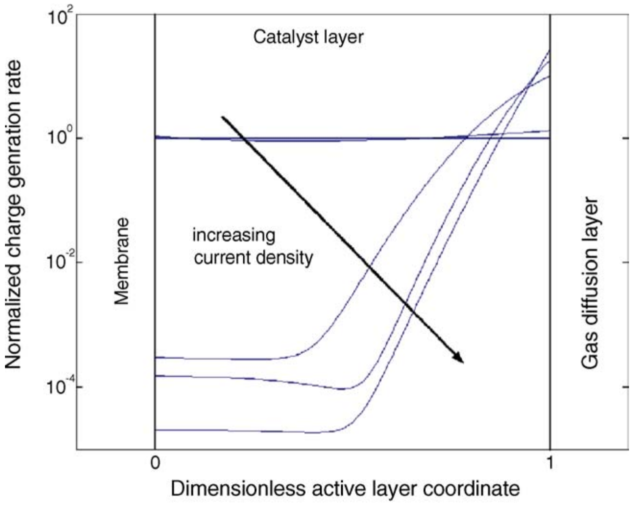


Fig. 1. The catalyst layer of the cathode side of a PEM fuel cell.

PEMFC. At present, catalyst coated membranes are widely used in PEMFCs.

Since the electrochemical oxidation and reduction reactions take place at the three-phase boundary interface, which consists of a proton conductive polymer, an electron conductive catalyst and/or a catalyst support, and gas passages, which should be hydrophobic. The properties of the MEA interface appear to have a strong impact on the PEMFC performance. To date, most of the research focuses on the water transportation properties of gas diffusion layers. In fact, the electrochemical reaction takes place in the catalyst layer where the three-phase interface has the most important role. From simulation results, it is known that the three phase interface shifts during the fuel cell operation. Based on a mathematical fuel cell model that accounts for the generation and transport of liquid water [3], the influence of the liquid water distribution on the activity of the cathode can be investigated. In Fig. 1, the catalyst layer on the cathode side of a PEM fuel cell is shown. The solid lines indicate the normalized charge generation rate. At low current densities, the charge generation is distributed uniformly across the electrode since oxygen is accessible in all areas. With increasing current density, the product water that is generated by the electrochemical reaction accumulates in the catalyst layer. This effect increases the diffusion resistance for oxygen resulting in a shift of the electrochemically active region towards the gas diffusion layer. Naturally, the water transport properties of the catalyst layer will have a strong impact on the accumulation of liquid water within the catalyst layer and hence on the efficiency of the electrode.

In analogy with the transport of gases, one can describe the transport of water by using an effective diffusivity. This diffusivity is mainly governed by the permeability, the capillary pressure-saturation relation and the contact angle of the medium. Up to now, very little is known about the water transport properties of the catalyst layer. Nevertheless, the catalyst layer plays an important role in the water management in PEMFCs. In particular, if the permeability of the catalyst layer is small compared to the permeability of the gas diffusion layer, the contact angle of the catalyst layer is significant for the fuel cell behaviour at high current densities. Therefore, it is necessary to investigate the three-phase interface phenomena inside the catalyst layer.

When hydrophilicity and hydrophobicity are studied, contact angle measurement is one of the most popular experimental methods. Contact angle as a wetting phenomenon was originally defined two hundred years ago for solid, nonporous, non-absorbent surfaces for which the contact angle reading was taken at equilibrium. The spreading of a liquid on a solid surface is important for various practical processes, and contact-angle measurements provide an elegant method to characterize the interfacial properties of the liquid with the solid substrates. The complex physical processes occurring when a liquid contacts a solid play an important role in determining the performance of chemical processes and materials.

For investigating the hydrophobicity and hydrophilicity of key materials in fuel cells, some publications on the contact angle of polymer membranes and gas diffusion layers exist. Zawodzinski and Gottesfeld [4] investigated the contact angles of water on the surface of perfluosulphonic acid membrane Nafion, which is prehydrated. They found the time dependent contact angle on the surface of a Nafion membrane and they measured the advancing and receding contact angles, when a droplet is added and then evaporated from the surface respectively. From their interpretation, the advancing contact angle is much more feasible for membrane hydrophobicity and/or hydrophilicity analysis. Brack et al. [5] investigated the surface properties of selected proton-conducting radiation-grafted membranes by means of contact angle measurement. Brack et al. [6] also reported the investigation of membranes using contact angle measurements with several different liquids. They have measured fully water-swollen membranes. It was described that the contact angles of the water on the membranes increases when the membranes dried out.

For years, contact angles of liquids on polymer surfaces are widely used to predict wetting and adhesion properties of these solids by calculating their solid–vapor surface tension. Sessile drop method [7] is the most common method. While the theory is based on the equilibrium of an axisymmetric sessile drop on a flat, horizontal, smooth, homogeneous, isotropic, and rigid solid, it is generally found, in practice, that a whole range of contact angles is accessible experimentally causing wetting or contact angle hysteresis. The reason for this is that contact angle phenomena on polymer surfaces are not only influenced by the interfacial tensions according to Young's equation but also by many other phenomena, such as surface roughness, chemical heterogeneity, swelling, etc. These effects have to be considered when contact angle measurements are performed for polymers. For example, in Fig. 2, the surface of a polymer membrane in PEMFC is shown. The roughness of the surface is apparent. When a tra-

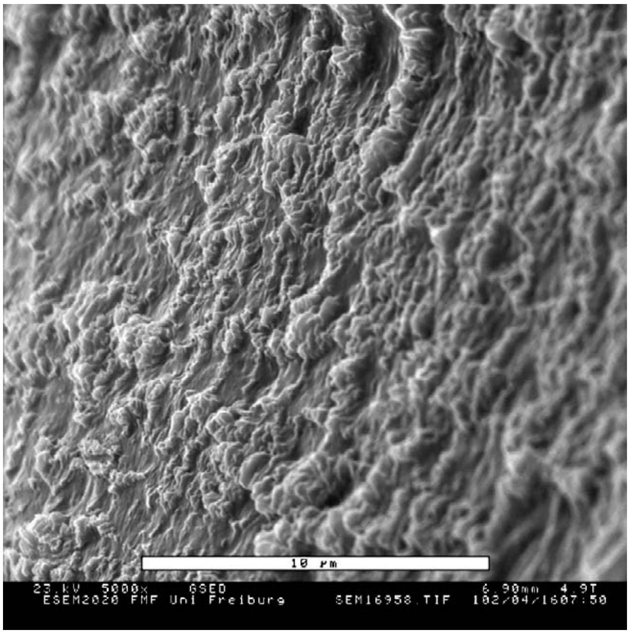


Fig. 2. Surface of a polymer membrane.

ditional contact angle measurement is performed on such a surface with at least 1 mm water droplet size, the measured value is an average value, which covers the peak and valley of the surface. When the material surface is porous, especially with different hydrophilicity/hydrophobicity characteristics, this average might give a false representation.

To characterize the flooding effect of a gas diffusion layer (GDL), Ihonen et al. [8] implemented contact angle measurements using the sessile drop method to investigate the hydrophobicity of GDLs. Williams et al. [9] tried to use different liquids with various liquid surface tensions to measure hydrophobic pores. Pasaogullari and Wang [10] measured water droplets on a GDL surface. They made use of the contact angle data in the GDL hydrophobic and hydrophilic characterization. Although the original approach was not defined for porous and sorptive surfaces like paper and powder, contact angle measurements have been used for many years in these areas of technology. These methods did not gain wide acceptance for applications, as it was difficult to find a reliable correlation with experienced production problems. It was later found that most wetting and sorptive phenomena happened within the first second after initial contact between the liquid droplet and the specimen surface.

It is known that for rough and porous surfaces, the sessile drop method has its disadvantages. Normally, when the sessile drop method is applied, the size of the droplets is on a millimeter scale. Since the surface is porous, it is possible for the droplet to penetrate into the bulk and spread when the droplet attaches. This is for hydrophilic surface. Here the contact angle does not reflect the real surface properties. Thus, the Wilhelmy method was developed to characterize the contact angle and the surface tension. In applying the Wilhelmy method, a rectangular-shaped piece of diffusion media is dipped vertically into water and the weight of the diffusion media is measured with a sensitive balance. In a static version of this method, the sample is inserted a known distance, and the force is measured. Since the Wilhelmy method requires that both surfaces of the diffusion media have identical wetting characteristics, and due to the fact that the sample should be put into water, this method is not suitable for catalyst layer coated membranes. Lim and Wang [11] applied capillary rise method instead of sessile drop method in a study on porous GDL hydrophobicity. For a contact angle study on non-homogenous porous material, e.g. catalyst layers, it is necessary to take the roughness or microstructure into account. The investigation on the micro-scale could be helpful.

To date, few publications on the hydrophobicity and the hydrophilicity properties of the catalyst layer. Since the electrochemical reaction occurs at the interface of the catalyst layer and membrane, it is necessary to develop useful methods to help understand catalyst layers in PEMFC. In this paper both the microstructure of MEAs as well as the hydrophobicity and hydrophilicity were investigated. The basic idea is to investigate the hydrophilicity and hydrophobicity characteristics of the catalyst layer. This is an important aspect in the three-phase interface, which might be useful for the water management in PEMFC.

2. Experimental

The catalyst layers measured in this paper are all from commercialized products. The catalyst loading of the samples CCM1, CCM2, CCM3 and CCM4 are all 0.3 mgPt/cm^2. The polymer membrane for CCM1, CCM2 and CCM3 are the same. As these samples stem from different suppliers, the preparation processes might be different. By combining contact angle measurements with other surface sensitive methods, such as environmental scanning electron microscope (ESEM), energy dispersive X-ray analysis (EDX) and porosity measurement, we obtained a better understanding of the hydrophobicity and/or hydrophilicity of PEMFC catalyst layer based on different microstructures.

2.1. Wetting properties and contact angle measurement

Contact angles measurements were performed for different catalyst layer samples. The samples were at least 3 cm × 3 cm to avoid significant changes of the samples' surface caused by the swelling effect. The contact angle was measured by optical contact angle measurement system OCA 20, from DataPhysics Instruments GmbH. For each measurement, a 15 μL deionized water droplet was made by placing the tip of the syringe close to the sample surface. The water droplet then attached to the sample surface. Before the water droplet attached to the sample surface, the wetting process was recorded until no significant change at the surface was observed any more. Then we measured the contact angle at different times during the wetting process. In this way, time dependent contact angles were obtained.

2.2. *Environmental scanning electron microscope (ESEM) measurement*

Environmental scanning electron microscope imaging was conducted with an environmental scanning electron microscope (ESEM 2020 from Electroscan Corp., Wilmington, USA). Imaging of the samples in a dry state was conducted in a water vapor (5 Torr) at room temperature with a voltage of 23–25 kV (LaB_6-cathode). The secondary electrons were detected using a GSED (Gaseous Secondary Electron Detector). Imaging of the samples in wet state was conducted by cooling the sample down to 5 °C with a Peltier device in a water vapor (7–9 Torr). The voltage of the electron beam was 23 kV (LaB_6-cathode). With this technique, no sputter coating is necessary for sample preparation.

A Peltier device, also known as a thermoelectric (TE) module, is a small solid-state device that functions as a heat pump. When a dc current is applied, heat is moved from one side of the device to the other, where it must be removed with a heat sink. By utilizing Peltier stage and high water vapor pressure in the specimen chamber, it is possible to achieve high levels of humidity (up to 100%). By this method, it is feasible to cool the sample below the dew point of the atmospheric water vapor. The condensation of vapor within the sample could be realized. In these conditions wet or hydrated specimens will not dry and introduce any artifacts. Dynamic experiments are also possible. For example, drying or wetting processes can be examined. The growth process of micro-water droplets could be seen, which is similar to the water formation in a PEMFC.

2.3. *Porosity measurements*

Because the catalyst layers of the CCM are porous, the influence of the pore distribution must be taken into account. For hydrophilic materials with large pores, the sessile drop contact angle measurement is not suitable [10]. The basic porosity data was measured with a Pascal 140 + 440 Mercury Porosimeter (Zentrum für Sonnenenergie und Wasserstoff-Forschung (ZSW), Germany), which operated up to 427 MPa. The pore sizes between 2 nm and 58 μm could be measured. The pore size distribution was measured under different mercury pressures. The pores inside the membranes are reported to be less than 10 nm [12–14]. From that it is assumed that the pores larger than 10 nm are all due to the catalyst layer.

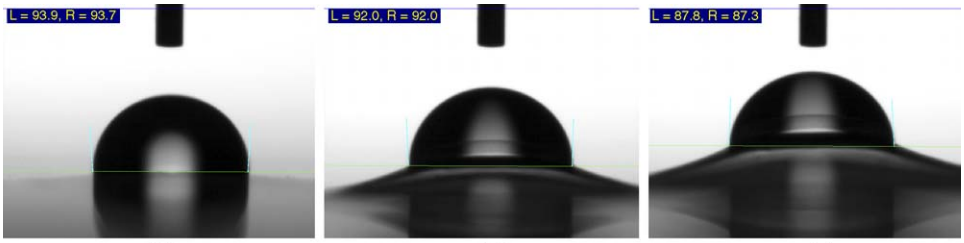
2.4. *Energy dispersive X-ray (EDX) analysis*

To analyse the chemical composition of the catalyst layer, EDX was applied. EDX measurements were conducted by a Si–Li detector, is manufactured by Oxford Instruments (Fachhochschule Esslingen, Germany). With regards to measurement accuracy, EDX is not a highly quantitative analysis tool. Therefore, different areas of the samples were scanned and chemical element distribution spectrums were obtained, giving valuable information.

3. Results and discussion

Since there is an ionomer in the catalyst layer, the wetting property of the ionomer effects the conventionally measured contact angle of the catalyst layer. From the time dependent contact angle measurement process, the wetting process of a membrane and catalyst layer could be observed. In Fig. 3, the baseline of a water droplet is defined as the line at the interface between the water droplet and the membrane surface. In the movie showing the time-dependent contact angle measurement, the water droplet as it first attaches at a dry Nafion membrane surface can be seen (Fig. 3(a)). At the first moment when the water droplet attaches to the dry membrane, the advancing contact angle shows a large value, 93.9° (0 s). When the water droplet stands at the surface, the Nafion membrane becomes wet and is swelling. Then, the following measured contact angle shows a reducing trend, 92.0° (6 s) in Fig. 3(b). After 3 min, the contact angle of the Nafion membrane seems to be in equilibrium, 87.8° (Fig. 3(c)). When the process continues even longer, the contact angle no longer changes significantly. Using contact angle measurements performed during this period, the wetting behavior of the ionomers can be investigated.

When the contact angles of the catalyst layers at a CCM are measured, the wetting process can be observed because of the



(a) (b) (c)

Fig. 3. The wetting process of a Nafion membrane when contact angle measurement is performed. (a) A water droplet first attaches to the surface of a dry Nafion membrane, 0 s. The contact angle is 93.9°. (b) At 6 s the membrane is getting wet and swelling, the contact angle is 92.0°. (c) After 3 min, the contact angle is 87.8°.

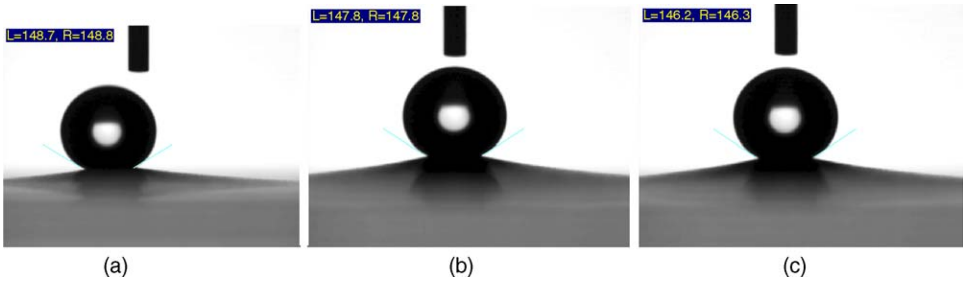


Fig. 4. The time dependent contact angle of a catalyst layer with wetting process (a) 0 s. The first attachment of the water droplet at the catalyst layer surface. The contact angle is 148.7°; (b) 60 s, the measured contact angle is 147.8°; (c) 100 s, the measured contact angle is 146.2°.

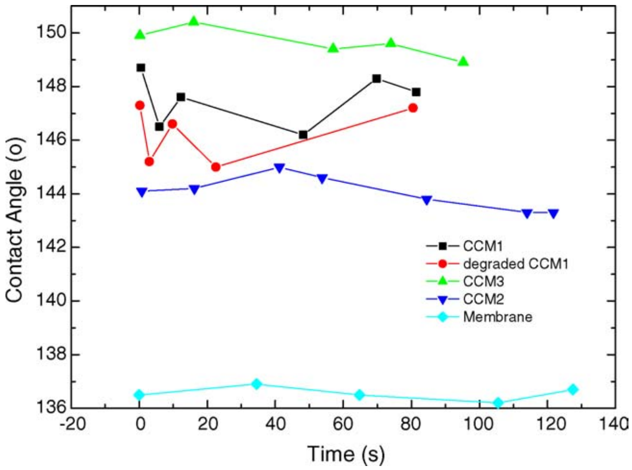


Fig. 5. Time dependent contact angles for several catalyst layers.

polymer. In Fig. 4 (a) it can be seen that the first attachment of a water droplet at the catalyst layer surface shows a relatively high contact angle. This could be due to the hydrophobicity of the catalyst material. Later, when the water droplet stands at the porous surface, some water might be absorbed by the polymer material in the porous catalyst layer, and the wetting phenomena appears. The catalyst coated membrane "rises" when the water droplet attaches. This is similar to the phenomena when a water droplet attaches to the blank membrane.

All catalyst layers in Fig. 5 have the same catalyst loading, 0.3 mgPt/cm^2. In Table 1, the difference in pore size among the CCM samples was shown. Although CCM1, CCM2 and CCM3 use the same polymer membrane and have the same catalyst loading, these three CCMs have different pore size distributions. With a high percentage of 10–100 μm pore distribution (CCM2: 14.1%, CCM1: 12.2%, CCM3: 11.54%) and a slightly higher porosity (CCM2: 35.3%, CCM1: 34.4%, CCM3: 20.45%), CCM2 shows a lower time dependent contact angle in Fig. 5. This may be due to water, which penetrates through some large pores and is absorbed by the polymer membrane under the catalyst layer. Meanwhile, from Fig. 5, it is known that CCM1 and CCM2 are less hydrophobic than CCM3. The high hydrophobic characteristic of CCM3 is beneficial to a high current density operation, where it is easier to get rid of the flooding problem. In Fig. 6, with humidified gases fed in at 60 °C, the *I*–*V* curves of CCM1 and CCM3 show that at the high current density zone, the performance of CCM3 is much better than CCM1. Meanwhile, the high proportion of large pores (1000–100 μm) also contributes to the improved mass transport, which results in a higher performance at the high current density zone.

Table 1
Porosity distributions of some catalyst layers

	CCM1	CCM2	CCM3	CCM4
Average pore radius (μm)	0.03852	0.03423	0.03788	2.1741
Total porosity (%)	34.3967	35.2958	20.45	37.2672
Relative volume in different pore radius range (%)				
1000–100 (μm)	0	0	9.62	0
100–10 (μm)	12.22	14.140	11.54	35.48
10–1 (μm)	21.11	16.160	11.54	14.84
1–0.1 (μm)	3.33	3.030	0	3.23
0.1–0.01 (μm)	61.11	53.540	65.4	38.71
0.01–0.001 (μm)	2.22	13.130	1.92	7.74

It is difficult to measure the contact angle of CCM4 with the traditional method. On one hand, the percentage of large pores (10–100 μm) in CCM4 is 35.5%. This is much higher

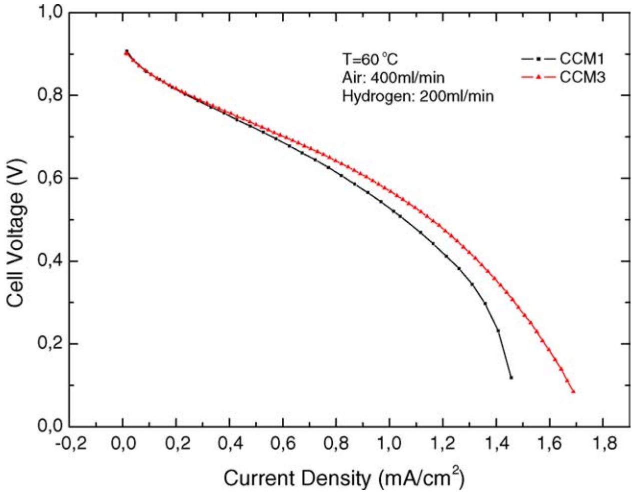


Fig. 6. Different CCM polarization curves in a test cell CCM3 with highly time-dependent contact angles shows higher fuel cell performance at high current densities (>800 mA/cm^2). It implies a lower mass transport resistance.

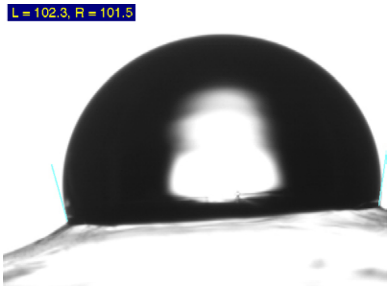


Fig. 7. Contact angle on highly porous surface.

than CCM1 (12.2%), CCM2 (14.1%) and CCM3 (11.54%), see Table 1. On the other hand, the total porosity of CCM4 is 37.3%, which is higher than the other three samples. When the traditional contact angle measurement is applied to such a CCM, a consistent result can hardly be attained, see Fig. 7. Because of the non-uniform pore distribution, the shape of the water droplet depends on its location. For 15 μL of deionized water, a water droplet of about 1 mm in diameter will form on the sample surface. From the porosity measurement shown in Table 1, such a catalyst layer has an average pore radius of several micrometers. This implies that a water droplet might cover several pores. The pore size distribution in the catalyst layers reflects the microstructure differences of different catalyst layers. Because the pores are not evenly distributed in the catalyst layers, the microstructure of the catalyst layer has an impact on the normal contact angle measurement. Therefore, in Fig. 7, the left side and the right side of the water droplet show significant differences. Water penetrates easily into the non-flat sample surface through large pores. Different hydrophobic and hydrophilic pores can also be mixed together. Therefore, the real contact angle can hardly be detected by the traditional equipment. For the samples with a high percentage of large pores, the microstructure ought to be considered when the hydrophicility and/or hydrophobicity are detected.

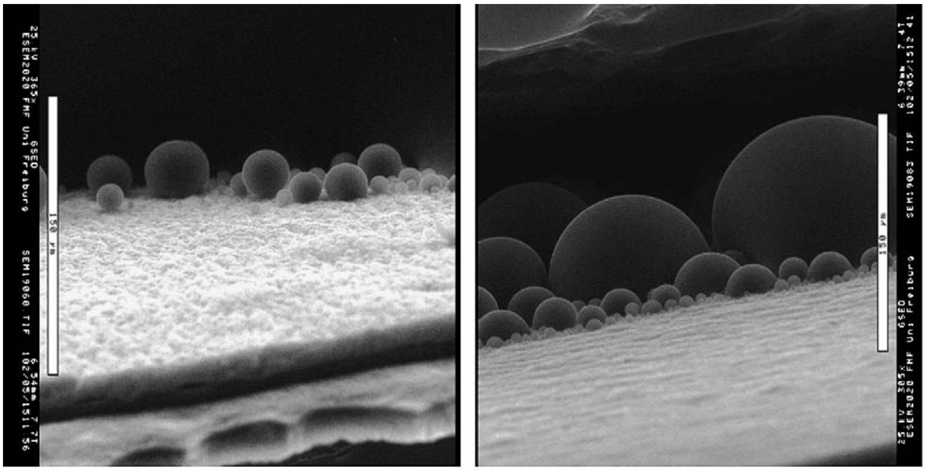
3.1. *Contact angle based on microstructure by means of ESEM*

In the earlier description of the ESEM, it is possible for water droplets to condensate inside the porous sample. Nam and Kaviany [15] have shown some water droplets at the surface of a Toray carbon paper, but there is no further investigation reported. An early work about ESEM applications on MEA is reported mainly for the qualitative analysis [16]. In our experiments, when the sample platform (the upper side of the Peltier device) is cooled down to 4–5 °C, water droplets will form at the sample surface even in the bulk of the sample. In Fig. 8(a) and (b), water droplets are distributed over the catalyst surfaces of the CCM1 and CCM2. Even if the water droplets are not the same size, they show the hydrophobic characteristics of the catalyst layer. The difference among these water droplets is most probably caused by the microstructure differences. The pores in the catalyst layer have a certain distribution, which makes the bulk and the surface inhomogenously porous. When water droplets condense at different solid microstructure locations, the differences in the hydrophobicity and hydrophilicity are apparent. Some of the high ionomer content locations show some flat-water droplets, while the low ionomer locations show sphere-like water droplets.

Since this is the first attempt to use ESEM as a contact angle analysis tool to investigate hydrophobicity and hydrophilicity on inhomogenous material, it is necessary to define the contact angle on a micro-scale, i.e. a micro-contact angle.

3.2. *Definition of micro-contact angle*

The base line connects the left and right point when the droplets contact the substrate. The angle between the base line and the tangent of the gas-liquid-solid interface is a micro-contact angle. In Fig. 9(a), some water droplets are condensed



(a) Water droplets at CCM1 (b) Water droplets at CCM2

Fig. 8. Water droplets on a micrometer scale at the catalyst layer CCM1 and CCM2.

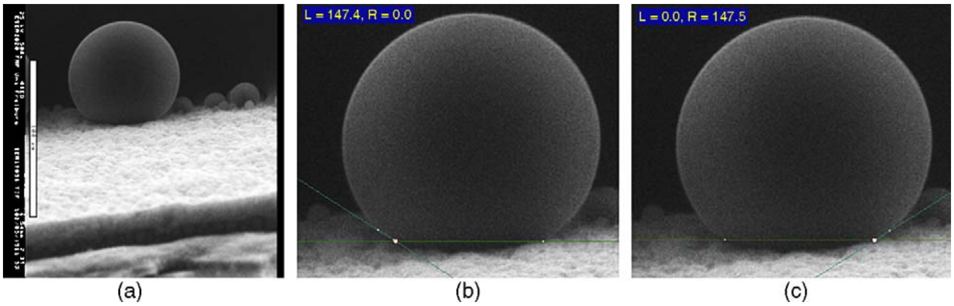


Fig. 9. Micro-contact angle at catalyst layer surface. (a) Original location of the water droplet; (b) left side micro-contact angle; (c) right side micro-contact angle.

on the catalyst layer of CCM1 in the ESEM. The diameter of the defined droplet is about 55 μm. In Fig. 9(b) and (c), the micro-contact angle of sample CCM1 is 147.4 and 147.5° for the left and right side, respectively. Because of the roughness of the sample surface, the interface between water droplets and the catalyst layer are not symmetrical, and therefore, water droplets to the left and right side of the micro-water droplet could be different. The position of the micro-contact angle should be specified when the micro-contact angles are measured.

By this method, the surface of the catalyst layer has been scanned after the ESEM sample chamber reaches 5 °C, at 6–7 Torr, since water droplet condensation and evaporation has reached a dynamic equilibrium. The process looks like a sweating process (Fig. 10). At the beginning, some small water droplets appear, i.e. water droplets 1, 2 and 3 in Fig. 10(a). They gradually increase in size (Fig. 10(b)). But, when the water droplets 1, 2, and 3 merge together to form one big droplet of about 150 μm in diameter (Fig. 10(c)), the contact angles can not be measured. This could also be evidence that for such a porous material, the irregular results obtained by the false conventional contact angle measurement, which uses water droplets on the millimeter scale, might come from merged droplets.

Since the catalyst layer is made up of a catalyst and a polymer, it is not a homogenous material. The value of the surface contact angle depends on the local composition of the catalyst layer. From different locations of the catalyst layer, a micro-contact angle distribution could be measured. From the ESEM picture of CCM2, three different locations are measured and the mean values are obtained. The average value of the contact angles is 144.9° (Table 2). The difference between these water droplets could come from the different roughnesses of the surface as well as from the composition inhomogenity. Although the average value for this sample does not show too much difference from the conventional contact angle measurement, detailed information based on the microstructure can be obtained.

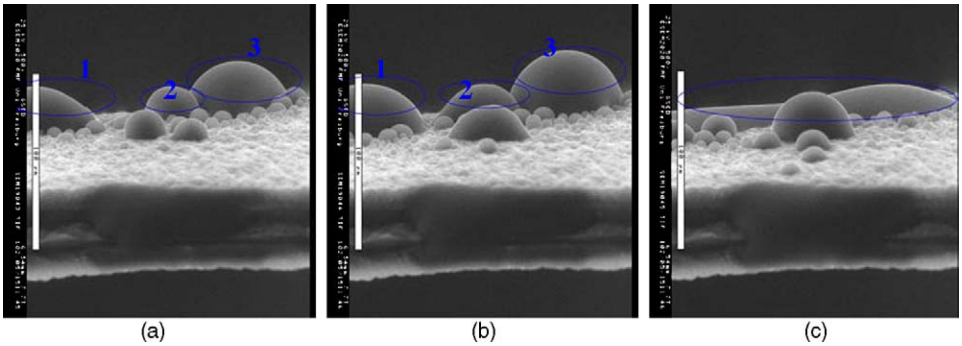
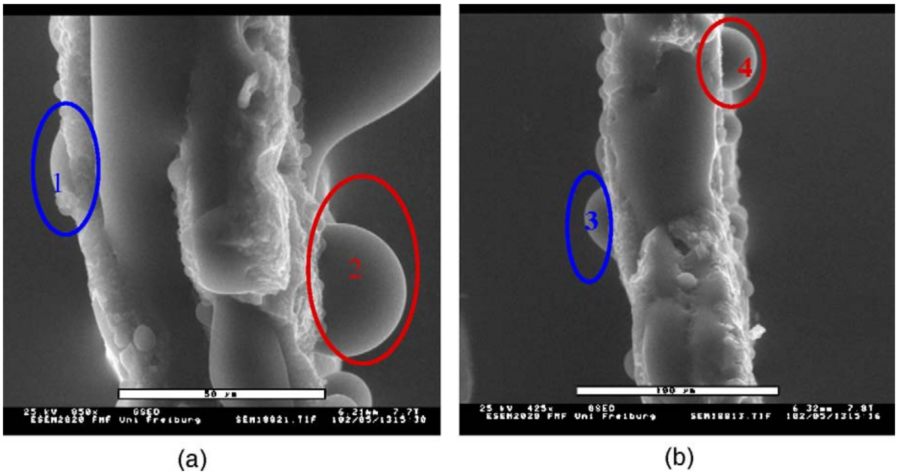


Fig. 10. Water droplet growing and merging process under ESEM. (a) At the beginning, some small water droplets appear, i.e. water droplets 1, 2 and 3. (b) Water droplets 1, 2 and 3 increase in size. (c) Water droplets 1, 2, and 3 merge together to form one big droplet. The contact angle of this water droplet is not be used.

Table 2
Micro-contact angle measurements of CCM2

	No. of water droplets[a]						
	1	2	3	4	5	6	Average
Contact angle (left)	144.0	148.0	147.3	141.3	143.5	144.4	144.8
Contact angle (right)	Not seen	147.6	147.2	141.2	143.8	Not seen	145.0

[a] From the first line of the water droplets, left to right.



(a) (b)

Fig. 11. ESEM pictures for degraded MEA. (a) The cathode catalyst layer and (b) the anode catalyst layer.

Compared with the conventional contact angle measurement, ESEM is able to provide detailed information about the micro-contact angle for inhomogenous material. The water droplets used for the micro-contact angle measurement are on a scale of several micrometers. This is far less than the 1 mm achieved in the conventional sessile droplet method. Because the sample was fixed on the Peltier device, the top of the sample has the highest local temperature. Within the water vapor environment, water droplets are generated inside the bulk of the sample, since the bulk has a lower temperature than the surface. From Fig. 10(a)–(c), it can be seen that while the water droplets increase in size, the cross-section of the sample is always covered by water droplets. Therefore, to some extent, the water droplet at the surface could show the hydrophobicity and/or hydrophilicity of the bulk of the material.

3.3. Hydrophilicity analysis of degraded catalyst layer by means of ESEM

Generally, the degradation of MEAs in PEMFC might have several reasons i.e.: catalyst agglomeration, membrane degradation, hydrophobicity change and pollution effect of impurity, etc. Since ESEM is suitable for analyzing the microstructure and micro-contact angle, it is used to characterize the hydrophobicity and/or hydrophilicity of the catalyst layer of a degraded MEA on the micro-scale. The degraded MEA is from a fuel cell stack, which showed a performance loss of 14% when the fuel cell operated at 260 mA/cm^2. In Fig. 11, the left side is the cathode catalyst layer and the right side is the anode catalyst layer. Some hydrophilic parts shown at the cathode side and marked as 1 and 3 in Fig. 11(a) and (b), correspond to flat water droplets. Smaller contact angles demonstrate a typical hydrophilicity. For water droplet 3 in Fig. 11(b), the measured micro-contact angle is 58.5° on the left side and 58.7° on the right side, respectively. For droplet 1, the micro contact angle of 33° is even smaller on the right side. Most of the microstructure of the degraded catalyst layer still retains it original hydrophobicity, marked as 2 and 4. The micro-contact angles are 94.5° and 98°, respectively.

To confirm the difference between the CCM1 and the degraded CCM1 which were obtained from contact angle measurements, the sample of degraded CCM1 was analyzed by EDX. Several different areas of the samples were scanned by EDX. It was found that there is some silicon distributed in the degraded catalyst layer, shown in Fig. 12, however, the elements distribution is not uniform throughout the sample. Non-uniform distributed silicon inside degraded CCM1 could give some explanation as to why the degraded CCM1 became more hydrophilic.

The results from ESEM and EDX lead to the similar conclusion: the used MEA has a non-uniform degradation effect with regards to the hydrophobicity of the catalyst layer at the cathode. The sealing material and preprocessing could be possible reasons for the existence of silicon at the MEA. Although silicon itself does not have a strong impact on a fuel

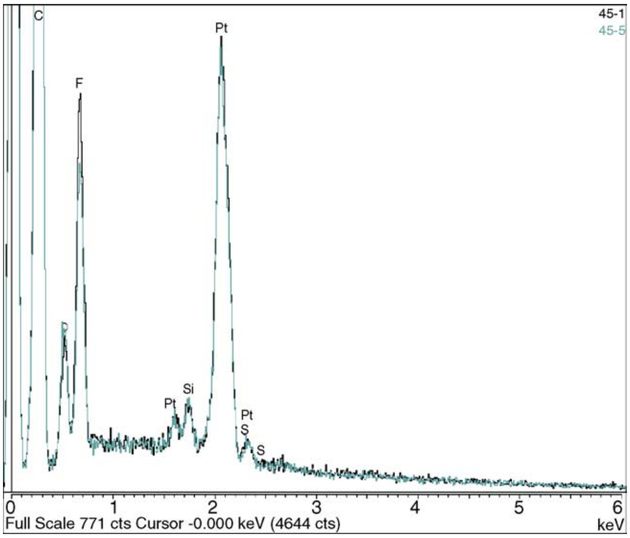


Fig. 12. EDX analysis of the degraded MEA.

cell performance, the change in hydrophobicity influences the fuel cell performance.

4. Conclusion

To investigate the hydrophobicity and/or hydrophilicity of catalyst layers in PEMFCs, conventional contact angle measurements have been performed. Combined with microstructure analyses, porosity measurements and EDX analyses, different catalyst layers were compared. For the first time, it has been proposed to apply ESEM to analyse the hydrophobicity and/or hydrophilicity of the catalyst layer. The micro-contact angle distribution could be obtained as a function of the catalyst microstructure. ESEM has been shown to be a useful tool for characterizing the hydrophobicity and/or hydrophilicity of porous materials.

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