

Analysis of membrane electrode assembly (MEA) by environmental scanning electron microscope (ESEM)

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Accepted 21 December 2005

Abstract

To date, the available equipment for characterising the microstructure of membrane electrode assembly (MEA) is still not well developed. For example, applying the normal scanning electron microscope (SEM) only provides information on the dry structure of MEAs. This paper presents a microstructure analysis method of MEAs in proton exchange membrane fuel cells (PEMFC). The microstructure analysis in this paper utilises the environmental scanning electron microscope (ESEM), which shows its advantage on the sample microstructure analysis in wet mode. When water is present, the characteristics of the MEA, especially the hydrophobic and/or hydrophilic properties, are distinguishable on the ESEM images. With proper temperature and pressure control, the water distribution within both the membrane and the catalyst layer can be viewed by ESEM. Based on ESEM measurement and mercury porosity measurement, the distributions of hydrophobic and hydrophilic pores in MEA have been analyzed. By means of ESEM and energy dispersive X-ray (EDX), a degraded MEA is characterized. The microstructure change of the degraded MEA has been discussed. The results provide helpful information for the understanding of MEAs in PEMFC.

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Keywords: PEM fuel cell membrane electrode assembly; Environmental scanning electron microscope; Microstructure; Degradation

1. Introduction

Fuel cells, especially low temperature fuel cells, such as proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) show, with their high power density, their easy and convenient operation, their environmentally friendly characteristics and their long operation time, that they are promising power supply for portable applications in the near future. Many efforts on improving fuel cells performance have been made in the past two decades [1].

The core of a PEMFC is the membrane electrode assembly (MEA). It consists of a membrane and catalyst layers, and sometimes gas diffusion layers are also included. At the anode, the hydrogen is broken down into two components: the hydrogen nucleus (also known as a proton) and an electron.

The proton migrates from the anode to the cathode through the electrolyte. At the cathode, the proton (H^+) reacts with the electron (e^-) coming from the load and with the oxygen molecule. They combine to form water, which is the only chemical product of the fuel cell. The interface in a MEA is often referred to as the triple or three-phase interface, since in some PEMFC fuel cell designs, the fuel (or oxidizer) is gas, the electrolyte product is liquid and the electrode/catalyst surface is solid. The state of this three-phase interface plays a critical role in determining the electrochemical performance of a fuel cell; hence, this triple interface has been the focus of much research in improving fuel cells [2,3]. As water is the only chemical product in PEMFC, it is essential to observe what happens inside the MEA morphology when water is present. Water has an influence on the three-phase interface properties in MEA, for example, the hydrophilicity of the membrane and some polymer containing catalyst layers. It will be useful to understand the material properties with water existence.

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In the past research work, the scanning electron microscope (SEM) is one of the most widely used pieces of equipment for analyzing the morphology of MEAs. One disadvantage of SEM is that it is normally not possible to examine samples that produce any significant amount of vapor when placed in a vacuum. Because of this limitation, samples must be dried. For MEA microstructure analysis, conventional SEM means that it is impossible for water to be involved. Some vapor-producing samples can be examined using cryogenic SEM. However, even cryogenic SEM cannot be used to observe the drying or wetting process of materials. In an attempt to overcome these disadvantages, progress has been made in recent years in perfecting the environmental scanning electron microscope (ESEM). ESEM is a new innovation in scanning microscopes specifically designed to study wet, oil bearing or insulating materials. Polymers, biological cells, plants, soil bacteria, concrete, wood, asphalt and liquid suspensions have been observed in the ESEM without prior specimen preparation or gold coating. Samples may be examined in water vapor or other gases such as CO₂ or N₂ at near atmospheric pressures due to the unique vacuum system of the ESEM.

In this paper, ESEM is used to detect the morphology of MEAs in wet mode. Since we lack a method to investigate the in situ phenomena during water generation in the electrochemical reaction, the ESEM technique is adapted as a pseudo in situ method for the interface phenomena with water existence.

2. Experimental

Environmental scanning electron microscope imaging was conducted at the Freiburger Materialforschungszentrum (FMF, Freiburg, Germany) with an environmental scanning electron microscope (ESEM 2020 from Electroscan Corp., Wilmington, USA). Imaging of the samples in wet state was conducted by cooling the sample down to 5 °C with a Peltier device in a water vapour (7–9 Torr). The voltage of the electron beam was 23 kV (LaB₆-cathode). The detection of the secondary-electrons was carried out with a gaseous secondary electron detector (GSED). With this technique, no sputter coating is necessary for sample preparation.

In ESEM, a Peltier device is used. This thermoelectric (TE) module is a small solid-state device that functions as 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 cooling Peltier stage and high water vapor pressure in the specimen chamber, it is possible to achieve high levels of humidity (up to 100%). In these conditions, wet or hydrated specimens will not dry and introduce any artifacts. Dynamic experiments are also possible; for example, wetting, drying or crystallization processes can be examined.

The surface phenomena of Nafion[®] 117, a polytetrafluoroethylene (PTFE)/Nafion composite membrane and a

sulfonated poly ether ether ketone (SPEEK)/PTFE composite membrane (56.6% degree of sulfonation, EW = 590) are investigated by means of ESEM. The cross section of the samples is obtained in the following ways. The sample is put into liquid nitrogen for at least 10 min. Afterwards, it is suddenly broken to get the “fresh” cross section.

The EDX measurement was conducted using a Si–Li detector equipped with INCA, manufactured by Oxford Instruments (Fachhochschule Esslingen, Germany).

To compare the hydrophilicity and/or the hydrophobicity of the material, the contact angle was measured by the contact angle measurement system OCA 20, manufactured by Dataphysics Instruments GmbH, according to the sessile and captive drop method.

The porosity was measured by a Pascal 140 + 440 Mercury Porosimeter (Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW), Germany), which operates up to 62,000 PSI. The pore size could be measured between 2 and 57,000 nm.

3. Results and discussion

3.1. ESEM measurement of membrane

Nafion[®] is one of the most popular polymers used in PEMFC. In this paper, Nafion[®] 117 is the first sample to evaluate the possibility of ESEM measurement. The formation of water droplets on the surface of Nafion[®] 117 can be seen by ESEM. Every 15 s, an ESEM picture is taken.

From the wetting process on the surface of Nafion[®] membrane, the hydrophilicity of Nafion could be easily seen from this ESEM image series (Fig. 1(a)–(e)). Although some of the water droplets size grows with time, the contact angle does not change. In other word, ESEM could show the hydrophilicity. The surface phenomena could be studied by ESEM during water droplet formation. As Zawodzinski et al. [5,6] showed, the surface of this ionomer exhibits a wide range of contact angle with water. It seems that this is due to the wetting process of this ionomer. Here the hydrophilicity is obvious. Since Nafion[®] 117 is a homogenous material, the wetting phenomena on the surface shows that the process of wetting in Nafion[®] is very quick. Meanwhile, the cross section of Nafion[®] in Fig. 2 shows consistency in the bulk and the surface.

The swelling effect of membranes could be detected by ESEM. Two composite membranes (CM1 which is a perfluorinated ionomer/PTFE composite membrane and CM2 which is SPEEK/PTFE composite membrane) have been measured by ESEM in wet mode. The ESEM images of CM1 and CM2 are shown in Figs. 3 and 4. The swelling effect of the hydrophilic material could be measured by means of ESEM. In Fig. 3, the middle part of the perfluorinated ionomer/PTFE membrane is PTFE. Here, no difference between dry mode and wet mode measurement in ESEM is observed. This confirms the hydrophobic characteristics. Meanwhile,

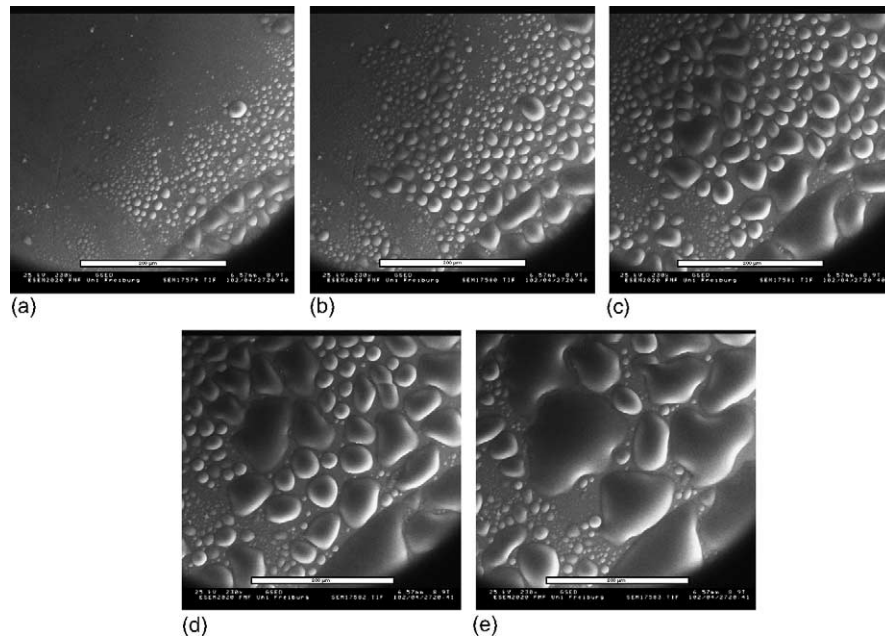


Fig. 1. The process of water droplet formation on Nafion® 117.

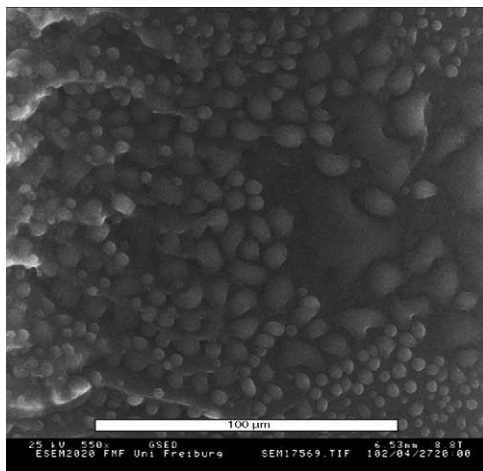


Fig. 2. Cross section of Nafion® 117 in wet mode.

the composite part, which is perfluorinated ionmer shows its hydrophilicity.

From Fig. 4, the SPEEK (left side in Fig. 4) and PTFE layer (right side in the picture) can be easily distinguished by their hydrophilicity and hydrophobicity under the water circumstance. Especially, at the SPEEK surface, there is a big flat water droplet which shows its hydrophilicity. Compared with the EDX measurement results [4], it is found that the high fluorine content area shows the hydrophobic part in the ESEM pictures. This characteristic could be used to distinguish the hydrophobic and hydrophilic area of the MEA microstructure under the wet mode in ESEM.

3.2. ESEM measurement of membrane electrode assembly

Measurement of the catalyst layer hydrophilicity is an important issue in order to characterize the catalyst-coated membrane MEA. Although there are some publications on

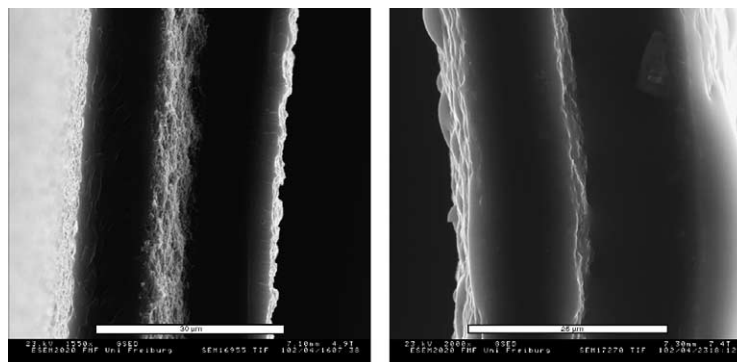


Fig. 3. Perfluorinated ionmer/PTFE composite membrane (CM1) in dry and wet mode.

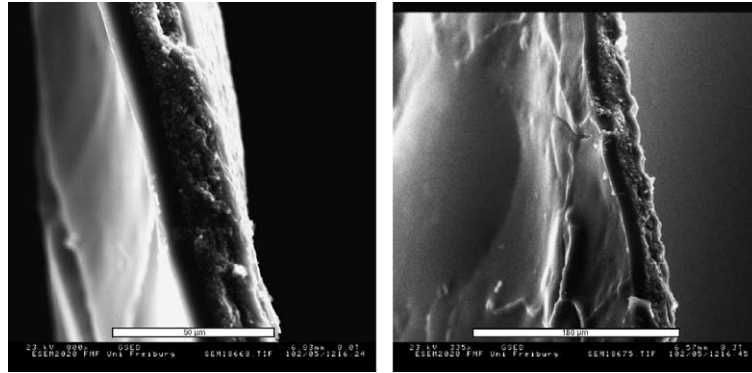


Fig. 4. ESEM pictures of SPEEK/PTFE (CM2) composite membrane. Left side with water sensitive material is SPEEK, the right side is PTFE substrate which has no influence by water existence.

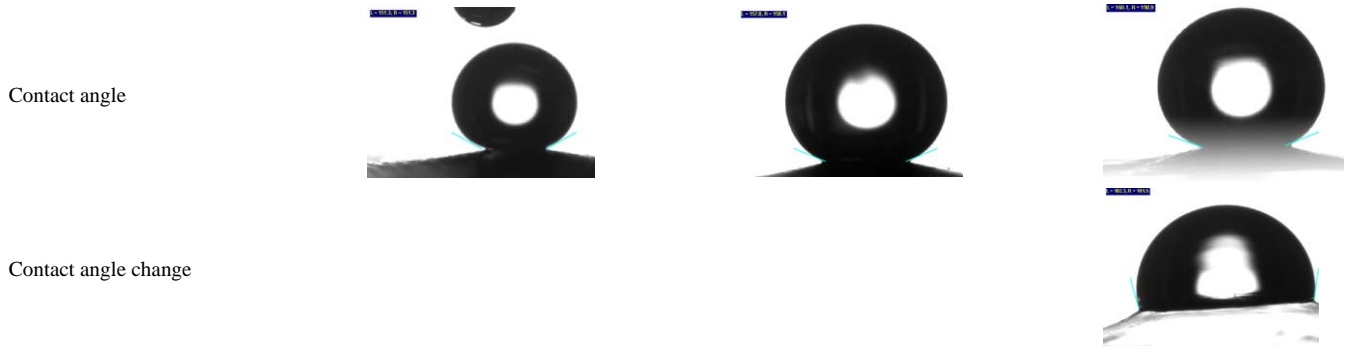
the hydrophobicity and/or hydrophilicity of membranes and gas diffusion media [7–10], only a few publications exist on the measurement of the catalyst layer. One of the reasons is that the catalyst layer is already attached to the membrane. When the contact angle measurement system is used, the pores inside the catalyst layer are not able to avoid the influence of the polymer material. For catalyst layers with big pores (several 10 μm), the contact angle measurement shows significant changes during the wetting process. We have investigated a catalyst-coated membrane from DuPont which catalyst loading is 0.4 mg Pt cm⁻² at cathode and anode side, and other two catalyst-coated membranes CCM1 and CCM2, which have the same platinum loading 0.4 mg cm⁻² for each side. The results of the pore distribution are shown in Table 1. CCM2, which has a big average pore size of 2.17 μm, eas-

ily has a strong impact on measuring the contact angle by the OCA 20 system. The DuPont MEA and CCM1 have an average pore radius of 0.0275 and 0.0385 μm, respectively. It is possible to measure the static contact angle of these two samples by OCA 20.

The ESEM measurement shows its advantage here. In Fig. 5(a), a cross section of a catalyst-coated membrane is shown. A laser has burned some parts of the catalyst layer. EDX measurement results of original and burned MEA are shown in Fig. 6. From the EDX result in Fig. 6(b), it can be known that the part burned by the laser has no platinum peak and is only the blank membrane. In Fig. 5(b), the water droplets are on the blank membrane, Fig. 5(c) shows the water droplets on the surface of the catalyst layer. They show that the water droplets on the blank membrane are flatter than

Table 1
Porosity and contact angles of different catalyst-coated membranes

	DuPont MEA	CCM1	CCM2
Average pore radius (μm)	0.02752	0.03852	2.1740
Total porosity (%)	22.03	34.40	37.27
Relative volume in different pore radius range (%)			
10000–1000 (μm)	3.42	0	0
1000–100 (μm)	4.27	0	0
100–10 (μm)	8.55	12.22	35.48
10–1 (μm)	0.85	21.11	14.84
1–0.1 (μm)	0	3.33	3.23
0.1–0.01 (μm)	60.68	61.11	38.71
0.01–0.001 (μm)	22.22	2.22	7.74



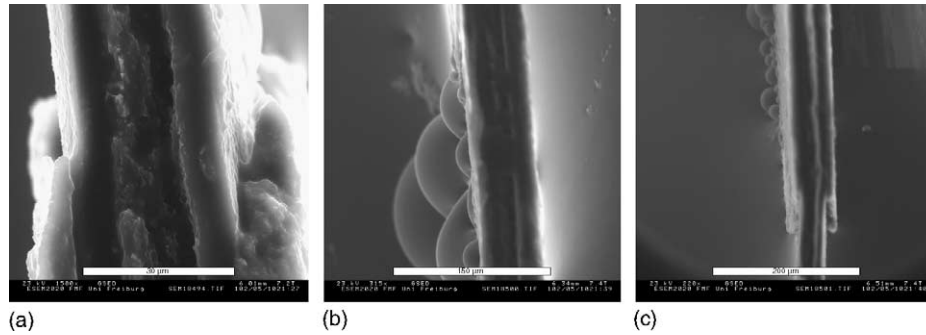


Fig. 5. ESEM pictures of laser burned MEA (CCM1): (a) cross section; (b) water droplet on the blank membrane; (c) water droplet on the surface of the catalyst layer.

those on the catalyst layer surface. This means the catalyst layer is more hydrophobic than the blank membrane. In this way, we could see the difference in hydrophilicity between the catalyst layer and the blank membrane. This measurement concludes that the catalyst layer is not as hydrophilic as the membrane. From the ESEM picture, it is hopeful to measure the contact angle of the catalyst layer. As the catalyst layer is not a real homogenous material, the contact angle based on the microstructure has ranges from being slightly hydrophobic to very hydrophobic (Fig. 7). Nevertheless, it is possible to evaluate the hydrophilic structure of a catalyst-coated membrane.

When the temperature in the ESEM chamber rises, the water droplets evaporate. After the water droplets evaporate from the surface of catalyst layer, the agglomerate and pore sizes can be measured. In Fig. 8, the measured hydrophobic

pore sizes of CCM1 are between 150 and 400 nm. The big pores range from 100 to 1000 μm and all show a high contact angle ($>90^\circ$) which means hydrophobic. Although there is a possibility that some small pores are hydrophobic, it is assumed that the macro-pore in the catalyst layer is more hydrophobic than micro-pore. With the combination of the mercury porosimetry analysis and the hydrophobic macro-pore assumption, the porosity of hydrophobic pores in the catalyst layer is calculated as:

$$\varepsilon_{\text{Hydrophobic}} = \varepsilon V_{\text{Hydrophobic}}$$

in which, ε is the sum porosity, $\varepsilon_{\text{Hydrophobic}}$ is the hydrophobic porosity and $V_{\text{Hydrophobic}}$ is the relative volume of the hydrophobic pores.

According to the ESEM analysis, the pores larger than 0.1 μm are taken as the hydrophobic pores. Then, based on

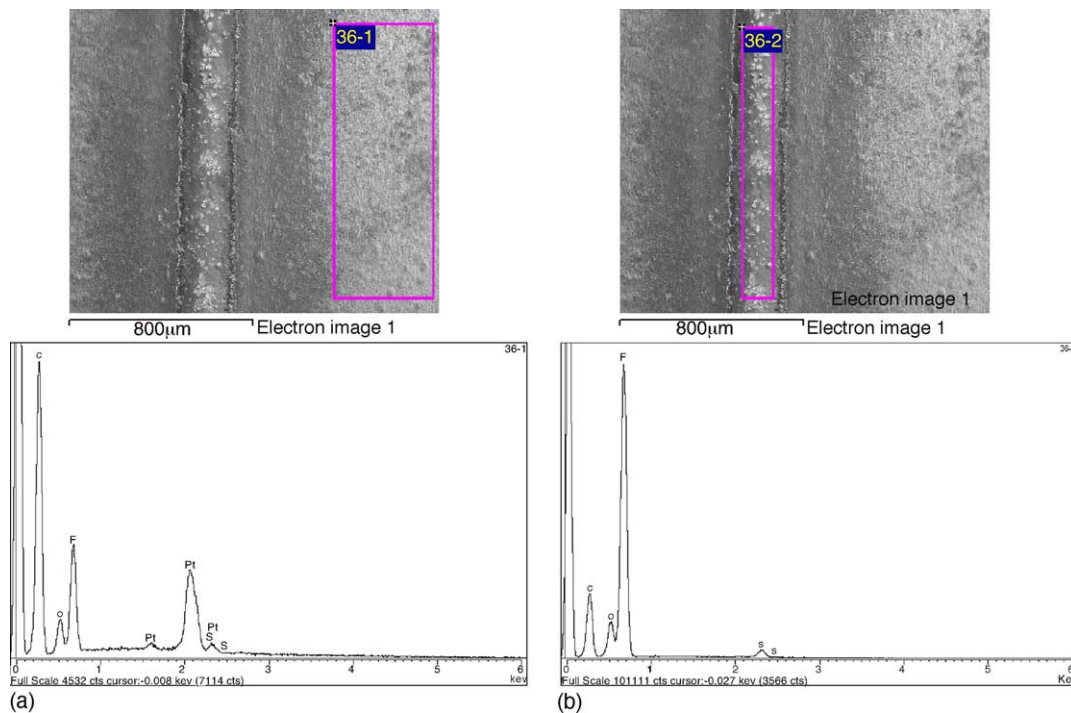


Fig. 6. EDX spectrum of original and burned MEA (CCM1). The picture and EDX result of the (a) catalyst and (b) blank membrane.

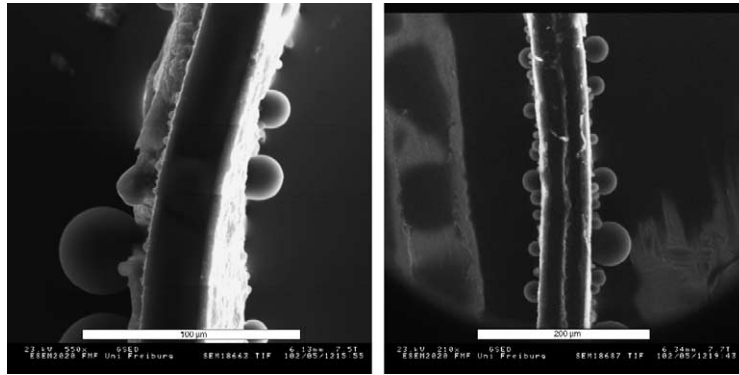


Fig. 7. Contact angle range of different catalyst layers.

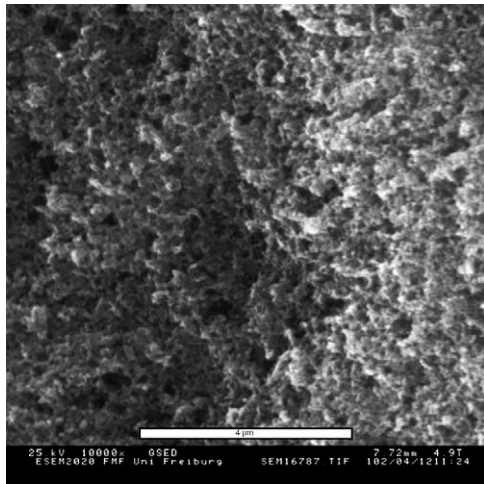


Fig. 8. MEA catalyst surface morphology of CCM1.

Table 2
Hydrophobic porosity of different catalyst-coated membranes

	DuPont MEA	CCM1	CCM2
Total porosity (%)	22.03	34.40	37.27
Relative volume of hydrophobic pores (%)	17.09	36.66	53.55
Calculated hydrophobic porosity (%)	3.76	12.61	20.0

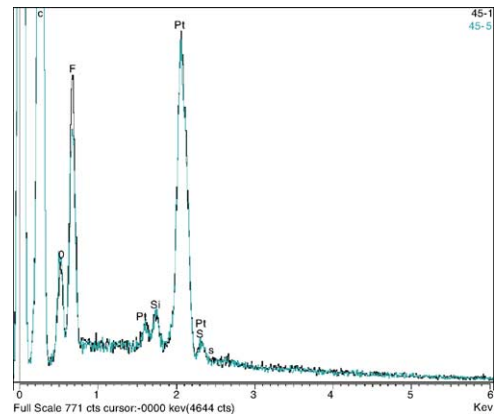


Fig. 9. EDX analysis of the degraded MEA.

the data in Table 1, the hydrophobic porosity of the samples could be calculated. The results are shown in Table 2.

3.3. MEA hydrophilicity and degradation analysis

A degraded MEA which has operated in a fuel cell over 700 h is analyzed by EDX and ESEM, shown in Figs. 9 and 10. Fig. 9 shows the result of the EDX analysis of

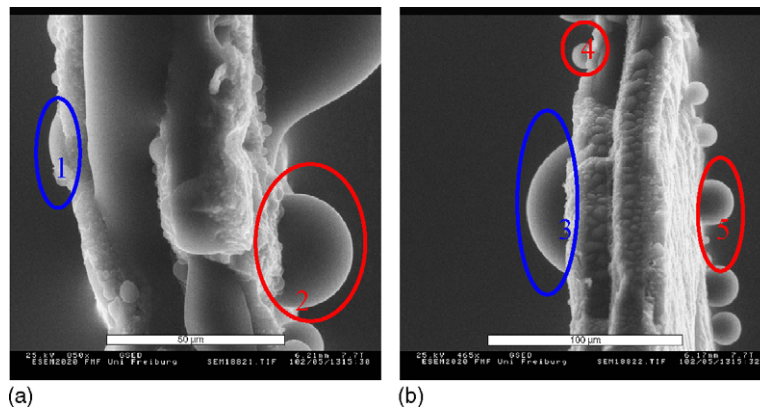


Fig. 10. ESEM pictures for degraded MEA.

the degraded cathode catalyst layer and anode catalyst layer, which are marked dark (45-5) and grey (45-1), respectively. The EDX analysis shows that in the catalyst layer of the degraded MEA, the fluorine peaks for cathode and anode are different. There is also a significant silicon peak, which might come from the sealing of the inlet of the gas. In the corresponding EDX spectrums, it could be known that the cathode side has less fluorine than the anode side. Meanwhile, the surface EDX analysis shows that the cathode side has more silicon than the anode side. Due to these two reasons, the cathode side shows more hydrophilicity than the anode side. In Fig. 10(a) and (b), it is found that in the cathode catalyst layer (left side in Fig. 10(a) and (b)), there are some flat water droplets, which are marked as 1 and 3, indicating the hydrophilicity. Some other parts still show high contact angles, which are marked as 2, 4 and 5, indicating the hydrophobicity. But the hydrophilicity is not uniformly distributed.

4. Conclusion

When water exists, ESEM has shown its advantage in the hydrophilicity and hydrophobicity analysis for fuel cell membrane electrode assemblies. The contact angles in the ESEM pictures are available to evaluate the hydrophobicity and/or hydrophilicity of the material. ESEM is available for the contact angle qualitative analysis, especially for the catalyst layer, which is easily influenced by the surface properties and porosity. By means of ESEM measurement, it is possible to calculate the hydrophobic and hydrophilic porosity based on porosity results. The ESEM result and the EDX measurement have shown their consistency on MEA degradation analysis. It is possible to implement ESEM in MEA microstructure analysis.

Acknowledgements

This work was partially funded by the Forschungsallianz Brennstoffzellen Baden-Württemberg and National Natural Science Foundation of China (Grant No. 20206030). The authors appreciate the assistance of the ESEM measurement conducted by Mr. Andreas Pfister at Freiburger Materialforschungszentrum (FMF, Freiburg, Germany) and the EDX analysis conducted by Dr. Juergen Kraut at the Labor für Rasterelektronenmikroskopie u. Mikroanalyse, Fachhochschule Esslingen. Dr. Danming Xing, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, is appreciated for supplying the PEEK/PTFE composite membrane. Mr. Manfred Grünerbel at Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW), Germany, is also appreciated for the help on the porosity measurement.

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