Degradation of sealings for PEFC test cells during fuel cell operation

M. Schulze [a,*], T. Knöri [a], A. Schneider [b], E. Gülzow [a]

[a] *Institut für Technische Thermodynamik, Deutsches Zentrum für Luft-und Raumfahrt, D-70569 Stuttgart, Germany*
[b] *Adam Opel AG, GAPC, IPC 81-90, 65423 Rüsselsheim, Germany*

Abstract

For long-term operation of fuel cells the stability of all components is needed under extreme conditions. Especially the components in polymer electrolyte fuel cells (PEFCs) may show corrosion problems caused by the acid character of the solid electrolyte. One of the parts, which is commonly neglected, is the sealing material. Sealings are necessary for separating the gas compartments from the each other in order to avoid mixing of hydrogen and oxygen. A typical sealing material is silicone.

Fuel cell components are characterized after operation in single cells under typical fuel cell conditions. After fuel cell operation frequently an alteration is visible on the sealing and the membrane parts which were in direct contact with each other. Those parts of the membrane, which were in contact with the sealing surface, became colored. Motivated by this observation membranes and sealings were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). In addition, electrodes and backings were investigated by X-ray photoelectron spectroscopy (XPS).

With the XPS measurements of the electrodes operated in a silicone sealed cell, residues of the silicone were detected on its surface. This indicates that the decomposition products of the silicone seals have a high mobility. In SEM/EDX mappings, an enrichment of silicone residues on the platinum was observed. Therefore, the decomposition products may contribute to a poisoning of the catalysts and may also change the hydrophilic/hydrophobic characteristic of the electrodes.
© 2003 Elsevier B.V. All rights reserved.

Keywords: PEFC; Silicone; Sealing; Degradation; Scanning electron microscopy; Energy dispersive X-ray analysis; X-ray photoelectron spectroscopy

1. Introduction

In the last decade worldwide energy consumption continued to climb. It increased in the last decade by some 10% up to approximately 3.6×10^{20} J in the year 1999. According to the International Energy Agency's (IEA) World Energy Outlook, the global demand for primary energy will increase by 57% (corresponding to 2% a year) from 1997 to 2020 at an annual economic growth of roughly 3%. The IEA anticipates an annual rise in global CO_2 emissions between 1997 and 2020 of almost 14 billion tons. This corresponds to a total increase of 63% or 2.1% a year [1,2]. If this increase of consumption is maintained, fossil energy resources will be spent within a few generations and the problem of environmental pollution will become a key issue for the future of mankind. Therefore, the future of energy supply lies in renewable energy sources and developing new energy conversion technologies such as fuel cells. Due to their potential in converting chemical energy with high efficiency directly into electrical energy and their environmen-

tally friendly character, fuel cells and especially the polymer electrolyte fuel cell (PEFC) have the chance to become a sustainable, resource-saving energy source for diverse applications, e.g. for the mobile sector [3].

The modular design of a PEFC suggests that manufacturing will in future will be of low-cost and permits mass production. Recent improvements in fuel cell technology have led to a degree in development, which allows to envisage commercial fields. Within the next decades a successive replacement of conventional energy conversion technologies is likely, even if certain technical obstacles remain still to be overcome. For long-term operation of fuel cells stability of all components is needed. At present, the status of fuel cell development can not guarantee sufficient life times of several thousands of hours for mobile or portable applications and several ten thousands of hours for stationary applications. Therefore, the investigation of degradation mechanisms is a main topic in fuel cell research [4]. However, only a few publications exist concerning the investigation of degradation effects of polymer electrolyte membrane fuel cells [5–16].

One component commonly neglected in the research of degradation effects is the sealing material. In a PEFC sealings are necessary to separate the gas compartments from

* Corresponding author. Tel.: +49-711-6862-456;
fax: +49-711-6862-747.
E-mail address: mathias.schulze@dlr.de (M. Schulze).

the each other and to avoid mixing of hydrogen and oxygen respectively. A faulty or inappropriate sealing leads to fuel losses and reduced voltage due to the formation of a mixed potential at the electrodes. Usually the resulting gas mixture can explode if the ratio of oxygen and hydrogen lies in a certain range. In a fuel cell, the hazard of an explosion is improbable due to the presence of the noble metal platinum. Platinum acts as a catalyst and stimulates the reaction of the fuel and the oxidant gas. But the heat of reaction of this catalytic combustion generates hot spots in the MEA. Thus, temperature rises until the membrane will be destroyed. The resulting holes enhance mixing of the gases that finally may lead to an open fire. Besides these safety aspects, it is also necessary from the manufacturer's point of view that the sealing materials should be easy to handle, low priced and chemically inert, even under the corrosive environment caused by the acid electrolyte and the chemical conditions. Typical sealing materials are fluorine caoutchouc, EPDM and silicone.

2. Experimental

2.1. Sample preparation

For the experiments membrane–electrode assemblies (MEAs) with two different types of electrodes were used. The first one contains commercial electrodes purchased from E-TEK with 20 wt.%. Pt/C and a Pt-loading of 0.4 mg/cm^2. The second one was a proprietary development prepared with the DLR dry spraying technique. In contrast to typically used preparation methods for commercial electrodes from a catalyst-containing suspension, the DLR manufacturing way is a dry process avoiding solvents and complicated process steps and can fit to a fully automated mass production [17–22]. It is a consequent further development of the manufacturing technique for alkaline fuel cell electrodes [23–30], with a new deposition type of the powder mixture for the reaction layer. The resulting electrodes contained 20 wt.% Pt/C and a Pt-loading of 0.2 mg/cm^2 on each electrode. On each electrode E-TEK single sided backings were used as gas diffusion layers. In both cases the MEAs were prepared by hot pressing the electrodes (1.6 MPa, 2 min, 160 °C) onto a Nafion® membrane (purchased from DuPont). The active area of each MEA was 4.8×4.8 cm^2.

2.2. Electrochemical experiments

All electrochemical experiments were carried out in a 23 cm^2 single cell. On the cathode side, a stainless steel electrode holder with moulded meander structures was used as gas distributor. The current collector on the anode had a flow-field with a chocolate wafer structure which was divided into 4×4 quadratic segments of stainless steel. By means of this device, the value of the current which is generated in a certain region of the membrane electrode assembly

was recorded separately for each segment, so that the MEAs can be characterized by V–I curves and local current densities. At DLR, the segmented cells are used for the investigation of hydrogen supplied polymer electrolyte membrane fuel cells as well as for the investigation of direct methanol fuel cells (DMFC). More details of this device can be found in [31]. Between the membrane electrode assembly and the segmented cell, a sealing of silicone-red® was used for separating the gas compartments against the environment. On both sides of the MEA, silicone sealings were used.

The cells were fixed in test setups which were developed for automatic, continuous and safety controlled operations with hydrogen and oxygen or air. These facilities allow the variation of the operating conditions in a wide range of parameters [21,31,32]. In our experiments the cells operated in the dead-end-mode at a temperature of 80 °C with pure hydrogen and oxygen (H$_2$ 5.0 and O$_2$ 4.8, Messer Griesheim) at 2.0 bar absolute. Both gases were not humidified. The anode side was purged by opening the outlet valve with pulses of 0.5 s every 900 s. On the cathode side, the outlet was opened for 0.5 s every 120 s at the beginning. Later on, the intervals were extended to 240 s. For the start-up, the MEAs were humidified by an injection of liquid water directly into the test-cell. The cell voltage was 500 mV. Under these conditions, the cathode became flooded over the operational time.

2.3. Physical characterization

The different fuel cell components were characterized after operation.

After preparation and electrochemical stressing by fuel cell operation, the MEAs were investigated by scanning electron microscopy (SEM) [33] combined with energy dispersive X-ray spectroscopy (EDX) [33], X-ray photoelectron spectroscopy (XPS) [33] and porosimetry (with mercury intrusion) [34,35]. For the SEM and EDX measurements, a Zeiss Gemini microscope (LEO) was used in combination with a NORAN VOYAGER 3000 EDX-detector. This SEM allows high magnification imaging at low and high beam voltages (1–30 keV). The SEM and EDX measurements were performed on the backside surface as well as on cross sections of the MEAs.

The XPS measurements were performed in a XSAM 800 (Kratos). The XPS equipment is described in more details in [36]. XPS yields information about the chemical composition of the surface and the method shows a very high surface sensitivity. In contrast, EDX has a low surface sensitivity and yields information about the bulk composition of the volume close to the surface. SEM yields information about the surface structure and gives information about the bulk character. The used XPS does not allow to investigate the samples with a high lateral resolution, the possible resolution amounts to a few mm^2; therefore, no XPS investigations on cross sections were performed, but only the electrode surfaces, reaction layers and backings, as well as the membrane surface of the MEAs.

3. Results and discussion

After an operational time of several days, a leakage test showed that the mechanical function of the silicone sealings still remain. After these tests, the fuel cells were opened and the different parts of them were examined. At first, it can be noticed that the sealings always stuck on the Nafion® membrane and an alteration of those membrane areas which were in direct contact with the sealings was visible. Those parts of the membrane surface became colored yellow, which indicates a chemical reaction of the sealing material. A thermal change of the sealing could be excluded, because their range of application was from −90 up to 250 °C according to the manufacturers specification.

Motivated by the change of the silicone appearance, the MEA was studied with different physical methods to investigate alterations in the structure and in the chemical composition. On the cathode backside, numerous particles were visible. The particles were imaged with optical and scanning electron microscopy. The particle sizes are in the range of below 1 μm to few hundred μm. Different forms of the particles were observed; compact particles, which were determined by EDX as platinum oxide shown in [37] and more structured particles.

Fig. 1 shows a photography of the MEA taken with a light microscope. The displayed area is approx. 5.5×3.9 mm^2. The bright region at the left upper corner shows the membrane, below the diagonal in the figure the cathode backing is displayed. On the cathode backing, bright domains can be observed. Thus, depositions were observed on the whole cathode backing. On the anode backing, no particles were visible by light microscopy.

Fig. 2 shows a SEM image of such a structured particle. The first explanation for particles on the cathode backside would be a kind of impurities, but the displayed particle has a form like a crumpled foil and such a form of a particle is untypical for dust, abrasion or similar impurities. Therefore, the particles were investigated by EDX. In the EDX analysis silicon and oxygen were determined as main components. Silicon oxide particles in the form of sand (crystalline structure) as well as in form of glass (amorphous structure) typically have a different particle shape. In addition, if the particles were abrasion fragments of the silicone sealing, similar particles should also be found on the anode side, which was not case. Therefore, the displayed particle seems to be a separated part of the silicone sealing or is formed by a reaction with decomposition fragments of the silicone sealing. A significant concentration of carbon and fluorine in the particles was not observed. In the carbon mapping, the structure of the carbon cloth is shadowed by the particle. From the silicon, oxygen, carbon and fluorine signal, it cannot be distinguished if the particle is a fragment of the sealing or a decomposition product. In addition to the silicon and oxygen, some platinum can be detected. The platinum in the particle is observed in the edges of the investigated particle. The platinum decoration of the edges indicates an alteration in the electrodes. The mobility of platinum and its agglomeration in PEFC electrodes is a known effect [37,38], where the platinum migrates in the direction from the anode to the cathode [37].

The particles on the cathode backing are distributed over the complete area. Consequently, the decomposition products from the silicone sealing must be mobile.

On the anode backing no particles, neither platinum oxide [37] nor the silicone-containing particles could be observed. Two different hypotheses allow to explain why no silicon is observed on the anode backing: on the one hand, the decomposition components of the silicone move in the
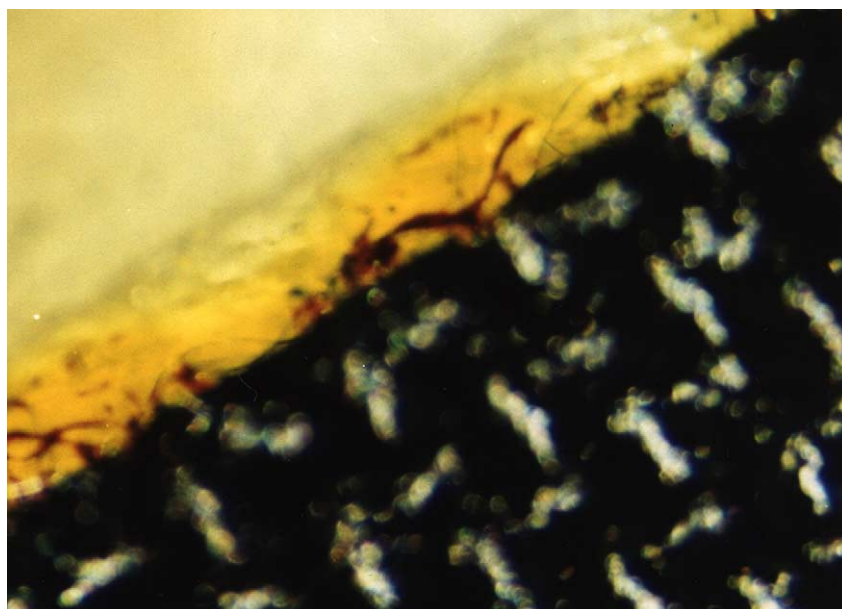

Fig. 1. Photography of membrane electrode assembly made by a light microscope on the cathode backing. The displayed area is 5.5×3.9 mm^2.
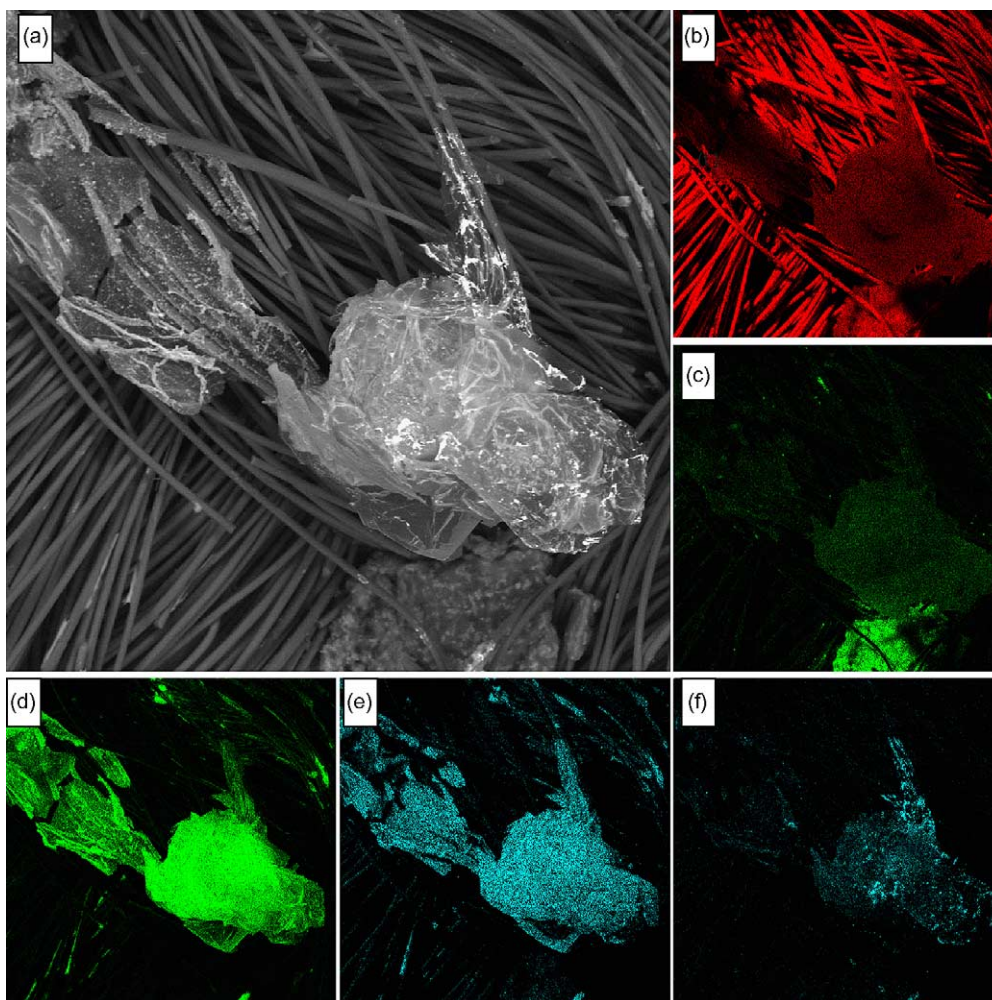
Fig. 2. SEM micrograph of a particle of the backside of the cathode backing after fuel cell operation (a) and the corresponding EDX mappings for carbon (b), fluorine (c), silicon (d), oxygen (e) and platinum (f). The imaged area is $460 \times 460\,\mu m^2$.

same direction as the platinum; possibly the driving force for the mobility is the electrical field for both. On the other hand, the reaction conditions on anode and cathode differ extremely; therefore, it is possible that the silicone sealing decomposes only on the cathode side. Which explanation is correct cannot be derived from these investigations on the reaction layer. Therefore, additional measurements are needed.

In an independent XPS investigation on the reaction layer surface of a used commercial electrode applied as anode in the reaction layer silicon was detected (Fig. 3). Also, in this case, silicone red® was used as sealing material for the cells. For the XPS analysis of used electrodes using commercial electrodes, there is the advantage that the electrodes can be better separated from the membrane electrode assemblies after operation. This is due to the preparation technique; the commercial electrodes are manufactured as self contained units; in contrast the reaction layers prepared with the DLR dry spraying technique [20,21,39] are fixed on the membrane and cannot be separated. The XP spectrum is dominated by the carbon, oxygen and fluorine signal. The platinum cata-

lyst in the commercial electrodes is covered by a polymer film [21,40]. Additionally, the signal of silicon, enlarged in Fig. 3, was observed. This is a second indicator for a high mobility of the silicone decomposition products. Combining the high mobility of the silicone decomposition fragments and the attraction between these and the platinum catalyst a poisoning of the catalyst becomes more likely.

Furthermore, the sealings have a hydrophobic character. Therefore, the decomposition products could also be hydrophobic and may change the wetting behavior of the electrodes, which is determined by the content of polytetrafluoro-ethylene PTFE [41]. The influence of the silicone decomposition fragments on the wetting behavior of the electrodes cannot be determined, because the PTFE in the electrodes is also changed by the electrochemical stressing due to fuel cell operation [42].

The silicon in the anode reaction layer is a clear indicator that the silicon decomposition fragments move in the same direction as the platinum—from the anode backing in the direction to the cathode backing. In addition, the XPS measurements show clearly that the silicone on the anode side
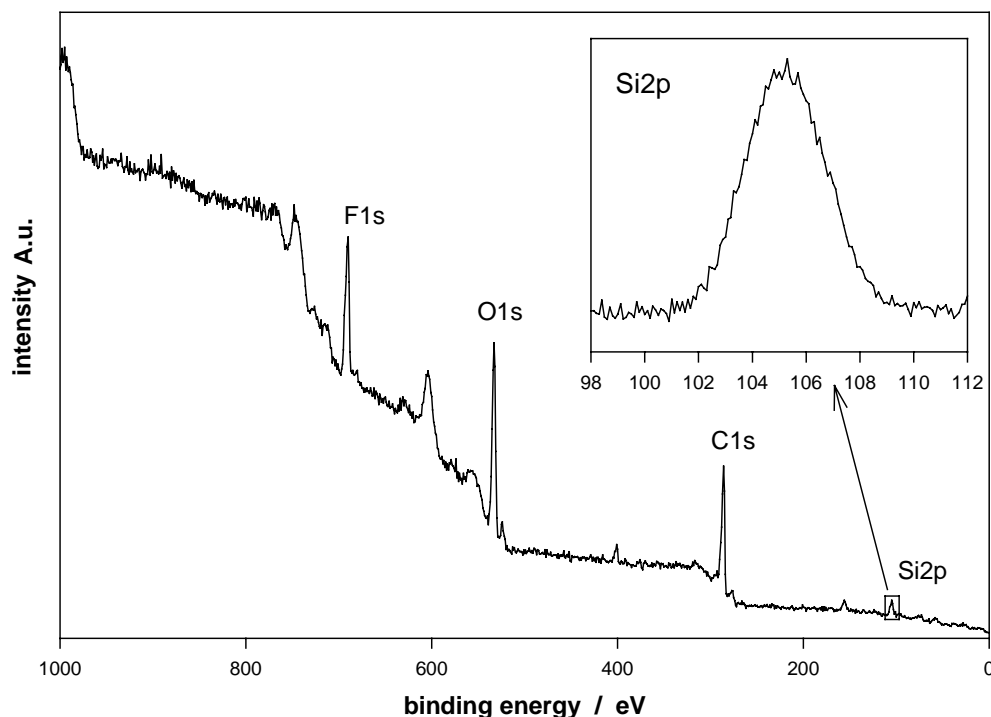
Fig. 3. XP spectrum of an used electrode (The Si2p-region is enlarged).

decomposes, too. An alternative explanation for the silicon on the anode reaction layer could be given, if the silicone decomposition products migrate from the cathode side through the membrane to the anodic reaction layer. This should be excluded because no silicon was detected on the cathodic reaction layer as well as no silicon was observed in the membrane (see below). Therefore, the silicone decomposes also on the anode side, this means, the reaction conditions are not the reason why the silicon-containing particles are only observed on the cathode backing and not on the anode backing. Therefore, it can be concluded that the movement of the silicone decomposition fragments is not induced by the different reaction conditions on anode and cathode, but is induced by a directed movement of the silicone decomposition fragments.

In order to get more information about the movement of the silicone decomposition fragments and the commonly observed platinum and silicon a cross section of the used DLR MEA operated with silicone red® as sealing material was investigated by SEM and EDX (Fig. 4). Fig. 4a and b show the SEM micrographs imaged with back-scattered electrons and with secondary electrons. Using the back-scattered electrons for the imaging, the contrast is determined by the difference in the efficiency to back-scatter electrons. Heavy elements are displayed brighter than light elements in this imaging mode. If the secondary electrons are used for the imaging, the contrast is determined by the differences in the electron work function. In addition, the secondary electrons are detected in a high angle to the sample normal, therefore, the shadowing effect yields a more steric impression. In both imaging modes, the platinum is displayed bright and

the membrane is displayed dark. The thickness of the membrane is approximately 90 μm.

In the EDX mapping, carbon is detected in the electrodes, while the carbon concentration in the membrane is significantly lower. The fluorine is bound in the polymers, PTFE and Nafion®. Consequently, the fluorine concentration is maximum in the polymer electrolyte membrane and the hydrophobic layer. The electrolyte membrane also contains a significant concentration of sulfur. The platinum is concentrated in the reaction layer as expected. Very interesting is the distribution of the silicon in the cross section. The decomposition products of the silicone sealing could only be found on the reaction layer of the anode whereas the cathode reaction layer remains silicon-free. Only particles containing silicon are found in the cathode backing.

The electrolyte membrane contains oxygen and sulfur. In addition, the oxygen of the air can oxidize the catalyst in the reaction layers after operation and separation of the membrane electrode assemblies from the fuel cell. Consequently, oxygen is found in the reaction layer and in the membrane. The oxygen concentration in the anode reaction layer is higher than in the cathode reaction layer. In addition, a high oxygen concentration is found in the silicon containing particle in the cathode backing. Both, the higher oxygen concentration in the anode reaction layer and the oxygen in the silicon particles, show that oxygen is found accompanying the silicon—this means the silicon is in an oxidized form.

In the membrane, no silicon is observed. Consequently, the transport of the silicone decomposition fragments in the membrane and in the electrode must be completely different.
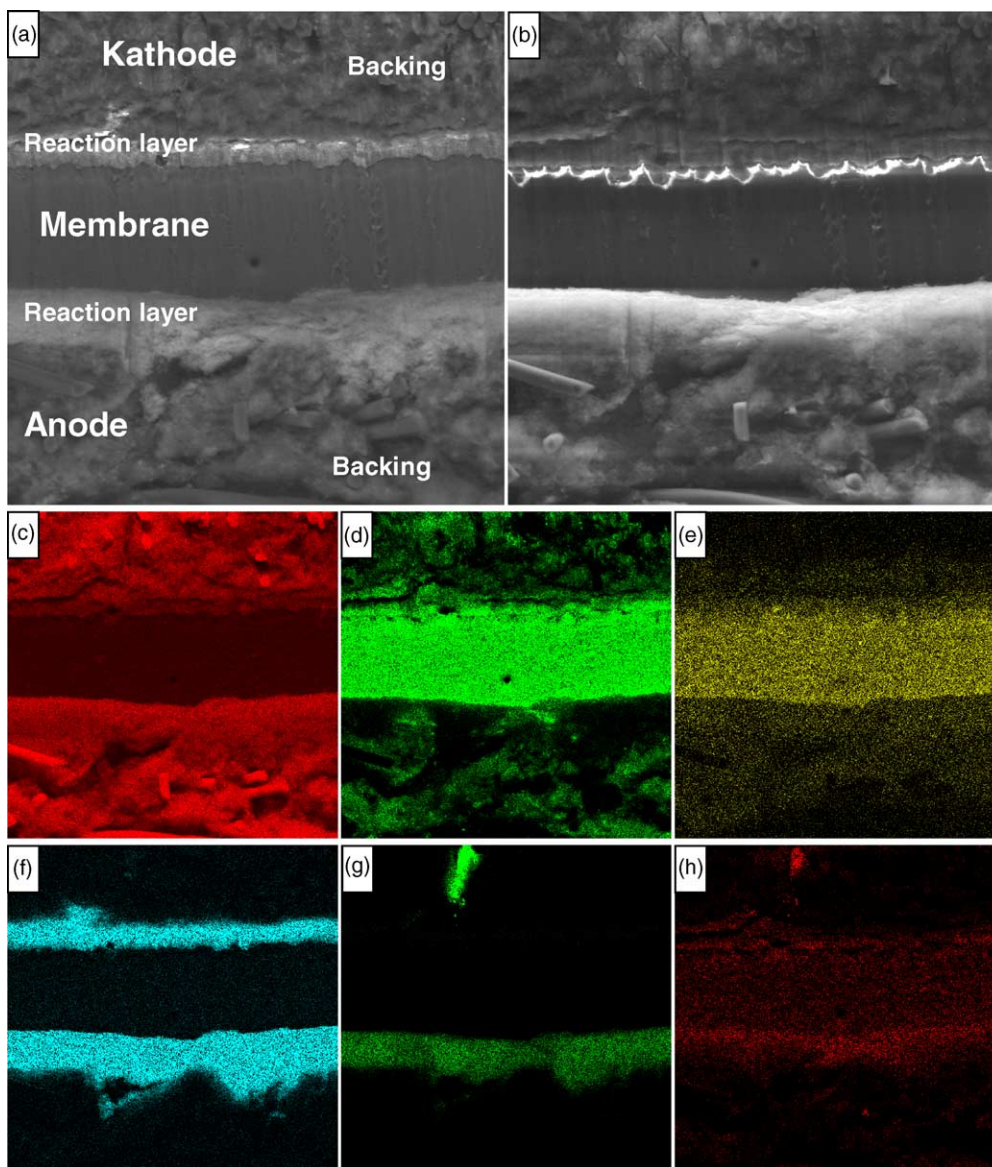
Fig. 4. SEM micrograph and EDX-mappings of a MEA cross section: (a) SEM micrograph image with back-scattered electrons; (b) imaged with the secondary electrons, (c–h) EDX mappings for the elements: (c) carbon, (d) fluorine, (e) sulfur, (f) platinum, (g) silicon and (h) oxygen. The imaged area is $190 \times 190\,\mu m^2$.

If the transport in the membrane were to would be fast, a low silicon concentration in the membrane is possible, but in the cathode reaction layer silicon should also be observable. Therefore, the absence of the silicon in the membrane is effected by the hindering of the diffusion into the membrane from the electrode side. Consequently, it can be concluded, that the Nafion® membrane is a diffusion barrier for the silicone decomposition fragments.

The combined appearance of silicon and platinum especially in the EDX analysis of the particles on the cathode backing indicates that an attractive interaction between platinum and the silicone decomposition fragments exists. The attractive interaction could be the cause for the directed movement of the silicone decomposition fragments, because

the silicone fragments follow the moving platinum, but in this case also silicon should be detected in the cathode reaction layer. Therefore, most likely for the movement of the silicone decomposition fragments a directed driving force exists like that for the platinum migration.

A risk for fuel cells is that the probability of a poisoning of the platinum catalyst increases due to the attractive interaction. The poisoning of the catalyst is more critical in the anode than in the cathode, because for the silicone decomposition fragments the driving force yields a migration away from the cathode reaction layer.

In addition to a poisoning of the catalyst, the silicone decomposition fragments may change the wetting behavior of the electrodes. On the anode side, mainly the reaction layer

is influenced; on the cathode side, mainly the gas diffusion layer. In both electrodes, the transport processes will be influenced by the decomposition of the silicone. Caused by the barrier function of the polymer electrolyte membrane, the silicone decomposition fragments will be enriched on the interface between the membrane and the anode reaction layer. This will increase the transition resistance, whereas the problem is more critical in MEAs with self-contained electrodes assemblies than in MEAs with reaction layers directly fabricated onto the membrane, because the transition resistance between electrode and membrane is higher using self-contained electrodes and therefore, the migration of the ions in the interface zone is enhanced, which is also observed for the platinum [37]. In any case, the silicone decomposition fragments in the electrodes as well as the enrichment in the interface between membrane and anode should influence the media transport in the electrodes and should effect the behavior near the limiting current. During the operational time of the tested MEA here the electrochemical performance did not change significantly, the behavior near the limiting current was not investigated.

4. Conclusion

If sealings fabricated of silicone-red® are used for fuel cell operations, they are subjected to a degradation process. This decomposition proceeds at both electrodes. Therefore, the different conditions in the two gas compartments, the oxidizing environment at the cathode side the reducing one at the anode side of the membrane electrode assembly, cannot be the cause for that reaction. Most likely, the acid character of the polymer electrolyte membrane in combination with the thermal stressing of the sealing material induces the alteration, even if the mechanical function of silicone sealings remains. Hence, the sealings stick on both sides of the membrane which leads to the observed coloration to yellow.

The products of this reaction have a high mobility and try to move from the anode to the cathode forced by the electrical field. On the anode side, the fragments of the sealing material diffuse from the edge of the MEA to the reaction zone, on the cathode they get to the backside of the gas diffusion layer, where they are able to react with the catalyst, forming particles containing silicon, oxygen and platinum. The Nafion® membrane itself is a barrier for the different decomposition products and remains silicon-free, so that the fragments have to accumulate in the reaction layer of the fuel cell's anode.

This accumulation of silicone decomposition products may change the wetting character of the electrodes, the water balance of the cell and finally the mass transfer within both electrodes due to the wetting behavior of silicone which is different from that of electrode materials. Especially if there is an alteration of the water balance in the cathode due to silicone, this may strongly change the electrochemical behavior and requires an adaptation of the operation conditions to the changed cathode character. Furthermore, the platinum catalyst of the anode can be poisoned due to an interaction of the noble metal to the silicone fragments. Impedance studies on MEAs have shown, that the contribution of the anode towards the total impedance usually can be neglected [43]. According to this result, a distinct change of the anode's condition should effect the behavior and the performance of the MEA close to the limiting current.

A lot of different degradation processes, agglomeration of the catalyst [37], changes of PTFE [42] and so on, proceed simultaneously. So, it is impossible to quantify the influence of the individual degradation effects separately at the present state of knowledge. Therefore, further investigations of degradation processes are necessary.

Acknowledgements

References

[1] The Federal Ministry of Economics and Technology, Germany, Energy Report: Sustainable Energy Policy to Meet the Needs of the Future, Documentation 508, June 2002, http://www.bmwi.de.
[2] IEA World Energy Outlook 2000.
[3] K. Kordesch, G. Simader, Fuel Cells and Their Applications, VCH–Verlag, Weinheim, 1996.
[4] For example: BMBF-Project: Langlebige PEFC als Voraussetzung für eine Wasserstoffenergiewirtschaft, supported by the German Bundesministerium für Bildung und Forschung.
[5] E. Gülzow, M. Schulze, N. Wagner, T. Kaz, R. Reißner, G. Steinhilber, A. Schneider, J. Power Sources 86 (2000) 352.
[6] M.S. Wilson, J.A. Valerio, S. Gottesfeld, Electrochim. Acta 40 (1995) 355.
[7] M.S. Wilson, F.H. Garzon, K.E. Sickafus, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 2872.
[8] B. Mattsson, H. Ericson, L.M. Torell, F. Sundfolm, Electrochim. Acta 45 (2000) 1405.
[9] G. Hübner, E. Roduner, J. Mater. Chem. 9 (1999) 409.
[10] M. Schulze, M. Lorenz, N. Wagner, E. Gülzow, Fresenius J. Anal. Chem. 365 (1999) 106.
[11] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, J. Power Sources 86 (2000) 237.
[12] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, J. Appl. Electrochem. 30 (2000) 101.
[13] P.G. Dirven, W.J. Engelen, C.J.M. Van Der Poorten, J. Appl. Electrochem. 25 (1995) 122.
[14] J.M. Rheaume, B. Müller, M. Schulze, J. Power Sources 76 (1998) 60.
[15] F.N. Büchi, B. Gupta, O. Haas, G.G. Scherer, Electrochim. Acta 40 (1995) 345.
[16] S. Gupta, D. Tryk, S.K. Zecevic, W. Aldred, D. Guo, R.F. Savinell, J. Appl. Electrochem. 28 (1998) 673.
[17] D. Bevers, E. Gülzow, A. Helmbold, B. Müller, Innovative production technique for PEFC electrodes, in: Proceedings of the Fuel Cell Seminar, Orlando, 1996, p. 668.
[18] A. Helmbold, German Patent DE 197 57 492 A 1, 1999.
[19] D. Bevers, N. Wagner, German patent DE 195 09 749 C2.

[20] E. Gülzow, et al., Fuel Cell Bull. 15 (1999) 8–12.

[21] E. Gülzow, A. Helmbold, T. Kaz, R. Reißner, M. Schulze, N. Wagner, G. Steinhilber, J. Power Sources 86 (2000) 352.

[22] E. Gülzow, T. Kaz, J. Power Sources 106 (2002) 122.

[23] H. Sauer, German patent DE 2 941 774 (CI H01M4/88).

[24] A. Winsel, German patent DE 3 342 969 (CI C25B11/06).

[25] E. Gülzow, K. Bolwin, W. Schnurnberger, Dechema-Monogr. Bd. 117 (1989) 365.

[26] E. Gülzow, W. Schnurnberger, Dechema-Monogr. Bd. 124 (1991) 675.

[27] E. Gülzow, K. Bolwin, W. Schnurnberger, Dechema-Monogr. Bd. 121 (1990) 483.

[28] E. Gülzow, B. Holzwarth, M. Schulze, N. Wagner, W. Schnurnberger, Dechema-Monogr. Bd. 125 (1992) 561.

[29] M. Schulze, E. Gülzow, G. Steinhilber, Appl. Surf. Sci. 179 (2001) 252.

[30] E. Gülzow, M. Schulze, G. Steinhilber, J. Power Sources 106 (2002) 126.

[31] E. Gülzow, T. Kaz, R. Reißner, H. Sander, L. Schilling, M.V. Bradke, J. Power Sources 105 (2002) 261.

[32] S. Weißhaar, R. Reissner, W. Schröder, E. Gülzow, J. Power Sources 118 (2003) 405.

[33] G. Ertl, J. Küppers, Low Energy Electron and Surface Spectroscopy, VCH–Verlagsgesellschaft, Weinheim, 1985.

[34] Carlo Erba Microstructure Line No. 5, 1987, p. 1.

[35] Carlo Erba Microstructure Line No. 19, 1987, p. 2.

[36] M. Schulze, E. Gülzow, K. Bolwin, W. Schnurnberger, Fresenius J. Anal. Chem. 353 (1995) 778.

[37] M. Schulze, A. Schneider, E. Gülzow, Alteration of the distribution of the platinum catalyst in membrane–electrode assemblies during PEFC operation, in: Proceedings of 8th UECT, 20–21 June 2002, Ulm, Germany.

[38] P. Staiti, A.S. Arico, V. Antonucci, S. Hocevar, J. Power Sources 70 (1998) 91.

[39] E. Gülzow, T. Kaz, J. Power Sources 106 (2002) 122.

[40] J.M. Rheaume, B. Müller, M. Schulze, J. Power Sources 76 (1998) 60.

[41] M. Schulze, M. Lorenz, T. Kaz, XPS study of electrodes formed from a mixture of carbon black and PTFE powder, Surf. Interface Anal. 34 (2002) 646.

[42] R. Reissner, B. Thoben, T. Kaz, M. Schulze, E. Gülzow, Degradation of the hydrophobicity of fuel cell electrodes, in: Proceedings of the 8th UECT, 20–21 June 2002, Ulm, Germany.

[43] N. Wagner, J. Appl. Electrochem. 32 (2002) 859.