

Investigation of structure and ORR reactivity of fuel cell catalysts by in-situ STM

R. Hiesgen · D. Eberhardt · E. Aleksandrova ·
K. A. Friedrich

Received: 10 November 2006 / Revised: 14 August 2008 / Accepted: 20 August 2008 / Published online: 9 September 2007
© Springer Science+Business Media B.V. 2007

Abstract In order to provide insight into the interfacial relationships at fuel cell electrodes, a measuring technique based on a scanning tunneling microscope working in an electrochemical cell has been developed. The structure of model electrodes consisting of carbon supported Pt and ionomer mixtures as well as MEA electrode surfaces is imaged by the electrochemical scanning tunneling microscope (EC-STM) from microscale to nanoscale. Images with subnanometer resolution are obtained indicating that some ordering of the particles on the carbon support is present in the model system and in the MEA. It is demonstrated that in both cases nanometer structures can be imaged reliably and that the interface is rather clean and active under reaction conditions. In addition, a technique has been developed to measure the local reactivity by using the STM tip as a sensor electrode for the ORR.

Keywords Electrochemical scanning tunnelling microscopy · Platinum nanoparticles · Fuel cell · Reactivity · Oxygen

1 Introduction

To become commercially viable, polymer electrolyte fuel cells (PEFC) have to overcome the barrier of high catalyst costs caused by the use of platinum and platinum-based catalyst in the fuel cell electrodes. The electrodes have a complex structure: the porous electrodes typically consist of the catalyst, most often platinum nanoparticles, in most cases supported on carbon particles, and mixed with ionomer (e.g. Nafion). The reaction is assumed to take place at the three-phase boundary. However, the detailed surface structure like the real space distribution of the catalyst on the surface and the extension of covering of the carbon surface with catalyst particles, as well as details of the structure/activity relationship of the electrode remain largely unknown.

Recently research on the proton exchange membrane fuel cell (PEMFC) has focused on improving the catalytic activity of the cathode electrocatalysts, where the oxygen reduction reaction (ORR) occurs. Although a huge variety of catalysts have been investigated, so far Pt-based catalysts are the best material for oxygen reduction. However, at relatively low temperatures typical for PEMFC applications, the strong kinetic inhibition of the cathodic ORR leads to a high overpotential, amounting to several hundreds of millivolts. Therefore, the slow ORR kinetics is one of the limiting factors in the energy conversion efficiency of PEMFCs [1, 2].

The reactivity of a catalyst particle is not only determined by the composition of the particle but also by their size, structure and surroundings. Up to now the optimum composition, nanostructure and size of catalyst particles for the ORR is still unclear. Numerous groups have observed improved kinetics of the ORR when platinum is alloyed with other transition metals, typically the 3d transition

R. Hiesgen (✉) · D. Eberhardt
Hochschule Esslingen, Kanalstr. 33, 73728 Esslingen, Germany
e-mail: Renate.Hiesgen@hs-esslingen.de

E. Aleksandrova
Institut für Physikalische Chemie, Universität Stuttgart,
Pfaffenwaldring 55, 70569 Stuttgart, Germany

K. A. Friedrich
Institut für Technische Thermodynamik, Deutsches Zentrum für
Luft- und Raumfahrt, Pfaffenwaldring 38-40, 70569 Stuttgart,
Germany

metals like Cr, Co, Ni, Fe [3, 4]. The improved kinetics of the ORR in these alloys has been attributed to geometric and electronic changes such as shorter Pt–Pt bonds and increased d-band vacancies that are brought about when Pt is alloyed. Other factors such as surface roughening by electrochemical dissolution of transition metals have also been proposed as reasons for the observed increase in the kinetics of the ORR [5]. Another aspect is the high price of noble metals which makes it desirable to look for platinum-free catalysts with comparable activity.

Important factors which may influence the local ORR activity are the surface structure, the size and distribution of the catalyst particles on their support, the coverage of the carbon support and the nature of active sites on the catalyst [6]. Therefore it is necessary to obtain information about the local reactivity in addition to the investigation of the structure with a high resolution.

It is preferable to perform the investigation under conditions which are at least to some extent comparable to the situation in a working fuel cell, i.e. in a humid environment and during electrochemical reactions. Since the structure of a real electrode found in a membrane electrode assembly (MEA) is complicated, different aspects of the components of an electrode, especially the catalyst, have been investigated mostly as model systems i.e. with spectroscopic techniques and scanning probe methods [7–10].

Another important research activity in fuel cell development is improvement of the polymer electrolyte membrane (PEM). The currently well-developed PEM fuel cell technology is based on perfluorosulfonic acid (PFSA) polymer membranes as electrolyte [11]. The critical features of the membrane in PEM fuel cells are high protonic conductivity, low permeability to reactants, low electronic conductivity, chemical stability and good mechanical properties. Nafion membranes are widely used and accepted as the industry standard [12, 13].

Scanning tunneling microscopy has been established as a method for characterizing surface structures down to the nanometer scale in real space [14]. It has the advantage to work under vacuum conditions as well as in ambient air and in an electrochemical cell under potentiostatic control of tip and sample. In addition to the surface information, a variety of different properties have been measured including electronic [15] and electrochemical properties [16]. A measuring technique based on an EC-STM therefore has the potential to give insight into the structure of even complex composite materials like fuel cell electrodes and to provide details of the structure-reactivity correlation on the nanometer scale [9]. In many respects the present approach of using STM for fuel cells components has similarities to a scanning electrochemical microscope (SECM) approach as electrochemical reactions are

involved in the imaging. SECM has been pioneered by Bard and his group [17].

In this study we want to demonstrate the possibilities of STM measurements of fuel cell electrode components. Although the imaging mechanisms of complex fuel cell relevant systems are not fully understood it is obvious from the measurements that useful information about structure and reactivity can be derived. In particular, we have investigated the structure of a Nafion layer with pure ionic conductivity as well as of a model electrode composed of carbon-supported platinum catalyst and Nafion, and of the electrode on a real MEA in a fuel cell configuration with a mixed electronic/ionic conductivity. All samples are measured in the presence of electrochemical reactions. In addition, we present a method using the in-situ STM to investigate the local reactivity of a catalyst sample concerning the oxygen reduction reaction.

2 Experimental

The experiments were performed using a commercial STM (Nanoscope III, Digital Instruments, Santa Barbara, USA) equipped with an electrochemical cell and a bipotentiostat. An oxidized gold wire ($E = 1200 \text{ mV}_{\text{RHE}}$) or a platinum wire ($E = 750 \text{ mV}_{\text{RHE}}$) was used as reference electrode. A platinum wire served as counter electrode. All potentials quoted are given with respect to the reversible hydrogen electrode scale (RHE). As tunnelling tips electrochemically etched Pt:Ir (80:20) wires or gold wires were used and the tips were insulated with an electrochemically applied lacquer or with Apiezon[®] wax in order to minimise Faradaic currents. Without potentiostatic control a voltage was applied to the sample holder with respect to the STM tip. The tunnelling current used for imaging was always in the order of 1 nA.

2.1 Sample preparation

The model electrodes consisted of a thin catalyst containing layer deposited on a suitable substrate like flame annealed gold film on glass (with gold (111) orientation) or highly orientated pyrolytic graphite (HOPG). A thin catalyst layer was prepared by suspending a fine powdered catalyst sample in a solution of Nafion (Fluka) using an ultrasonic bath and dripping the suspension onto the substrate. Afterwards, the samples were annealed for a few minutes at about 80 °C. After evaporation of the solvent the catalyst sample was ready for use. The Nafion layers were prepared in the same way without adding catalyst powder.

The electrodes at the membrane electrode assemblies (MEA) used were prepared by a dry layer technique at the Institute for Technical Thermodynamics of the German Aerospace Centre (DLR), Stuttgart [18]. They are based on Nafion[®] 112 membranes and have differently composed electrodes.

2.2 Electrochemical measurements

All measurements were carried out at room temperature in an aqueous solution of 0.1 M sulphuric acid prepared with supra pure sulphuric acid (Merck) and Milli-Q[®] water in the electrochemical cell of the STM. If not otherwise stated, the measurements were performed under potentiostatic control of STM tip and sample.

For the reactivity measurement small lithography programs (Nanoscope III software) were used to control the potentials of the tunnelling tip and the sample electrode as well as the distance between tunnelling tip and sample surface. The measurements were recorded with a data acquisition device from National Instruments (*PCI-6035E*) by a second computer.

3 Results and discussion

3.1 Structure investigation of Nafion

As ionically conductive component in the electrode Nafion[®] from DuPont was used. This is a perfluorinated polymer with perfluorosulfonic acid side groups. The anions (SO_3^-) are tethered to the polymer and the cations (H^+ , Na^+) are mobile and solvated by water.

In the STM images the different parts of the composite electrode material can only be separated by their structure. In order to distinguish the catalyst particles, the carbon support, and the ionically conducting phase from each other a pure thin Nafion[®] layer without additional components was prepared. For that reason a pure Nafion[®] film subjected to a heat treatment equivalent to that used in fuel cell electrodes was prepared on HOPG and investigated in dilute sulphuric acid.

The measurements were performed in an electrochemical cell in which potentials of tip and HOPG were controlled by a potentiostat. The potential difference used was 100 mV with the tip at the more positive potential ($E_{(\text{substrate})} = +0.3$ V (RHE), $E_{(\text{tip})} = +0.4$ V (RHE)). In an oxygen containing electrolyte oxygen reduction takes place at both tip and substrate electrodes. Since imaging was not possible in the dry state electrochemical reactions must be involved. The high lateral resolution can only be explained by a tunnelling current between tip and Nafion surface. Nafion has a

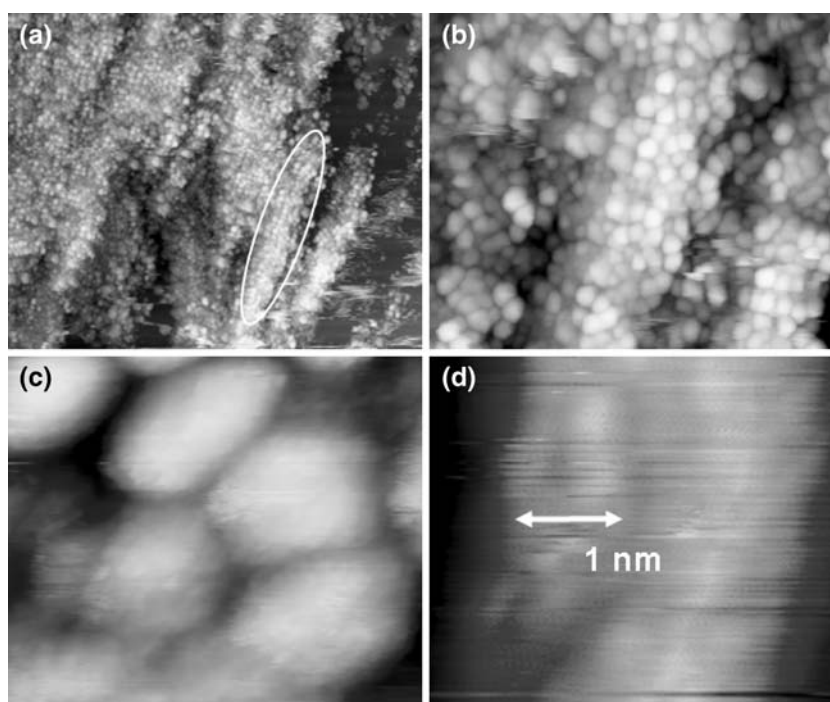
negligible electronic conductivity but is a good ionic conductor. The Nafion[®] films are much thicker than the tunnelling distance and therefore the observed currents can only be explained by a combination of tunnelling with ionic currents involving electrochemical reactions. The imaging mechanism is not understood in detail and has led to some controversy in the literature [17]. However, it is clear that high resolution images of Nafion[®] surfaces can be obtained and be interpreted regarding structural information.

The STM images in Fig. 1 reveal a structured film showing an anisotropic rod-like structure at lower resolution. Zooming with STM into one of these rods at the marked area reveals the images shown in Fig. 1b and c. Here, a substructure consisting of circular globules with a size in the order of 6–8 nm is visible. Similar structures have been detected on Nafion[®] films coated onto mica in humid environment [17]. In this study the Nafion film has been measured in liquid, whereas the other measurements have been performed only under humid conditions. Since the sample is imaged in the electrochemical cell and is embedded in electrolyte solution, the visible outer parts of the Nafion are hydrophilic surfaces. Hydrophobic parts on the surface can not be imaged by the tip due to the absence of ionic conductivity. Inside the globules brighter spots can be seen in Fig. 1c and d. They have a distance of 0.5–1 nm. The STM method shows bright spots when the current becomes larger or the surface exhibits an elevation. We interpret the bright spots as the sites of SO_3^- groups where the proton assisted electronic current is larger. The distance of about 0.5 nm between the SO_3^- groups is roughly the same value as reported in the literature [17, 19]. The STM images are consistent with the ionic cluster model for the hydrophilic regions of Nafion[®] at a humidity of 100%, but a detailed interpretation requires better understanding of the imaging process.

3.2 Structure of model electrodes on gold

In Fig. 2 the surface of a model electrode deposited onto a flame annealed gold sample is shown. The measurement was also performed by STM in sulphuric acid under potential control. The electrode was composed of a carbon supported commercial fuel cell catalyst with 40 wt.% Pt with a particle size of 1–2 nm diameter mixed with Nafion[®]. The STM measurement was performed directly after preparation of the catalyst layer to avoid ageing processes. The Pt particles are distributed on the surface of the larger carbon particles from the support, which have a diameter of 10 nm–15 nm. Here, the distribution and arrangement of catalyst particles on the surface can be studied directly, whereas in TEM measurements this information is not readily available. It can be seen that the

Fig. 1 STM image of an annealed Nafion layer on graphite (HOGP) in $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ $E_{(\text{Nafion})} = +0.3 \text{ V}$ (RHE), $E_{(\text{tip})} = +0.4 \text{ V}$ (RHE) (a) image size $500 \times 500 \text{ nm}$, (b) detail of one globule, image size $140 \text{ nm} \times 120 \text{ nm}$, (c) globules with internal structure, image size $12 \text{ nm} \times 10.6 \text{ nm}$, (d) image size $5 \text{ nm} \times 4.3 \text{ nm}$



particles are not randomly arranged on the surface but form somewhat ordered structures at certain sites. A preference for chain formation of particles as well as for hexagonal structures is observed. However, a separation of the particles is discerned in the images so that full agglomeration can be excluded. This ordering may be caused by preferable docking sites on the carbon or be a consequence of particle-particle interactions which may lead to further agglomeration after some time. Coverage of the carbon surface with catalyst particles is incomplete, a fact that has also been found in the other measurements made on electrodes but containing different catalysts.

In Fig. 3 the surface structure of the same catalyst but after storage of the dispersion for about 2 weeks under

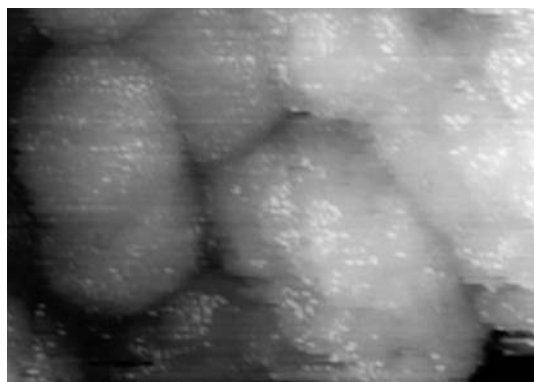


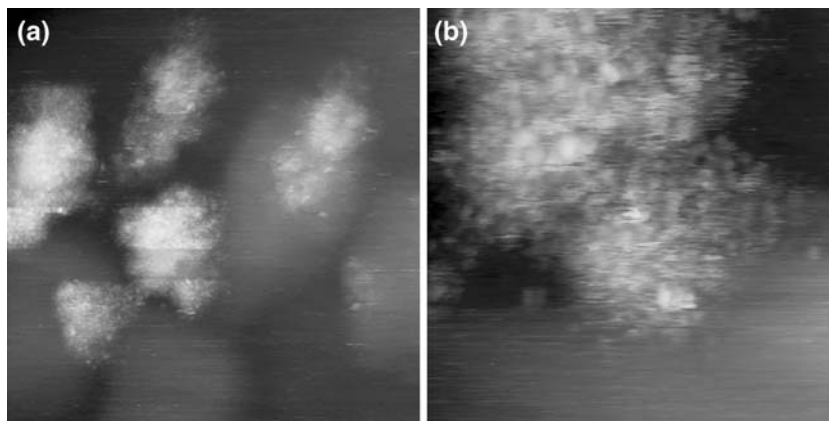
Fig. 2 STM image of a commercial Pt/C catalyst with Nafion on gold in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, $E_{(\text{Nafion})} = +0.3 \text{ V}$ (RHE), $E_{(\text{tip})} = +0.4 \text{ V}$ (RHE), image size $40 \times 30 \text{ nm}$

ambient conditions before preparation of the catalyst layer is shown. Thus, this procedure is representative of ageing of the dispersion and not of fuel cell operation. It is well known that catalyst dispersions and slurries are prone to fast ageing. In the STM image differently shaped platinum crystals of about 5–8 nm diameter are visible. Although, the overall shape of the crystals is clearly detected, i.e. a triangle crystal in the lower left corner in Fig. 3a, the surface of the crystals does not show a perfect atomic crystal structure but has a granular substructure with a size of 1–2 nm (Fig. 3b). Probably, the primary 1–2 nm large Pt particles from the fresh solution have formed larger agglomerates. In addition, these surfaces must be partly oxidized. The growth of the platinum particles decreases the efficiency of the catalyst by loss of platinum surface. This effect has been studied by Gasteiger et al. in fuel cells working under different conditions [20]. The authors conclude that the loss of the platinum surface in combination with carbon oxidation of the support is the most important factor limiting the long term stability of a fuel cell.

3.3 Electrodes on membrane electrode assemblies (MEA)

Besides the surface structure of model electrodes real membrane electrode assemblies (MEA) have also been imaged by STM. Similar to the case of Nafion[®], STM measurements of the upper electrode surface of a MEA surface are only possible in solution or under quite humid

Fig. 3 STM image of a commercial Pt/C catalyst with Nafion on gold in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ after storing the catalyst solution for about 2 weeks, $E_{(\text{catalyst})} = +0.3 \text{ V (RHE)}$, $E_{(\text{tip})} = +0.4 \text{ V (RHE)}$, (a) image size $40 \times 40 \text{ nm}$, (b) detail of one crystal, image size $10 \text{ nm} \times 10 \text{ nm}$



conditions. When imaging a MEA, the upper electrode does not have a direct electronic contact to the lower Pt containing electrode which is in contact to the voltage biased sample holder. It is connected to the ionically conductive Nafion membrane, which thereby has electronic contact to the sample holder. Therefore electrochemical reactions supporting the tunnelling current of about 1 nA need to take place at the upper and lower interface of the Nafion membrane with ionic transport of the current in-between. Figure 4 shows a scheme of the sample in the cell having a fuel cell configuration. The measurements on the MEAs were performed in electrolyte but without potentiostatic control. Current flow is observed when the negative voltage applied to the lower electrode (in contact with the sample holder) against the STM tip exceeds about 100 mV . Due to the significant higher resistance of the tunneling gap compared to the membrane, the voltage drop between the lower and upper electrode on both sides of the membrane is small and most of the voltage drop is located between upper electrode and the tip. Although the natures of the reactions are not controlled in this arrangement we assume that oxygen reactions take place due to the presence of oxygen in the environment. Following this argument at the lower electrode, having a slightly more negative potential compared to the upper electrode, a net oxygen reduction reaction is expected resulting in a net proton current through the Nafion membrane. Due to the closed current circuit and the fixed bias voltage between upper electrode and tip, normal electrochemical STM tunneling images can be obtained. An STM image on an area of $100 \text{ nm} \times 100 \text{ nm}$ of an electrode from an MEA is given in Fig. 5. The electrode is composed of carbon supported platinum catalyst without the addition of Nafion[®]. The image was measured directly after preparation of the MEA and without working in a fuel cell. The elliptical carbon particles are clearly visible and have a diameter of about 10 nm . On the surface of the carbon the individual platinum catalyst particles are visible. They have a diameter of about $1\text{--}2 \text{ nm}$. Their distribution on the

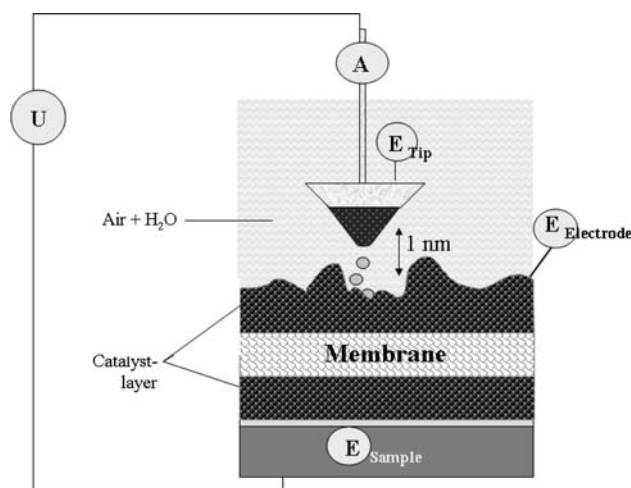


Fig. 4 In-situ method for imaging of the membrane electrode assembly using an electrochemical STM



Fig. 5 STM image of one electrode of a membrane electrode (MEA) with carbon supported Pt 1 mg cm^{-2} catalyst in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, $U = -0.1 \text{ V}$, $I_{(\text{tip})} = 1 \text{ nA}$, image size $100 \text{ nm} \times 100 \text{ nm}$

surface can be directly seen and is similar to the distribution found on the carbon surface of the model electrode. Also here, the carbon surface is not fully covered with catalyst particles. They are also not randomly distributed, but some ordering is visible. This non-random distribution is already present before exposing the MEA to the electrolyte. We can conclude that this ordering is a property of the catalyst and is not associated with electrochemical ageing. It might be caused by particle-particle interactions. The similarities between both surfaces, the model electrode and the MEA electrode, give some confidence that these measurements represent the typical distribution of a freshly prepared electrode surface.

Figure 6 shows an area of 15 nm by 15 nm of the surface of the electrode of a differently prepared MEA, composed of Pt black and Nafion[®] (30%) without carbon. An individual platinum catalyst crystal with a diameter of about 5 nm is visible and marked in the image. The image shows the existence of a subnanometer structure. Although, a detailed interpretation is difficult, in the marked area which may show a crystallite, nine bright spots, two appearing as double spots, are visible, which have a separation of about 0.7–0.3 nm. Other single bright spots can also be seen at other sites on the surface. The nature of these bright spots cannot be determined from the picture. However, in STM images bright areas indicate a higher current flow. It is obvious that an unprecedented high resolution is observed for such complex and rough surfaces. A detailed interpretation regarding surface structure requires further investigation.

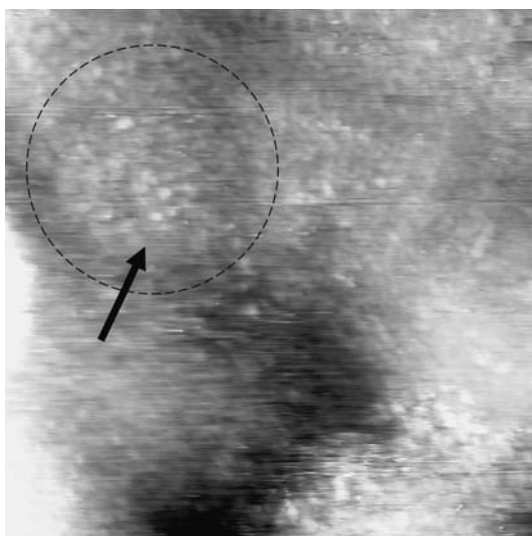


Fig. 6 STM image of one electrode of a membrane electrode (MEA) with 1 mg cm^{-2} Pt black catalyst and Nafion (30%) in 0.1 mol L^{-1} H_2SO_4 , $U = -0.4 \text{ V}$, $I_{(\text{tip})} = 0.5 \text{ nA}$, image size $15 \text{ nm} \times 15 \text{ nm}$

3.4 Reactivity measurements

The diffusion limited current or the current at a fixed potential can be used as a measure for the oxygen concentration under otherwise fixed conditions. Here, the reactivity of a catalyst on the sample should be investigated due to its reactivity for the oxygen reduction reaction. For this purpose, the STM tip was used as an electrochemical sensor for oxygen and the current through the STM tip during oxygen reduction was measured. The measurement of the local reactivity of a catalyst sample for oxygen reduction by STM starts with recording a topographic image (Fig. 7a). After positioning the tunnelling tip over a selected area on the catalyst sample the feedback control was switched off and the tip was moved up some nanometers (Fig. 7b). The total measurement included two separate current measurements under the same conditions. At the beginning of each measurement, the potential of the tunnelling tip was increased for a short time until a defined quantity of oxygen was generated electrochemically. During the oxygen evolution oxidation of the tip metal surface takes place (Fig. 7c). The diffusion of the generated oxygen into the solution forms a spatially restricted area of high concentration around the tunnelling tip. After reduction of the tip metal the tunnelling tip serves as a sensor electrode for oxygen. Now the reactivity measurements can be performed with two consecutive measurements: First, in order to obtain a baseline sensor signal the potential of the tip is switched into the oxygen reduction potential region. Consequently, the reduction of the previously generated oxygen takes place. As long as the potential at the sample electrode is not changed the current through the tunnelling tip decreases slowly because of the diffusion of oxygen into the solution away from the tip and due to oxygen reduction at the tip. In the second measurement the sample electrode potential is also set to the oxygen reduction potential causing an additional reduction of oxygen at the sample electrode. Near surface active areas the oxygen concentration is reduced and the oxygen reduction current through the tip decreases clearly in comparison to passive areas (Fig. 7d, e). At the end of the measurement cycle the potentials are set to the original values, the tunnelling tip is approached to the surface, and the automatic control is switched on again. The difference current between both measurements is taken as a relative measure for the reactivity of the catalyst sample for oxygen reduction at the sample.

As a model sample a Pt foil was used. Both current measurements and the resulting difference current are demonstrated in Fig. 8. At $t = 4.5 \text{ s}$ on the time axis the potential of the tip was set to oxygen reduction and after a capacitive current peak the upper curve shows a steady current decrease (region “A”) caused by the diffusion of

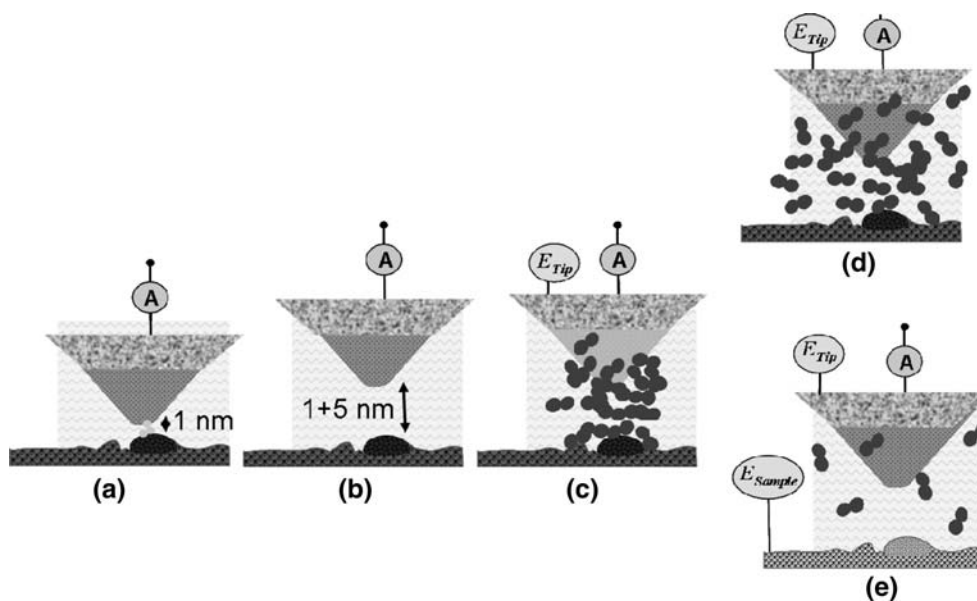


Fig. 7 Principle of the method for determining the reactivity of a sample concerning the oxygen reduction reaction: (a) tunnelling increase of distance; (b) increase of gap-no more tunnelling current;

(c) evolution of oxygen at the tip; (d) measurement of the resulting oxygen concentration by the tip during reduction of oxygen at the sample with inactive catalyst, and (e) with active catalyst

oxygen away from the tip region. The diffusion is rather slow because the system resembles a thin film cell with a small gap between sample and tip. The two rough surfaces of tip and Pt foil hinder diffusion. This curve was measured without reduction of oxygen at the sample. The second measurement started in the same way. In addition, the potential of the catalyst sample was also set to oxygen reduction. In Fig. 8 this measurement is shown in the lower curve and the reduction starts at $t = 6\text{ s}$ (region “B”). The steep decrease of the lower current curve is caused by the immediate decrease of the oxygen concentration close to the tip caused by oxygen reduction at the catalyst sample. After switching off the reduction and returning it to its former potential value at $t = 8.5\text{ s}$ the concentration of oxygen rises again due to back diffusion from the surrounding solution. The difference current between the upper and lower curve is attributed to the reduction of oxygen at the platinum foil and is shown in the inset of Fig. 8.

In Fig. 9 the difference currents for 3 different catalyst test samples are given. The dotted line marks the maximum possible difference current assuming an immediate decrease of the oxygen concentration to zero. This would lead to a vertical slope of the difference current. Therefore, the slope of the difference current, as well as the resulting maximum current height can be used as a (relative) measure for the reactivity under otherwise constant conditions.

The upper curve has been measured with a commercial Pt/C (40 wt.%) catalyst and its reactivity is superior to that of a Pt foil measured under the same conditions visible in the curve below, although the current was not normalized

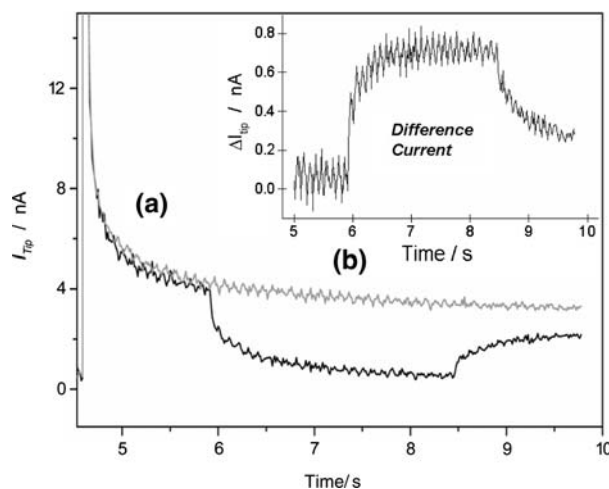


Fig. 8 Current through the STM tip after oxygen evolution at the tip without oxygen reduction (upper curve) and with oxygen reduction (lower curve) at a Pt foil. Time interval “A”: reduction of oxygen at the tip, time interval “B”: reduction of oxygen at the tip and at the sample (Pt foil)

to the free platinum surface. The lowest curve shows the signal recorded at a pure gold surface with no significant reactivity for oxygen reduction under these conditions.

The major aim of this novel method is to correlate the structure and the reactivity of a catalyst. For this goal, the lateral resolution of the reactivity measurement should be as high as possible. An estimation of the actual lateral resolution for an inhomogeneously coated sample leads to a value of about a micrometer. An increase in the lateral resolution is possible by leaving out the evolution of oxygen at the tip. In

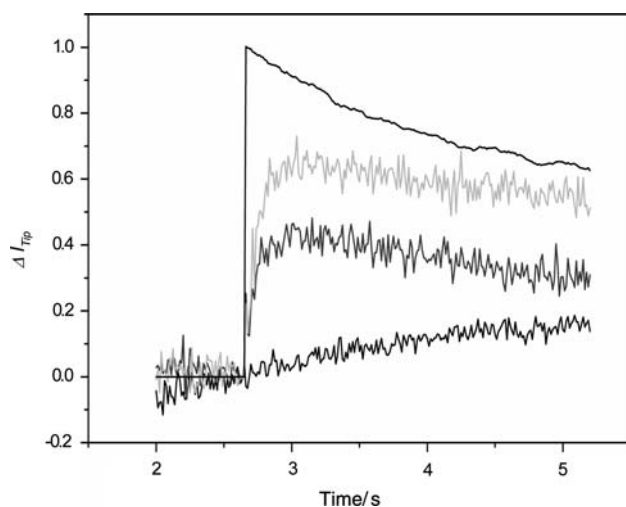


Fig. 9 Difference current between current through STM tip with and without reduction of oxygen at the sample (bottom to top) for a Au ($E_{(Sample)} = +0.2$ V (RHE)), Pt foil ($E_{(Sample)} = +0.3$ V (RHE)), and gold/glass with Pt/C (40 wt.%) catalyst with Nafion ($E_{(Sample)} = +0.3$ V (RHE)), thin black line: maximum possible difference current

this case a high and constant oxygen concentration in the solution is needed. Under these conditions shorter time intervals during the measurement steps can be applied. The local change in the oxygen concentration is constricted to a smaller area. Thereby the lateral resolution of the reactivity measurement can be reduced by one order of magnitude which has already been demonstrated.

4 Summary and conclusion

By using a STM working in an electrochemical cell not only the complex material of a fuel cell electrode with its mixed electronic and ionic conductivity can be imaged, but also the electrodes of complete MEAs. For all samples, and especially in the latter case, the current is not solely due to the flow of electrons but also of protons and imaging is only possible while electrochemical reactions are taking place at the interfaces. Consequently, the investigations are only possible under quite humid conditions or in-situ in an electrochemical cell. The imaging conditions and therefore the properties of the catalyst surface are, to some extent, comparable to the situation in a working fuel cell. The STM images indicate a degree of ordering of the platinum nanoparticles on the carbon support surface even on freshly prepared samples both on model electrodes as well as MEA electrodes. In addition, incomplete coverage of the carbon surface with catalyst has been found. Although ambient conditions are present, a subnanometer resolution of the surface is observed. Bright atomic spots at the corner of a platinum particle have been imaged and may be associated to electrochemically more reactive sites.

Pure Nafion® as an ionic conductor has also been investigated and its structure in an environment close to the conditions in a working fuel cell has been visualized. The results from the in-situ STM measurements fit well to the structure model of ionic clusters given in the literature. It has also been shown that the relative reactivity concerning the oxygen reduction can be measured using the STM tip as an electrochemical sensor. Further measurements using the measuring technique with increased lateral resolution will be performed. Although, in this case the resolution of the reactivity measurement is below the resolution of the STM image, it is apparent that this route may yield more insight into structure–reactivity correlations.

Acknowledgements The authors gratefully acknowledge financial support by the BMBF within the network: “Efficient oxygen reduction for electrochemical energy conversion” (O₂-RedNet) and by the “Forschungsallianz Brennstoffzellen Baden-Württemberg (FABZ)”. We also thank Till Katz, DLR, ITT, Stuttgart, for providing us with the MEAs.

References

- Gottesfeld S, Zawodzinski TA (1997) In: Alkire RC, Gerischer H, Kolb DM, Tobias CW (eds) *Advances in electrochemical science and engineering*. Wiley-VCH, Weinheim, pp 195
- Paulus U, Schmidt TJ, Gasteiger HA, Behm RJ (2001) *J Electroanal Chem* 495:134
- Friedrich KA, Beck T, Garche J, Stimming U (2002) *Abstracts of Papers of the American Chemical Society* 223:U442
- Toda T, Igarashi H, Uchida H, Watanabe M (1999) *J Electrochem Soc* 146:3750
- Paffett MT, Beery JG, Gottesfeld S (1988) *J Electrochem Soc* 135:1431
- Friedrich KA, Geysers KP, Dickinson AJ, Stimming U (2002) *J Electroanal Chem* 524:261–272
- Collins JA, Stimming U (2003) In: Wieckowski A, Savinova ER, Vayenas GG (eds) *Catalyst and electrocatalysis at nanoparticle surfaces*. Marcel Dekker, Inc, New York
- Dickinson AJ, Carrette LPL, Collins JA, Friedrich KA, Stimming U (2002) *Electrochim Acta* 47:3733
- Kibler LA, Kolb DM (2002) In: Vielstich W, Lamm A, Gasteiger H (eds) *Handbook of fuel cell technology*. Wiley, Chichester
- Bönemann H, Nagabhushana KS (2004) *Encyclopedia Nanosci Nanotechnol* 1:739
- Savadogo O (1998) *J New Mat Electrochem Systems* 1:47
- Hickner MA, Pivovar BS (2005) *Fuel cells* 5:213
- Barbir F (2005) *PEM Fuel cells: theory and practice*. Elsevier Academic Press
- Meier J, Friedrich KA, Stimming U (2002) *Faraday Discuss* 121:365
- Hiesgen R, Meissner D (1997) *Electrochim Acta* 42:2881
- Hiesgen R, Eberhardt D, Meissner D (2005) *Surf Sci* 597(1–3):80
- Fan FR, Bard A (1995) *Science* 270:1851
- Gülzow E, Schulze M, Wagner N, Kaz T, Reissner R, Steinhilber G, Schneider A (2000) *J Power Sources* 86:352
- Kreuer KD (2001) *J Memb Sci* 185:29
- Ferreira PJ, Ola GJ', Shao-Horn Y, Morgan D, Makharia R, Kocha S, Gasteiger HA (2005) *J Electrochem Soc* 152A:2256