J Appl Electrochem (2010) 40:877–883
DOI 10.1007/s10800-009-9919-x

ORIGINAL PAPER

The use of in situ X-ray absorption spectroscopy in applied fuel cell research

Virginie Croze · Frank Ettingshausen ·
Julia Melke · Matthias Soehn ·
Dominic Stuermer · Christina Roth

Received: 13 November 2008 / Accepted: 27 April 2009 / Published online: 13 May 2009

Abstract For a detailed understanding and systematic optimization of fuel cell systems, in situ studies are an indispensable tool, as they provide information on the catalyst structure in different operation conditions. X-ray absorption spectroscopy (XAS) is in particular suitable for *operando* investigations, since it does not require ultra high vacuum conditions or long-range order in the sample. Furthermore, it provides in situ information on oxidation state, adsorbed species and catalyst structure, and thus complements ex situ information, e.g. from X-ray diffraction (structure), X-ray photoelectron spectroscopy (oxidation state) and FTIR (adsorbates) nicely. In a spectroelectrochemistry experiment, XAS can be combined with different electrochemical techniques in order to satisfy different needs and scientific aims. Spectra of both a Pt–Ru anode catalyst and a Pt–Co cathode catalyst were recorded at different potentials, while measuring the current-potential characteristics of a single cell. So-called half-cell measurements, where the former fuel cell cathode was used with hydrogen as the reference electrode, were performed in water and ethanol to obtain a more detailed mechanistic insight into the ethanol electrooxidation. From a more industrial point of view, different catalysts were tested with a fast potential cycling protocol simulating rapid load changes in a vehicle.

Keywords In situ · Fuel cells · X-ray absorption spectroscopy · Spectroelectrochemistry · Operando

1 Introduction

Fuel cells are assumed to become a major component in tomorrow's energy economy, as they offer the attractive perspective of efficient and clean energy conversion. High and intermediate temperature fuel cells will be used in stationary applications, while low temperature fuel cell systems are expected to provide solutions in the mobile and portable market segment. Among the main obstacles so far preventing the rapid market-introduction of low temperature proton exchange membrane fuel cells (PEMFC) are their high cost and poor durability [1]. Nowadays, platinum is the catalyst material used at both the anode and the cathode side, and, unfortunately, high platinum loadings are needed to speed up the sluggish oxygen reduction reaction (ORR) contributing to the high cost of fuel cell systems [2]. A lot of effort has been spent on replacing Pt by less expensive, non-precious metal alternatives [3–5], but so far largely to no avail. Moreover, although platinum is comparatively stable in the harsh conditions of a PEMFC, still a not negligible fraction of the platinum is leached out off the electrode and dragged into the membrane [6–9]. There it can re-precipitate and form huge crystals, which are no longer active in catalyzing the electrode reactions and thus lost for the fuel cell performance. Less noble metals, which are often applied as co-catalysts, e.g. Ru in the anode, are expected to show even less stability during long-term operation [10, 11].

V. Croze · F. Ettingshausen · D. Stuermer · C. Roth (✉)
Renewable Energies, Institute for Materials Science,
TU Darmstadt, Petersenstr. 23, 64287 Darmstadt, Germany
e-mail: c_roth@tu-darmstadt.de

J. Melke
Fraunhofer Institute for Solar Energy Systems, Freiburg,
Germany

M. Soehn
Renewable Energies, Institute for Electrical Power Systems,
TU Darmstadt, Landgraf-Georg-Str. 4, 64283 Darmstadt,
Germany

From the above it is easy to conclude, that the selection of a suitable catalyst material poses one of the critical aspects of the PEM fuel cell technology. And this selection should not only be made on the basis of ex situ data, but also information on the catalyst's in situ behaviour is needed in order to closely adapt it to the real life situation. Many studies have demonstrated that the efficiencies of both the anodic and cathodic reactions are improved, when one or more transition metals are alloyed to the pure Pt catalyst [12–18]. However, the fundamental mechanisms are still not completely understood, so that a rational catalyst optimization is not yet feasible. Furthermore, in complex compositions the long-term stability of each catalyst component becomes an even more important issue in order to prevent changes in the optimum composition over operation time. In this background, novel in situ characterization techniques are required, which can be performed in an environment as close to the real operation conditions as possible (*operando* studies).

In this respect, X-ray absorption spectroscopy (XAS) comes to mind as a versatile tool, which neither requires UHV conditions, nor long-range order in the material [19]. These enviable features make it a suitable method for in situ studies of the kind of nanostructured materials, which are used in heterogeneous catalysis and electrocatalysis [20, 21]. By analysis of the extended X-ray absorption fine structure (EXAFS) in the absorption spectrum, information on the catalyst's geometric structure can be obtained expressed by the number of nearest neighbours (N) of the absorber atom and their distance (R) from it. The novel delta μ XANES approach [22, 23], which focuses on the systematic analysis of the X-ray absorption near edge structure (XANES) region, furthermore provides information about adsorbates on the catalyst surface. Accordingly, in situ information on oxidation state, adsorbates and structure can be obtained in just one experiment [19, 24], nicely complementing standard ex situ information, as obtained from, for instance, X-ray diffraction (XRD; structure), X-ray photoelectron spectroscopy (XPS; oxidation state) and Fourier-transformed infrared spectroscopy (FTIR; adsorbed species). Another advantage of the XAS technique is its flexibility. Due to the flexible beamline set-up, plenty of space is available between the first and the second ion chamber allowing for bulky equipment like a fuel cell test bench (Fig. 1). Thus, in a spectroelectrochemistry experiment, XAS can be combined with different electrochemical techniques in order to satisfy different needs and scientific aims [25]. In this respect, the design of the in situ cell plays a crucial role, which has been reported in recent work by Principi et al. [26, 27], but also in earlier publications by the Smotkin [28, 29] and Russell group [30].

In this work, three spectroelectrochemical experiments with entirely different objectives will be presented: (a) full cell measurements, in which a Pt–Ru anode catalyst and a Pt–Co cathode catalyst were tested, (b) half cell measurements to obtain a more detailed mechanistic insight into the ethanol electrooxidation reaction, and (c) fast potential jumps to simulate rapid load changes in a vehicle.

2 Experimental

2.1 Catalysts and preparation of membrane-electrode assemblies (MEA)

Commercially available carbon-supported pure Pt/C (20 wt.% Pt on Vulcan XC 72), carbon-supported Pt–Ru/C [20 wt.% Pt–Ru (1:1) on Vulcan XC 72], all purchased from E-TEK Inc., and carbon-supported Pt/C (50 wt.% Pt on

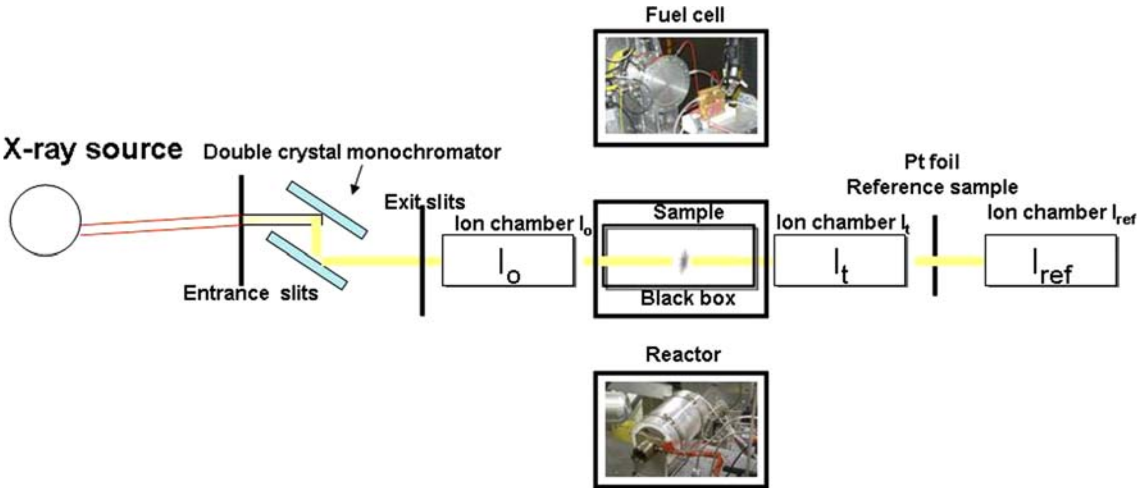


Fig. 1 Principle set-up of an X-ray absorption spectroscopy experiment underlining the flexibility of the spectroelectrochemical approach

Vulcan XC 72), purchased from Johnson Matthey were applied for the measurements. As cathode materials, Pt–Co catalysts with increasing cobalt content have been prepared in our laboratory using an impregnation method and ethylene glycol as the reducing agent in a process slightly modified to the one described in [31] (Pt–Co 3:1, Pt–Co 1:1 and Pt–Co with Co excess, 20 wt.% metal on Vulcan XC 72).

Membrane-electrode assemblies (MEA) with an active electrode area of 25 cm^2 were manufactured by an airbrush technique, assembled with 60% hydrophobized Toray® carbon paper as gas diffusion layer and mounted in a commercially available fuel cell hardware. Both electrodes were airbrushed using a catalytic ink prepared from 0.2 g of the respective catalyst mixed with 1 ml of Nafion (5 wt.% in solution, Aldrich). A metal loading of approximate 0.4 mg cm^{-2} per electrode was applied, and in all experiments Nafion©117 (DuPont) served as the proton conducting membrane.

2.2 X-ray absorption spectroscopy measurement and data processing

All experiments were carried out in transmission mode at the beamline X1 at Hasylab, Hamburg, in an energy range from $E = 11{,}300$ to 12,800 eV (Pt L_3-edge at 11,564 eV) using a thin Pt metal foil as reference. A Si(111) double-crystal monochromator was used and detuned to 50% intensity to avoid higher harmonics present in the X-ray beam. The intensities of the focused beam and the transmitted beam were detected by three gas-filled ion chambers in series. Extraction of the EXAFS data from the measured absorption spectra was either performed with the program XDAP developed by Vaarkamp [32] or using ATHENA by Ravel et al. [33]. The pre-edge was approximated by a modified Victoreen curve, and in the case of XDAP analysis the background subtracted using cubic spline routines with a continuously adjustable smooth parameter [34]. Normalization was performed by dividing the data by the height of the adsorption edge at 50 eV.

2.3 Spectroelectrochemical experiments

The idea of spectroelectrochemical experiments is to combine spectroscopy with electrochemistry in a way suitable to investigate electrocatalysts in great detail in their actual working conditions or at least close to these. However, very often the requirements necessary for the electrochemical experiment hamper the spectroscopic measurement and vice versa. A typical example of that situation is the thin layer of electrolyte needed for a good signal-to-noise ratio in an FTIR experiment in contrast to the impeded diffusion this will cause in the electrochemical experiment [35]. The combination of XAS with different electrochemical techniques is no exception from this rule [26, 27].

In fuel cell research, XAS takes advantage of three essential features: (1) no UHV needed, (2) no long-range order in the sample required, and (3) flexible experimental set-up with space for bulky equipment. This allows the design of very different experiments complying different needs and with different scientific focus. Three examples will be given here.

2.4 Current-voltage curves (*U*/*i*)

Recording the current-voltage characteristics of a fuel cell is a very straight-forward tool to test the general catalyst suitability of both the anode and the cathode catalyst. Spectra can be recorded in the activation, resistivity (Ohm) and diffusion regime and the catalyst's behaviour monitored. In the anode experiment, a commercial Pt–Ru catalyst was used, whereas in the cathode experiment an in-house synthesized Pt–Co catalyst was applied. The measurements were performed with a commercial automatic fuel cell test bench purchased from MAGNUM (Darmstadt) and specifically designed for portable use at experimental beamlines. Prior to the measurements, the fuel cell was heated to the correct working temperature and purged with nitrogen for a couple of minutes to free the hydrogen pipe from air. In hydrogen operation, 150 ml min^{-1} H_2 (N 5.0, Linde) were loaded with water in a humidifier ($T = 75$ °C) and fed into the fuel cell anode. As cathode feed, high-purity oxygen (N 4.5, Linde) was supplied at 75 ml min^{-1}. CO could be added to the fuel feed if necessary in concentrations between 75 and 150 ppm to demonstrate catalyst poisoning effects. Current-voltage curves (*U*/*i* curves) were recorded galvanostatically, and after a short equilibration period spectra were recorded at specific potentials. A photograph of the experimental set-up for operando fuel cell tests at beamline X1, HASYLAB, Hamburg is shown in Fig. 2. Figure 3a shows a current-voltage characteristics recorded during an operando measurement, while the arrows mark the potentials, at which transmission spectra were recorded.

2.5 Half-cell tests

In full cell tests, no reference electrode was used, and only the total cell potential recorded under the assumption that in H_2/O_2 operation the anode potential would stay close to 0 V. For detailed mechanistic studies, however, this method is not sufficient, and a precise potential measurement had to be introduced, which is possible by so-called half cell measurements. The electrochemical characterization is carried out in the standard fuel cell set-up but using

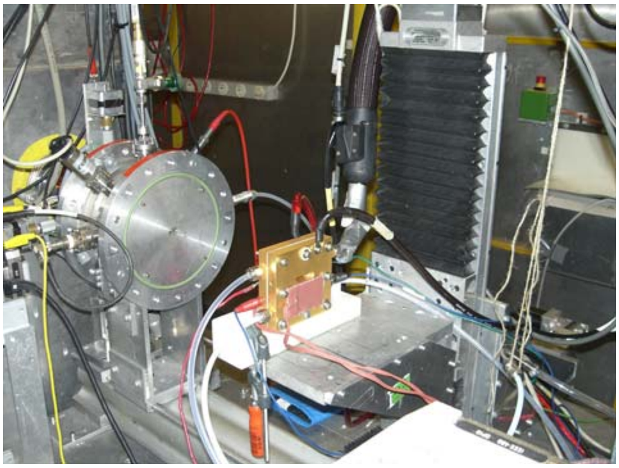
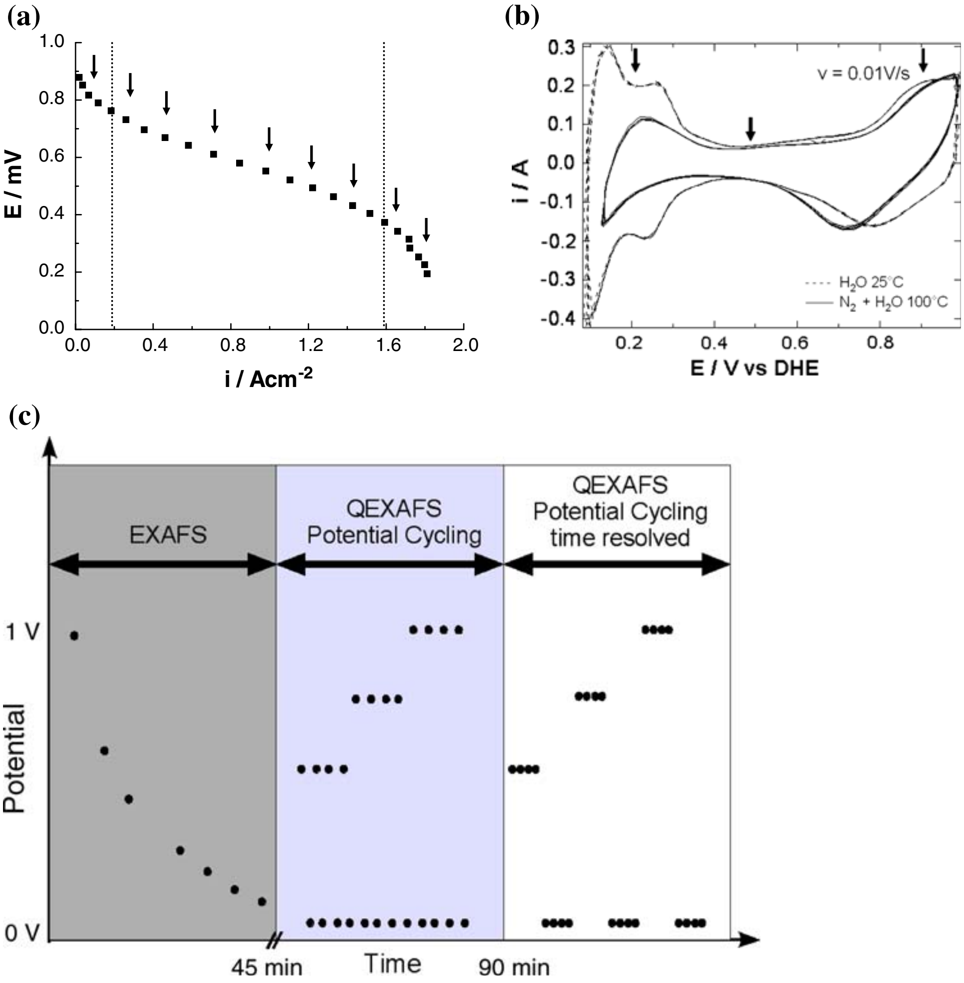


Fig. 2 Photograph of an operando fuel cell experiment at the beamline X1 at Hasylab, Hamburg; commercial single cell hardware mounted on x–y table, second ion chamber in the background

the hydrogen-fed counter electrode as a reference electrode. In this paper, the half cell characterization of the former fuel cell anode is reported, while the former cathode side is fed with hydrogen and used as reference. The former anode side was either fed with a nitrogen stream saturated with water at 80 °C or with 1.2 ml min^{-1} evaporated ethanol supported by a nitrogen gas stream to investigate the ethanol electrooxidation mechanism at carbon-supported Pt and Pt–Sn catalysts. Cyclic voltammetry measurements were obtained to investigate the catalyst's activity (Fig. 3b). Then, EXAFS spectra were recorded at several potentials in the hydrogen adsorption (H_{ad}) region [approximately 0.15 V vs. DHE (dynamic hydrogen electrode)], double layer (DL) region (approximately 0.45 V vs. DHE), and at potentials, where O(H) adsorption is visible (approximately 0.95 V vs. DHE).

From the XAS analysis, no ad-hoc conclusions can be drawn as to the nature of the adsorbed oxygen-containing species. The conventional EXAFS analysis is sensitive to the geometric structure and as such identifies Pt–O nearest neighbours. The height of the white-line gives a first indication of oxidation and/or adsorbates on the surface. However, only in delta μ XANES the electronic structure is probed, which can be used to identify adsorbates at the Pt

Fig. 3 Designs of the spectroelectrochemical experiment vary with objective; **a** current-voltage characteristics obtained in a full cell measurement, **b** voltammetric sweeps recorded in a half cell measurement with the former Pt/C fuel cell anode in water (base voltammogram), while the former cathode was used as a reference electrode, **c** example of a rapid load change protocol using the Quick EXAFS (QEXAFS) mode



surface. Two slightly shifted signals are obtained, one for an atop-adsorbed species and one for an adsorbate in a bridge-bonded or fcc site. From chemical intuition, one would call the atop-adsorbed species OH, the bridge/fcc species O. Recent literature, e.g. by Wang et al. [36, 37], provides details on potential regions, where O and/or OH exist on a Pt surface in electrochemical conditions. A transition from OH to O adsorption on Pt(111) in acidic conditions has been observed at approximate 0.8 V vs. RHE.

2.6 Potential cycle protocols

Potential cycle protocols are of increasing interest for industrial applications, since dynamic processes play an important role in ageing phenomena. Furthermore, rapid ageing protocols are being developed for industrial customers, which should simulate the actual situation in a fuel cell closely, but in a much shorter period of time. A Pt–Co cathode catalyst has been studied in dynamic operation applying a certain ageing protocol, which has been devised with an industrial partner (Fig. 3c). However, since the standard EXAFS scan lasts at least 30 min, the quick EXAFS (QEXAFS) mode at beamline X1, which allows for a much faster data acquisition in the range of seconds to minutes, is applied. In this technique, the monochromator is stepped rapidly, at the expense of a slightly downgraded signal-to-noise ratio in the obtained spectra. The protocol is composed of three parts: at first, a standard current-voltage curve is recorded and spectra obtained at several potentials. Then, rapid potential steps are applied in the following sequence: 0–400–0 mV (three times), 0–600–0 mV (three times) and 0–800–0 mV (three times). In the last part, time-dependent changes were followed closely by successively recording at least three very short QEXAFS spectra at the same potential, before jumping to a new potential. Rapid potential changes were applied between the same potentials as before, i.e. 0, 400, 600, and 800 mV.

3 Results

In full cell measurements, *U*/*i* curves were recorded and spectra taken at characteristic potentials in order to test the general suitability of catalyst materials and to compare specific features of different catalysts in an environment as close to normal operation as possible. In this background, operando XAS studies are particularly helpful, since both the catalyst structure as well as adsorbates on their surface can be investigated. For example, in a previous study two differently synthesized Pt–Ru catalysts with significantly different electrocatalytic performance were tested at the fuel cell anode, and the XAS data used to pinpoint the origin in their different activities (structure–activity correlation, [38]). Another comparatively important aspect is the changes catalysts suffer, when first put into operation [39] as compared to the slow degradation they suffer during long-term operation. For the design of tailor-made catalysts for a specific reaction, detailed knowledge on both aspects will be extremely helpful.

Figure 4 depicts the processes, which occur at a catalyst during operation, in the form of a cartoon. In the figure's upper part, a commercial Pt–Ru catalyst is shown in its as-received form, when it is put into first contact with the hydrogen feed and then into operation at 0 mV. The as-received Pt–Ru catalyst consists of a Pt core predominantly covered by an oxide-shell of the less noble, oxophilic second element. Following first contact with the anode feed, e.g. hydrogen or methanol, the oxidic ruthenium shell becomes reduced, and the metallic ruthenium is free to move towards the particle core. The operation potential then leads to the formation of an increasingly homogeneous Pt–Ru alloy. In the lower part of Fig. 4, the same depiction as a cartoon has been chosen for the morphology of the cathode catalyst particles. A home-made carbon-supported Pt–Co cathode catalyst is shown at three characteristic potentials of 0.93, 0.69, and 0.57 V. Fitting the EXAFS data, mainly Pt–Pt contributions and no Pt–Co nearest neighbours were observed indicating a very inhomogeneous alloy formation. It is assumed that Co oxide islands stick to the surface of a Pt particle core.

Analysis of the XANES region points towards adsorption of oxygen-containing groups on the platinum surface. In agreement with literature [36, 37], it is proposed that at high potentials O exists at the surface, whereas at low potentials OH is suggested. At the intermediate potential of 0.69 V the reaction proceeds fast and the Pt surface appears largely free from adsorbates within the resolution limit of this technique. Due to the adsorption process and the change in surface energy also the particle shape changes (comp. [40]), which can be seen from significant changes in the N values and which has also been indicated in Fig. 4. The detailed analysis of adsorbates at the anode side, however, is much more complex, in particular in CO-containing anode feeds. In this case, O(H), CO, and H adsorbates have to be considered and their competition for free adsorption sites followed in dependence on potential. A systematic study of the enhancement observed after Ru addition to platinum by the so-called bifunctional mechanism and the electronic effect using the delta μ XANES technique can be found in [39]. It is the first report monitoring these phenomena in a real working fuel cell.

In contrast to the results presented above, Fig. 5 shows the R and N values during half cell operation for a Pt/C catalyst to be used at the anode of a direct ethanol fuel cell (DEFC). The term ex situ here refers to the catalyst already

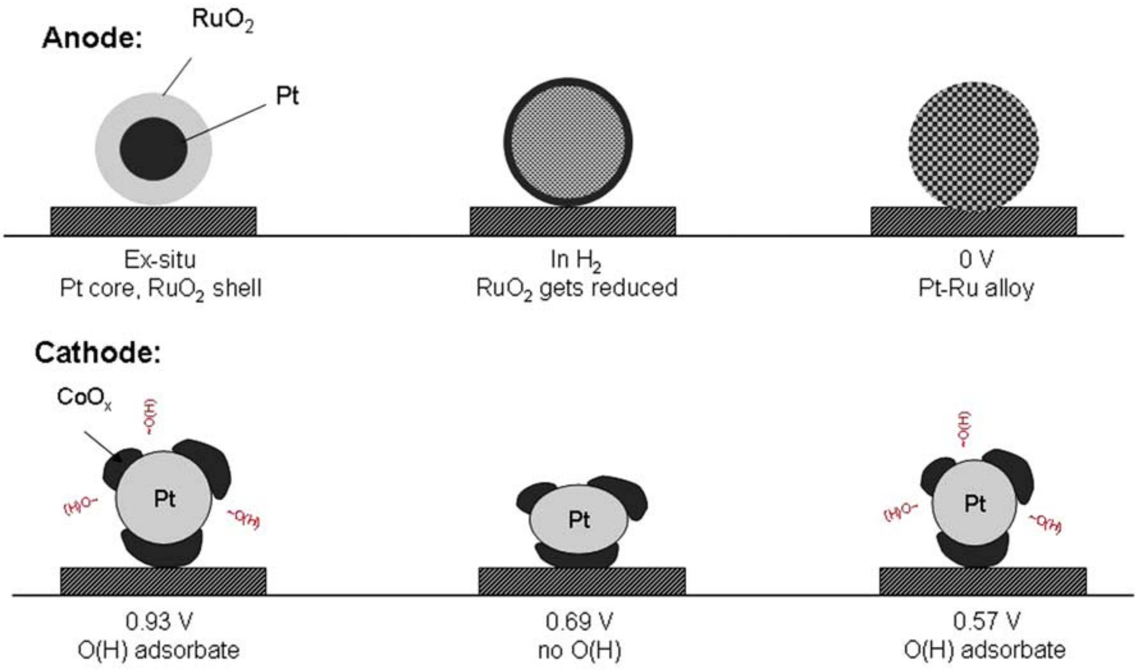


Fig. 4 Cartoons of the structure of the Pt–Ru anode catalyst (*top*) and Pt–Co cathode catalyst (*bottom*) in different operation conditions. It is suggested that at 0.93 V the cathode is covered with O in an fcc site, whereas at 0.57 V the catalyst surface is covered by OH [37]

prepared as an MEA, but before operation (no potential applied). From the EXAFS analysis, it is observed that the $N_{Pt–Pt}$ and the $N_{Pt–O}$ values vary with operation conditions, whereas the R values remain largely the same. In the ex situ measurement, $N_{Pt–O}$ is close to 2, but as soon as put into contact with hydrogen or ethanol the catalyst becomes reduced and only the Pt–Pt contribution is observed. At rather high potentials of 950 mV in the base voltammogram the catalyst becomes oxidized and a small Pt–O contribution appears in the EXAFS. In ethanol, however, this is not the case. The catalyst structure itself seems to be largely unaffected by the potential. The delta μ XANES approach has been applied to get a more detailed insight into the ethanol electrooxidation process. With this technique, different adsorbates can be distinguished and thus possible reaction mechanisms postulated. Adsorbed H, O(H) and other fragments of the ethanol oxidation may result in different signatures, and the experimentally obtained data can be compared to theoretically calculated signatures. Analysis of the data suggests the presence of significant coverage with ethanol or other intermediate species such as acetaldehyde bonded through a C atom in an atop position at all potentials between OCV and 0.95 V, and this coverage appears to be relatively constant with potential. The exact nature of the adsorbates may also be determined with the help of specific model experiments, e.g. using acetaldehyde as a fuel. More detailed investigations are on the way comparing a standard Pt/C catalyst to the more active Pt–Sn/C.

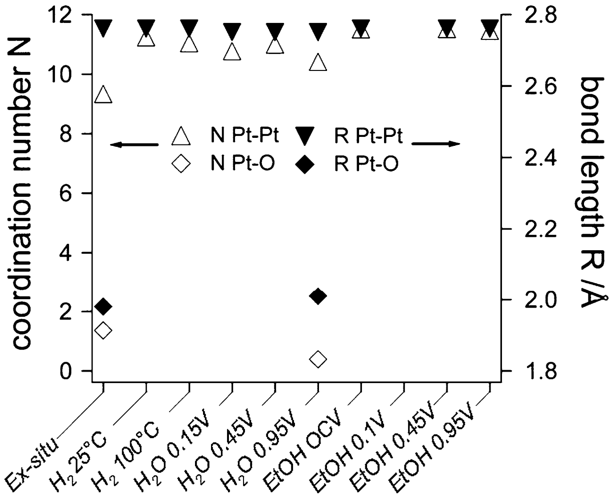


Fig. 5 Results of a half cell experiment with a carbon-supported Pt catalyst at well-defined electrode potentials; R and N values of Pt–Pt (*triangle*) and Pt–O (*diamond*) contribution are depicted

4 Conclusions

It has been shown that combining XAS with different electrochemical techniques in a spectroelectrochemical experiment is a suitable tool in fuel cell research. The electrochemical technique chosen strongly depends on the aim of the study. In full cell measurements, suitable anode and cathode catalysts can be identified and studied in an environment close to the real-life situation. In contrast, half cell measurements are chosen, if detailed mechanistic information is required and the processes have to be referred to precise potentials. Furthermore, time-resolved studies are feasible using the QEXAFS technique, by which the acquisition time for a spectrum can be reduced significantly. This set-up can help to identify degradation mechanisms and to design rapid ageing protocols closely matching reality. The above techniques have been applied to study different Pt–Ru anode catalysts and different Pt–Co cathode catalysts during their operation in PEMFC and DMFC mode. In other studies the bifunctional mechanism has been followed in a fuel cell for the first time using the delta μ XANES technique, and using this technique also the mechanism of the ethanol electrooxidation on Pt/C will be further unveiled in future studies.

Acknowledgement Thanks are due to the staff of beamline X1 at HASYLAB, Hamburg, in particular A. Webb and M. Hermann.

References

1. de Bruijn FA, Dam VAT, Janssen GJM (2008) Fuel Cells 8:3
2. He T, Kreidler E, Xiong L, Luo J, Zhong CJ (2006) J Electrochem Soc 153:A1637
3. Garsuch A, MacIntyre K, Michaud X, Stevens DA, Dahn JR (2008) J Electrochem Soc 155:B953
4. Bashyam R, Zelenay P (2006) Nature 443:63
5. Charreteur F, Jaouen F, Ruggeri S, Dodelet J-P (2008) Electrochim Acta 53:2925
6. Ferreira PJ, lao GJ, Shao-Horn Y, Morgan D, Makkharia R, Kocha S, Gasteiger HA (2005) J Electrochem Soc 152:A2256
7. Yasuda K, Taniguchi A, Akita T, Ioroi T, Siroma Z (2006) Phys Chem Chem Phys 8:746
8. Zhang J, Litteer BA, Wenbin G, Liu H, Gasteiger HA (2007) J Electrochem Soc 154:B1006
9. Kim L, Chung CG, Sung YW, Chung JS (2008) J Power Sources 183:524
10. Liang ZX, Zhao TS, Xu JB (2008) J Power Sources 185:166
11. Park GS, Pak C, Chung YS, Kim JR, Jeon WS, Lee YH, Kim K, Chang H, Seung D (2008) J Power Sources 176:484
12. Colmenares L, Wang H, Jusys Z, Jiang L, Yan S, Sun GQ, Behm RJ (2006) Electrochim Acta 52:221
13. Grgur BN, Markovic NM, Ross PN (1999) J Electrochem Soc 146:1613
14. Stamenkovic V, Grgur BN, Ross PN, Markovic NM (2005) J Electrochem Soc 152:A277
15. Maillard F, Lu G.-Q, Wieckowski A, Stimming U (2005) J Phys Chem B 109:16230
16. Long JW, Stroud RM, Swider-Lyons KE, Rolison DR (2000) J Phys Chem B 104:9772
17. Lu GJ, Cooper JS, McGinn PJ (2006) J Power Sources 161:106
18. Stevens DA, Rouleau JM, Mar RE, Atanasoski RT, Schmoeckel AK, Debe MK, Dahn JR (2007) J Electrochem Soc 154:B1211
19. Weckhuysen BM (2004) In: Weckhuysen BM (ed) In situ spectroscopy of catalysts. American Scientific Publishers, CA, USA, pp 1–10
20. Roth C, Benker N, Mazurek M, Scheiba F, Fuess H (2007) Appl Catal A 319:81
21. Russell AE, Ball SC, Maniguet S, Thompsett D (2007) J Power Sources 171:72
22. Teliska M, O'Grady WE, Ramaker DE (2005) J Phys Chem B 109:8076
23. Koningsberger DC, Oudenhuijzen MK, de Graaf J, van Bokhoven JA, Ramaker DE (2003) J Catal 216:178
24. Russell AE, Rose A (2004) Chem Rev 104:4613
25. Gale RJ (ed) (1988) Spectroelectrochemistry: theory and practice, Springer, NY, USA
26. Principi E, Di Cicco A, Witkowska A, Marassi R (2007) J Synchr Rad 14:276
27. Witkowska A, Dsoke S, Principi E, Marassi R, Di Cicco A, Rossi V (2008) J Power Sources 178:603
28. Stoupin S, Chung EH, Chattopadhyay S, Segre CU, Smotkin ES (2006) J Phys Chem B 110:9932
29. Viswanathan R, Liu R, Smotkin ES (2002) Rev Sci Instrum 73:2124
30. Wiltshire RJK, King CR, Rose A, Wells PP, Hogarth MP, Thompsett D, Russell AE (2005) Electrochim Acta 50:5208
31. Chen Z, Xu L, Li W, Waje M, Yan Y (2006) Nanotechnology 17:5254
32. Vaarkamp M, Linders JC, Koningsberger DC (1995) Physica B 208/209:159
33. Ravel B, Newville M (2005) J Synchr Rad 12:537
34. van Dorssen GE, Koningsberger DC, Ramaker DE (2002) J Phys Condens Matter 14:13529
35. Hind AR, Bhargava SK, McKinnon A (2001) Adv Colloid Interface Sci 93:91
36. Wang JX, Zhang J, Adzic RR (2007) J Phys Chem A 111:12702
37. Wang JX, Uribe FA, Springer TE, Zhang J, Adzic RR (2008) Faraday Discuss 140
38. Scott FJ, Roth C, Ramaker DE (2007) J Phys Chem C 111:11403
39. Roth C, Benker N, Buhrmester Th, Mazurek M, Loster M, Fuess H, Koningsberger DC, Ramaker DE (2005) J Am Chem Soc 127:14607
40. Hansen PL, Wagner JB, Helveg S, Rostrup-Nielsen JR, Clausen BS, Topsoe H (2002) Science 295:2053