Proc. Int. Conf. SRMS-2
Jpn. J. Appl. Phys. Vol. 38 (1999) Suppl. 38-1, pp. 36-39

Characterization of Electrocatalysts by in situ SAXS and XAS Investigations

H.-G. Haubold, P.Hiller, H. Jungbluth, T. Vad

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH,
D-52425 Jülich, Germany

Size distributions, oxidation states and surface coverage of Pt catalyst particles on carbon supports were studied by anomalous small angle scattering (ASAXS) and X-ray absorption (XANES) with X-ray energies near the Pt-L3 absorption edge. The measurements were performed in electrochemical cells to trace electrochemical reactions in situ as a function of the applied electrochemical potential. In potential sweep experiments combined in situ ASAXS and XAS measurements give direct information on the electrochemical processes of methanol oxidation and iodine adsorption on the catalyst surface.

Keywords: Electrocatalysts, Pt/C, in situ SAXS, in situ XAS, ASAXS, XANES

1. Introduction

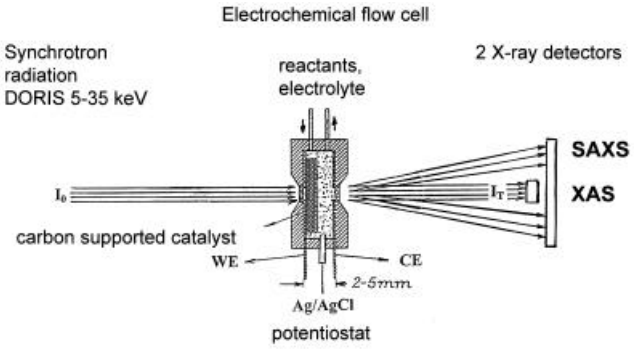
Electrocatalysis is of widespread importance for fuel cells and electrochemical sensor applications. The evaluation of the structure of the electrode surfaces itself, their adsorption layers and the identification of reactions at the catalyst-electrolyte interface are of interest in both fundamental and applied research. Ex situ studies of electrodes, that are removed from the potential environment in the electrochemical cell are of limited value, since changes can occur during the washing and drying procedures.

X-ray methods such as X-ray small angle scattering (SAXS) and X-ray absorption spectroscopy (XAS) with X-rays in the 10 keV energy regime were found in our studies to be excellent in situ probes for both the structure of the commonly used fine dispersed supported electrocatalysts as well as for electrochemical reactions, in which adsorbed intermediates are created on their surfaces. Hard X-rays in this energy regime easily penetrate even mm thick electrode-electrolyte assemblies in electrochemical cells. This allowed us to perform our studies in situ in electrochemical cells under electrochemical working conditions.

We used in situ SAXS as a direct technique to achieve the particle size distribution of nm sized Pt catalyst particles on carbon supports and in situ XAS to get direct information on surface processes such as catalyst oxidation and layer adsorption on the catalyst surfaces. This becomes possible because of the large fraction of surface atoms in small particles and the extremely large catalyst surface of more than 0.1 m² per cm² sample area for electrodes with typical catalyst loads of 1 mg / cm² which are used in low temperature fuel cells. With the "white line" absorption in the XANES Pt-L3 absorption spectrum we traced the Pt d-band occupancy as a probe for catalyst oxidation under operating conditions. Under the flow cell conditions used for our experiments, potential dependent variations of the XAS in the out-of-edge region are direct measures for the amount of adsorbates, which were accumulated in the surface layers of the catalysts during operation.

2. Experiment and sample preparation

We performed the experiments at our JUSIFA beamline (1).



The setup is shown in Fig.1. The sample was mounted as the working electrode in an electrochemical flow cell.

Fig.1. Electrochemical cell and experimental setup for in situ XAS/SAXS studies with synchrotron radiation.

In situ potential-hold and potential-sweep experiments were performed using a potentiostat. For the XAS measurements, a pin diode was used for the measurement of both direct and attenuated beam. The small angle scattering patterns were collected with a position sensitive multi wire proportional counter (MWPC). It's anode counts were counted as a measure for the integrated SAXS intensity in pre-selected Q-ranges, Q=scattering vector. The sample electrodes were prepared from 10wt% Pt/C carbon supported catalyst powder from the E-TEK company (see Fig. 2).

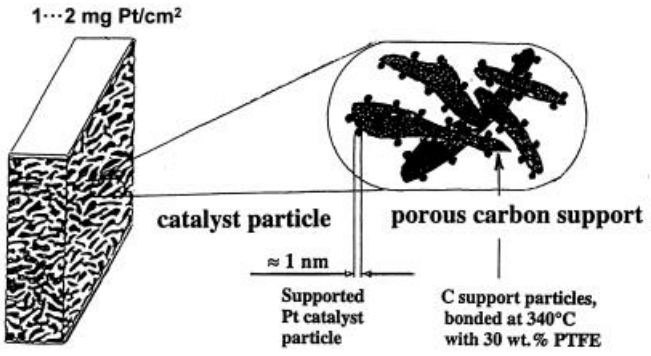


Fig.2. Pt electrocatalyst particles in carbon supported fuel cell electrodes.

3. Catalyst structure

Anomalous scattering in contrast variation small angle scattering experiments allowed to separate the scattering contributions from the catalyst particles and the pores in the porous carbon support (2). Fig. 3 shows the scattering curves for two energies 10.2 keV and 11.55 keV near the Pt-L3 absorption edge and their difference with fits for bimodal size distributions of the Pt particles.

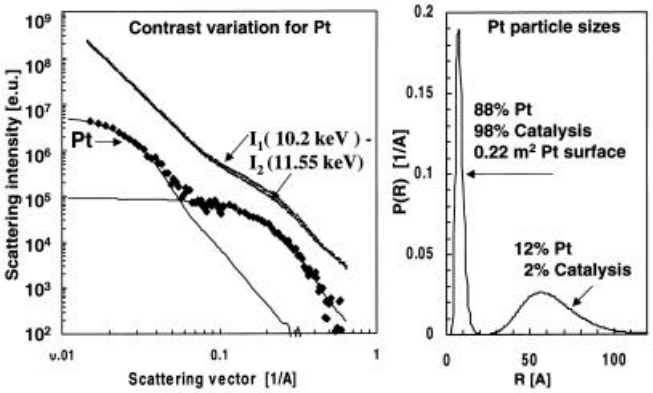


Fig.3. Scattering intensities I_1, I_2, intensity difference I_1-I_2 with fits for log-normal size distributions and corresponding bimodal size distributions P(R).

In the sample with a platinum loading of 1.5 mg Pt /cm^2 88% of the Pt resides in small particles with a mean radius of 8.1 Å, 12% in a second size distribution with a mean radius of 62 Å. The smaller particles contribute 98% to the electrocatalysis, the total particle surface of this fine dispersed platinum amounts to 0.22 m^2 per cm^2 sample surface.

4. Catalyst oxidation

The catalyst oxidation was studied in 1m sulfuric acid. Results from small angle scattering are given in Fig. 4 and 5. In a cyclic potential sweep experiment between an electrochemical potential of -300mV and 1100 mV vs. Ag/AgCl the integrated SAXS intensity drops sharply at about 600mV in the anodic sweep and remains at a low value up to 400 mV in the reverse sweep in cathodic direction. This can be attributed to a particle growth due to the onset of electro-oxidation of the platinum. Fig. 5 gives the full separated scattering curve for the platinum particles at 250mV in the reduced state and at 1100 mV in the oxidized state. The fitted size distributions give mean radii of 0.86 nm for the reduced and 1.06 nm for the oxidized particles. This size increase can be attributed to the formation of a PtO oxide with a reduced number density of Pt atoms (2).

The catalyst oxidation can be traced also by the height of the white line in the Pt-L3 absorption spectrum in the XANES region. It monitors the density of empty electronic 5d-states near the Fermi level which is lowered by oxidation. Thus, in equivalence to the particle size increase from SAXS, an increase of the white line is observed in the XAS measurement. This becomes possible, since about 60% of the Pt Atoms in these small particles reside on their surface and are subject to the oxidation.

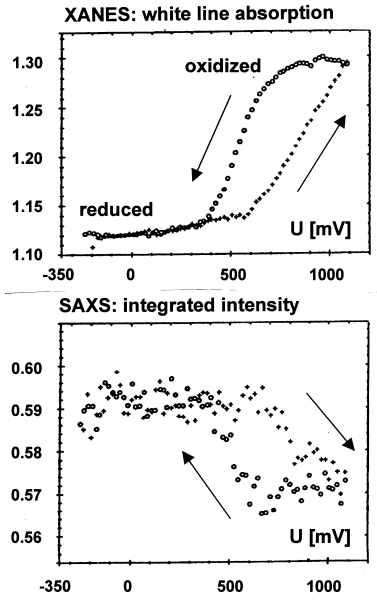


Fig.4. Normalized "white line" X-ray absorption and integrated SAXS intensity [a.u.] as measured in a real time experiment (t_{meas}=10s) at a sweep rate of v=1 mV/s.

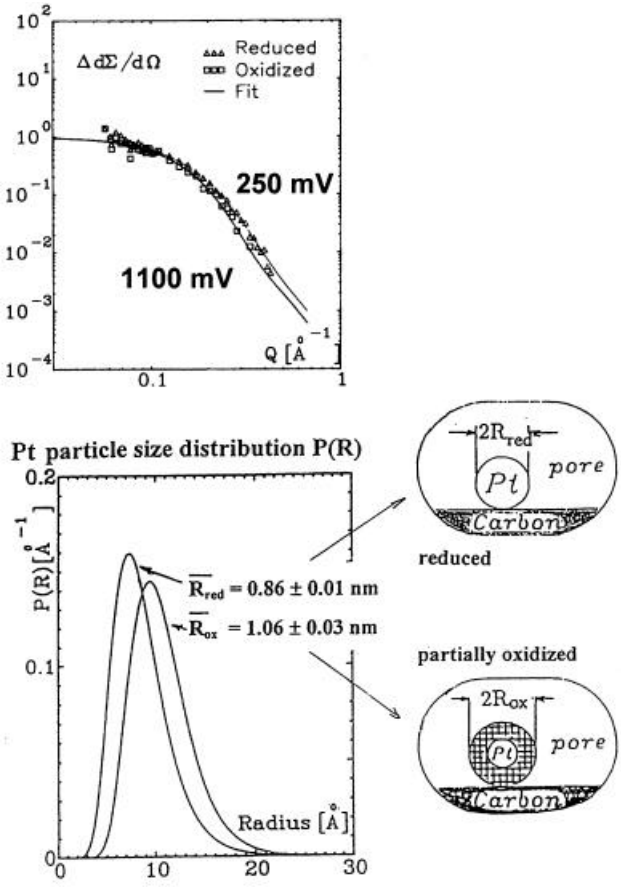


Fig.5. Normalized scattering curves and particle size distributions of the Pt-particles in the reduced and oxidized state at 0.25 V and 1.1 V vs. Ag/AgCl, respectively.

5. Iodide adsorption

Iodide adsorption in 0.1m KI solution was studied by in situ XAS, XANES and SAXS. X-ray absorption spectra between X-ray energies 11542 and 11582 eV were taken in potential hold experiments at -400, -200, 400 and 500 mV vs. Ag/AgCl (Fig. 6) and in potential sweep experiments between -1280 mV and 1250 mV (Fig. 7).

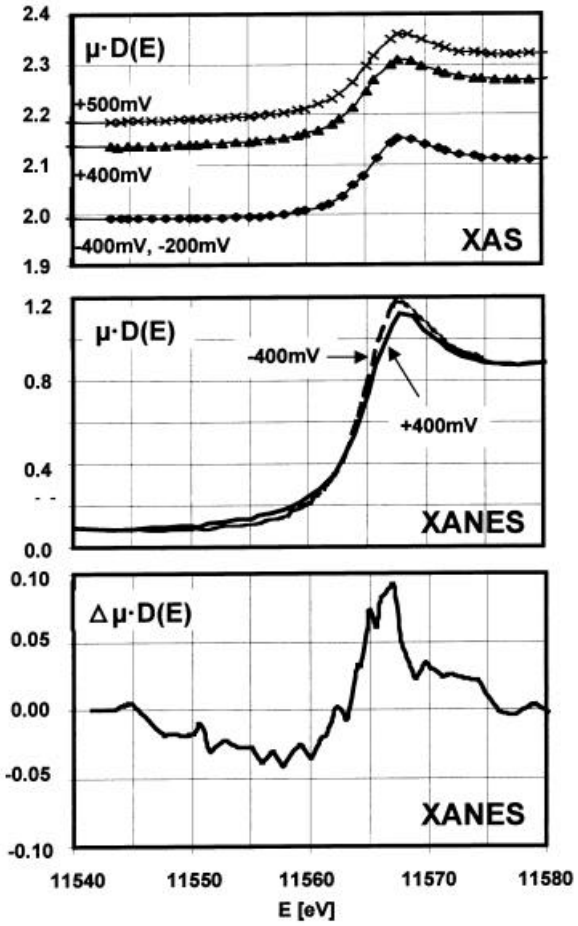


Fig.6. X-ray absorption spectra from potential hold experiments at U= -400, -200, 400 and 500 mV vs. Ag / AgCl, normalized absorption spectra at U= -400 and 400 mV and the difference $\Delta\mu{\cdot}D=\mu{\cdot}D(-400mV)-\mu{\cdot}D(400mV)$.

The huge catalyst surface adsorbs the considerable iodide amount of about 5 mg per cm^2 sample area or 3.3 µg per cm^2 platinum surface under the flow conditions for the KI solution. These numbers can be deduced from the overall shift in the absorption spectra or from the variation in the absorption as measured at the white line energy E1, respectively. For the platinum surface of 0.17 m^2 per cm^2 sample area of the sample under study, this corresponds to a very dense packing of 1.6 iodide ions per 1 $Å^2$ for an assumed mono layer coverage directly on the top layer of the metal surface or to 0.6 iodide ions per 1 $Å^2$ on top of a 5 Å water sheath in between. These numbers may be compared to the distance of closest approach for elemental iodine of 2.7 Å and indicate either a very dense packed simple mono layer or a more complex structure of the iodide layer.

As shown in the potential dependent recorded height of the white line (Fig. 7), we observe a significant change in the XANES spectrum at a potential of about 0 V. It can be attributed to a partial charge transfer from platinum to the previously adsorbed iodide. An interpretation is a transformation of the iodide ions to elemental iodine. The iodine is then oxidized to iodate and stripped at about 900 mV into solution, probably by the onset of catalyst oxidation in our oxygen containing electrolyte.

At the starting point of our experiment –1280 mV, the electrostatic repulsion between iodide ion and the platinum surface hinders the iodide adsorption. This was investigated by molecular dynamics calculations (3) on the electrochemical transfer of solvated iodide ions from an aqueous solution to an atomic adsorbate state on the platinum surface.

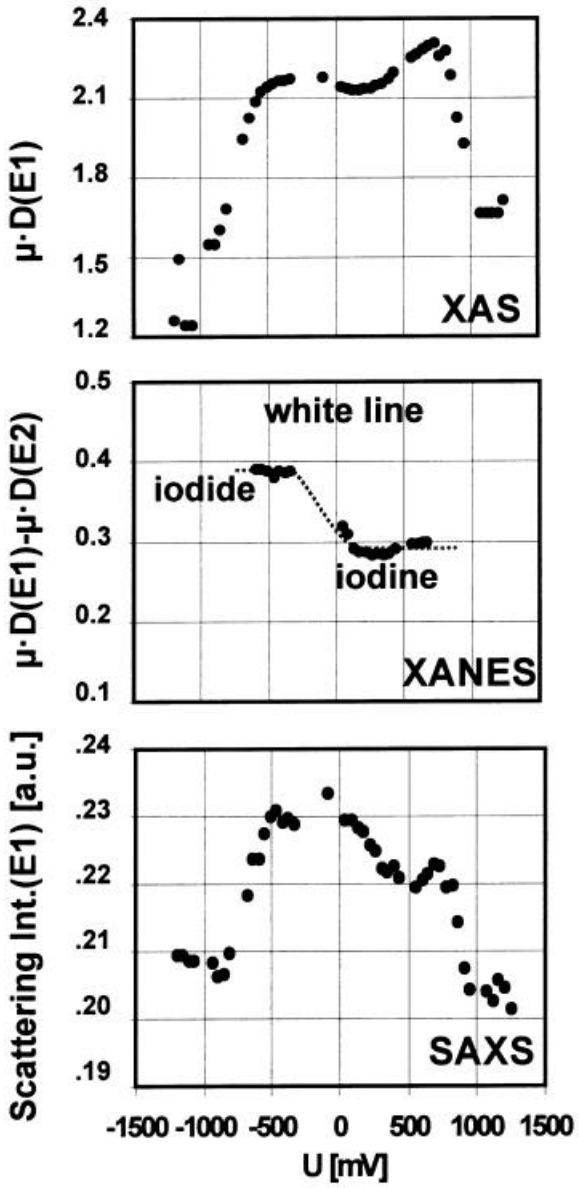


Fig.7. X-ray absorption, change of the height of the white line in arbitrary units, and integrated small angle scattering intensity vs. potential U from potential sweep experiments: t_{meas}=50s, v=0.2 mV/s, E1=11565 eV (white line), E2=11544 eV (pre edge).

6. Methanol oxidation

Adsorption of intermediates by partial oxidation of methanol was studied in a solution of methanol in 1 m sulfuric acid, figs. 8 and 9. A Faradaic current due to the complete electro-oxidation of methanol to carbon dioxide is observed in the potential region between 300 mV and 600 mV. At higher potentials the catalysis is hindered by the electro-oxidation of the catalyst itself, at lower potentials methanol is only partially oxidized (4, 5) and adsorbed intermediates like carbon monoxide or =CHOH are observed .

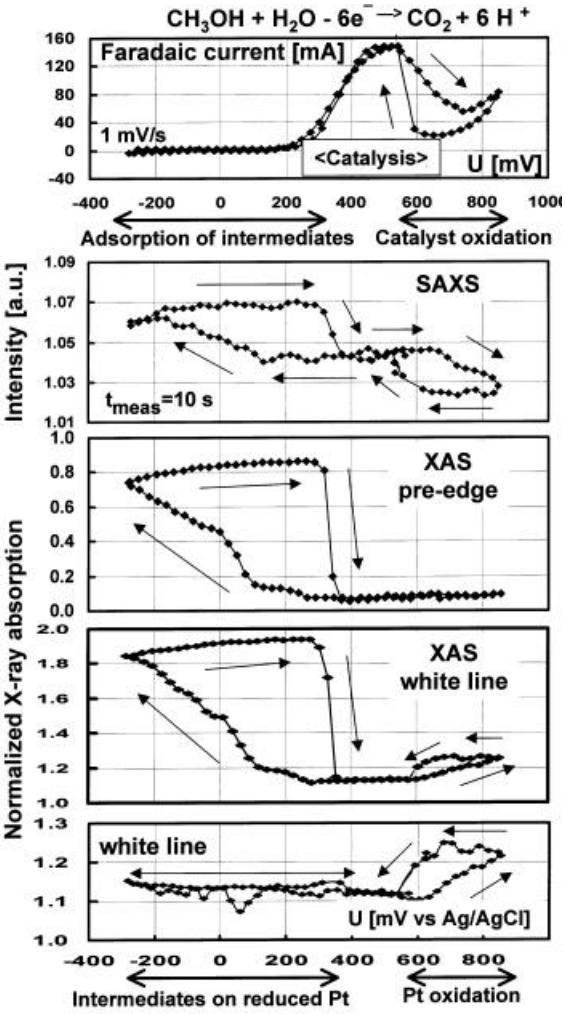


Fig.8. Faradaic current, integrated small angle scattering intensity and X-ray absorption vs. potential U from in situ studies of the electro – oxidation of methanol.

Fig. 9 allows to identify clearly three reaction steps in the partial oxidation range. Stripping is observed at negative potentials of –300 mV. For a more detailed discussion and the identification of the individual intermediates measurements of the complete scattering curves are required – both for the methanol oxidation itself as well as for possible intermediates like formic acid. This will provide SAXS/XAS reference data which then can be used as fingerprints for the identification of intermediate products in the electrochemical reaction.

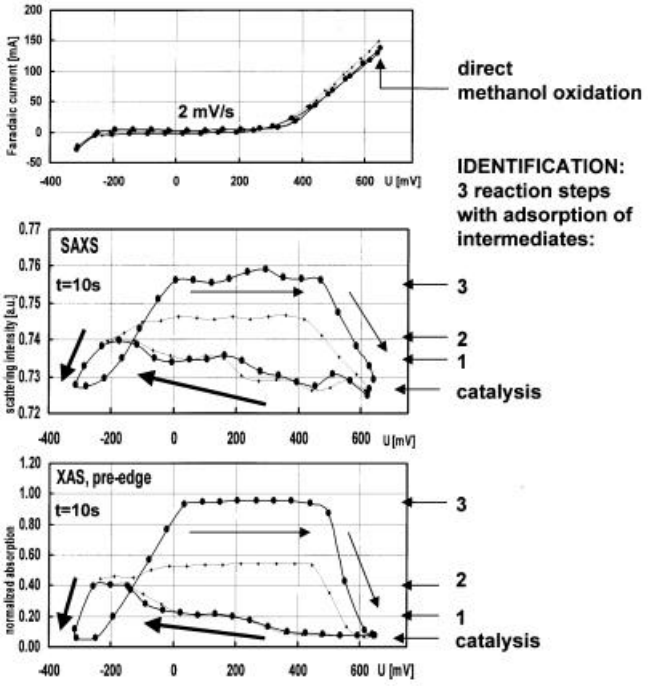


Fig.9. Faradaic current, integrated SAXS intensity and X-ray absorption in the potential range –300mV ≤ U ≤ 650mV of partial methanol oxidation. Adsorbate stripping at H_2 evolving potentials < -300 mV

7. Conclusions

Nano-structures of supported electrocatalysts can be determined unambiguously from small angle scattering studies, since anomalous scattering can be used in ASAXS experiments to separate the catalyst scattering from the background scattering which arises from the porous electrode. Intermediate reaction steps in electro catalyzed reactions can be identified and characterized in combined SAXS, ASAXS, XAS and XANES experiments in situ under operating electrochemical conditions. Here, SAXS gives in situ information on the size of adsorbed intermediates on the catalyst surfaces, whereas XAS is a measure for their quantity. The combination of SAXS and XAS in situ data then allows to retrieve the magnitude of their molecular volume and in this way to identify the various intermediates in complex electrochemical reactions. Applications were tested by characterizing electrochemical reactions as in electrochemical sensors and fuel cells.

References

1. H.-G. Haubold et al., Rev. Sci. Instr. **60** (1989), 1943–1946.
2. H.-G. Haubold, X.H. Wang, G. Goerigk and W. Schilling, J. Appl. Cryst. **30** (1997), 653– 658.
3. O. Pecina, W.Schmickler, E. Spohr, J. Electroanal. Chem. **394** (1995) 29-34.
4. A. Wieckowski, K. Itaya eds., Electrode Processes VI, Methanol Fuel Cells and Related Topics, Proc. Sixth Int. Symposium on Electrode Processes, 189th ECS Meeting, Proc. Vol. **96-8**, ISBN 1-56677-160-9 (1996) 322-480.
5. H.-G. Haubold, H. Jungbluth, P. Hiller, X.H. Wang, G. Goerigk and W. Schilling, Electrode Processes VI, Proc. Sixth Int. Symposium on Electrode Processes, 189th ECS Meeting, Proc. Vol. **96-8**, ISBN 1-56677-160-9 (1996) 383-393.