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A new approach for QEXAFS data acquisition

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Quick-scanning EXAFS (QEXAFS) data were recorded by direct readout of the ionization chambers by means of current amplifiers and a high speed analog to digital converter (ADC) which enables the simultaneous measurement of 4 individual channels with sampling rates of up to 200 kHz. QEXAFS spectra covering an energy range of more than 2000 eV as well as XANES data are presented. The results show that near edge spectra of metal foils can be measured in about 5 ms with an excellent reproducibility. First applications of this setup in catalysis research will be discussed.

Keywords: Quick-EXAFS, Piezo-QEXAFS, catalysis

1. Introduction

Time dependent phenomena such as chemical reactions can be monitored using the quick-scanning EXAFS setup, where the goniometer of the monochromator is continuously rotated while the absorption spectrum is measured (Frahm (1989)). Up to date, a time resolution of about 1 s for a complete EXAFS spectrum and 200 ms for near edge spectra can be achieved using the Quick-EXAFS (QEXAFS) technique (Frahm (1995)). However, a further reduction of the acquisition time is very desirable. During the QEXAFS data acquisition, each amplified detector current is usually converted into a voltage which subsequently is transformed to a frequency which is integrated in a CAMAC counter (see, e.g. Frahm (1989)). Using this setup, the integration time for each data point is limited by the voltage to frequency conversion, i.e. if the integration time is very small, the number of counts detected in each channel is too small to give accurate values for the absorption, especially in the EXAFS region. This limits the minimal data acquisition time which can be used. In this contribution present the first results obtained with high speed analog to digital converters (ADC) controlled by a PC computer, which directly monitored the output voltage of the current amplifiers.

2. Experimental details

A high speed ADC board (DATEL PCI-416M2 with 4 individual 16 bit ADCs on board) in a Pentium PC (166 MHz, 96 MB

RAM) was used for the direct measurement of the output voltages of the current amplifiers (Keithley 428). Our setup enables the simultaneous measurement of 4 individual channels with 16 bit resolution at sampling rates of up to 200 kHz. While the absorption coefficients of the sample and a reference material were obtained by the quotient of the related ionization chamber currents, the energy scale was calculated from the stepper motor controller pulses which are directly related to the Bragg angle of the monochromator crystals. In a second series of experiments, the monochromator crystals were mounted on piezo-driven tilt tables. These tilt tables can be actuated by a sinusoidal voltage with frequencies of more than 100 Hz, resulting in very fast energy scans up- and downwards. In this case, the piezo voltage directly defines the energy scale. Further details are given elsewhere (Bornebusch (1998)). In this contribution, we report on the first QEXAFS experiments with both setups at the undulator beamline BW1 at HASYLAB (Frahm *et al.* (1995)). The results presented here were measured in the transmission mode using a Si(111) fixed exit double crystal monochromator and N₂-filled ionization chambers as detectors.

3. Results and Discussion

In Fig. 1, raw experimental QEXAFS data obtained in 143 s from a 4 μm thick platinum foil cooled to 77 K are displayed. The scan covered the Pt L₃-, L₂- and L₁-edges, i.e. a scan range of 2500 eV. Data simultaneously measured using the CAMAC counters are compared to those using the ADC; no significant differences are visible. In the insert of Fig. 1, the k-weighted absorption fine structure measured above the Pt L₃-edge is presented for both spectra after subtraction of the smooth background. Obviously, the CAMAC data exhibit a slightly higher noise level for k ≥ 14 Å⁻¹, i.e. the performance of the data acquisition with ADCs is better than that of the common voltage to VFC counter system.

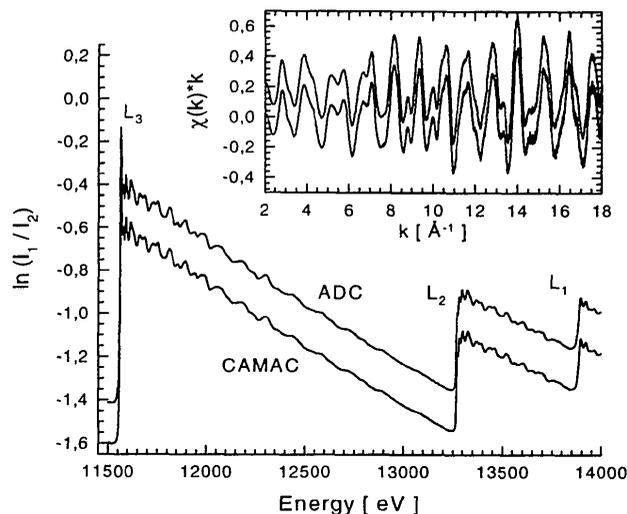


Figure 1

Experimental QEXAFS scans of a platinum foil cooled to 77 K covering all Pt L-edges measured in 143 s using the CAMAC counters and the PC ADC setup (2 kHz sampling rate), all ADC data are shifted +0.2 units upwards. The data reduction of the ADC-data set was performed so that the total number of data points is identical for both methods. The insert depicts the k-weighted absorption fine structure $\chi(k)*k$ at the Pt L₃-edge of both spectra.

A piezo-QEXAFS scan obtained at the Cu K-edge of a 7 μm Cu foil is presented in Fig. 2(a); the displayed voltage corresponds to an energy range of about 50 eV. This XANES spectrum was obtained in 4.5 ms using a 111 Hz modulation of the monochromator piezo stages and an ADC sampling rate of 200 kHz. Fig. 2(b) shows a near edge spectrum, obtained in 7.6 ms at the Pt L_3 edge of a platinum foil with 66 Hz modulation of the piezo stages and an ADC sampling rate 200 kHz; the energy range amounts to approximately 65 eV. Spectral features which are typical for each of the investigated metals (marked A-C and A'-C') are clearly visible in these spectra. However, compared to conventional step-by-step EXAFS measurements, these structures appear to be slightly smeared out. Nevertheless, the described setup using the ADCs gives reproducible, high quality results and dynamical processes can be investigated in situ on this time scale.

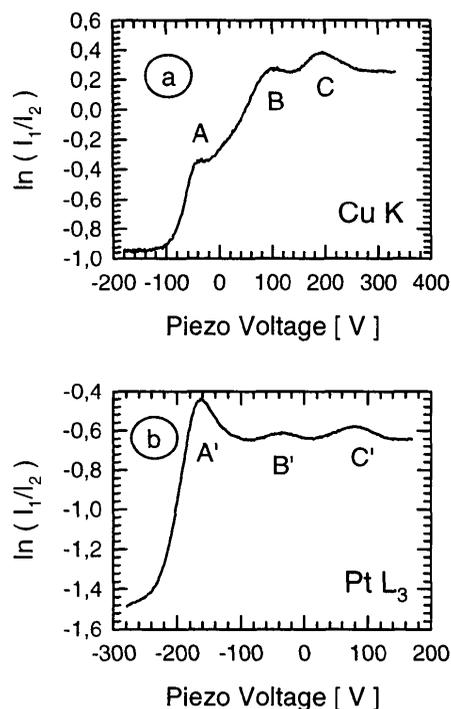


Figure 2

(a) Piezo-QEXAFS of a Cu-foil at the Cu K-edge obtained in 4.5 ms with an ADC sampling rate of 200 kHz (111 Hz modulation of the monochromator crystals). The displayed voltage range corresponds to an energy range of about 50 eV. (b) Piezo-QEXAFS of a Pt-foil at the Pt L_3 -edge obtained in 7.6 ms with an ADC sampling rate of 200 kHz (66 Hz modulation of the monochromator crystals). The displayed voltage range corresponds to an energy range of about 65 eV.

The application of this setup seems to be promising for time resolved in situ EXAFS experiments of chemical reactions which occur in a time scale of some milliseconds such as combustion or decomposition reactions, and research in the field of catalysis and electrochemistry. Results obtained in situ at the Cr K-edge during the reduction of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ to Cr_2O_3 in a H_2 atmosphere at $T \approx 192^\circ\text{C}$ are presented in Fig. 3 (30 spectra, each measured in 20 ms); a capillary micro reactor (Clausen *et al.* (1991)) was used for this experiment. The intense feature at around 0 V piezo voltage corresponds to the Cr^{6+} preedge peak at 5993 eV (see e.g.

Davenport and Isaacs (1990)). Though Cr_2O_3 does not reveal a prepeak in the investigated photon energy range (Davenport and Isaacs (1990)), the intensity of the Cr^{6+} peak can be used as a measure for the progressing thermal decomposition of ammoniumdichromate to Cr_2O_3 . Obviously, only two spectra with an intermediate intensity were measured; i.e. the reaction occurs on a time scale of less than ≈ 150 ms. This can be seen more clearly in the insert of Fig. 3, where the integrated intensity of the Cr^{6+} preedge peak is displayed as a function of the reaction time.

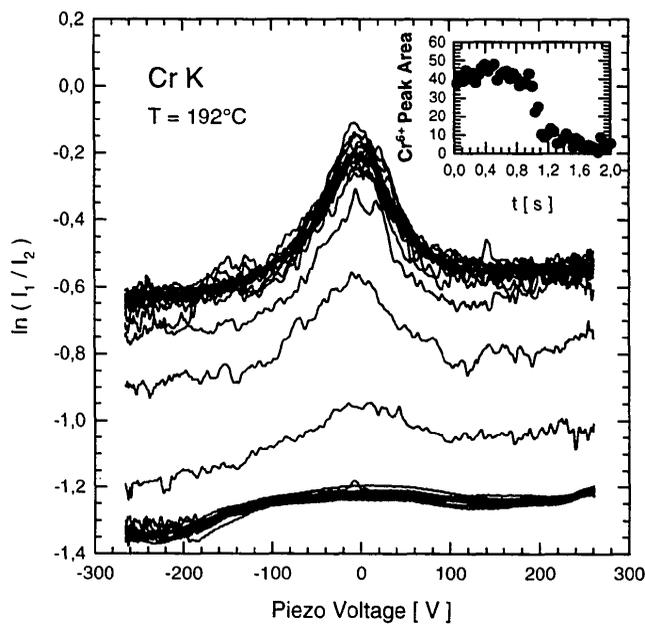


Figure 3

In situ reduction of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in a gas flow of H_2 at $T \approx 192^\circ\text{C}$ measured in the vicinity of the Cr K-edge (20 ms/spectrum, 30 spectra are shown, 25 Hz modulation of the monochromator crystals, 200 kHz ADC sampling rate); the displayed voltage range corresponds to an energy range of about 20 eV. The rapid thermal decomposition of the Cr-compound can clearly be monitored as can be seen in the insert, where the integrated intensity of the Cr^{6+} preedge peak at about 5993 eV (0 V piezo voltage) is displayed as a function of time.

4. Conclusion

For the future, real time investigations of catalytical, electrochemical and combustion reactions are planned with a time resolution of few milliseconds. In addition to XANES experiments, improvements of the monochromator piezo stages will enable the data collection in extended energy regions, i.e. complete EXAFS spectra extending over an energy range of at least 500 eV photon energy will be accessible.

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