

## Electrochemistry

*J. Synchrotron Rad.* (1999), 6, 591–593

### Time-resolved EXAFS investigations of the anodic dissolution of Mo

Dirk Lützenkirchen-Hecht and Ronald Frahm

*Institut für Angewandte Physik, Heinrich-Heine-Universität Düsseldorf, Universitätsstr.1, 40225 Düsseldorf, Germany. Email: hechtd@uni-duesseldorf.de*

The corrosion products formed during the anodic polarization of molybdenum in 1M KOH were investigated with time resolved X-ray absorption spectroscopy in the vicinity of the Mo K-edge. Near edge spectra as well as EXAFS scans extending over approximately 1000 eV above the Mo absorption edge were measured as a function of the corrosion time. Time dependent values for the concentration of the dissolved Mo species in the electrolyte were calculated from the change of the absorption coefficient at the absorption edge. The detailed analysis of the XANES and EXAFS data suggests the presence of  $\text{MoO}_4^{2-}$  ions in the solution.

**Keywords:** corrosion, molybdenum, electrochemistry, QEXAFS

#### 1. Introduction

Electrochemical methods such as rotating ring disk electrode measurements are capable to detect corrosion products with a high accuracy in very low concentrations (see, e.g. Albery and Hitchman (1971)). These methods are governed by thermodynamic properties (oxidation and reduction potentials), i.e. generally it is not possible to determine structural information about corrosion products in the liquid phase. Although X-ray diffraction (XRD) is a powerful tool providing detailed structural data of liquids, the information obtained by XRD is the sum of all atomic pair correlation functions in the solution. Besides the employment of the anomalous scattering technique, XRD is usually not element specific. Therefore it is generally very difficult to separate the contributions of different electrolyte components. In addition, further problems arise if the investigated species are inhomogeneously distributed in the liquid phase, if the absolute concentrations of the investigated species are low compared to the basic electrolyte or if the concentration of the species of interest changes with time as it is the case for corrosion products. In the present study, time dependent extended X-ray absorption spectroscopy (QEXAFS) was used for the investigation of the corrosion products formed during the anodic polarization of Mo in alkaline KOH solution.

#### 2. Experimental details

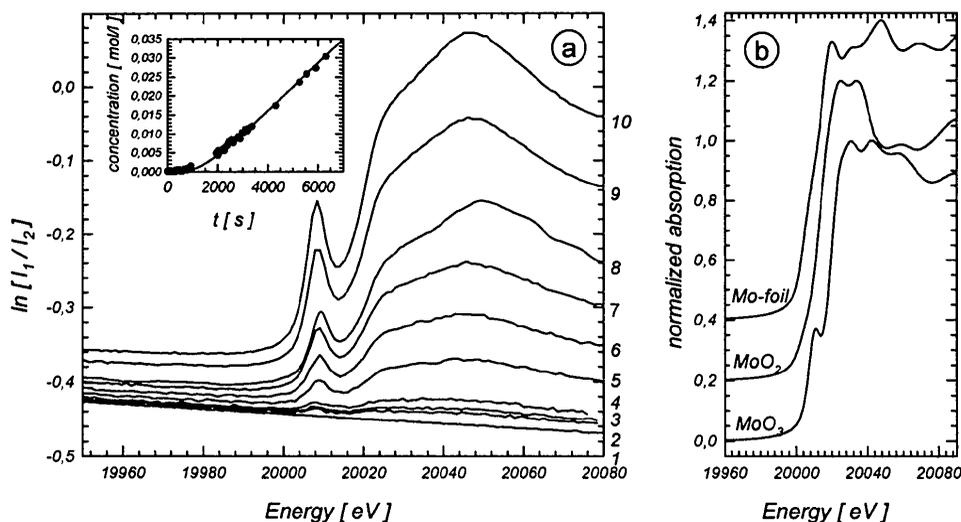
EXAFS spectra were recorded at the ROEMO II beamline (Frahm (1989)) at the DORIS III storage ring (HASYLAB, DESY, Hamburg) operating at a positron energy of 4.43 GeV with 75 - 100 mA of stored current. A double-crystal monochromator with two flat Si (311) crystals and an energy resolution of about 5 eV at around 20 keV was used. The crystals could be detuned with respect to each other using a piezo crystal

tilt stage to reduce the amount of harmonics in the Bragg-reflected beam. EXAFS data were collected in situ under potential control in the vicinity of the Mo K-edge at 20 keV. The incident x-ray beam was collimated vertically by a 50  $\mu\text{m}$  slit. Ar filled ionization chambers were used to monitor incident and transmitted intensities. Using integration times between ca. 0.05 s and ca. 0.2 s for each data point, the time resolution ranged from about 10 s up to 60 s for the XANES scans and from 150 s to 300 s for the EXAFS scans. For the measurements, the monochromatic X-ray beam passes the electrochemical cell (length 20 mm) approximately in 3 mm distance parallel to the corroded Mo-metal surface. The energy scale of the monochromator was calibrated with a molybdenum foil measured in transmission between the second and a third ionization chamber simultaneously with each energy scan. The anodic dissolution of Mo in 1M KOH (pH 13.8) was initiated by a potential step from  $-1.0$  V to  $-0.2$  V. While a gold wire served as counter electrode, a Hg/HgO/1M KOH electrode ( $+0.14$  V vs. standard hydrogen electrode (SHE)) was used as reference electrode. The working electrode was a 0.5 mm thick Mo foil (Aldrich Chemicals, 99.99% purity). A molybdenum foil, crystalline  $\text{MoO}_2$  and  $\text{MoO}_3$  powders pressed in polyethylene were measured in transmission to obtain standard spectra. Further details about the experimental setup are given in a previous publication (Lützenkirchen-Hecht *et al.* (1998)).

#### 3. Results and Discussion

The XANES regions of Mo K-edge absorption spectra recorded at different times after a potential step from  $-1.0$  V to  $-0.2$  V are presented in Fig. 1(a). The increasing magnitude of the Mo absorption indicates an increasing concentration of Mo in the solution. An intense preedge feature is measured at about 20010 eV in the XANES spectra of the dissolved Mo species for  $t > 400$  s. Time dependent values for the Mo concentration in the electrolyte calculated from the edge heights of the spectra are given in the insert. A detailed analysis of these concentrations yields information about the diffusion coefficient of the electrochemically dissolved species: With the boundary condition that the concentration  $c$  of the corrosion product in a distance  $x$  from the surface of the corroded metal electrode is  $c(x,t)=0$  for  $t=0$  and  $c(x,t)=0$  for  $x \rightarrow \infty$ , Fick's equation of diffusion can be solved analytically (see, e.g. Bockris and Reddy (1977)). The analysis shows that  $c(x,t)$  is a function of the corrosion current density  $j$ , which can be measured in situ, the valency of the corroded species  $z$ , the distance  $x$  and the diffusion coefficient  $D$ . Though  $x$  and  $j$  were directly measured, while  $z$  was determined from the XANES data (see below),  $D$  is the only independent variable, i.e. the value of the diffusion coefficient can be determined from the measured time dependance of the concentration. The fit line is presented in the insert of Fig. 1(a), which results in a value  $D=1.2 \cdot 10^{-5}$   $\text{cm}^2/\text{s}$  (Lützenkirchen-Hecht and Frahm (1998)). Similar values were found for the diffusion coefficients of  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  or  $\text{IO}_3^-$  ions in aqueous solutions (Heyrovský and Kuta (1966)).

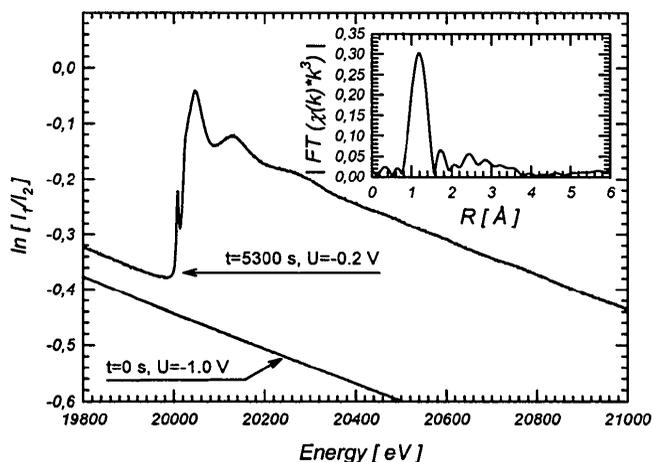
In Fig. 1(b), XANES spectra of several Mo reference compounds are presented for comparison. Obviously, the preedge feature observed in the XANES spectra of the Mo corrosion products can be correlated with the presence of a  $\text{Mo}^{6+}$  species: Such a pronounced prepeak could only be observed for  $\text{MoO}_3$  ( $\text{Mo}^{6+}$ ) but not for  $\text{MoO}_2$  ( $\text{Mo}^{4+}$ ) or metallic molybdenum.



**Figure 1**

(a) XANES region of Mo K-edge spectra obtained during the electrochemical corrosion of a Mo-electrode in 1M KOH after a potential step from  $-1.0$  V to  $-0.2$  V. The X-ray beam passes the electrochemical parallel to the surface of the Mo electrode. In situ spectra 1-10 denote 0 s, 400 s, 650 s, 920 s, 1950 s, 2500 s, 3400 s, 4300 s, 5300 s and 6300 s of oxidation time. The spectra were measured in 8.8 s with an integration time of 0.08 s for each data point. The insert depicts the concentration of Mo in the solution as calculated from the edge height of the spectra (dots) as a function of time and the fit to theory (see text). (b) Mo K-edge XANES spectra of a Mo metal foil, MoO<sub>2</sub> and MoO<sub>3</sub>.

An extended XAFS spectrum recorded after 5300 s of electrooxidation is presented in Fig. 2. Each data point was integrated for 0.15 s resulting in a total time of  $\approx 150$  s for a complete spectrum ranging from 19800 eV to 21000 eV. Besides the distinct preedge feature which was already discussed, EXAFS modulations are clearly visible in this absorption spectrum. For comparison, the spectrum recorded at  $-1.0$  V, i.e. before the initiation of the corrosion of the Mo-metal at  $t=0$  s is also shown.



**Figure 2**

Transmission EXAFS-spectrum recorded in situ in an electrochemical cell after 5300 s of oxidation at  $-0.2$  V: The X-ray beam passes the electrochemical cell parallel to the surface of the Mo electrode. For comparison, the spectrum recorded at  $-1.0$  V is also presented. In the insert, the magnitude of the Fourier transform of the  $k^3$ -weighted fine structure oscillations is shown ( $k$ -range:  $2 \text{ \AA}^{-1} \leq k \leq 10 \text{ \AA}^{-1}$ , data not phase shift corrected).

The magnitude of the Fourier transform (FT) of the  $k^3$ -weighted fine structure oscillations obtained after the subtraction of a smooth background signal is presented in the insert of Fig. 2. The nearest neighbor peak is clearly visible at a radial distance of about  $1.2 \text{ \AA}$ . After isolation of this first coordination shell by means of a filter function, the data were back transformed into  $k$ -space and fitted with phases and amplitudes calculated for a Mo-O coordination (Rehr *et al.* (1992)). The mean values obtained for the nearest neighbor distance  $R_1$ , the coordination number  $N_1$  and the mean square displacement  $\sigma_1$  of the first coordination shell are  $R_1=1.75 \pm 0.02 \text{ \AA}$ ,  $N_1=4.06 \pm 0.11$  and  $\sigma_1=0.061 \pm 0.005 \text{ \AA}$ . From the determined coordination number of about  $N=4$ , the absence of further coordination shells in the Fourier-Transforms of our EXAFS data and the presence of a Mo<sup>6+</sup> species, the formation of a MoO<sub>4</sub><sup>2-</sup> ion during the corrosion of Mo in alkaline media is very likely.

#### 4. Conclusions

Time resolved X-ray absorption spectroscopy (QEXAFS) was applied to the investigation of the corrosion of molybdenum in 1M KOH. The results show that QEXAFS is well suited for the in situ investigation of inhomogeneously distributed corrosion products in the liquid phase. While XANES data indicate the presence of a Mo<sup>6+</sup> species, the detailed analysis of the extended X-ray absorption fine structure suggests the formation of MoO<sub>4</sub><sup>2-</sup> ions during the electrochemical dissolution of Mo in the alkaline KOH solution.

#### Acknowledgement

Financial support by the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and general support by HASYLAB is gratefully acknowledged.

**References:**

- Albery, W.J. and Hitchman, M.L. (1971). *Ring Disk Electrodes*. Clarendon Press, Oxford.
- Bockris, J.O'M. and Reddy, A.K. (1977). *Modern Electrochemistry, Vol. 1*. Plenum Press, New York, 287 - 460.
- Frahm, R. (1989). *Rev. Sci. Instrum.* **60**, 2515 - 2518.
- Heyrovský, J. and Kuta, J. (1966). *Principles of Polarography*. Academic Press, New York.
- Lützenkirchen-Hecht, D., Waligura, C.U. and Strehblow, H.-H. (1998). *Corrosion Sci.* **40**, 1037 - 1042.
- Lützenkirchen-Hecht, D. and Frahm, R. (1998), unpublished.
- Rehr, J.J., Albers, R.C. and Zabinsky, Z.I. (1992). *Phys. Rev. Lett.* **69**, 3397 - 3400.

(Received 10 August 1998; accepted 29 January 1999)