ESRF	**Experiment title:** **An Electrochemical In-Situ Study of the 1T phase MoS_2 by SAXS and EXAFS: The behavior of Lithium in Phase Transformation and Hydrogen Evolution Reaction (HER)**	**Experiment number**: 26-01-1154
Beamline: BM26	**Date of experiment**: from: 3 May 2018 to: 7 May 2018	**Date of report**: 27 June 2018
Shifts: 12	**Local contact(s)**: Dr. Alessandro Longo	*Received at ESRF:*

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Report:

We carried out an *in-situ* X-ray scattering and absorption study to probe the catalytically active species in 1T-MoS_2 during the electrochemical hydrogen evolution reaction. Specifically, *operando* X-ray absorption spectra will be recorded to analyze the local binding environment of Mo during hydrogen evolution.

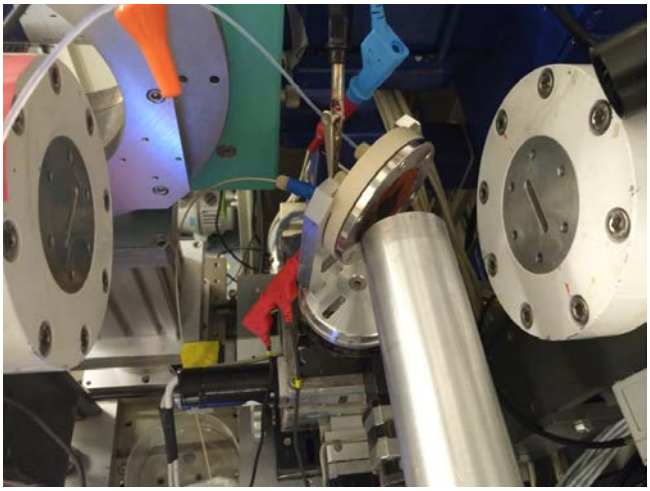

Fig. 1 *Photograph of the experimental setup to do X-ray absorption spectroscopy with fluorescence mode under electrochemical in-situ conditions.*

1T phase MoS_2 films were prepared at TU Eindhoven via immersing ALD deposited 2H-MoS_2 on glassy carbon substrates in butyllithium solution (20 wt. % in hexane) for 24 hours. The thickness of MoS_2 films is ~80 nm. The 1T-MoS_2 films on glassy carbon substrates were investigated by Mo K edge x-ray absorption in fluorescence detection mode at the BM26 (DUBBLE) beamline. The measurements were conducted in an electrochemical cell (as shown in Figure 1) to check the stability of the 1T and 2H phases of the MoS_2. The beam size has been approximately 2 (height)$\times$0.5 (width) mm^2.

X-ray absorption near edge structure (XANES) measurements were collected for 2H-MoS_2 and 1T-MoS_2 (Figure 2). According to the normalized XANES of 2H-MoS_2, there is negligible changes in peak positions and intensities; while the intensity of second peak of 1T-MoS_2 at ~20075 eV increases once in contact with

electrolyte. In addition, a new feature at ~20005 eV appears under HER conditions compared with pristine 1T-MoS_2.

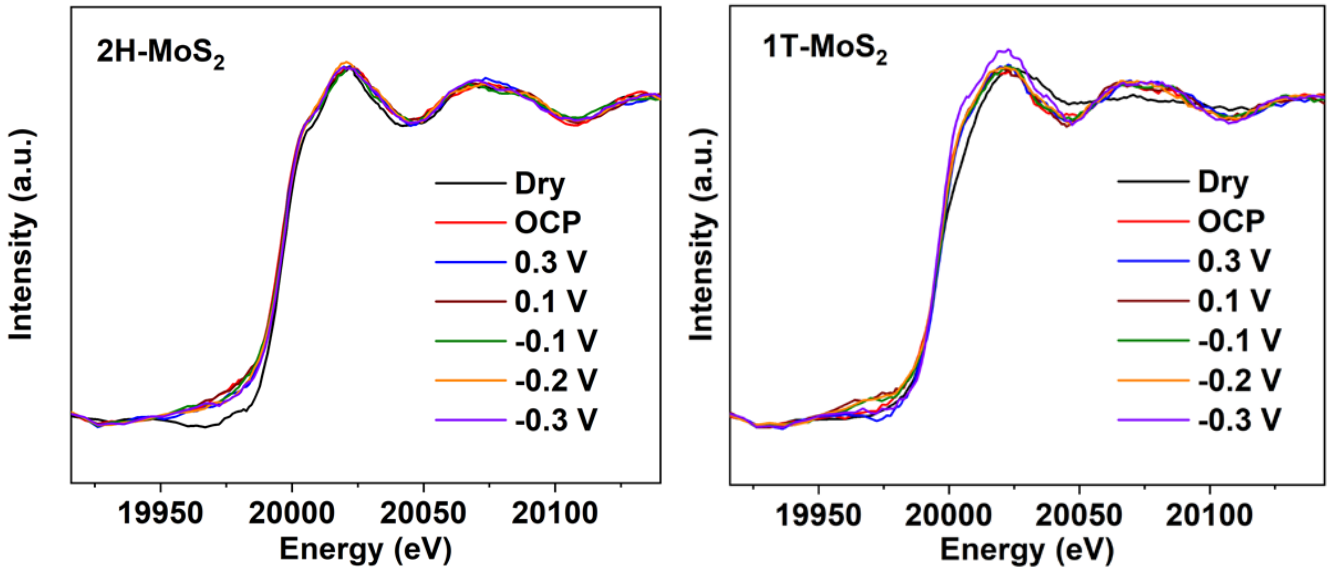

Fig. 2 *In-situ Mo K edge XANES spectra of 2H-MoS_2 and 1T-MoS_2 at different potentiials (vs. RHE) in N_2 saturated 0.1 M H_2SO_4.*

To evaluate the phase stability of 1T-MoS_2, the local bond nature was investigated by EXAFS at Mo K edge. The FT profile comparison of EXAFS data in R space exhibits a distinct distorted Mo-S bond for 1T'-MoS_2 under operando conditions; however, the coordination number (CN) of distorted Mo-S bond decreases 5.9 (dry) to 0.3 (-0.3 V RHE), which indicates that the components of 1T'-MoS_2 in the films decreases under HER electrocatalysis conditions. The EXAFS data analysis is also consistent with the XANES spectra which shows the feature of 2H-MoS_2 under potentials in electrolyte. With this knowledge, together with other results from Raman spectroscopy and XPS, we may conclude that 1T-MoS_2 is gradually changing back to 2H phase under HER conditions.

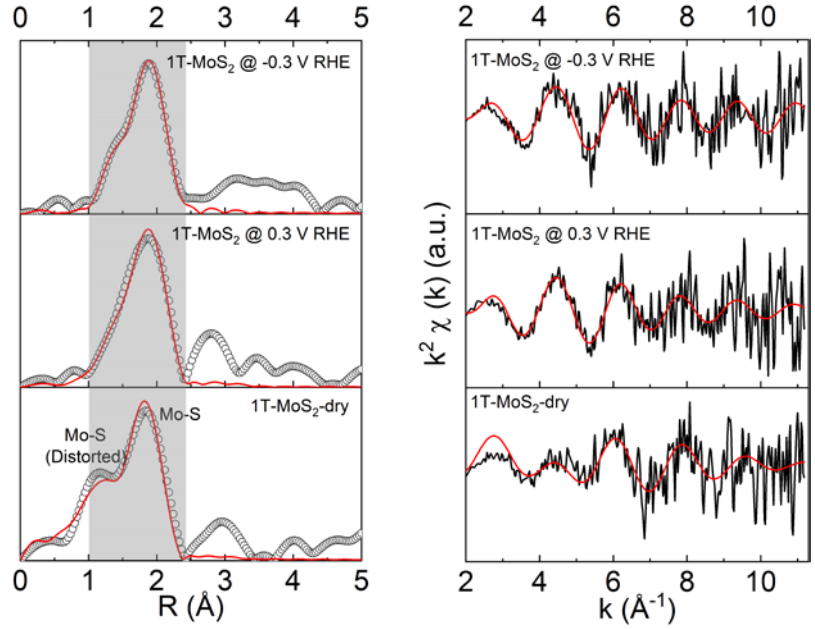

Fig. 3 *Fitting results corresponding to the Mo K edge EXAFS Fourier Transfer (left)and χ(k)spectra of 1T-MoS_2 films collected under different conditions. Data are ploted as open circles and fits as red curves.*

SAXS has not been employed in this beamtime. A manuscript is currently in preparation.