Experimental report

13/11/2019

Proposal: 5-23-717 **Council:** 10/2018

Title: Structural evolution of molybdenumcompound catalysts

Research area: Materials

This proposal is a resubmission of 5-23-710

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Samples: Mo2C on carbon
MoS2 on carbon

Instrument	Requested days	Allocated days	From	To
D20	1	1	30/09/2019	01/10/2019

Abstract:

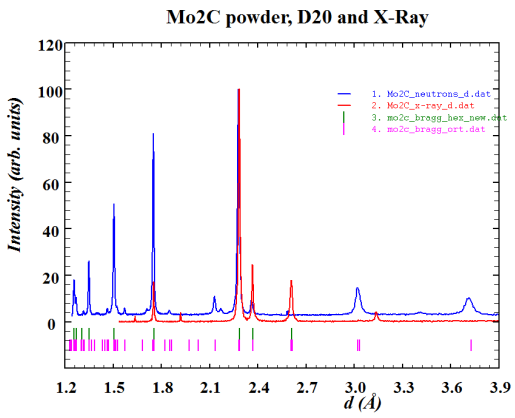
Power-to-gas is one of the most promising concepts to store renewable energy. Hydrogen gas is produced from water when excess energy is available and reconverted when energy is in demand. For the hydrogen evolution reaction (HER) molybdenum disulfide, MoS2, is an intensely studied catalyst and Mo2C is one of the emerging candidates. Recent electrochemical studies have led to substantial improvements in our knowledge about the catalytic activity of MoS2 and it is clear that the hydrogen sorption and diffusion dynamics play a crucial role, however the microscopic mechanisms of the catalytic activity remain largely unsolved.
Using neutron diffraction we will study the evolution of the microscopic structure of MoS2 and Mo2C catalyst particles on carbon electrodes at different stages of the catalytic process.

Experimental report exp.5-23-717

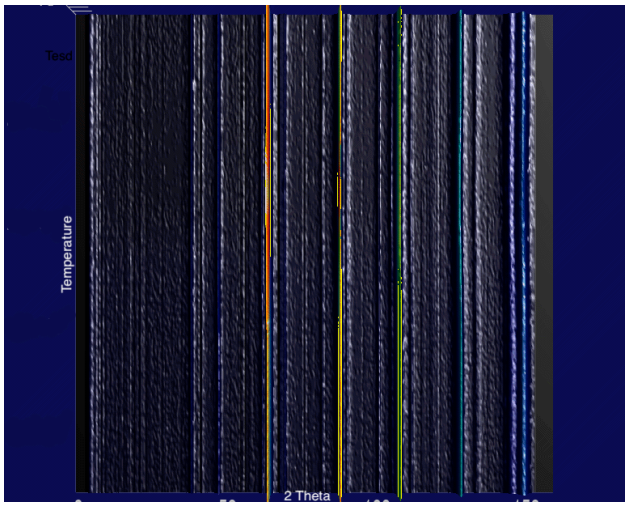
We performed a series of neutron diffraction experiments on the powder diffractometer D20 at ILL. The samples studied: MoS_2 on exfoliated graphite sheet with H_2O adsorbed via 12 hours of electrolysis, exfoliated graphite sheet as received, Mo_2C powder with adsorbed hydrogen, MoS_2 and Mo_2C on porous glassy carbon deuterated and non-deuterated.

We start our description of results with the measurements of the Mo_2C powder. At 100 K the phase is clearly orthorhombic (Pic. 1) and those additional orthorhombic reflections do not disappear during a temperature scan (Pic. 2). However on an XRD pattern of another Mo_2C sample only hexagonal peaks can be seen. The difference in the preparation of the samples was the temperature during adsorption process, 100 K for neutron experiment and 300 K for X-ray. Taking into account the fact that orthorhombic Mo_2C phase is stable under ambient conditions we assume that the critical temperature of phase transition under hydrogen adsorption should be between 100 K and 300 K.

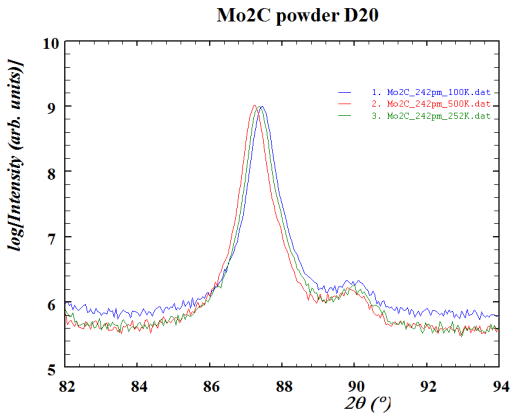
Comparing scans at different temperature points (Pic. 3) one can see the decrease in incoherent background level when heating from 100 K to 500 K, which can be attributed to hydrogen desorption. Peak position shifts (Pic. 3) need more detailed treatment in order to distinguish between thermal expansion and hydrogen desorption contributions.



Pic. 1. Mo_2C neutron (blue) and X-ray (red) powder diffraction spectra. Vertical green sticks - Bragg positions for hexagonal Mo_2C, vertical pink sticks - Bragg positions for orthorhombic Mo_2C.

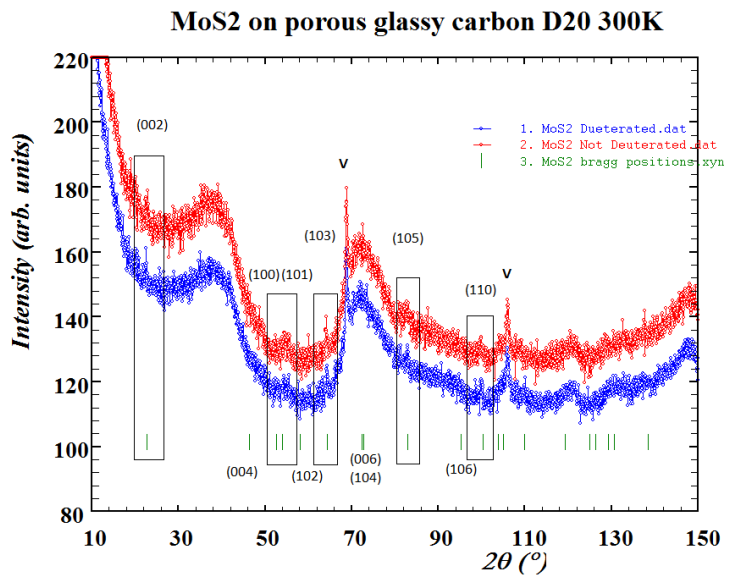


Pic. 2. Mo_2C powder diffraction temperature scan. All reflections remain almost the same during the heating process, no intensity changes can be seen.

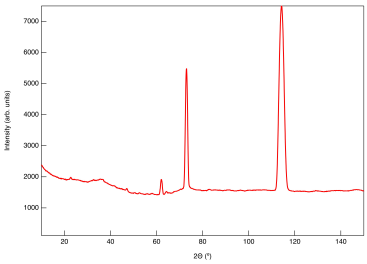


Pic. 3. Sum of (221) and (202) reflections (at 87.3 2Theta) of Mo_2C powder. Lines in blue, red and green stand for 100 K, 500 K and 252 K after heating respectively. Background falls when heating from 100 K to 500 K and does not increase when cooling back down to 250 K, meaning that hydrogen desorps at elevated temperature and does not adsorb when cooling back down.

For MoS_2 on porous glassy carbon we already have some data from our previous D20 experiment. For that experiment we used glassy carbon with large pores and this time we used the one with much smaller pores. The intensities of MoS_2 peaks in the current experiment are extremely lower the the ones from the previous one, meaning that the change in pore size drastically decreases the amount of sample that can be deposited on a substrate.
However even with such a poor data we can extract some informations from the spectra. Deuterated and non-deuterated samples exhibit different behaviour (Pic. 4). The non-deuterated sample yields higher incoherent background level, probably due to hydrogen sorption from the atmosphere or from the coating process, which does not happen to a deuterated sample because a significant part of adsorption sites is occupied by deuterium. The widths of the reflections also look slightly different. However, the data quality may hinder the extraction of quantitative results.

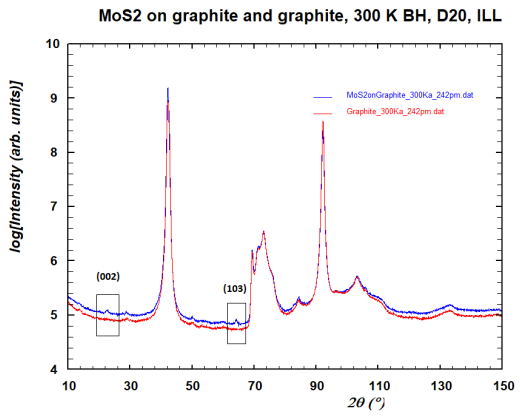


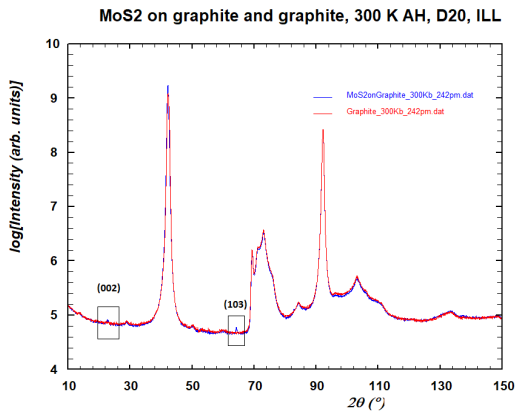
Pic.4. MoS_2 on porous glassy carbon diffraction spectra. Blue and red points represent deuterated and non-deuterated samples respectively, green vertical sticks show the positions of Bragg reflections, V indicates vanadium peaks.



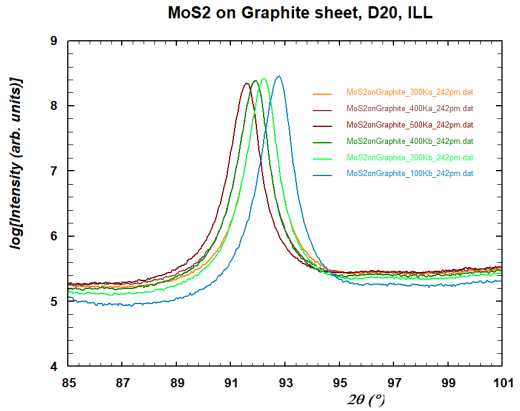
Pic. 5. MoS_2 on porous glassy carbon with large pores, data from previous D20 experiment.

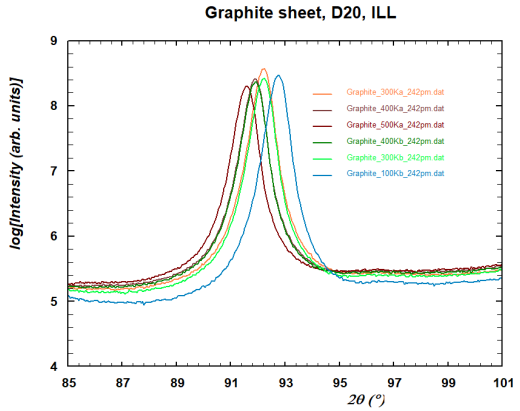
We also measured MoS_2 on exfoliated graphite and the amount of sample is very low as well. The difference in the incoherent background between MoS_2 on graphite and the substrate itself is attributed to the hydrogen adsorbed by MoS_2 as this difference disappears after heating to 500 K and cooling back to 300 K. The graphite peak exhibits different behaviour depending on whether it is clean or with MoS_2 on top. For the substrate with the sample, graphite reflections at the same temperatures before and after heating have exactly the same intensity and profile, the difference is only in the background because of hydrogen desorption. While the the same reflections are different in terms of intensities for the clean exfoliated graphite.





Pic. 6. Spectra of MoS_2 on exfoliated graphite (blue line) and the clean substrate (red line) at 300 K before heating (left) and after heating to 500 K and cooling back to 300 K (right).





Pic. 7. Graphite peak for the exfoliated graphite with (left) or without (right) MoS_2. The colour-temperature notations are as follows, before heating: orange - 300 K, light brown - 400 K, brown - 500 K; after heating: dark green - 400 K, light green - 300 K, blue - 100 K.