Experimental report

11/02/2019

Proposal: 7-05-491 **Council:** 4/2018

Title: Dynamics of hydrogen in molybdenumdisulfide and molybdenum carbide electrodes

Research area: Materials

This proposal is a new proposal

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Samples: hydrogen sorbed in Mo2C/Carbon electrode
hydrogen sorbed in MoS2/Carbon electrode

Instrument	Requested days	Allocated days	From	To
IN11	9	5	27/09/2018	02/10/2018

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 neutron spin echo we propose to study the evolution of the diffusivity of hydrogen in MoS2 and Mo2C catalyst particles on carbon electrodes at different stages of the catalytic process.

Experimental Report 7-05-491 „Dynamics of hydrogen in MoS_2 and Mo_2C electrodes“

1. Introduction

Recently, there has been immense progress in technologies related to the production of renewable energy, however storage concepts have not yet reached the same maturity. ‘Power-to-gas’ is one of the most promising concepts: Hydrogen gas is produced from water when energy is available and reconverted when energy is in demand. Each conversion process needs to be carried out as efficiently as possible using optimized materials.

In the frame of this technology molybdenum disulfide, MoS_2, is an intensely studied catalyst candidate for the hydrogen evolution reaction (HER) in water electrolyzers [1,2], i.e., the reaction in which hydrogen is created out of water. Recent electrochemical studies allow detailed conclusions about its catalytic activity [3-7]: Besides the remarkable progress in structural studies, the reasons for the activity of the catalysts remain elusive. On platinum catalysts it is well-known that hydrogen diffusion below the surface plays a role in the activity [8].

2. Samples and Experiment

It was the aim of this experiment to explore if hydrogen dynamics are visible in model electrode samples consisting of a graphite foil substrate [9] coated with MoS_2 nanopowder catalyst. Since we had only very limited beam time agreed by the subcommittee, we have decided to scan a range of samples with only a few representative sample temperatures. Three samples had been operated in water electrolysis prior to the spectroscopy experiments, two of them using D_2O, the third sample using H_2O. The forth sample was unprocessed graphite foil in as-received state. On all samples spin echo experiments were performed on IN11C (using the 30 degree detector bank for maximum signal) at a wavelength of λ = 5,5 Å with a *Q* range of 0.1 .. 0.7 $Å^{-1}$ and on four representative temperatures: 2 K (resolution), 100 K, 300 K, and 500 K.

Mo_2C catalyst powder, which had been originally proposed for an experiment of 9 days, was not studied, because the experiment had to be shortened to 5 days.

3. Results

As a first important result, we can confirm that we have found strong incoherent dynamics that shows a Q-dependence and temperature dependence. Fig. 1 shows spectra recorded in the Q range 0.1 .. 0.55 $Å^{-1}$ for a MoS_2-loaded graphite sample, which had been operated for 4 hours in water electrolysis. At 100 K there is negligible diffusion, but at 300 K clear signal from diffusion is found. At 500 K the diffusive signal is similar in strength to the signal at 300 K and the diffusion is clearly faster, as expected for a thermally activated process.

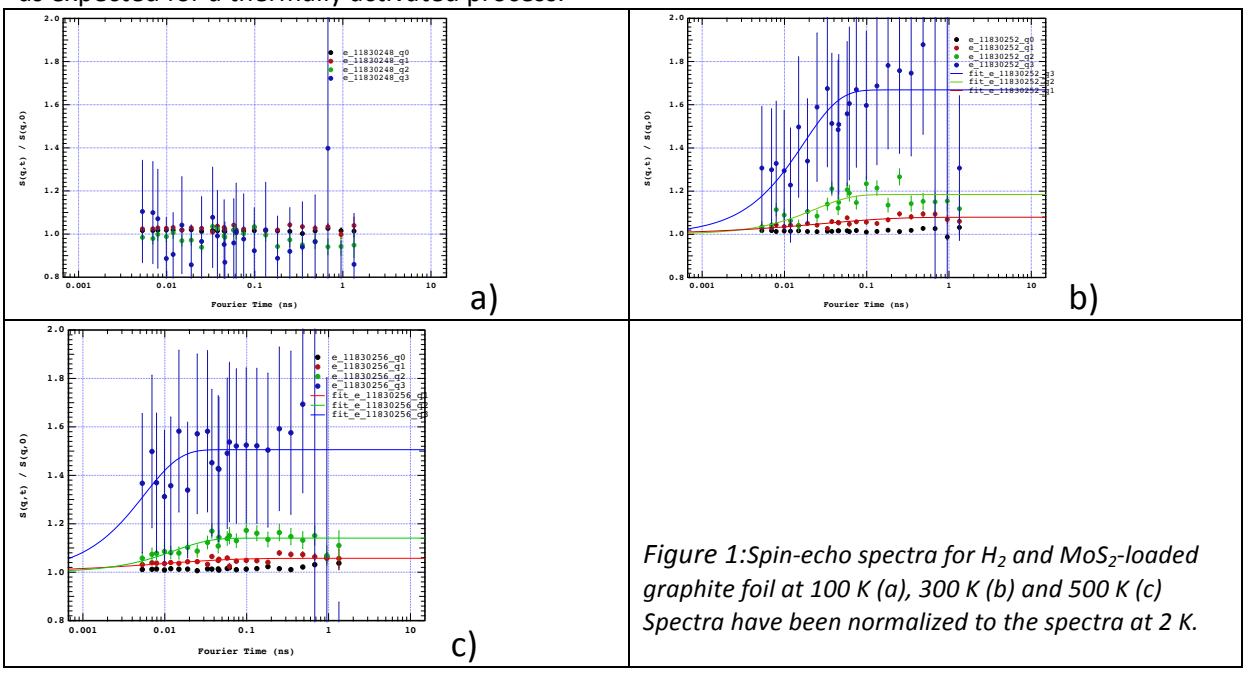

Figure 1:Spin-echo spectra for H_2 and MoS_2-loaded graphite foil at 100 K (a), 300 K (b) and 500 K (c) Spectra have been normalized to the spectra at 2 K.

From our preparatory experiments with nuclear reaction analysis employing the reaction $^{1}H(^{15}N,\alpha\gamma)^{12}C$ it became clear that hydrogen is stored in the MoS_2 through the electrochemical loading, but there is also hydrogen present in the substrate. So it would be a serious challenge to distinguish between hydrogen and water incorporated in the carbon substrate and the hydrogen loaded into the MoS_2 catalyst itself. Therefore both, D_2O and H_2O were used in electrolysis, resulting in loading of the samples with deuterium atoms and hydrogen atoms, respectively. Fig. 2 shows the spin echo signal for three samples at 300 K. First of all, it is found that the unloaded sample and the sample loaded with D2O show the strongest diffusive signal (of the incoherent signal), which suggests that the hydrogen/water mobility in the graphite substrate provides the strongest signal. A first analysis suggests that the diffusion is about three times as fast as room temperature diffusion in bulk water. The diffusivity in the hydrogen loaded sample appear somewhat slower at first analysis. At 100 K there is no discernible diffusion in any of the measured samples. A more detailed analysis of the electrode samples will be performed and further analysis of the data is required. It would be highly interesting to have the spectra for more temperatures and at better statistics for a better characterisation of the activation behaviour.

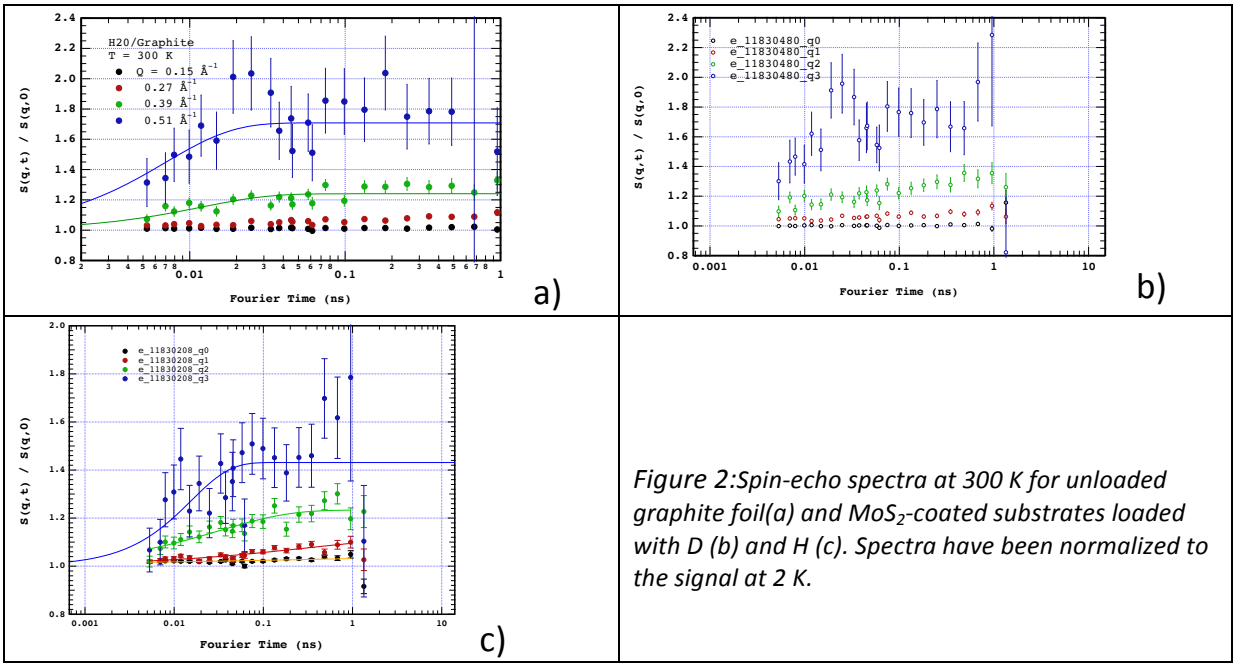

Figure 2:Spin-echo spectra at 300 K for unloaded graphite foil(a) and MoS_2-coated substrates loaded with D (b) and H (c). Spectra have been normalized to the signal at 2 K.

4. References

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