QENS study of the diffusivity of hydrogen in MoS_2

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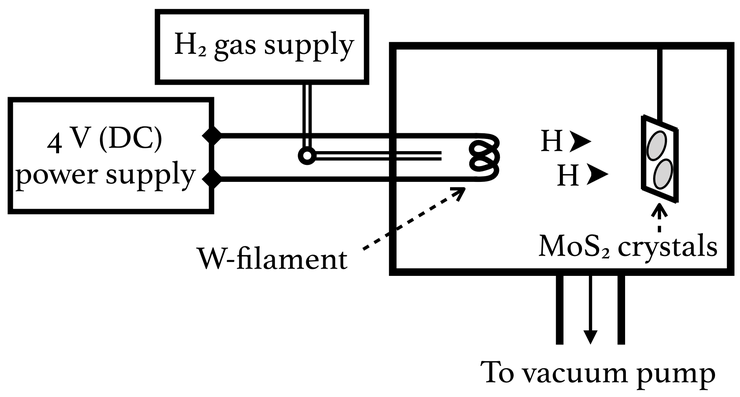
Abstract

Understanding of diffusion patterns of hydrogen inside the promising HER catalyst, MoS_2, is crucial for a deliberate development of its properties for future use in hydrogen electrolysis. Hence the diffusion of various hydrogen species adsorbed inside layered MoS_2 crystals has been studied by means of quasi-elastic neutron scattering, nuclear reaction analysis and X-ray photoelectron spectroscopy. The neutron time-of-flight measurements demonstrate fast diffusion of hydrogen molecules parallel to the basal planes of MoS_2, and slower motion of atomic hydrogen. Penetration of MoS_2 layers by hydrogen was observed by nuclear reaction analysis on a completely different timescale.

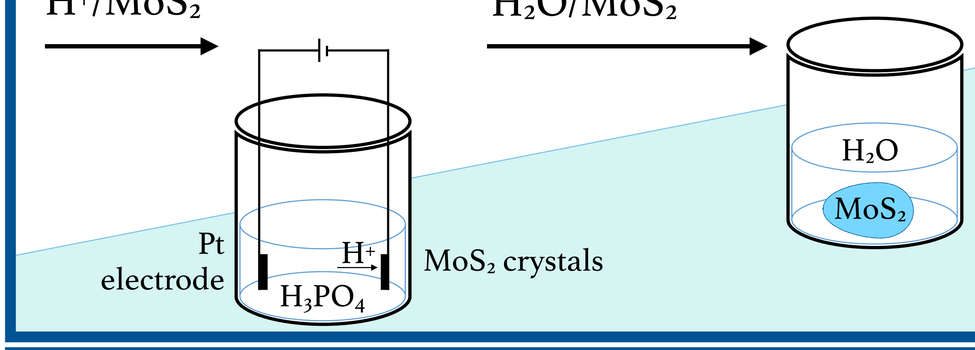
H-Loading

Atom beam loading → H/MoS_2



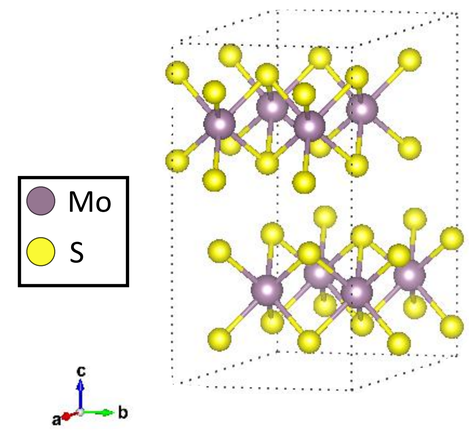
Electrolysis H^+/MoS_2

Water soaking H_2O/MoS_2

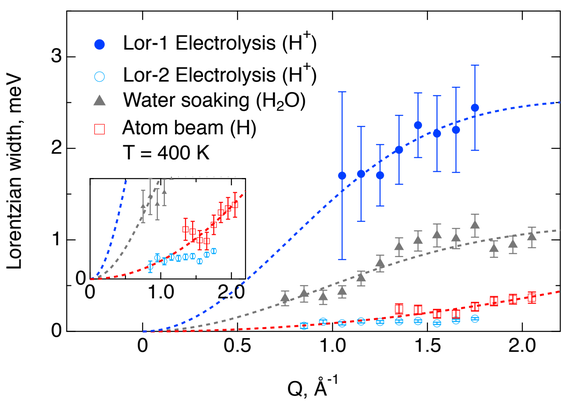


Sample

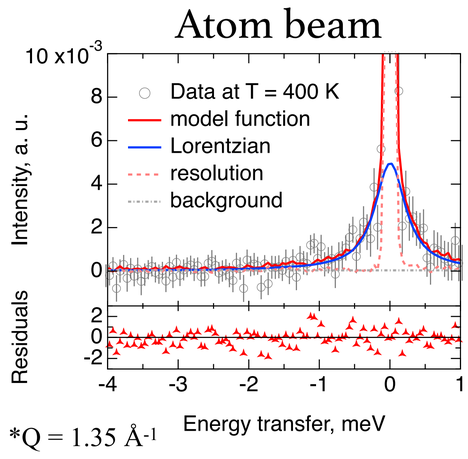
- Molybdenum disulfide is a layered material, which has shown decent catalytic properties for the hydrogen evolution reaction (HER);
- It is widely used and thus easily obtainable;
- It has $P6_3/mmc$ hexagonal structure with a = 3.15 Å and c = 12.30 Å



TOF QENS, in plane

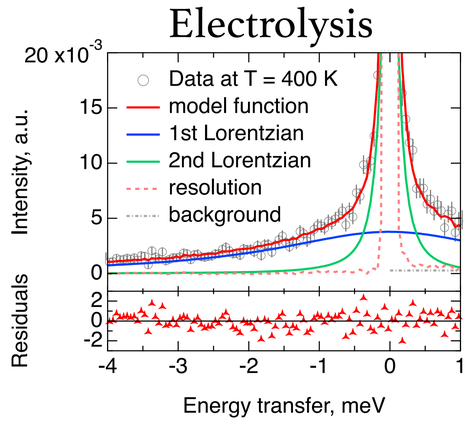


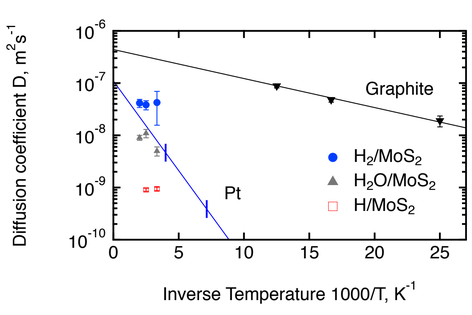
Atom beam



*Q = 1.35 Å^{-1}

Electrolysis

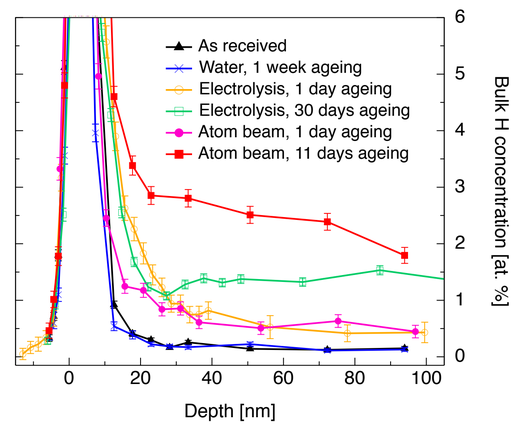




The three loading processes result in completely different hydrogen diffusion profiles observed. H^+/MoS_2 exhibits two motion modes, most probably it is due to generation of H_2 during electrolysis.

Neutral H atoms seem to diffuse relatively slow, with $D \sim 0.1 \cdot 10^{-8}$ m^2/s. Recombined H_2 molecules are fast, but trapped inside the material, since at 500 K the signal for H/MoS_2 is lost and for electrolytically loaded MoS_2 it persists.

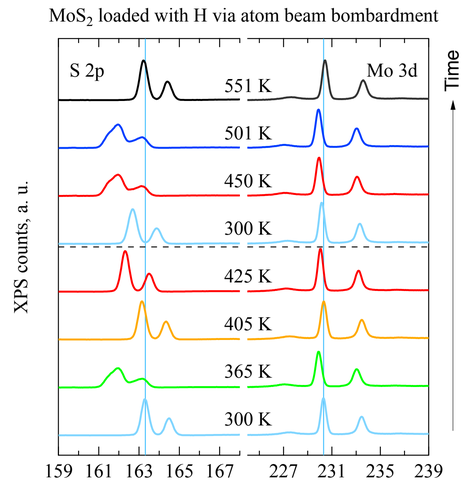
Nuclear Reaction Analysis, out-of-plane



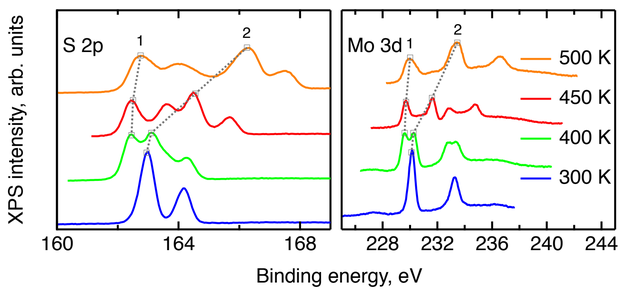
*The scale is not fully applicable below ~10 nm

NRA shows that the highest initial bulk H concentration is achieved by loading via electrolysis. Water, as expected, does not penetrate MoS_2 layers. The estimated diffusion coefficient for the two other loading processes is $D \sim 10^{-21}$ m^2/s.

XPS



XPS scans of the H/MoS_2 exhibit several reduction sequences along heating, indicating that in this sample hydrogen should be bound in at least two different environments with different binding energy.



The surface of the electrolysis loaded crystal, on the other hand, mostly shows oxidation pattern during heating, suggesting either hydrogen desorption, or charging of the part of the surface.

Conclusion

The diffusion of various hydrogen species in a promising HER catalyst, MoS_2, have been studied via QENS, NRA and XPS. The rate of atomic H diffusion along the MoS_2 basal planes appeared to be slower than the reported one for H on Pt surface, ~10^{-9} m^2/s as compared to ~10^{-8} m^2/s, respectively, which may be one of the reasons why the Tafel reaction step ($H_{ad} + H_{ad} \rightarrow H_2$) is hindered for this material. Electrolysis process most probably generates a large amount of H_2 in the bulk of MoS_2. These molecules are generally trapped within the matrix and do not desorb easily. Hydrogen atoms can penetrate MoS_2 layers, however, the process is extremely slow.