$[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ as active site models for amorphous molybdenum sulphides in HER-catalysis

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Abstract: Amorphous molybdenum sulphides are known for their high catalytic activity and robustness in the hydrogen evolution reaction (HER). Meanwhile the reaction mechanism is still subject of debate. In this study, the activity of molybdenum sulphido clusters was tested as homogeneous as well as heterogeneous catalysts in order to contribute to the elucidation of possible reaction pathways.

Keywords: HER, molybdenum sulphides, catalysis.

1. Introduction

The best known electrocatalyst for the production of hydrogen is platinum.[1] As this is a rare and precious metal, non-toxic and earth-abundant alternatives are needed. Amongst them are amorphous molybdenum sulphides (MoS_x), which show excellent catalytic activities for proton reduction.[2] However, the mechanism of the hydrogen evolution reaction (HER) catalyzed by MoS_x is still a subject of debate. Molecular molybdenum sulphido clusters like $[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ can be considered as molecular structural models for the active sites of molybdenum sulfides (Fig. 1) and their study could thus contribute to solve this problem. Not much is known about the chemical properties and catalytic performance of these clusters so far.[3]

2. Experimental

The molybdenum sulphido clusters $[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ were prepared following literature procedures.[3,4] For this, an aqueous ammonium polysulfide solution ($pH \approx 11$) was mixed with ammonium heptamolybdate and heated to 90°C for 15h, from which $(NH_4)_2[Mo_3S_{13}]$ precipitates as red crystals. Further addition of ammonium polysulfide solution to the filtrate then yields $(NH_4)_2[Mo_2S_{12}]$ as a black powder. The clusters were characterized by Raman spectroscopy, X-ray powder diffraction and mass spectrometry. In chemical proton reduction set-ups their catalytic activity was studied with Eu^{II}-DTPA as reducing agent.[5] In addition, electrochemical measurements were performed testing the clusters' behaviour in homogeneous as well as heterogeneous catalysis. For electrocatalytic HER, electrodes were prepared by drop-casting solutions of the clusters on graphite paper.

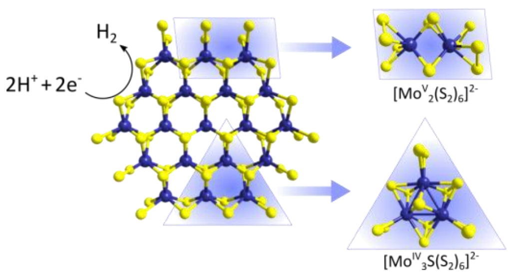

Figure 1. $[Mo_3S_{13}]^{2-}$ and $[Mo_2S_{12}]^{2-}$ as molecular structural models for the active sites of molybdenum sulphides.[3]

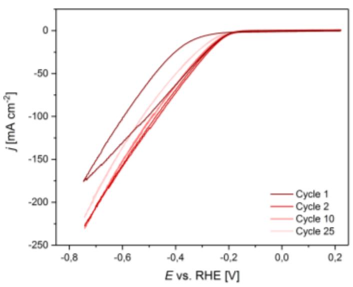

Figure 2. Cyclic voltammograms of immobilized $[Mo_3S_{13}]^{2-}$ at pH 0.3

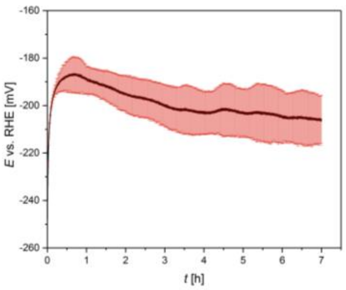

Figure 3. Chronopotentiometric measurements of immobilized $[Mo_3S_{13}]^{2-}$ at pH 0.3.

3. Results and discussion

In cyclovoltammetric and chronopotentiometric measurements, clusters immobilized on carbon electrodes showed high HER-activity with overpotentials of $\eta = 220\text{-}230$ mV in strongly (pH = 0.3) or $\eta = 400\text{-}470$ mV in weakly acidic solution (pH = 4.5) at a current densities of $j = 10$ mA cm^{-2} (Fig. 2). In chronopotentiometric measures over 7 h, immobilized $[\text{Mo}_3\text{S}_{13}]^{2-}$ showed better longterm stability than $[\text{Mo}_2\text{S}_{12}]^{2-}$ (Fig. 3). This result could be confirmed for homogeneous catalysis in the presence of Eu^{II}-DTPA at different pH values with varying concentrations.

4. Conclusions

In chemical as well as in electrochemical set-ups $[\text{Mo}_3\text{S}_{13}]^{2-}$ and $[\text{Mo}_2\text{S}_{12}]^{2-}$ showed high catalytic HER-activities. Therefore the clusters have a high potential to act as molecular structural models for amorphous molybdenum sulphides building a bridge between homogeneous and heterogeneous catalysis. Thus further investigations by our group will follow, especially for the homogeneous system in solution where more detailed studies on the reaction mechanism are possible.

References

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