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Mechanistic insights of molecular metal polyselenides for catalytic hydrogen generation†

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Molecular metal chalcogenides have attracted great attention as electrocatalysts for the hydrogen evolution reaction (HER). However, efficient utilisation of the active sites and catalytic performance modulation has been challenging. Here we explore the design of immobilized molecular molybdenum polyselenides [Mo₂O₂S₂(Se₂)(Se_x)]²⁻ that exhibit efficient hydrogen evolution at low overpotential and stability over 1000 cycles. Density functional calculations provide evidence of a unimolecular mechanism in the HER process via the exploration of viable reaction pathways. The discussed findings are of a broad interest in the development of efficient molecular electrocatalytic materials.

Development of catalysts for the hydrogen evolution reaction (HER) is one of the key challenges in the realisation of a hydrogen economy based on electrocatalytic water splitting. The best performing HER catalyst is platinum, however its high cost and low natural abundance makes the development of noble-metal free catalysts an important area of research.¹ A variety of transition metal chalcogenides (ME_x) (M = Co, Fe, Ni, V, Nb, Ta, Mo, W; E = S, Se, Te) have been explored^{2–9} in a quest for discovery of low production cost catalysts with high catalytic activity, and stability under aqueous corrosive conditions. Despite the extensive research conducted in this area, even the well explored chalcogenide, MoS₂^{9–11} significantly underperforms as electrocatalyst for HER compared to Pt. This is due to the fact that most of the activity in MoS₂ comes from the edge sites which

represent only a small fraction of the overall number of active sites in solid state materials like MoS₂. Interestingly, molecular oxochalcogenides can incorporate by design a significant number of functional groups (which mimic very effectively the edge of solid-state chalcogenides) and have been shown to be at least as stable and effective as solid-state analogues. For example, the [Mo₂(S₂)₆]²⁻ cluster contains three disulphides per molybdenum,¹² while the hybrid family of LMo^{VI}O(S₂)₂ (where L = bidentate ligand) type catalysts exhibited an indicative cooperative electronic effect between the inorganic and organic components.^{13–15} When immobilised on an appropriate surface, they can effectively act as heterogeneous catalysts. Additionally, the design of the catalyst's key components (*e.g.* metal centres, type and number of chalcogens) can be pre-determined using a precise molecular chemistry approach. The all-inorganic molybdenum- and tungsten-based sulphide catalysts has shown overpotentials as low as -114 ± 3 mV at 10 mA cm⁻².¹⁶ The presence of well-defined molecular structures rendered the computational modelling more informative and reinforced our understanding of the HER mechanism. Theoretical calculations demonstrated that the reduction occurs on the disulphide ligand, while the terminal oxo ligand stabilise the negative charge developed during the catalytic process. Interestingly, investigation of other molecular chalcogenide equivalents^{17–20} for the HER and exploration of the edge based catalytic sites has not previously been attempted.

In this work, we investigated the effects of stoichiometric and structural control resulting from the appropriate combination of chalcogen elements and their ratio (*e.g.* O²⁻/Se₂²⁻) within the coordination sphere of earth abundant transition metals and compare their mechanistic differences with their sulfur analogues.

The dimeric nanocluster, [Mo₂O₂(μ-Se)₂(Se₂)(Se₂)]²⁻ **1**, was synthesised following a facile method under mild conditions. The synthetic approach exploits the selenophilicity of molybdenum by exposing an alkaline molybdate solution to selenizing conditions. Alternatively, at elevated temperature and pressure regimes, the equilibrium shifts towards the formation of a mixture of species with the general formulae [Mo₂O₂(μ-Se)₂(Se₂)(Se_x)]²⁻ (where *x* = 2–4) **2**.

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During the reaction the species $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_2)]^{2-}$, $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_3)]^{2-}$ and $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_4)]^{2-}$, seem to be in an equilibrium under harsh experimental conditions and found to co-crystallise within the same unit cell. Each method yielded orange-red crystals which were characterized by single crystal and powder X-ray structural analysis, FT-IR, ^{77}Se NMR and high-resolution electrospray ionization mass spectrometry (ESI-MS). Subsequently, the $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)]^{2-}$ **1** species was investigated as potential electrocatalyst to produce H_2 gas from acidic media where was found to exhibit excellent activity towards the hydrogen evolution reaction (HER). The oxoselenometalate compounds were synthesized under nitrogen atmosphere, following an optimised facile two-step process (see ESI†) utilizing low-cost materials, thus illustrating their potential for economically viable scalability.

The facile two-step synthetic procedure yields orange-red crystals and their single crystal X-ray diffraction (XRD) analysis shows that $[(\text{CH}_3)_4\text{N}]_2[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)_2]$ **1** crystallises in the orthorhombic system space group $Pca2_1$ with unit cell dimensions of $a = 18.614(10)$, $b = 11.422(6)$, $c = 11.422(6)$ Å. The powder X-ray diffraction study conducted on the freshly synthesised material **1** (Fig. S5, ESI†) further confirm the purity of the synthesised material in the hexa-selenide form. Alternatively, the more challenging high temperature and pressure synthesis gives crystals containing a mixture of seleno-containing species with the formula $[(\text{CH}_3)_4\text{N}]_2[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)_{0.25}[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_3)]_{0.25}[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_4)]_{0.5}]$ **2** which crystallises in the triclinic space group $P\bar{1}$ with unit cell dimensions of $a = 10.098(4)$, $b = 12.766(5)$, $c = 18.713(7)$ Å, ($\alpha = 78.432(4)^\circ$, $\beta = 80.140(4)^\circ$ and $\gamma = 86.939(4)^\circ$). Fig. 1 displays the crystal structures of the $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)]^{2-}$ **1** and the $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_4)]^{2-}$ anion found in **2** respectively. The $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)]^{2-}$ and $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_4)]^{2-}$ anions are constructed by two molybdenum centres that are mutually linked by two $\mu\text{-Se}^{2-}$ bridges, and a $\text{Mo}^{\text{V}}\text{-Mo}^{\text{V}}$ separation of 2.885(1) and 2.884(2) Å. In addition, the coordination sphere of each molybdenum centre is completed by a terminal oxo group of $\text{Mo}=\text{O}$ bond distances 1.687(8) and 1.68(1) Å and two selenide bridging atoms with an average $\text{Mo}-(\mu\text{-Se})$ bond distances of *ca.* 2.447 and 2.461 Å, respectively.

Finally, in the case of the $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)]^{2-}$ anion the coordination sphere of Mo is completed by two terminal diselenide (Se_2^{2-}) groups with an average Se–Se bond distance of *ca.* 2.323 Å, while in the case of $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_4)]^{2-}$

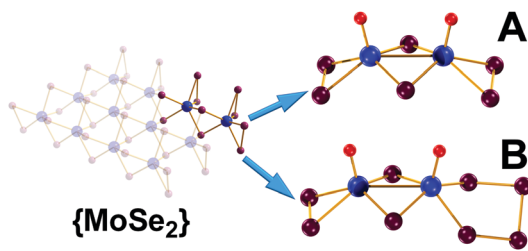


Fig. 1 Ball-and-stick representation of: (A) $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)_2]^{2-}$ and (B) $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_4)]^{2-}$. Colour code: Mo, Blue; Se, plum; O, red; Counterions are omitted for clarity.

that is by a diselenide (Se_2^{2-}) and a tetraselenide (Se_4^{2-}) group with average Se–Se bond distance of *ca.* 2.333 Å. The overall charge of the compound is compensated by two tetramethylammonium, $(\text{CH}_3)_4\text{N}^+$, cations per dimeric cluster.

In an effort to further characterize the isolated compounds, we employed high resolution electrospray ionization mass spectrometry (ESI-MS)^{21–23} to determine the composition of the oxoselenometalate species in solution. The ESI-MS studies were performed in CH_3CN . A series of singly charged distribution envelopes were observed, all in the region of 500–1000 m/z (Fig. S4, ESI†). More specifically, the distribution envelopes centred at 699.18 m/z value can be assigned to the intact compound $[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)]^{2-}$. Additionally, ^{77}Se NMR spectrum of **1** recorded in DMF. The spectrum shows two distinct peaks corresponding to the two unique environments in the dimer located at shifts of 134 and 711 ppm relative to Me_2Se (Fig. S6, ESI†).

To investigate the HER activity of the molecular catalyst we immobilised the catalyst on a glassy carbon electrode (GCE) support (see ESI†).

The amount of catalyst on the electrode surface was controlled by adjusting the loading concentration and volume. The performance of the catalyst improves as a function of the catalyst loading up to the value of $3.38 \mu\text{mol cm}^{-2}$. Beyond this value the quality and mechanical stability of the produced electrocatalytic film degrades which leads either to similar or inferior performance due to detachment of the film from the electrode's surface. The results reported in Fig. 2 indicate that the cluster is highly active towards HER revealing a very small onset (40 mV) and low overpotential of -165 ± 3 mV (at $j = 10 \text{ mA cm}^{-2}$) as a function of the catalyst loading. Consequently, further increase of the applied overpotential results in a rapid rise of the cathodic current, which is

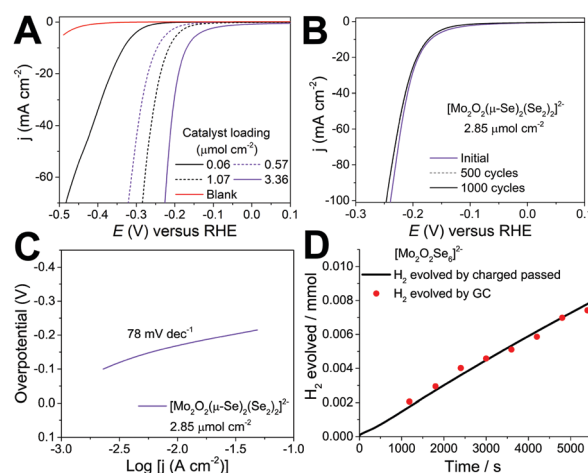


Fig. 2 Electrochemical measurements of the molecular chalcocide for HER electrocatalysis in 1 M H_2SO_4 . (A) Observed polarisation curves as a function of the concentration of the catalyst; (B) Stability of the catalyst after 1000 cycles; (C) Corresponding Tafel plot and (D) Hydrogen evolved over time determined by charge passed (black line) and gas chromatography (red squares) $(\text{Me}_4\text{N})_2[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)]$ deposited on glassy carbon electrode.



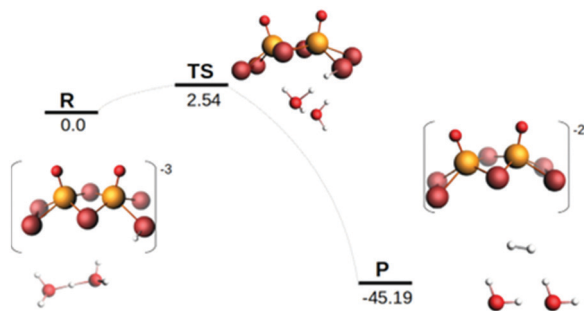


Fig. 4 Activation energy and transition state for **B1** $\text{H}[\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)_2]^{3-}$.

(BB1, Fig. S24, ESI†, $\Delta G^\ddagger = +16.52 \text{ kcal mol}^{-1}$). Interestingly, when the interaction takes place on the bidentate $\kappa^{1,4}\text{-Se}_4^{2-}$ terminal site the calculated activation energy and transition state for $[\text{H}_2\text{Mo}_2\text{O}_2(\mu\text{-Se})_2(\text{Se}_2)(\text{Se}_4)]^{2-}$ (BB3) was found to be lower ($\Delta G^\ddagger = +14.4 \text{ kcal mol}^{-1}$ (Fig. S25, ESI†).

It is worth noting that single-protonated forms have significantly lower activation energies than the double-protonated ones. The activation barriers for compounds **1** (B1) and **2** are only 2.54 (Fig. 4) and 5.18 kcal mol^{-1} (Fig. S23, ESI†), respectively. Thus, the model of the transition state for single protonated forms is the most probable candidate. For the non-reduced, single- and double-reduced species, their double-protonated forms are the most thermodynamically stable. Considering electrochemical routes, $2e^-$ addition to double-protonated non-reduced species is non-favourable. In contrast, reduction reactions from single protonated and non-protonated forms are more feasible (Fig. 3). Thus, our results clearly point towards the Heyrovsky mechanism based on thermodynamic favourability and the high activation energies observed for the alternative Tafel step.

In conclusion, a more accessible and high-yield synthesis for the selenium analogue to the well-known $[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2)_2]^{2-}$ structure makes it possible to explore the electronic and chemical properties of the molecule, which have previously remained unexplored. The performance of the molecular catalyst for the hydrogen evolution reaction was evaluated while we propose viable mechanistic pathways in relation to the interaction between catalysts and substrate while we identified intriguing differences with their sulphur analogues. The initial $1 e^-$ reduction is easier compared to the sulphur containing analogue however the second reduction is more energetically demanding which is reflected to the observed slightly elevated Tafel slope. This indicates the significant electronic changes of the selenium containing structure relative to the sulphur. Notably, these results represent an attractive strategy for preparing next generation HER electrocatalysts. Understanding the electronic underpinnings of trends in activity as a function of the metal or chalcogen incorporated in the molecular

species, can help inform the design of new catalysts and exploitation of cooperative and structural effects. Moreover, the development of facile low-cost synthesis of a molecular catalyst is highly desirable for the easier scale up in large scale applications.

Conflicts of interest

There are no conflicts to declare.

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