Molybdenum sulfide for energy applications

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MOLYBDENUM SULFIDE FOR ENERGY APPLICATIONS

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SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES

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MOLYBDENUM SULFIDE FOR ENERGY APPLICATIONS

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Summary

This thesis examines the use of molybdenum sulfide material for energy related applications, specifically into electrocatalysis for hydrogen evolution reaction (HER). It looked into some of the fundamental aspects of the practical application of molybdenum sulfide material when use as a starting material or for the electroanalysis measurements. This thesis is broadly separated into two sections, where **Section I** explores the variations in the electrocatalytic performances of molybdenum disulfide from various commercial sources while **Section II** investigates into the use of various solvents as dispersion medium for molybdenum sulfide materials.

Chapter 1 introduces the motivation and reviewed some of the state-of-the-art molybdenum sulfide materials as an efficient catalysis. In **Chapter 2**, the electrocatalytic performances of molybdenum disulfide from various commercial sources were investigated and extensive characterization tools were employed to discuss the differences. Effects of various solvents as a dispersion medium for molybdenum disulfide was explored in **Chapter 3** while the effects on molybdenum trisulfide will be discussed in **Chapter 4**. The conclusion of the thesis can be found in **Chapter 5**.

Authors' Contribution

The author would like to acknowledge the collaboration with Prof. Zdeněk Sofer's group from Czech Republic. The data listed as follows were contributed by our collaborators: X-ray diffraction (XRD), X-ray fluorescence (XRF), particle size analysis of the samples in Chapter 2 and the synthesized material (MoS_2) used in Chapter 3. Lastly, the author would also like to acknowledge Naziah for the XPS raw spectrum for powder- MoS_3 in Chapter 4.

List of Abbreviation

$^{\circ}\text{C}$	Degree centigrade
ΔE_p	Peak to peak separation
k^0_{obs}	Observed Heterogeneous Electron Transfer Rate
ACN	Acetonitrile
BE	Binding Energy
CV	Cyclic Voltammetry (Voltammogram)
DMF	N,N-dimethylformamide
EtOH	Ethanol
GCE	Glassy Carbon Electrode
HER	Hydrogen Evolution Reaction
HET	Heterogeneous Electron Transfer
IGA	Inorganic Graphene Analogues
LSV	Linear Sweep Voltammetry (Voltammogram)
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PBS	Phosphate Buffered Solution
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscope
XPS	X-ray Photoelectron Spectroscopy

Chapter 1

Introduction

1.1 Motivation

The problem facing today's technologically-savvy and knowledge based population is to deal with the consequences of our burgeoning fascination with energy intensive lifestyle. The unrestricted use of fossil fuels has brought about consequences unintended. There is reportedly an increase in the occurrences of floods and droughts, and many have attributed the cause to escalating global temperature caused by greenhouse gases such as CO₂.¹⁻² The threat to survival and continuity of all life forms is universal. However, energy security is central to sustain our modern way of life.³ As such, the scientific community is now eager to look for energy sources that are carbon-neutral or environmentally sustainable and realizing it to the market. With exploding and constantly growing demand for energy due to increase in population and affluent lifestyle, alternative clean energy must be realized before the exhaust of fossil fuel and/or the environmental consequences becomes irreversible. Hydrogen as one of the most abundant element,⁴ presents itself as a solution to both sustainability and energy security.⁵

Fuel cell, present itself as an alternative to combustion driven system. It converts chemical energy directly to electrical energy,⁶ utilizing hydrogen as its fuel. Hydrogen has long been known as a clean fuel, with the largest energy density amongst the known fuel,^{5, 7} and hence, promising to replace the carbon economy that the world is now based on. It is considered clean as only water is produced as its side product when it is oxidized.^{3, 8} It also has a high energy yield that is "2.75 times greater than hydrocarbons fuel".^{2, 9} Furthermore, fuel cell powered by compressed hydrogen is experimented to produce lesser emissions as compared to conventional diesel-powered buses and would

improve air quality significantly.¹⁰⁻¹¹ The current convention of hydrogen gas production is through steam reforming of hydrocarbons where carbon-oxides (CO_2 and CO) are also formed as a mixture with hydrogen gas. Further separation would also be required and it is energy intensive. The conversion of corn to yield ethanol, which act as a liquid fuel for generation of hydrogen is attractive. This means of production of liquid fuels from biomass appears to be renewable and clean.¹² With intensive research conducted over the years, efficiency would be much better in time to come. However, the direct competition of using these biomass (such as corn) for energy to food in this resource constrain world where hunger is not fully eradicated does not seems to be the best way forward. A carbon-neutral method with less complications with food security would be the splitting of water either through (1) photochemical method¹³ or (2) electrochemical splitting of water using energy generated from renewables such as solar or wind energy.^{5, 14-15} However, the gap between realizing the science into large scale application is limited by several factors.¹⁶⁻
¹⁷ (1) Economic and, (2) technology bottleneck. Firstly, the most efficient catalyst to date for hydrogen evolution reaction (HER) is Pt,¹⁷⁻¹⁸ a rare earth metal, and its prices has been constantly increasing.¹⁸ This prevents the large scale implementation in an economical fashion as it is not cost-competitive. Other issues would include the huge infrastructure cost to shift from the current gasoline system.¹⁹ Next, the storage of hydrogen gas is also a problem, associating not just with high capital cost but also major safety concerns.^{3, 16, 20} Metal hydrides are currently the top-choice material for hydrogen storage, with better and improved efficiencies, recovery and safety.²¹ In order to achieve carbon-neutrality when hydrogen is used as a fuel, we have to consider the

production process of hydrogen gas itself. This thesis focuses on the electrochemical method of splitting water, where the effectiveness of the material as an electrocatalyst is studied. The pursuit towards an efficient electrocatalyst that move away from noble metal continues to be important research area throughout the decade^{17-18, 22-23} and this motivates the purpose of this thesis.

1.2 Hydrogen Evolution Reaction (HER)

Moving forward, it is the goal of environmentalists and scientists to move towards achieving the goal of a “hydrogen economy” and an economical production of hydrogen is therefore, pertinent. Although hydrogen is one of the most abundance element, it does not exist freely in nature and it has to be synthesized. This renders hydrogen as a secondary form of energy.⁹ The direct thermal splitting of water is highly energy intensive requiring temperature of more than 2500 K and an efficient system to separate the hydrogen and oxygen produced.^{5, 24} Electrolysis of water would separate the products formed at the cathode and anode respectively. The electrochemical splitting of water is widely and extensively studied, drawing conclusions to its pathway.²⁵⁻²⁹ In general, HER in an acidic solution (pH 0) is given by the following chemical equation:

And the corresponding half reaction occurring at the anode is known as the oxygen evolution reaction (OER):³⁰

The cathodic HER is regarded as a classic example in the field of electro-kinetics.^{25, 28, 31} HER in acidic medium is thought to involve an adsorption and desorption process where the evolution of molecular hydrogen occurs at the electrode surface. The following shows the HER pathway when occurred in acidic medium:^{25-28, 31-33}

Table 1-1: HER Mechanism in Acidic Medium

Volmer	$H_3O^+ + e^- \rightarrow H_{ads} + H_2O$
Heyrovsky	$H_3O^+ + e^- + H_{ads} \rightarrow H_2 + H_2O$
Tafel	$H_{ads} + H_{ads} \rightarrow H_2 + H_2O$

HER can possibly occur in two different pathways, being either (a) Volmer-Heyrovsky or (b) Volmer-Tafel. The adsorption of hydrogen ion to the electrode surface occurs during the Volmer step. In (a), an adsorbed hydrogen atom combines with a hydrogen ion to form molecular hydrogen; while in (b), the Tafel step is commonly known as the combination step where two adsorbed hydrogen combines to give the final product. The electrode surface function to transfers the electron to hydrogen ion in the electrolyte and to the adsorb hydrogen atom.³¹ As such, the composition or morphology of the electrode's surface is highly crucial to its performance as a HER electrocatalyst. The free energy of hydrogen adsorption (ΔG_H) is an important factor in affecting the reaction kinetics since adsorbed hydrogen atom is involved in both of the possible pathway.³³⁻³⁵ As both the adsorption (Volmer) and desorption (Heyrovsky or Tafel) of hydrogen atom occurs simultaneously for HER, the best catalyst would have a hydrogen adsorption energy that is close to thermoneutral value ($\Delta G_H = 0$). This means that the catalyst itself does not bind too strongly nor too weakly to the hydrogen atom. If the surface and hydrogen atom binds too strongly, desorption would be difficult and the catalytic surface would be poisoned; and if it binds weakly, the hydrogen adsorption step (Volmer step) would be limited and activation is hard.³⁶ This relationship of binding ability of electrodes' surfaces to hydrogen atom adsorbed is first discussed by Parsons³⁴

and resembles that of the Sabatier principle. The Sabatier principle is exemplified by the ‘volcano’ plot which is main tool to predict the best electrocatalyst for HER, where the exchange current density (j_0) is plotted against ΔG_H (Figure 1-1).^{29, 36-37} It predicts that the best catalyst would have moderate binding affinities to the intermediates. Hinnemann *et al.*, concluded that the use of free energy of hydrogen adsorbed is a good parameter for the prediction of active catalyst for HER, and it is useful for both metals and enzymes alike.³⁸

Figure 1-1: Exchange current density as a function of the free energy of adsorbed hydrogen (ΔG_H). (top) Experimentally determined values; (bottom) theoretical kinetic model. (Reproduced from reference 37)

Pt is the benchmark as a HER electrocatalyst, situating at the top of the ‘volcano’ plot.^{18, 36-37} Till date, the search for an equally high performance electrocatalyst composed of inexpensive precursors is still actively on-going.^{23, 39} This is a critical phase in advancing towards the goal of a hydrogen economy.⁴⁰ Non-precious metal⁴¹⁻⁴² and metal-free catalyst are gaining much attention with their cost advantage and further development of the catalyst can allow it to achieve similar efficiency as some of the benchmark materials.³⁹

Transition metal (TM) chalcogenides,⁴³⁻⁴⁵ TM-nitrides,⁴⁶ TM-carbide⁴⁷⁻⁴⁹ and TM-phosphides⁵⁰⁻⁵² are some of the current emerging materials developed for HER. Metal-free catalyst containing only C and N were reported to be as efficient HER electrocatalyst as their metal-based counterparts.⁵³ The hybridized structure (g-C₃N₄@NG) containing graphitic-carbon nitride (g-C₃N₄) with N-doped graphene (NG) shows excellent HER activity (0.24 V) with a Tafel slope of 51.5 mV dec⁻¹. g-C₃N₄@NG is much more active than the individual pure g-C₃N₄ or NG which lacks conductivity and active sites respectively. This illustrates some of the design and research directions for future HER catalyst. Molybdenum Sulfide for HER will be discussed in greater detail in the following sub-section.

1.3 Oxygen Reduction Reaction (ORR)

Hydrogen evolved is used as the fuel for fuel cell such as a proton exchange membrane fuel cell (PEMFC). PEMFC is widely studied and advanced in the mobile electronic devices and vehicles sector due mainly to its functionality in low temperatures, and other advantages such as compactness and fast start-ups.⁵⁴⁻⁵⁵ In a fuel cell, hydrogen oxidation reaction (HOR) would occur at the anode and the corresponding cathode reaction is the oxygen reduction reaction (ORR).

Table 1-2: The Electrochemical Reaction Occurring in a Fuel Cell.

Anode (HOR)	$H_2 \rightarrow 2H^+ + 2e^-$
Cathode (ORR)	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

ORR is kinetically much more sluggish than HOR. The cathode requires a much higher catalyst loading even with the use of Pt. To achieve the needed fuel cell performance, the cathode requires about 8 times higher in terms of catalyst loading as compare to the anode.⁵⁵ This provides a much needed urgency to improve the catalytic performance of the cathode so that it is much more economical, allowing a more widespread utilization of this technology in the near future. Till date, Pt still remains as the top choice for incorporation in technological devices involving fuel cells.⁵⁶ Toyota Mirai, the world's first fuel cell vehicle sold commercially utilizes PtCo catalyst as its cathode for ORR. Despite the improvement of the ORR efficiency from its 2008 model, the use of rare earth metal has not yet been fully eradicated.⁵⁷ As such, the pricing of such a fuel cell vehicle (FCV) is still not as compelling and attractive as a conventional combustion engine vehicle⁵⁷ and this would have limited the adoption of clean-technology. Thus, only when technological advancement is tied together with economic consideration will we see success in its wide-spread adoption. This prompts environmentally conscious scientists to work towards achieving a 'low rare earth metal loading catalyst with equally good activity'.

Towards approaching this goal, the research community has studied and developed efficient ORR catalyst, mainly divided into 2 groups: (1) precious-metal based alloys and (2) non-precious metal catalyst (NPMC). Precious-metal based alloys reduce the usage of the precious rare earth metal such as Pt and also ensures the high catalytic performance of such alloys. One of the notable alloys with the best activity is observed with those having the bulk Pt₃Ni (111) surface. Metal-doped Pt₃Ni octahedral was recently developed with enhanced ORR catalytic activity and stability superior to that of Pt-Ni nanostructures. Mo-

Pt₃Ni/C shows the best performance for ORR catalysis as compared to the other transition metal-doped (V, Cr, Mn, Fe, Co W) Pt₃Ni/C. It also improves the robustness of the undoped-Pt₃Ni/C catalyst.⁵⁸ In order to reduce dependency on rare earth metal, the community turns towards the development of the broader based NPMC. This can include abundant-metal based catalyst,⁵⁹⁻⁶⁰ metal-free catalyst⁶¹⁻⁶³ or more common would be the hybrid metal-carbon based composites.⁶⁴⁻⁶⁵ Transition metal oxides are reported to be promising catalyst for ORR.⁶⁶⁻⁶⁷ More interestingly, there have been developments in transforming organic waste materials into functional material.⁶⁸⁻⁷⁰ Seaweed-derived material and treated organic-rich amaranthus waste were demonstrated to be applicable as a catalyst for ORR.^{71 72}

1.4 Molybdenum Disulfide

Riding on the waves of the Nano-era, transition metal dichalcogenides (TMDs) have gained significant interest in the recent decade due to their structural and electronic properties when reduced from bulk. In the bulk form, it closely resembles that of graphite with similar layered structure.⁷³ With the ground-breaking discovery of the successful synthesis of free-standing graphene in 2004,⁷⁴ its inorganic analogue (known as inorganic graphene analogues, IAG) have benefited from the spotlight. The IAG would include the likes of TMDs, and in particular, molybdenum disulfide (MoS₂) is one of the materials that garners the most attention.

Structure

MoS₂ is a group VI metal dichalcogenide and it is naturally occurring as molybdenite ore.⁷⁵ It is one of the most stable TMDs.⁷⁶ In its bulk form, it is described as a layered structure, with each layer being tri-atomically thick. It was reported that the interlayer forces are about 100 times weaker than the intralayer forces.⁷⁷ Each layer consists of S-Mo-S covalently bonded together and weak van der Waals forces of attraction exist between the layers as in graphite. And because of this additional variability, there are different structural allotropes of MoS₂ based on its coordination and stacking pattern. The Mo atom could be coordinated to the S atoms in a trigonal prismatic manner (2H or 3R) or octahedrally (1T). The type of coordination determines the phase of the structure. The three more common polytypes are: hexagonal 2H, rhombohedral 3R and tetragonal 1T phase. The pre-suffix numeric represents the number of layer in a unit cell along the *c* axis while the alphabets represents the symmetry type. For the 1T-phase, each single layer in the unit cell follows the repeating pattern of AbC and the only sequence in bulk structures would be AbC AbC AbC. For the 2H-phase, the two layers in the unit cell follows the repeating pattern AbA BaB; 3R-phase, the unit cell contains three layers following the sequence AbA CaC BcB (Figure 1-2).⁷⁸

Figure 1-2: The pictorial representation of the 3 polytypes of MoS₂. (Reproduced from reference 78)

Applications

MoS₂ is a highly functional material which has applications spanning across many areas. Traditionally, MoS₂ application focuses on its use as a dry lubricant⁷⁹ and as an effective catalyst for hydrodesulphurisation process.⁸⁰⁻⁸¹ Moving forward, MoS₂ has find itself useful in the area of sensing,⁸²⁻⁸⁷ flexible devices,⁸⁸ energy storage,⁷⁵ and for biological applications such as being a plausible future antibiotics with its antibacterial properties,⁸⁹ as drug delivery-vector⁹⁰ or as bioimaging probes.⁹¹ Before diving deeper into MoS₂ applications in HER, some of its emerging applications will be mentioned briefly.

Figure 1-3: Shows wide arrays of MoS₂-based sensing devices. (Reproduced from reference 87)

MoS₂ has recently seen its application in the area of sensing, whether is it for detection of biomolecules or gas molecules (such as NO_x or CO). Figure 1-3 shows some of the various platforms where MoS₂ has been studied for sensing. Some examples are briefly described as follows. Single layer reduced-MoS₂ is demonstrated to be able generate distinct oxidation peak to selectively detect dopamine in a mixture of ascorbic acid, dopamine and uric acid.⁸⁴ These biologically important molecules are hard to distinguish from each other using voltammetry techniques.⁸⁴ MoS₂-based tactile sensor was recently reported to show high sensitivity, good uniformity and outstanding mechanical flexibility. Performance reproducibility were also obtained even on unconventional substrate such as a human fingertip.⁸⁵ With the emergence of super bacterial pushing the limits of medical advancement, nanomaterials serve as a plausible alternative. Till date, there has yet to be any report on the resistant of bacterial against gold nanoparticles-based antibiotics. Positively functionalised-MoS₂ was reported to have antibacterial properties against methicillin-resistant *S. aureus* (MRSA) and *P. aeruginosa* but exhibited low eukaryotes cell toxicity, hinting at its application as a future medicine. When compared to other small

molecules, functionalised-MoS₂ was found to have a lower antibacterial dosage. This makes it an even more promising antibacterial drug.⁸⁹

Molybdenum Disulfide (MoS₂) for HER

Molybdenum Sulfide have emerged as an important class of materials for HER. Earlier in the chapter, the criterion for an effective HER catalyst has been discussed. The popularity of MoS₂ for HER can be attributed to the study in 2005 by Hinnemann *et al.*³⁸ Indeed, nature has been the solution and has provided clues with its beauty. The computational work of Hinnenmann *et al.* uses density functional theory (DFT) to calculate the functionality of nanoparticulate MoS₂ as an efficient HER catalyst, based on natural enzyme (nitrogenase) which is an efficient HER catalyst. MoS₂ was found to fit computationally into their calculations and that the MoS₂ edge sites closely resembles to nitrogenase's active sites. Subsequently, Jaramillo *et al.* further confirmed this computational result by showing the high catalytic efficiency of MoS₂ nanocrystals and identifying the active sites as the edge sites. The authors found that the current response scaled linearly with the number of edge sites present.⁹² Tan *et al.* also concluded that the edge sites are much more active than the basal plane when using macroscopic crystals for measurements.⁹³

The precious metal-free MoS₂ with high activity presents itself as a practical and useful material for the electrochemical production of hydrogen.³³ MoS₂ would have been an ideal candidate in the quest to replace Pt as leading position for HER catalyst. MoS₂ from mineral molybdenite is abundant and hence cheaper than Pt.⁷⁵ Tsai *et al.* conducted DFT calculations of the ΔG_H on

the basal plane, Mo and S edges and again confirming that the active sites are the edge sites, with Mo-edge having a more thermoneutral value compared to the S-edge (Figure 1-4).⁹⁴

System	Surface	Stable structure	θ_S (ML)	θ_H (ML)	H adsorption ΔG_H (eV)
MoS ₂	Basal plane (0001)			0.0625	1.92
	Mo-edge (10 $\bar{1}$ 0)		0.5	0.25	0.06
	S-edge ($\bar{1}$ 010)		1.0	1.0	-0.45

Figure 1-4: Shows the ΔG_H of the basal plane, Mo edge and S edge. Legend: blue spheres – Mo; yellow spheres – S. (Reproduced from reference 94)

There has been an explosion of interest in MoS₂ for electrocatalytic HER performance since. These tap on the intrinsic properties of MoS₂ and to further enhance it in their catalyst design. In order to maximise MoS₂ potential as a catalyst for HER, there are several broad classes of design-engineering that researchers worked on. The anisotropic properties of the structure provided a motivation to preferentially enhance the density of the more catalytic edge site in place of the relatively inert basal plane; or to try to activate the basal plane. These strategies are broadly categorized into (1) increasing the density of the active edge sites of the material and (2) enhance the intrinsic properties of MoS₂ for catalytic activity. Some of the research findings prominent or recent in this field would be presented.

(1) Increasing density of catalytic edge sites

Many research teams tried to increase MoS₂ catalytic performance for HER by designing a catalyst with a higher number of edge sites per area. This can be done either through a variation in synthesis method⁹⁵⁻⁹⁶ to expose more edge sites or by specific catalyst design.⁹⁷⁻⁹⁹

Defect engineering could be used as an approach for structural design to specifically exposed certain crystal plane to increase the accessible internal surface area. This concept can be utilized to introduce defects on the inert basal plane to expose more catalytic edge sites thereby enhancing its catalytic performance. Xie *et al.* have demonstrated that the use of excess thiourea is necessary for defect formation.⁹⁶ This defect rich MoS₂-nanosheets that were formed exhibited extremely high activity for HER, requiring a low onset potential of 0.12 V. When compared with the defect-free sample, a lower onset potential and Tafel slope were obtained for the defect-rich MoS₂. This provided evidence as a proof of concept for the use of defect engineering. Kong *et al.* intentionally designed MoS₂ structures with vertically aligned layers on its film to maximise the exposed active edge sites and to reduce resistance of electron transport across the layers (Figure 1-5).⁹⁷ Such edge terminated-structure was generally considered to be metastable but not for MoS₂ where the surface energy of the edge site is 2 orders of magnitude greater than the terrace sites.⁹⁷ One other notable example includes the double-gyroid MoS₂ structure. Its nanoscale curvature limits the formation of extended inert basal plane hence it preferentially exposes more active edge sites.⁹⁸

Figure 1-5: Schematic diagram of the vertically aligned MoS₂ sheets.
(Reproduced from reference 97)

(2) Enhancing the intrinsic properties of MoS₂

Another strategy commonly used would be to enhance the intrinsic properties of the material. It could be an activation of the (0001) basal plane which is deemed to be inert or less catalytic,¹⁰⁰⁻¹⁰¹ tuning towards a more thermoneutral neutral value for the free energy of hydrogen adsorption either at the Mo or S edge¹⁰² or improving the conductivity of the material to improve electron transfer rate.¹⁰³⁻¹⁰⁴

Li *et al.* demonstrated both theoretically and experimentally, the use of strain engineering to produce eventual S vacancies in MoS₂ in the basal plane act as a highly catalytic site for HER.¹⁰⁰ Using first principles calculation, Ouyang *et al.* investigated 16 types of structural defects and found that 6 types of defects (Figure 1-6) can activate the inert basal plane thus leading to an enhancement in its catalytic performance. These defects, if present on the basal plane would provide catalytic sites for HER.¹⁰¹

Figure 1-6: The 6 types of defects that has shown to activate the basal plane using first principles calculation. Legend: V_s – monosulfur vacancy; V_{MoS_3} - vacancy complex of Mo and nearby three sulfurs; Mo_{S_2} - a Mo atom substituting a S_2 atom; $4|8a$ - 60° - tilt composed 4-8 rings; S bridge; Mo–Mo bond. (Reproduced from reference 101)

Doping is commonly used as a strategy to tune the structure, properties and hence activity of a material.¹⁰⁵ Theoretically, DFT study have also identified 14 types of transition metal dopants (Pt, Ni, Ru, Rh, Co, Fe, Mn, Ta, V, Nb, Cr, Os, Ir, and Re) to be able to enhance the ΔG_H at the S-edge.¹⁰² Experimentally, V- and Co-doped-MoS₂ was found to be catalytically more active than the undoped-MoS₂.^{103, 106} Sun *et al.* reported that the presence of V-dopant successfully enhanced its conductivity with a higher carrier concentration and hence a faster electron transfer process. This explains the lower onset potential (−0.13 V) achieved by the V-doped MoS₂ nanosheets. Its conversion to semi-metallic properties without causing a parallel phase change is an important finding as most enhanced conductivity is accompanied by a corresponding phase change to the 1T-metallic polytype.¹⁰³ Hybrid materials thriving on the synergistic effect of the different components are commonly designed and reported to be of good catalytic activity. MoS₂ nanoparticles on reduced graphene oxide (rGO) has shown to be exceptional for its HER catalytic activity,

with both a low onset potential (~ 0.1 V) and small Tafel slope (41 mV dec^{-1}). One of the reason cited for the exceptional activity was the enhanced conductivity due to the electrical coupling to the rGO support which results in a rapid transfer of electron.¹⁰⁴ Lastly, inducing phase transformation to the metallic 1T phase is also a strategy being commonly pursued.¹⁰⁷⁻¹⁰⁸

1.5 Amorphous-Molybdenum Sulfide (MoS_x)

Beyond crystalline MoS_2 , amorphous molybdenum sulfide ($\text{a-MoS}_x, x \geq 2$), with composition typical of MoS_3 , have shown to be highly active as an electrocatalyst for HER.^{40, 109-113} MoS_3 has no crystalline counterpart¹¹⁴⁻¹¹⁵ and amorphous materials typically lack long range order but exhibit define short range arrangement.¹¹⁶ Highly crystalline- MoS_2 obtained at 1000°C was found to be an inferior HER catalyst.¹¹¹ Similarly, higher growth temperature beyond 420°C is observed to exhibit decreasing HER catalytic activity. Interestingly, a-MoS_x was not only reported to be active for HER, but has shown to exhibit consistently lower Tafel slope as compared to their crystalline counterparts. The chalcogen to Mo ratio was found to be less decisive in defining the Tafel slope range.¹¹⁷ a-MoS_x is less well-known when compared to MoS_2 , which have a huge amount of literature reviews and articles recording intensive theoretical and experimental research data. On the other hand, the amount of literature on this branch of molybdenum sulfide (a-MoS_x) pales in comparison but is growing steadily since its emergence as an effective electrocatalyst in 2011 by Hu's group.¹¹⁸ The allure of such amorphous material stems not only from its exceptional catalytic (electro- or photo-catalytic) HER performance, but also from its milder synthesis conditions, hence more energy and cost effective. It is only logical that a less energy-intensive synthesis method be applied for the

preparation of materials for clean energy or energy-saving applications. On the contrary, crystalline MoS₂ (nanoparticles) instead, are commonly synthesised under elevated temperature and/or high vacuum.¹¹⁹⁻¹²⁰ This is counter intuitive if it were to be used for clean energy applications and the harsh conditions might limit the scalability and practicality of such processes.¹¹⁰

Amorphous-MoS_x for HER

Recent development with a-MoS_x for HER catalyst will be discussed in the following sub-section. Similarly, the catalyst design for a-MoS_x thus far can be divided into two categories: (1) increasing the conductivity and (2) increasing the catalytically active sites or electrochemically active surface sites.

(1) Increasing the conductivity

MoS₂ nanoparticles grown on rGO which is a highly efficient HER catalyst reported by Li *et al.* is an epitome.¹⁰⁴ Drawing parallels, many functional catalyst design closely resembles such strategy. Hybrid structures containing both the a-MoS_x and a conductive substrate has been a common and effective strategy employed to combat the MoS_x slow electron transport rate and low conductivity. Multiwalled Carbon Nanotubes (MWCNTs) was added to as-prepared MoS₃ solution (MoS₃ sol) as a conducting additive and the authors found a positive correlation of the MWCNT loading and the current density recorded.¹²¹ Mo-supported-a-MoS₃ were not only shown to exhibit outstanding HER catalytic performance, but also demonstrated to be functional in solar-water splitting devices. The incorporation of the prepared material into a practical device justifies the functionality of the material.¹²² The Mo-supported-a-MoS₃ is described to have a porous and nanostructured morphology. The

enhanced performance is again, attributed to the Mo support, which improves conductivity and hence the electron transport and interfacial charge transfer. Its porous and nanostructured morphology is thought to be responsible for the larger electrochemically active surface area. The hybrid structure of a-MoS_x on N-doped Carbon Nanotube (CNT) forest hybrid achieved the standard –10 mA cm⁻² current density at a low overpotential of 0.11 V, rivalling some of the best molybdenum sulfide HER electrocatalyst to date. This result is explained by the interplay of the nanometer thick a-MoS_x, dense catalytic sites and the deliberate design of the NCNT forest, with NCNT having a high electro-conductivity.¹²³ Other examples include the use of nanoporous gold as a substrate for a-MoS_x which is active for HER in both acidic and neutral medium;¹¹² Graphene-a-MoS_x composite;¹²⁴ the hybrid structure of a-MoS_x on Graphene-CNT (GCNT) as a highly active HER catalyst (Figure 1-7).¹²⁵ Electrochemical deposition was chosen as it would ensure all of the electrically accessible sites of the GCNT be coated.

Figure 1-7: Illustration of the GCNT/CP support and the MoS_x/GCNT/CP electrode. Legend: GCNT – Graphene Carbon Nanotube; CP – carbon paper. (Reproduced from reference 125)

(2) Morphology control to increase catalytic sites

The higher activity of a-MoS_x is attributed to the higher number of unsaturated Mo and S site^{118, 126} and it has catalytic sites across the entire surface.¹²³

In contrast, 2D-MoS₂ is only catalytic at the well-defined edges.⁹² Despite the intrinsically higher amount of active sites, efforts can be taken to further enhance this property. Active site maximization can be engineered by directing the morphology or surface sites to ensure the active sites are preferentially exposed. Defect engineering, such as the introduction of S vacancy through the use of hydrogen plasma not only helped to increase the active sites density, but also altered its surface energy. After plasma treatment, the a-MoS_x is determined as MoS_{1.7} (before: MoS_{3.1}) and becomes hydrophilic. It releases H₂ bubbles much faster than Pt surfaces. Hence, at high current density, the plasma-a-MoS_x (MoS_{1.7}) becomes comparable and even better than Pt, where the release of H₂ bubbles from the Pt surface is thought the limit the reaction.¹²⁷ 0-dimensional (no sides were greater than nm range) a-MoS_x quantum dots with small diameter (< 3 nm) showed extremely good HER catalytic efficiency in neutral medium. The smaller dimensions hence more Mo vacancies and a higher proportion of S active sites, with the presence of more bridging S₂²⁻ explains the performance.¹⁰⁹ Other examples includes the growth of MoS_x on graphene-protected 3D Ni foam which results in high catalyst loading thus number of active sites and reduced resistance.¹¹¹ Specific morphology design such as hollow prism structure of Co-MoS₃ was found to be highly efficient as compared to spheres or polyhedron Co-MoS₃ which were rather mediocre.¹²⁸

From the recent developments, some of the structures are superior than others. Apart from morphology control or tapping on the synergistic effect of hybrid structures which more often than not provide both larger surface area and enhanced conductivity, specific tuning can also be done with the incorporation of other metals such as Co or Ni. and in such cases, certain metal ions were found to be more effective than others.¹²⁸⁻¹²⁹

Much of the research finding discussed were only very recent, with many of them published just in 2016. This explains the great potential in the research of a-MoS_x materials. There is much more for the research community to discover. Although the activity for HER is not yet well understood as of now, extensive efforts by various research groups will accelerate our understanding and aid in the eventual design of a highly functional catalyst.

1.6 Parameters for Electrochemical Measurements

In the pursuit of a highly functional catalyst with activity comparable to Pt and to lead to its eventual replacement, the alternative must not only offer high HER (or ORR) performances, but also be robust and stable in addition to being cheaper. In this thesis, the focus is to investigate the catalytic efficiency of the molybdenum sulfide materials.

In order to quantify the efficiency of the various catalyst reported, various groups often used different parameters for HER performance. In this work, the overpotential at which a fixed current density of -10 mA cm^{-2} was used as the basis of catalytic efficiency and for comparison. Normalization to the electrode surface area is necessary to be able to allow quantitative comparison across electrode of various surface area.¹³⁰ The overpotential required to reach this fixed current density can be used to estimate the efficiency of the electrode material.⁸ A cost-effective 12.3% -efficient solar water splitting device can produce this fixed current density of -10 mA cm^{-2} .^{33, 41} It is now a commonly used parameter across many literature when discussing HER activity.^{123, 127, 131-132} The Tafel slope is another common and useful parameter used to evaluate for the material's HER catalytic efficiency.^{50, 97, 99, 111, 123, 132-133} Tafel slope is recorded in mV dec^{-1} can divulge information about the possible reaction mechanisms in some cases.^{25, 104, 128, 134} It tells us the additional amount of energy required to lead to the same magnitude increase in current density. It also provides clues to the electron transfer rate between the electrode and analyte.¹³⁵ A lower Tafel slope is hence desirable for an ideal electrocatalyst. The Tafel equation can be simplified to $\eta = a + b \log i$, where a and b are

constants. A Tafel plot consist of $\log |i|$ vs η .¹³⁰ The Tafel slope, b , is commonly evaluated experimentally for the various HER electrocatalytic materials.

For ORR, the onset potential is the key factor to evaluate the materials' efficiency. The onset potential is defined by the potential in which 10% of the maximum current density is reached.¹³⁶ The more positive onset potential achieved by the various electrode materials would define a better ORR electrocatalyst as less potential is required for the reduction to occur.

Electrochemical reactions generally occur at the interface between the electrode and electrolyte. The heterogeneous nature¹³⁷ would have meant that surface properties are important in defining its catalytic properties, however this would also depend on the redox couple used. A useful electrochemical electrode material would thus be able to perform rapid electron transfer kinetics.¹³⁷ Heterogeneous electron transfer (HET) rate would thus be useful in defining the functionality of the material especially for sensing applications. The ferro/ferricyanide redox probe was deemed to be surface sensitive and makes this an excellent redox probe for the various electrode materials.¹³⁸ A faster HET rate would warrant a lower overpotential required. The observed HET rate is quantified by k_{obs}^0 . It is calculated by the method developed by Nicholson which can indirectly relate the peak separation of the anodic and cathodic peak in the cyclic voltammetry (CV) for a reversible redox probe to k_{obs}^0 .¹³⁹ The faster k_{obs}^0 is depicted by a smaller peak separation between the anodic and cathodic peak current in the CV. The peak separation is first correlated to a dimensionless kinetic parameter, ψ , which is related to k_{obs}^0 according to the following equation: $\psi \left[\pi D_o \left(\frac{nvF}{RT} \right) \right]^{\frac{1}{2}} = k_{\text{obs}}^0$. The parameters n , v , R , T and F stands for

the number of electron transferred, scan rate, gas constant, temperature, and Faraday's constant, respectively. The diffusion coefficient, $D_0 = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probe¹⁴⁰ and the roughness factor was not taken into account.

Introduction to Section I

Electrocatalytic Performances of Molybdenum Disulfide from Various Sources

Section I will focus on the different phase purity of MoS₂ and its electrocatalytic performance for HER.

MoS₂ is one of the more popular TMDs in the scientific community with a vast amount of literature devoted to its synthesis, properties and applications.^{73, 84, 141-145} This can date as far back into the 1980s.¹⁴⁶ Growing excitement surrounding nanomaterials have heightened interest in layered materials which can be thinned down to 2-dimensional (2D) form.¹⁰⁸ These commercially available MoS₂ are rarely characterized for composition and phase purity. There is, a wide range of overpotentials and Tafel slopes reported when dealing with MoS₂ of varying synthesis methods, pre-treatment or structure.^{95, 98-99, 104, 106, 131, 147-149} MoS₂ now also emerges as a promising material for electronic device fabrication with its increasing presence in the field of energy storage and conversion.¹⁵⁰⁻¹⁵³ However, erratic performances and inconsistencies have been observed in devices using exfoliated geological MoS₂.^{141-142, 154} As much of the research today are geared towards the monolayer or few-layers MoS₂, the possible differences of the commercially available MoS₂ which could be used as a source of starting materials through a top down approach for synthesizing the 2D or thin layer MoS₂ were investigated. Thin layer MoS₂ can be achieved by the following methods which includes scotch-tape based micromechanical exfoliation, solvent exfoliation, intercalation assisted exfoliation, hydrothermal synthesis, chemical vapour deposition and

thermolysis of precursors containing Mo and S.¹⁵⁵⁻¹⁵⁷ The mechanical exfoliation method is deemed as the most reliable method for achieving single-layered MoS₂.¹⁵⁸ However, sonication-assisted solvent exfoliation is thought to be highly advantageous due to the facile synthesis pathway. Hence, the use of commercially available MoS₂ is a likely source of precursor for many research and development team, especially in recent years with the flourishing of top-down synthesis method using liquid exfoliation.¹⁵⁹⁻¹⁶² **Chapter 2** will present and compare the electrocatalytic performances of MoS₂ from various commercial sources and elucidate the structural differences behind it.

Introduction to Section II

The Effects of Different Solvents as a Dispersion Medium for Molybdenum Sulfide

Section II will explore the effects of different solvents, when used as a dispersion medium for molybdenum sulfide on their electrochemical response. In **Chapter 3**, the solvent effects on MoS₂ will be explored while in **Chapter 4**, the solvent effects on MoS₃ will be discussed.

The excitement surrounding molybdenum sulfide as functional material has sprouted exponential growth in this research area. The need for a facile synthesis method arise, prompting the development of simple and efficient top-down approaches. Among these, sonication-assisted liquid phase exfoliation present itself as an efficient and facile preparation method. Thus, solvent effect is commonly explored in terms of its efficiency for exfoliation in producing nanomaterials.^{159-160, 163-168} Extensive research was previously done for the method of liquid exfoliation of graphene, which utilises organic solvents, water/surfactant system and ionic liquids.¹⁶⁶⁻¹⁷⁰ In recent years, with heightened interest in IGA such as TMDs, solvent effect on TMDs exfoliation have also been explored. Many different solvents were investigated for their efficiencies in thinning the bulk form through the use of top-down sonicated-assisted liquid exfoliation method.^{159-160, 163-165}

Apart from the interest in the solvents' efficiency for exfoliation, solvents effects were more commonly explored for fundamental studies in electrochemistry. It probes into the porosity effect and kinetics of the electrochemical reactions.¹⁷¹⁻¹⁷⁸ Such studies, were however limited to mainly

carbon materials (such as carbon nanotubes or graphene) for specific redox couple (such as ferro/ferricyanide) but not its effect on electrocatalysis of HER.^{171-172, 174-175, 178} These studies gave significant insights into the role of solvents and caution the readers that certain enhanced properties are sometimes due to mass transport effects and not due to the inherent property of the material itself.^{171-174, 176} However, the fundamental differences between the redox probe for heterogeneous electron transfer (HET) rate determination and HER mechanism would have limited the transfer of the findings from the studies conducted to explain or predict the HER electrocatalytic efficiency. Caution should be taken as it is necessary to note that activation of the electrode in one redox system does not imply that it will affect all system equally.^{138, 179-180} Findings from previous works could not accurately relate a better (or worst) HET rate (using the ferro/ferricyanide redox probe) to a better (or worst) HER electrocatalytic performance.^{131, 181-182}

This section wishes to examine the application of molybdenum sulphides material for energy application, mainly, HER. The mechanism of HER (and ORR) differs in principle between the various redox probes studied. Hence, previous studies conducted cannot be directly implicated for the reaction of interest here. Furthermore, studies in such area for TMDs, specifically, molybdenum sulfide are lacking. As such, this section set to uncover the differences in terms of the use of different solvents as dispersion medium for molybdenum sulfide in terms of their electrocatalytic performances for HER and ORR catalysis, the area where molybdenum sulphides have attracted a vast amount of interest since. Contrary to conventional research direction where the solvents' proficiency for exfoliation was studied.

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Section I

Electrocatalytic Performances of Molybdenum Disulfide from Various Sources

Chapter 2

Electrocatalysis of MoS₂ from Various Sources

Part of the results and discussion presented in this chapter is published in Chem. Eur. J.

2.1 Introduction

This chapter seeks to investigate the discrepancy across literature on the reported catalytic effects for hydrogen evolution reaction (HER) catalysis by MoS₂. The electrochemical performance of MoS₂ obtained from seven sources were explored and that these sources provide MoS₂ of various phase purity (2H and 3R, respectively or their mixtures) and composition, which are responsible for their different electrochemical properties. The overpotential for HER at -10 mA cm^{-2} for MoS₂ from seven different sources ranges from 0.59 V to 0.78 V. This is of very high importance as with much fervour in 2-dimensional-MoS₂, the use of top-down approach would likely involve the application of commercially available MoS₂. This chapter will detail and compare the differences of MoS₂ from the different sources namely (1) Alfa Aesar, (2) Aldrich, (3) Acros Organics, (4) Chempur, (5) Natural, (6) Riedel-de Haën and lastly (7) Schuchard especially on its electrocatalytic efficiency for HER. Huge differences between MoS₂ from different sources were observed and the structural reasons behind these differences were elucidated. These key parameters are responsible for large variance of reported catalytic properties of MoS₂.

2.2 Result and discussion

Characterisation

Detailed materials characterization by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), X-ray diffraction (XRD) and size distribution measurement by laser diffraction were performed to investigate the possible differences between them. Distinct layering in the structure of the materials were observed in the SEM images, but the general surface morphology is not exactly similar. MoS₂ from Aldrich (Figure 2-1b) and Acros Organics (Figure 2-1c) appear to have smaller particle size as compared to the rest. Particle size analysis was done with laser diffraction and it is discussed in the later paragraphs. EDS was carried out to identify the surface composition of each material and the ratio of Mo: S is shown in Table 2-1 by EDS.

Figure 2-1: The scanning electron micrographs of MoS₂ from the various origins from (a) Alfa Aesar, (b) Aldrich, (c) Acros Organics, (d) Chempur, (e) Natural, (f) Riedel-de Haën and (g) Schuchard. Magnification at x 10,000; scale bar represents 1 µm.

Table 2-1: The ratio of Mo: S based on EDS data.

at. %			
Origins	Mo	S	MoS _x
Alfa Aesar	17.61	31.25	MoS _{1.77}
Aldrich	3.93	7.34	MoS _{1.87}
Acros Organics	8.56	15.87	MoS _{1.85}
Chempur	3.35	6.14	MoS _{1.83}
Natural	22.21	40.15	MoS _{1.81}
Riedel-de Haën	14.54	26.31	MoS _{1.81}
Schuchard	13.46	24.76	MoS _{1.84}

XPS analysis was done to further look into their surface chemical composition. Each element has characteristics binding energies (BE, in eV) which are used to identify the individual elements and their oxidation state. Figure 2-2 illustrates the high resolution XPS spectra of Mo 3d and Figure 2-3 the spectra of S 2p.

Figure 2-2: XPS high resolution spectra for MoS₂ of Mo 3d from various sources: (a) Alfa Aesar, (b) Aldrich, (c) Acros Organics, (d) Chempur, (e) Natural, (f) Riedel-de Haën and (g) Schuchard.

Figure 2-3: XPS high resolution spectra for MoS₂ of S 2p from various companies: (a) Alfa Aesar, (b) Aldrich, (c) Acros Organics, (d) Chempur, (e) Natural, (f) Riedel-de Haën and (g) Schuchard.

Distinct BE peaks were observed for Mo 3d core level. Two sets of BE correspond to two different oxidation state of Mo, with the higher oxidation state at a higher BE level. The Mo⁴⁺ BE corresponding to either the 2H or 3R-phase were observed generally for all of the MoS₂ samples at *ca.* 229 eV and *ca.* 232 eV corresponding to the Mo⁴⁺ 3d_{5/2} and 3d_{3/2} respectively. With the

exception of MoS₂ from Riedel-de Haën, all MoS₂ has a set of higher BE at *ca.* 233 eV and 236 eV representing the Mo⁶⁺ 3d_{5/2} and 3d_{3/2}. This is confirmed by literature with Mo⁶⁺ having BE around 232 – 233 eV and 235 – 236 eV for 3d_{5/2} and 3d_{3/2} respectively.¹⁻³ Deconvolution of the peaks of MoS₂ (Mo 3d) from Riedel-de Haën displays a second set of peaks (Mo^(A)) that are down shifted to lower BE compared to Mo⁶⁺, at *ca.* 231 eV and *ca.* 234 eV. Mo^(A) with BE of Mo 3d_{5/2} at *ca.* 231 eV corroborates well with literature value of Mo⁵⁺ 3d_{5/2}.⁴⁻⁵ According to a study conducted by Tang *et al.*,⁶ the BE between Mo⁴⁺ and Mo⁵⁺ has an approximate difference of 1.3 eV. This corresponds to the difference in BE between Mo⁴⁺ 3d_{5/2} 229.27 eV and Mo^(A) 3d_{5/2} 230.65 eV for the MoS₂ from Riedel-de Haën. Mo^(A) could be either Mo⁵⁺ or could possibly be attributed to Mo⁴⁺ in molybdenum oxysulfide (MoO_xS_y).^{5, 7-8} Similarly, deconvolution of the S 2p spectra of Riedel-de Haën again reveals it to be different from the rest of the samples (Figure 2-3). S^(A) doublet at *ca.* 162 eV and 163 eV corresponding to 2p_{3/2} and 2p_{1/2} respectively, could be due either to S²⁻ (as in MoS₂) or terminal S₂²⁻.^{5, 9} S^(B) at higher BE of *ca.* 163 eV and 164 eV could then be assigned to bridging S₂²⁻ or apical S²⁻.⁹⁻¹⁰ Further distinction between the two types are not possible due to their similar BE. This difference in BE between S²⁻ and S₂²⁻ in this study is *ca.* 1.33 eV is similar to the difference of *ca.* 1.4 eV that was reported by Pham *et al.*⁵ It is possible that the sample from Riedel-de Haën contains MoO_xS_y impurities or amorphous MoS₃ impurities which the latter could exist in the form Mo⁵⁺(S₂²⁻)_{1/2}(S²⁻)₂ accounting for the presence of Mo^(A).^{6-7, 11-12} The amorphous nature of MoS₃ hinders their identification by XRD that was performed (Figure 2-4).^{6, 13-14} The broad XPS peaks of Riedel-de Haën suggest a mixed valence states of Mo which has a distinctively different XPS

spectra from the rest of the samples. To probe further, the surface elemental composition of the MoS₂ were presented in Table 2-2. The ratios are calculated based on the area normalized to their relative sensitivity factor (RSF) using the high resolution scans. S composition varies from $2.11 \leq x \leq 2.49$. The high value of $x = 2.49$ for MoS₂ sample from Riedel-de Haën could be an indication of the presence of MoS₃ impurities. In retrospect, this could have also meant a deficient in Mo and the greatest deficiency comes from MoS₂ from Riedel-de Haën and this could have further impacted on its electrochemistry. However, we noted that XPS is a surface technique and the elemental composition by EDS (Table 2-1) and XRF (Table 2-4) shows that the bulk composition of sample from Riedel-de Haën still corresponds well to MoS₂ as the bulk composition (exact ratio of Mo: S = 1: 1.81 for EDS; and 1: 2.03 for XRF).

Table 2-2: Empirical elemental compositions of the MoS₂ from various sources based on XPS analysis of high resolution spectra.

Origins	MoS _x
Alfa Aesar	MoS _{2.41}
Aldrich	MoS _{2.24}
Across Organics	MoS _{2.11}
Chempur	MoS _{2.33}
Natural	MoS _{2.29}
Riedel-de Haën	MoS _{2.49}
Schuchard	MoS _{2.24}

The presence of various structure modifications can strongly affect the electrocatalytic performance and XRD was used to resolve the phase purity of the samples. MoS₂ can exist as several structural allotropes, which can be distinguished by XRD. The stable 2H-phase and metastable 3R-phase can be

differentiated with their unique diffraction patterns. The X-ray diffractogram and the wt. % of 2H and 3R phases are shown in Table 2-3 and Figure 2-4. MoS₂ samples from Aldrich, Acros Organics, Chempur and Natural MoS₂ exist as pure 2H-phase without the rhombohedral 3R-phase. The other samples (Alfa Aesar, Riedel-de Haën and Schuchard) contain 3R-phase in the range about 38 – 43 wt.%.

Further detailed characterization was performed by XRF. XRF can help to identify the overall chemical composition of the material. The depth of analysis for XRF is greater than that of XPS which is a surface technique. XRF would be able to give bulk analysis of the sample. XRF results have shown significant differences in the impurities concentration as well as slight changes in metal to chalcogen ratio. All compositions were in the range of MoS_{1.96} to MoS_{2.05} with the exception of the sample from Natural with composition of MoS_{1.66}. This discrepancy may originate from the relatively large particles used for the analysis. In the same sample (Natural), high concentration of Si was also detected, likely to be in the form of SiO₂. This is believed to have originated from the inclusion of quartz microcrystals within natural molybdenite crystals. Low concentration of W was detected in several other samples; only samples from Chempur, Riedel-de Haën and Schuchard are free of W impurity. Fe and Zn were found to exist in all the samples, with samples from Aldrich, Acros Organics and Schuchard containing high levels of Fe (> 1000 ppm) and sample from Riedel-de Haën having the highest level of Zn concentration (2500 ppm). The impurities can strongly influence the electrocatalytic activity and its assessment is necessary to avoid interferences. The effect of enhanced catalytic effect of carbon nanotubes has been suggested to be due to residual metal or

presence of metallic impurities in carbon nanotubes.¹⁵⁻¹⁷ Hence this presents the need to be much more cautious and to identify the chemical composition of these samples. The results of XRF analysis are shown in Table 2-4.

Table 2-3: The phase composition of MoS₂ originating from different sources.

Origins	2H wt.%	3R wt.%
Alfa Aesar	58	42
Aldrich	100	0
Acros Organics	100	0
Chempur	100	0
Natural	100	0
Riedel-de Haën	57	43
Schuchard	62	38

Figure 2-4: The X-ray diffractogram of MoS₂. The red line in diffractogram correspond to 3R phase and the black line to 2H phase. ‘X’ marks the diffraction patterns in natural MoS₂ to originate from SiO₂.

Table 2-4: The composition of MoS₂ obtained by different suppliers measured by XRF. Mo and S concentration in wt.%; S/Mo ratio recalculated in at. %; impurities in ppm (detection limit 10 - 30 ppm).

	Mo	S	S/Mo	W	Na	Mg	Al	Si	K	Ca	Ti	V	Mn	Fe	Co	Zn	Cu	Pb	As	Se
Alfa Aesar	59.2	40.51	2.05	164	0	0	410	560	297	252	0	0	65	940	0	168	0	0	0	0
Aldrich	60	39.66	1.98	136	0	0	362	540	176	0	0	0	59	1490	0	202	0	0	0	0
Acros	60.16	39.49	1.96	224	260	72	0	0	1910	0	0	0	0	1020	0	104	368	0	0	0
Organics																				
Chempur	59.83	39.91	1.99	0	0	0	395	470	248	173	0	0	151	740	0	168	0	198	0	0
Natural	62.37	34.55	1.66	165	0	0	5710	21200	1290	1520	217	0	0	510	0	127	0	0	0	0
Riedel-de Haën	58.95	40.11	2.03	0	0	0.06	2230	361	193	276	0	67	0	269	0	2500	91	0	0	262
Schuchard	59.32	40.09	2.02	0	400	199	590	0	0	610	0	52	0	3290	34	256	99	0	143	233

The edge site of MoS₂ was found to be the active catalytic site for HER.¹⁸⁻¹⁹ Thus, the particle size is of huge importance as smaller particle leads to a higher concentration of edges. Increasing the density of active edge sites has been a pertinent concept in the design of MoS₂ electrocatalyst.²⁰⁻²¹ Particle sizes of MoS₂ obtained from different origins were significantly different (Figure 2-5 and Figure 2-6). The MoS₂ obtained from Aldrich, Acros Organics, Chempur and Schuchard has a geometric mean diameter of particles 5 μm or even smaller, while samples from Alfa Aesar and Riedel-de Haën has particles larger than 10 μm (geometric mean diameter). The mean diameters of MoS₂ particles are summarized in Figure 2-5 and the particle size distribution for individual MoS₂ samples are shown on Figure 2-6. Natural MoS₂ crystals were grounded in agate mortar and subsequently separated by screen with 100 μm opening. This could have led to the relatively large particle sizes in comparison with commercially obtained MoS₂ samples.

Figure 2-5: The mean particle diameters of MoS₂ obtained from various sources.

Figure 2-6: The particle size distribution of MoS₂ obtained from various source by laser diffraction measurement.

Figure 2-7: CVs during the (i) anodic scans and (ii) cathodic scans of the MoS₂ from various sources. (a) Alfa Aesar, (b) Aldrich, (c) Acros Organics, (d) Chempur, (e) Natural, (f) Riedel-de Haën and (g) Schuchard. Conditions: PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s⁻¹; all potentials are relative to the Ag/AgCl reference electrode. Legend: Orange – scan 1; grey – scan 2; blue – scan 3.

To do a dutiful comparison between the MoS₂ from various origins, electrochemical study of the compounds using a blank phosphate buffer solution (PBS) at pH 7.2 were conducted. This would bring insights into the electroactive components of the material, MoS₂, especially when one of the main applications of MoS₂ is eletrocatalysis.²² Despite being commercially labelled as MoS₂, all of the MoS₂ have very different electrochemical profile (that is, inherent electrochemistry – oxidation and reduction – of the material itself) as shown in Figure 2-7. For all of the MoS₂, we are able to identify an obvious oxidation peak at both the anodic and cathodic scan at about +1.1 to +1.5 V (depending on their source) except for MoS₂ from Riedel-de Haën. Most MoS₂ in this study do not exhibit recurrence of the oxidation peak with the exception of MoS₂ from Aldrich and Acros Organics (Figure 2-7b and Figure 2-7c). The absence of recurrence peak points to the likelihood of irreversible chemical oxidation; while MoS₂ from Aldrich and Acros Organics exhibit the possibility of reversibility as seen by the presence of a reduction shoulder peak in both the anodic and cathodic scan, giving rise to the recurrence of the oxidation peak. The reduction can also occur without prior oxidation of the compound. The reduction peak is observed even during the cathodic scan of MoS₂ from Aldrich and Acros Organics, followed by a reduced current intensity of the main oxidation peak. The electrochemical property of MoS₂ from Riedel-de Haën seems to differ from the rest of the MoS₂ presented in this study and also defies the conventional electrochemistry of MoS₂ as presented in other studies.²²⁻²³ The oxidation peak is insignificant with no reduction peak observed. The deficient of Mo as shown by the lowest ratio of Mo: S = 0.80: 2 based on XPS analysis could have explained the smaller oxidation peak of Mo. MoS₂ from

Natural source also exhibited limited oxidative current. However, the oxidation peak, like others, is distinct and easily identifiable. Schuchard is the only other source of MoS₂ that exhibited a reductive shoulder peak but only for its cathodic scan. However, following this reduction, the oxidative current becomes lower than that in the anodic scan. This phenomenon is similarly observed for MoS₂ from Aldrich and Acros Organics where the reductive peak was observed. This highlights the fact that the same chemical species can be oxidize and reduced, depending on the initial scan direction, and that this reduction is likely to be chemically irreversible.

Hydrogen Evolution Reaction

Figure 2-8: Hydrogen evolution reaction at different surfaces. (a) Polarization curve for HER for MoS₂ from Alfa Aesar, Aldrich, Acros Organics, Chempur, Natural, Riedel-de Haën, Schuchard. Conditions: 0.5 M H₂SO₄; scan rate: 2 mV s⁻¹. (b) Bar chart for the comparison of the overpotential of each material at -10 mA cm⁻² current density. (c) Tafel plot and (d) the bar chart comparing the Tafel slope. Error bars correspond to standard deviations based on triplicate measurements. Potentials are with respect to RHE.

The MoS₂ from the different commercially available sources were tested for their catalytic activity for HER. There is a huge difference in terms of overpotential at -10 mA cm⁻², ranging from 0.59 to 0.78 V. The lowest overpotential is observed for MoS₂ from Acros Organics and the highest from Riedel-de Haën (Figure 2-8). From the polarization curve and the bar chart comparison, a wide spread in terms of HER catalytic activity was observed

despite being chemically equivalent in terms of chemical formula, MoS₂. Cao's group reported that molybdenum sulfide catalytic activity for HER 'strongly depends on the growth temperature'.²⁴ Thus, the large variation in overpotential could be due to the different synthesis method adopted by the different companies. However, no information could be gathered with regards to their methods of production. It could either be through a synthetic route or produced by the purification of natural molybdenite. The detailed chemical and structural analysis discussed have revealed significant differences in impurities concentration, particle sizes as well as phase composition. All these factors are of huge importance for electrocatalytic activity. The potency of its HER catalytic ability is in the following order, with MoS₂ from Acros Organics (0.59 V) being the best performing one, followed by Aldrich (0.60 V), Natural (0.66 V), Schuchard (0.66 V), Alfa Aesar (0.69 V), Chempur (0.73 V) and lastly MoS₂ from Riedel-de Haën (0.78 V). The high Tafel slope observed indicates the Volmer step as rate limiting²⁵ and hints at low HER efficiency. Consolidating the information from both the overpotential and Tafel slope, the top three performing MoS₂ for HER are (1) Acros Organics, (2) Aldrich and (3) Schuchard with consistently lower overpotential and lower Tafel slope amongst the MoS₂ studied here. The characterization data from above shed light on the wide range of overpotential for HER catalysis. A positive correlation between a smaller x value in MoS _{x} (by XPS analysis, Table 2-2) and a lower overpotential observed at the current density of -10 mA cm^{-2} for HER was observed. The greater Mo composition (as seen with a smaller x value) could possibly translate to a higher density of Mo edges resulting in the better HER catalytic activity as shown by the experimental results. It is experimentally and theoretically

determined that the active sites of MoS₂ is the edges and the Mo-edge have a value closer to thermoneutral for its free energy for hydrogen adsorption.^{18-19, 26} With reference to Table 2-2, Acros Organics has the greatest amount of Mo relative to the rest of the samples and this could have accounted for the better HER catalytic ability exhibited by MoS₂ from Acros Organics. In Table 2-2, data were represented in terms of MoS_x, hence a higher Mo: S ratio would be represented as a small *x* value. This ratio of Mo: S is calculated based on XPS analysis which is a surface sensitive technique; and electrocatalysis is governed by the surface properties of the catalyst. Thus, this could have explained the HER catalytic efficiencies. Furthermore, from the above particle size analysis, it is seen that the MoS₂ obtained from Acros Organics, Aldrich and Schuchard which has a small geometric mean diameter of particles (< 5 μm) also display greater electrocatalytic activity for HER. MoS₂ from Alfa Aesar and Riedel-de Haën with larger particle size (geometric mean diameter > 10 μm) exhibits lower electrocatalytic activity. The smaller particle size as mentioned earlier could have translated to a higher concentration of edge sides. The presence of 3R-phase in samples from Alfa Aesar (42%) and Riedel-de Haën (43%) could have also played a part in its lower electrocatalytic activities. However, it is noted that Chempur which has a small geometric mean diameter and a pure 2H-phase does not seem to obey this trend. Similarly, sample from Schuchard with a 38% 3R-phase composition displays a relative moderate electrocatalytic activity amongst the sample. This seems to suggest that relationship between electrocatalytic HER activity, particle size and phase composition is not so direct. From XPS analysis for Riedel-de Haën as discussed above, the doublet at the higher BE Mo^(A) were assigned to be likely Mo⁵⁺ in the form of MoS₃ or

Mo^{4+} in the form of MoO_xS_y . The presence of MoS_3 is expected to display a better electrocatalytic activity.^{3, 27} The deviation from expected results could be due a few reasons. Firstly, a ‘reductive-activation’ process is noted across many of the amorphous molybdenum sulfide literature.^{5, 8, 13, 27-28} Secondly, the Mo oxidation state identified in these studies were attributed to Mo^{4+} instead of the Mo^{5+} that is identified here for MoS_3 . This could have accounted for the discrepancy in electrocatalytic activity. It however, could also be due to the presence of MoO_xS_y instead of amorphous MoS_3 . These are possible reasons which could have explained the inferior HER electrocatalytic activity to the other samples.

Heterogeneous Electron Transfer (HET) rate at GCE modified with MoS_2 from different sources for Ferro/ferricyanide Redox Probe

Figure 2-9: (a) CVs for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at the MoS_2 modified electrodes from the various companies; conditions: 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 50 mM PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s^{-1} . (b) Bar chart representation of the peak separation, ΔE_p (V) between the anodic and cathodic peak current. Potentials are with respect to Ag/AgCl reference electrode. Bare GCE is included here as a reference.

Table 2-5: The calculated k_{obs}^0 based on the peak separation of the CVs. Bare GCE is included here for reference.

Origins	k_{obs}^0 (cm s⁻¹)
Alfa Aesar	1.43×10^{-4}
Aldrich	3.78×10^{-4}
Acros Organics	1.78×10^{-4}
Chempur	1.89×10^{-4}
Natural	1.69×10^{-4}
Riedel-de Haën	2.86×10^{-4}
Schuchard	2.61×10^{-4}
Bare GCE	6.69×10^{-4}

Apart from looking directly into their varying capabilities in HER electrocatalytic efficiencies, the observed heterogeneous electron transfer (HET) rate, k_{obs}^0 , using the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe was also investigated. The HET rate determines the material suitability for use in electrochemical sensing device.¹³ The $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe is known to be “surface sensitive” this can help to uncover the differences in surface conditions.²⁹ There seems to be no activation effect of the MoS_2 materials to the GCE as the peak separation gets further apart and k_{obs}^0 becomes correspondingly smaller. There is no simple and direct correlation between the HET rate and HER catalytic efficiencies simply because of their different redox mechanism. The CVs are shown in Figure 2-9a and the peak separation are compared in the bar chart as in Figure 2-9b. The fastest HET rate corresponds to the smallest peak to peak separation and that is displayed by MoS_2 from Aldrich ($k_{obs}^0 = 3.78 \times 10^{-4} \text{ cm s}^{-1}$). In contrast, MoS_2 from Alfa Aesar has the slowest HET rate, quantify by the smallest k_{obs}^0 value of $1.43 \times 10^{-4} \text{ cm s}^{-1}$. However, all of the MoS_2 under

investigation has a slower HET rate than bare GCE for this redox probe (Table 2-5). The bulk structure of MoS₂ used would present a larger number of layers, inhibiting the rate of electron transfer from the electrode to the analyte.³⁰

Testing the Capacitance of MoS₂ from Different Sources

Figure 2-10: The anodic current at -0.5 V (vs Ag/AgCl) of CV against varying scan rate. (a) Alfa Aesar, (b) Aldrich, (c) Acros Organics, (d) Chempur, (e) Natural, (f) Riedel-de Haën, and (g) Schuchard. Conditions: 1.0 M KOH; scan rates: 50, 100, 200 and 400 mV s⁻¹; all measurements are performed relative to the Ag/AgCl reference electrode.

Figure 2-11: Capacitance performance of the MoS₂ from various sources. (a) CV at scan rate: 400 mV s⁻¹, b) bar chart representation of gravimetric capacitance (F g⁻¹) based on CV measurements, (c) galvanostatic charge/discharge plot at a constant current density of 1 A g⁻¹ and, (d) bar chart comparison of the gravimetric capacitance (F g⁻¹) based on constant current measurement. Conditions: 1.0 M KOH; potentials are with respect to Ag/AgCl reference electrode.

With MoS₂ becoming an increasingly popular material in the field of energy storage,³¹⁻³⁵ an investigation into the intrinsic difference in capacitance is of interest in this work. CV measurements were conducted at various scan rates (50, 100, 200 and 400 mV s⁻¹). Graphs of current vs scan rate were plotted (Figure 2-10) and a linear relationship was found between them. Hence, within

this potential region, the current was assumed to be non-faradaic. However, only the CV of the 400 mV s⁻¹ is shown here for a comparison between the MoS₂ from the various sources (Figure 2-11). The gravimetric capacitance values obtained are generally lower than 6 F g⁻¹. Such low values could possibly be due to its bulk structure where similar results were obtained by Mayorga-Martinez *et al.* for bulk MoS₂.³⁵ Capacitance was calculated from the relationship between current (I) and scan rate ($\frac{dv}{dt}$), $I = C \times \frac{dv}{dt}$,³⁶ and gravimetric capacitance was normalized to the amount of catalyst loading. Galvanostatic charge–discharge was done to confirm the results as obtained by CV. A fixed current density of 1 A g⁻¹ was used in a fixed potential window of –1.0 V to –0.3 V (vs Ag/AgCl). From the above two different methods of measurements, similar trend was observed despite the absolute capacitance values being larger when using the galvanostatic charge/discharge method. MoS₂ from Aldrich having the best capacitive behaviour with MoS₂ from Chempur and Acros Organics being the next 2 better performing ones. In general, the differences in terms of capacitive values are not too great between the 7 origins, but a distinctively better performing MoS₂ would be from Aldrich (Figure 2-11).

2.3 Conclusion

Despite the common chemical name of the materials, it has displayed different electrochemical properties and electrocatalytic efficiencies for HER when obtained from various sources. More information needs to be known about its synthetic process to make a more informed comparison, which is unfortunately not possible in this case. From the experiments conducted and a side by side comparison of the efficiencies of the MoS₂ from various sources, differences were observed and these differences could have a carry-over effect and attribute to their efficiency in their 2-dimensional form. In this particular study, the MoS₂ from Acros Organics, Aldrich and Schuchard are better performing for electrocatalysis for HER with consistently lower overpotential and lower Tafel slope. There are intrinsic implications with the different structural factors such as Mo: S ratio, particle size and also phase purity. However, the relationship is not so direct as discussed. Ultimately, the different origins of MoS₂ is likely to play a role in determining its efficiency for use in various applications; while the influence of the different factors will be dependent on the mechanism of each particular system. This chapter has documented the varying capabilities of MoS₂ in HER, HET rate and capacitance from various sources.

2.4 Experimental

Materials

The MoS₂ are commercially available from the following sources: (1) Alfar Asear (Germany; Lot# P05A030), (2) Sigma-Aldrich (Czech Republic; Lot# MKBS1091V), (3) Acros Organics (Belgium; Lot# A0349660), (4) Chempur (Germany; Lot# 005570), (5) Natural (Sörumsaasen mine, Spikkestad, Drammen, Norway), (6) Riedel-de Haën (Germany; Lot# 6140) and lastly (7) Schuchard (Germany; Lot#MO076). Natural MoS₂ was pulverized in agate mortar and sieved using a sieve with 100 µm opening. Milli-Q water (resistivity: 18.2 MΩ cm) was used for the preparation of the dispersion.

Equipment

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were done using a JEOL 7600F SEM (JEOL, Japan).

X-ray photoelectron spectroscopy (XPS) were conducted using a Phoibos 100 spectrometer with a Mg K α radiation source (SPECS, Germany) at 1254 eV. High resolution scans were also performed for the element of interest (Mo and S). The evaluation of chalcogen-to-metal ratios and quantitative distributions of the oxidation states in Mo were normalized accordingly to their relative sensitivity factor (RSF).

Particle size analysis was performed by laser diffraction method with Particle Sizer Analysette 22 NanoTec from Fritsch Laborgerätebau GmbH (Germany). The measurements were done using aqueous dispersion (1g 100 mL⁻¹) of the materials. The impurities concentration was measured with X-ray fluorescence (XRF) spectrometer Axios from PANalytical (The

Netherlands). The measurements were performed using Rh lamp (4 kW), wavelength dispersive analyser and scintillation detector. Data was evaluated by standardless method with Omnic software.

X-ray diffraction (XRD) measurements were performed by using Bruker D8 Discoverer diffractometer from Bruker AXS (Germany). Diffractometer works in Bragg–Brentano parafocusing geometry with a Cu K α radiation source (40 mA 40 kV⁻¹). Diffraction pattern were collected between 5° and 80° of 2 θ . The obtained data were evaluated using HighScore Plus 3.0e software.

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were carried out using a μ Autolab type III electrochemical analyser (Eco Chemie, Utrecht, The Netherlands) connected to a personal computer and controlled by NOVA 1.10 software. All voltammetry experiments were performed in an electrochemical cell at room temperature using a standard three-electrode configuration. A platinum electrode operated as the counter electrode while an Ag/AgCl electrode was used as a reference electrode.

Procedures

The materials of interest in this work were prepared in suspensions of concentration of 1 mg mL⁻¹ in Milli Q water. It was sonicated for 4 hours in temperature kept under 30 °C to obtain a well dispersed suspension. The materials were then drop casted on the GCE (diameter = 3 mm) by transferring a 5.0 μ L of the suspended material on the electrode surface and allow the solvent to evaporate. The catalyst loading was 70.7 μ g cm⁻² per electrode. The GCE surfaces were renewed prior to every new measurement by mechanical

polishing, cleaning it with a 0.05 μm alumina particle on a polishing pad with Milli-Q water.

Electrochemical Measurements.

HER measurement: LSV HER measurements were performed in N_2 -saturated 0.5 M sulfuric acid at a low scan rate of 2 mV s^{-1} . *Inherent electrochemistry:* CV measurements were performed in 50 mM phosphate buffer solution (PBS) at pH 7.2 as the supporting electrolyte scan rate of 100 mV s^{-1} . *Ferro/ferricyanide redox probe:* 10 mM of ferro/ferricyanide in 50 mM of PBS as supporting electrolyte, scan rate: 100 mV s^{-1} . *Capacitance:* Capacitance measurements were done in a 1.0 M KOH electrolyte under N_2 -condition. All voltammetry experiments were repeated 3 times to ensure the reproducibility of the results with random electrodes. The potentials vs RHE is calculated based on the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\text{Ag/AgCl}}^0$ where $E_{\text{Ag/AgCl}}$ is the measured potential and $E_{\text{Ag/AgCl}}^0 = 0.235 \text{ V}$ which is the standard potential of Ag/AgCl (1 M KCl) at 25°C .

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Section II

The Effects of Different Solvents as the Dispersion Medium for Molybdenum Sulfide

Chapter 3

The Effects of Different Solvents as
the Dispersion Medium for MoS₂ in
its Catalytic Efficiencies for HER and
ORR

*Part of the results and discussion presented in this chapter is
published in Phys. Chem. Chem. Phys.*

3.1 Introduction

MoS₂ has been investigated intensively in the field of catalysis for hydrogen evolution reaction (HER) in particular. Much efforts have been made by various research teams world-wide to look into specific catalyst design such as nano-structuring, defects engineering or hybrid structures. But what evades us, is the fundamental preparation method of the dispersion of MoS₂ especially for powdered MoS₂. Individual research teams with their best practices might be subjective and not validated by extensive experimental results. There are varying standards for research findings, due to the different practices adopted by various groups and this makes quantitative comparison of results across different work difficult. Across literature, many different solvents are used as either dispersion medium or for liquid phase exfoliation.¹⁻⁶

Five solvents were investigated in this study to give a general overview of MoS₂ dispersion in these medium. The five solvents are acetonitrile (ACN), dimethylformamide (DMF), ethanol (EtOH), methanol (MeOH) and water. It spans from polar aprotic solvents (ACN, DMF) to polar protic solvents (EtOH, MeOH, H₂O). In this chapter, the focus will be on varying the solvent as the dispersion medium for MoS₂. Aliquots will then be obtained from this dispersion and drop-casted onto the electrode surface for electrochemical analysis. It is widely assumed that the solvent used have no impact on the material and the electrode surface.⁷⁻⁸

In this chapter, the overpotential for HER varies from 0.57 to 0.72 V (freshly prepared) when different dispersion medium is used. Aging study for HER electrocatalytic efficiencies was also briefly looked into. Electrochemical

characterisation such as the its inherent electrochemistry and the observed HET rate of the MoS₂ dispersed in various solvents were also investigated. The casting of various solvents on the bare glassy carbon electrode (GCE) leads to a large variation in the observed HET rate and this highlights the significance of surface modification for specific redox probe such as the ferro/ferricyanide.

3.2 Result and Discussion

Figure 3-1: XPS high resolution spectra for Mo 3d of MoS₂ dispersed in various solvents: (a) ACN, (b) DMF, (c) EtOH, (d) MeOH and (e) water.

The high resolution XPS spectra of the MoS₂ dispersed in various solvents are shown in Figure 3-1. The spectra highly resemble each other with the Mo⁴⁺ as the main component in all MoS₂ dispersions prepared. The Mo⁴⁺ has a binding energy (BE, in eV) of *ca.* 229 eV and *ca.* 232 eV being Mo 3d_{5/2} and 3d_{3/2} respectively. From the XPS analysis it seems that the use of different solvents does not have significant effect on its chemical structures. The oxidation of Mo is kept to less than 23% of the Mo being Mo⁶⁺ across all samples. Mo⁶⁺ has BE at *ca.* 232 eV and 235 eV. The greatest percentage of

Mo^{6+} occurs for the sample prepared in water as the dispersion medium, followed by EtOH, MeOH, ACN, DMF. The solvent could have hastened the oxidation of the Mo but to varying degree. MoS_2 dispersed in protic solvents (such as water, EtOH and MeOH) appears to have the higher percentage of Mo^{6+} .

Figure 3-2: Scanning electron micrographs of MoS_2 drop-casted on the silicon oxide wafer. The aliquots were taken from MoS_2 dispersed in various solvents as per conditions for casting on glassy carbon electrode (GCE). (a) ACN, (b) DMF, (c) EtOH, (d) MeOH and (e) water (Magnification x300).

The drying effect of the solvent could have affected its orientation and morphology on the electrode's surface, resulting in the observed differences. As such, scanning electron microscope (SEM) images of the drop casted aliquots were taken to look into the assembly and distribution of the MoS_2 when different dispersion medium was used. Figure 3-2 is captured using silicon oxide wafer as the substrate material while in all electrochemical measurements, bare GCE was used as the base substrate material. This would be a close representation of the actual situation on the GCE's surface. The solvents with a higher boiling

point (hence lower volatility such as DMF) shows a much more even distribution of the material on the surface as compared to the volatile solvents (ACN, EtOH, and MeOH). The drying effect on the surface morphology is highly similar for MoS₂ dispersed by ACN, EtOH and MeOH (Figure 3-2a, c, d). It is generally well dispersed with occasional small aggregates (< 40 μm) as seen. DMF and water have the highest boiling point amongst the solvents, and typically takes longer time to dry during drop-casting. This could have explained the resulting difference in surface morphology of the deposited materials. For DMF and water, the material generally covers the entire surface much more evenly, with the particles being more closely packed. This is more apparent when DMF is used and could be due to the slowest drying rate of DMF compared to all other solvent, allowing the material to slowly settle on the substrate surface.

Electrochemical Characterization

Inherent Electrochemistry

Figure 3-3: CVs of the prepared MoS₂ dispersions. (a) ACN, (b) DMF, (c) EtOH, (d) MeOH and (e) water; (i) represents the cathodic scans and (ii) anodic scans direction. Conditions: PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s⁻¹. Potentials are relative to the Ag/AgCl reference electrode.

Inherent electrochemistry could be used as a form of electrochemical characterization of the material itself. The use of a blank phosphate buffer solution (PBS) helps to provide a high conductivity background and allows the use of electrochemical techniques to elucidate the electroactive moieties of the material. In this case, what is of particular interest is whether the use of different solvent medium for dispersion affects the electrochemical properties of MoS₂. An apparent feature would be the oxidation peak observed at *ca.* +1.0 V which was consistently observed across all cyclic voltammograms (CVs) (Figure 3-3). This anodic peak is likely due to the oxidation of Mo⁴⁺ to Mo⁶⁺.⁹⁻¹⁰ Further inspection of the cathodic currents upon the application of cathodic potentials

in the initial scan, shows only MoS₂ dispersed in DMF gives a well-defined shoulder peak at *ca.* -1.0 V; while the rest show a broadening of the peak area at the cathodic potentials, indicating the occurrence of a reduction process. As mentioned earlier, the CVs all show an obvious peak at *ca.* +1.0 V except MoS₂ in DMF (cathodic scan). Instead, it shows two peaks with close potentials overlapping. This could possibly be due to the difference in oxidizing potentials of the edge site and basal plane of the MoS₂ as suggested by Bonde *et al.*,¹¹ where the basal plane has a higher oxidizing potential. This was explained by Jaegermann and Schmeisser, whom characterised the inertness of the basal plane due to the “coodinatively saturated chalcogen ions”.¹² This feature is probably enhanced with DMF being the dispersion medium. This shows how the use of different solvent as dispersion medium could possibly affect and/or mask the inherent electrochemistry.

Heterogeneous Electron Transfer (HET) rate at MoS₂/Solvent-modified GCE for Ferro/ferricyanide Redox Probe

Figure 3-4: (a) CVs of the Fe(CN)₆^{4-/3-} redox probe for MoS₂ dispersed in various solvents. (b) Bar Chart representation of the peak separation between the anodic and cathodic peak current. Conditions: 10 mM Fe(CN)₆^{3-/4-} in 50 mM PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s⁻¹. Error bars

correspond to standard deviations based on triplicate measurements. Potentials are with respect to the Ag/AgCl reference electrode.

Table 3-1: The calculated k_{obs}^0 for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe when MoS_2 is dispersed in various solvent. Bare GCE is shown here for reference.

MoS₂/ Solvent	k_{obs}^0 (cm s⁻¹)
ACN	2.99×10^{-3}
DMF	5.90×10^{-4}
EtOH	3.53×10^{-3}
MeOH	2.74×10^{-3}
Water	1.88×10^{-3}
Bare GCE	3.20×10^{-3}

Figure 3-4 shows the CVs and also a bar chart representation of the peak separation. The calculated observed HET rate, k_{obs}^0 , is given in Table 3-1, where the bare GCE is added as a reference. The peak separation was kept within a range of 0.1 – 0.2 V, with the exception of MoS_2 dispersed in DMF which has the largest peak separation of 0.25 V (Figure 3-4b). The peak separations of the MoS_2 dispersed in various solvents are all larger than bare GCE (except EtOH), meaning that their HET rates are all slower when compared to bare GCE ($k_{\text{obs}}^0 = 3.20 \times 10^{-3} \text{ cm s}^{-1}$). The only exception is the MoS_2 dispersed in EtOH ($k_{\text{obs}}^0 = 3.53 \times 10^{-3} \text{ cm s}^{-1}$) which exhibits a slightly faster HET rate. Since XPS analysis have found that there are no significant differences in terms of Mo oxidation states across the different samples. The coating of the solvent- MoS_2 dispersion on the electrode surface could have affected the HET rate. The use of organic solvents could have detrimentally impacted on the GCE surface as the adsorption of trace impurities decreases the HET rate (increases the peak separation).¹³⁻¹⁴ Pretreatment of the GCE surface with organic solvents (IPA,

ACN and cyclohexane) without the use of activated carbon was found to negatively affect the HET rate (increase peak separation) hence implying that trace impurities were introduced onto the GCE surface instead of being removed.¹⁴ A control study with the use of bare GCE, intentionally drop-casted with the blank-solvent (without MoS₂) was thus conducted in this study (Figure 3-5). Indeed, this control study found that DMF causes an increase in the peak separation much more significantly compared to the other solvents used; while, the use of EtOH decreases the peak separation and increases the corresponding peak current (Figure 3-5). In this case, DMF has a greater impact than the other solvents. These findings match the results when MoS₂ in various solvents are drop casted on the GCE where a larger peak separation was associated with the use of DMF and smaller peak separation when EtOH is used. Looking further into literature, Tan *et al.* who prepared transition metal dichalcogenides (TMDs) such as MoS₂, MoSe₂, WS₂ and WSe₂, using DMF as the dispersion medium found that the materials have a larger peak separation as compared to bare GCE.² With the obvious impact of solvent in HET rate even with bare GCE, it is difficult to quantitatively attribute the contribution to either the solvents, MoS₂ or ultimately the synergistic effect of MoS₂ in the particular solvent. The author explained the larger peak separation to be due to the electrostatic repulsion between the negatively charged redox species and the TMDs sheets with negative zeta-potential.^{2, 15} This could have explained the larger peak separations for TMDs but not how the solvent affects its HET rate specifically. As ferro/ferricyanide is a surface sensitive redox probe, it is thus not surprising to note that the use of different solvents can have varying impact on its observed

HET rate and this is likely to be attributed to the trace amounts of surface adsorbates introduced by the different solvents.

Figure 3-5: The control experiment for the $\text{Fe}(\text{CN})_6^{4-/3-}$ redox probe. (a) CVs of the bare GCE drop casted with various solvents. (b) Bar Chart representation of the peak separation between the anodic and cathodic peak current. Conditions: 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 50 mM PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s⁻¹. Error bars correspond to standard deviations based on triplicate measurements. Potentials are with respect to the Ag/AgCl reference electrode

The porosity of electrodes modified with the use the drop casting technique has been described to cause the “enhanced electrocatalytic” effect of materials such as carbon nanotubes and graphene.¹⁶⁻¹⁷ Punckt *et al.*, have also shown in his work that different solvents used in preparation for dispersion would result in the differing porosity in functionalized graphene sheets.¹⁸ This effect could have explained for the slight improvement of MoS_2 in EtOH observed HET rate due possibly to the increased surface area. In a separate study, the use of EtOH as the solvent for WO_3 nanoparticles also found to result in larger photocurrent observed. It was explained by the enhanced surface area due to the presence of cracks on the films.¹⁹ These findings have provided insights that one must be careful when dealing with using the term ‘enhanced’

HET rate and/or electrocatalytic activity when a material is used as it could be due to the influence of solvent instead of an intrinsic activity of the material itself.

Hydrogen Evolution Reaction

Figure 3-6: The control experiment for the HER where blank-solvents (without any material suspended) were drop-casted on bare GCE. (a) Polarization curve for HER and (b) the bar chart shows the overpotential required to reach the specific current density of -10 mA cm^{-2} . Conditions: $0.5 \text{ M H}_2\text{SO}_4$; scan rate: 2 mV s^{-1} . Error bars correspond to standard deviations based on triplicate measurements. Potentials are with respect to RHE.

A control experiment was similarly done for HER where the blank-solvent (without MoS_2) was drop-casted to modify the GCE in order to determine if the various solvents have any significant impact on its HER catalytic efficiency (Figure 3-6). From the data collected, it seems that the solvents do not have significant impact in altering the overpotential required to achieve the specific current density. Thus, the differences obtained in Figure 3-7 could be due to the effectiveness of the solvents as a dispersion medium for MoS_2 or due to the varying interactions between the solvent and MoS_2 itself.

Figure 3-7: The consolidated data for HER analysis. (a) Polarization curve for HER for MoS₂ dispersed in various solvents. (b) Bar chart for the comparison of the overpotential of each samples at -10 mA cm^{-2} current density. (c) Shows the Tafel plot for the freshly prepared dispersion and (d) the bar chart comparing the Tafel slope. Conditions: $0.5 \text{ M H}_2\text{SO}_4$; scan rate: 2 mV s^{-1} . Error bars correspond to standard deviations based on triplicate measurements. Potentials are with respect to RHE. Legend: solid line – freshly prepared; dotted line – after 2 weeks.

The HER efficiency of MoS₂ dispersed in various medium was tested and the results are presented in Figure 3-7. When the dispersions were freshly prepared (electrochemical measurements were taken on the same day when the dispersions were prepared), a range of overpotential between 0.57 V (ACN) to 0.72 V (MeOH) was observed. Since the material used in this case are the same MoS₂ from the same synthesis method, the drastic difference between the

different samples would suggest that solvents have a role to play. Research results from various research teams cannot be compared quantitatively across literature when different dispersion solvents were used. This is especially so if the material involves the use of powdered form being dispersed in a solvent for drop casting during electrochemical experiments. Particularly, the drop casting method is commonly used among the electrochemistry community.^{8, 19-23} It is not commonly mentioned in many electrochemical studies when the measurements were taken with respect to the time when the dispersions were prepared. Hence, in order to stimulate practical research conditions, it is of interest to find out if there would be significant differences in terms of HER electrocatalytic performance after 2 weeks of preparation. Recent work by Gao *et al.* reported the aging effects of monolayer-MoS₂ (and WS₂).²⁴ The material used in this study are of bulk-form and thus expected to be much more stable when compared to monolayer-MoS₂.²⁴⁻²⁵ No general trend was seen across the solvents after it was prepared for 2 weeks in terms of HER electrocatalytic efficiency. When dispersed in ACN or water, the variation between freshly prepared and after 2 weeks is much smaller compared to the rest. For ACN, EtOH and MeOH, a corresponding increase in overpotential was observed after 2 weeks; whereas for DMF and water, a subsequent decrease is observed instead. Tafel slope, an inherent property of the reaction kinetics gives an indication to which the amount of energy required to cause a significant increase in current density and also the possible mechanism of HER.²⁶⁻²⁷ The Tafel slope of the Volmer step where the adsorption of hydrogen to the catalyst surface: $\text{H}^+ + \text{e}^- + \text{M} \rightarrow \text{M-H}$ occurs is 120 mv dec⁻¹. Following this, either a Heyrovsky or a Tafel step will occur, with a Tafel slope of 40 mv dec⁻¹ and 30 mV dec⁻¹

respectively.²⁸ In Figure 3-7c, only the Tafel plot of the freshly-prepared dispersion were shown to ensure clarity. From Figure 3-7d, all of the dispersion medium gives a Tafel slope above 120 mV dec^{-1} indicating that the Volmer step behaves as the rate determining step. The variation in Tafel slope is not as huge and significant compared to the differences in overpotential. The Tafel slope follows the trend of the overpotential when the data was collected after 2 weeks. Xu *et al.*, investigated the use of different solvents in the preparation of MoS_2/WS_2 quantum dots. These as-synthesised materials were then tested for their electrocatalytic activity for HER. The authors then concluded that “the solvent has little or no effect on the chemical property and structure of these quantum dots”.⁵⁶ This is similar to the findings presented here according to XPS analysis (Figure 3-1) which found no significant differences between the chemical structures of MoS_2 dispersed in various solvents.

Testing the Catalytic Efficiencies of MoS₂/Solvents for ORR

Figure 3-8: ORR. (a) and (b) corresponds to data collected for GCE modified with MoS₂ dispersed in various solvents; (c) and (d) corresponds to the control experiments where the blank-solvent (without MoS₂) is drop-casted onto the GCE. (a) and (c) shows the LSVs; (b) and (d) the onset potential of the ORR using the potential at which 10% of the maximum current density is achieved. Conditions: 0.1 M KOH, scan rate: 50 mV s⁻¹; electrolyte saturated with nitrogen (dashed lines) and air saturated (solid line). Error bars correspond to standard deviations based on triplicate measurements. Potentials are with respect to Ag/AgCl reference electrode.

MoS₂ has begun to see its role in the field of oxygen reduction reaction (ORR) catalysis, with various groups looking into the design of ORR catalyst using MoS₂.²⁹⁻³⁴ Figure 3-8a and 3-8b shows the consolidated result for the ORR catalysis by MoS₂ dispersed in various solvents while Figure 3-8c and 3-8d shows the control experiment. It is apparent that the different solvents do not

significantly alter the catalytic property of the GCE. Thus it is possible to rule out any enhancement in electrocatalytic performances for ORR to be due to the effect of solvent on GCE. Instead, the variations would be due to the interactions between the solvent and MoS₂ material itself. Despite the greater contrast in onset potentials for GCE-modified with MoS₂ in various solvents (Figure 3-8b) than the control experiments (Figure 3-8d), the variations in onset potential for GCE modified with MoS₂ dispersions ORR is not as diverse as compared to that for HER (Figure 3-7). MoS₂ dispersed in ACN has the most positive onset potential *ca.* -0.25 V is only 0.03 V difference from MoS₂ dispersed in DMF which have the least positive onset potential. In this case, the dispersion medium does not have any pronounced impact for ORR electrocatalysis for MoS₂. But it is also interesting to note that the current intensity is enhanced when catalyzed by MoS₂, which suggest that it being more efficient than bare GCE, although the difference in onset potential is small. In a study conducted by Eng *et al.*, the author concluded that “neither TMD compositions nor the chemical exfoliation methods have any obvious effect on ORR”.¹ It seems that few factors can affect the rate of ORR catalysis by MoS₂. However, size-dependent effect, the choice of supporting carbon electrode and catalytic mass loading have been reported to impact MoS₂ catalytic efficiency in ORR.^{30, 35}

3.3 Conclusion

From XPS characterization, the chemical structures of the material are largely unaffected by the choice of solvent (within the time frame where the experiment is conducted). Hence, this could have pointed to the effect of the different drying mechanism of the solvents during drop-casting to explain the variations observed across experiments. In summary, the ferro/ferricyanide redox probe is highly sensitive to the use of different solvents, and blank-DMF (no MoS₂) was found to worsen the HET rate drastically while blank-EtOH shows slight improvement in the HET rate. The dispersion medium for MoS₂ seems to be much less of an effect in terms of ORR electrocatalysis as when compared to HER and HET rate. In the case of HER, the use of MeOH as a dispersion medium resulted in a high overpotentials as compared to the use of other solvents. The use of various dispersion mediums affects the electrocatalysis of different reaction differently as seen from the three reaction system (ferro/ferricyanide, HER, ORR) that were investigated. Electrochemical reactions are heterogeneous in nature and one single solvent cannot be assumed to affect all reactions equally. It is highly dependent on their individual reaction mechanism and hence, sensitivity to the electrode surface. This chapter has documented rigorously the effect of different solvents (ACN, DMF, EtOH, MeOH and water) on the catalytic efficiencies of MoS₂ in HER and going further, aging study was done. It brings insights and guides into future preparation method and also highlights the importance of the preparation steps. The reader should read with caution across literature.

3.4 Experimental

Synthesis.

A mixture of 8.0 g of K_2CO_3 , 16.0 g of S and 10.5 g of MoO_3 and were heated at 750 °C for the synthesis of MoS_2 . The heating was performed for 8 hours in a quartz glass tube placed in crucible furnace loosely capped with quartz lid. The heating and cooling rates were 5 °C min⁻¹. The synthesized MoS_2 was then leached with hot water and the unreacted sulfur was extracted with carbon disulfide using a Soxhlet extractor. The product was then ultrasonicated with hot water and separated by suction filtration.¹⁰

Materials.

Acetonitrile (HPLC/SPECTRO) was obtained from Fulltime (assay (by GC): 99.9% min; water: 100 ppm); ethanol (absolute) is of analytical reagent grade, obtained from Fisher Scientific UK; methanol (HPLC/SPECTRO) was obtained from Fulltime (assay (by GC): 99.9% min; water: 0.05%); *N,N*-dimethyl formamide (purity (GC) $\geq$ 99.8%, water $\leq$ 0.1%) was obtained from Merck specialities; Milli-Q water with a resistivity of 18.2 M Ω cm was used.

Equipment.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were carried out using a μ Autolab type III electrochemical analyser (Eco Chemie, Utrecht, The Netherlands) connected to a personal computer and using NOVA 1.10 software. All voltammetry experiments were performed in an electrochemical cell with a standard three-electrode configuration. A platinum electrode was employed as the counter electrode while an Ag/AgCl electrode was used as the reference electrode. All measurements are performed relative to Ag/AgCl reference electrode. X-ray

photoelectron spectroscopy (XPS) was conducted by utilizing a Phoibos 100 spectrometer with a Mg K α radiation source (SPECS, Germany) at 1254 eV. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were done using a JEOL 7600F SEM (JEOL, Japan).

Procedures.

MoS₂ was prepared in suspensions of concentration of 1 mg mL⁻¹ in Milli-Q water, while for organic solvents (ACN, DMF, EtOH, MeOH), a higher concentration of 5 mg mL⁻¹ was used. It was sonicated for 1 hour in temperature kept under 30 °C to obtain a well dispersed suspension. The materials were then immobilized on the GCE (3 mm diameter) by transferring a 5 μ L of the suspended MoS₂ in Milli-Q water; while only 1 μ L of the suspended MoS₂ in other organic solvents, were transferred on the electrode surface by drop-casting with subsequent drying of the solvent. The catalyst loading for the MoS₂ in the various dispersion medium was kept constant at 70.7 μ g cm⁻² per electrode. The GCE surfaces were renewed prior to every new measurement by mechanical polishing, cleaning it with a 0.05 μ m alumina particle on a polishing pad with Mili-Q water. All voltammetry experiments were repeated 3 times to ensure the reproducibility of the results with random electrodes. SEM images were taken with MoS₂ dispersed in various solvents: (a) ACN (5mg/mL; 1 μ L), (b) DMF (5mg/mL; 1 μ L), (c) EtOH (5mg/mL; 1 μ L), (d) MeOH (5mg/mL; 1 μ L) and (e) water (1mg/mL; 5 μ L). Legend: (X mg/mL, Y μ L), X refers to the concentration of the dispersion and Y refers to the volume used for drop-casting, with the final MoS₂ loading being constant.

Electrochemical Measurements.

HER measurements: LSV was conducted in 0.5 M sulfuric acid with a low scan rate of 2 mV s⁻¹. *ORR measurements:* LSV was performed in N₂-saturated and in air-saturated 0.1 M KOH separately with a scan rate of 50 mV s⁻¹. *Ferro/ferricyanide redox probe:* CV measurements were performed in N₂-saturated 50 mM phosphate buffer solution (PBS) at pH 7.2 as the supporting electrolyte for 10 mM using the ferro/ferricyanide redox probe at a fixed scan rate of 100 mV s⁻¹, taking only the second scan for data processing. The overpotential for HER was taken at -10 mA cm⁻² current density; while the onset potential for ORR was taken to be at the potential where 10% of the maximum current density is observed. The potentials vs RHE is calculated based on the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E_{Ag/AgCl}^0$ where $E_{Ag/AgCl}$ is the measured potential and $E_{Ag/AgCl}^0 = 0.235$ V which is the standard potential of Ag/AgCl (1 M KCl) at 25 °C

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Chapter 4

The Effect of Different Solvents as the
Dispersion Medium for MoS₃

4.1 Introduction

Amorphous molybdenum sulphides (a-MoS_x, $x \geq 2$) have recently attracted much attention showing promising potential as effective electrocatalysis for hydrogen evolution reaction (HER).¹⁻² Such include MoS₃ which has no crystalline counterpart.³⁻⁵ Synthesis of such materials in mild conditions were recently reported, avoiding cost and energy intensive preparation methods. These are thus, in line with the goal of applying such material for environmental applications such as for HER. Hu's group demonstrated that electropolymerization of [MoS₄]²⁻ and acidification of MoO₃ and Na₂S solution can produce a-MoS_x.⁶⁻⁷ Similarly, Tang *et al.* reported the deposition of a-MoS₃ on CdSe-seeded CdS nanorods with a one-step thermal synthesis using microwave heating to 90 °C for 50 minutes.⁸ A facile synthesis of the nanostructured a-MoS_x catalyst at room temperature was later reported by Jaramillo's group. This method further allows the deposition of the as prepared material on to a wide-range of substrate.⁹ Catalyst design to improve the catalyst performance appears to be pertinent. Recent developments¹⁰⁻¹² was introduced in **Chapter 1**, with hybrid structures dominating this field.^{7, 13-17} These catalyst designs are representative of the current a-MoS_x catalyst and have commonly cited the improved conductivity hence faster electron transfer rates; increased surface area and hence greater density of catalytic sites as reasons for enhanced HER catalytic performances. This tackles the issue of slow electron transfer.¹⁸ It is also in the very recent years where detailed theoretical and experimental studies to elucidate the structure and active sites sprouted,¹⁹⁻²³ with which older literature can also provide insightful knowledge about the specific structures.^{3-4, 24-28} Although the catalytic active sites of a-MoS_x for HER

is not yet well established or widely acknowledged as of now, extensive efforts by various research groups will accelerate our understanding and aid in the eventual design of a highly functional catalyst.

Activation of the as synthesised catalysts were commonly reported to be necessary for the transformation to the active species.^{7, 9, 13, 21, 29} Instead of looking at modifying synthetic procedures or specific engineering of the catalyst, the impact of four common solvents (ACN, DMF, EtOH and water) as dispersion medium for MoS₃ was explored for the activation process. In this series of experiments, commercially available MoS₃ was used. The duration after dispersion preparation were also investigated. This is kept within reasonable experimental timeframe as the focus of this chapter is to investigate the fundamental preparation method of MoS₃ dispersions for the investigation for electrochemical measurements. X-ray photoelectron spectroscopy (XPS) analysis was also discussed in an attempt to explain the observations.

4.2 Result and Discussion

Reductive peak current was observed for MoS_x in various solvents and of varying magnitude. It was also reported by Vrubel *et al.* and others^{9, 13, 20-21} that MoS_x exhibits a reduction peak in the first scan and it was postulated by the same group that this is an activation of the MoS_x precatalyst to the active form.⁷ MoS_x is commonly activated before any meaningful electrochemical measurements were taken. This is so to first, activate the catalyst to its active form and second, to ensure that it is stabilised before any subsequent measurements were taken.^{9, 29} What is of interest here is the varying effects of various solvents on MoS_3 electrochemical reductive activation.

Electrochemical Study of MoS₃/Solvents

Figure 4-1: LSV of MoS₃ dispersed in various solvents namely (a) ACN, (b) DMF, (c) EtOH and (d) water where the dispersions were (i) freshly prepared, and (ii) after 2 weeks. Legend: ‘Solvent-2’ refers to the second polarisation curve. Conditions: 0.5 M H₂SO₄; scan rate: 2 mV s⁻¹. Potentials are with respect to the RHE.

Figure 4-1 shows the detailed comparison of the linear sweep voltammograms (LSV) of MoS₃ dispersed in various solvents in acidic

condition within a fixed range of current density. A quick visual scan of the different LSV gives the general conclusions that different solvents indeed have an important role in this first reduction process. This role is further enhanced by the repeat of the experiment after a longer time period of 1.5 days and 2 weeks. Bare glassy carbon electrode (GCE) was drop-casted with the aliquots of the dispersion right after it is sonicated for 20 minutes (see procedure). Such is the condition for the collection of data labelled as 'fresh', where the electrochemical experiments were conducted on the same day as the preparation. The duration from where the dispersions were first prepared showed different electrochemical profiles (Figure 4-1).

The first reductive sweep is required to activate the catalyst no matter the time duration (fresh to 2 weeks) for ACN, EtOH and water. When DMF was used as the solvent, differences were observed with varying time periods. For DMF, the activation process is only required for the freshly prepared dispersion (Figure 4-1b). Subsequently, such reductive peaks were no longer observed for this dispersion medium that was prepared for a longer period of time (1.5 days and 2 weeks). Since there seems to be a change in the MoS_3 specie after the first reductive sweep, 'reduced- MoS_3 ' will be used throughout this text to refer to MoS_3 after being subjected to one reductive sweep. It seems to suggest that DMF itself is able to cause a change in MoS_3 without the application of a reductive potential and stabilises the reduced- MoS_3 . Still, an improvement in the form of lower overpotential to achieve the current density of -10 mA cm^{-2} for the second polarisation is observed, despite the change being small (Figure 4-1bii). When water was used as the dispersion medium, the electrochemical profiles were rather similar despite the time duration. The first polarisation does

not cause any obvious reductive current (current density is generally less than $|-10 \text{ mA cm}^{-2}|$) within the 0 – 0.8 V *vs* RHE range as compared to MoS₃ in ACN, DMF or EtOH. The presence of a broad pre-wave before a steeper increase in current density occurring at *ca.* -0.9 V *vs* RHE was generally observed. Subsequently, after the first polarisation, the reduced-MoS₃ was able to achieve a much larger current density at a lower potential.

The experiments were again repeated at an extended time period of more than 1 month. Similar trend to the voltammograms as when it was prepared after 1.5 days and 2 weeks were observed for each solvent: the current density has a steeper increase after the first reduction at a smaller absolute potential. Since the LSV gave similar trend, the dispersions were deemed to be in a relatively stable state after it was prepared for ~1.5 days. It is noted that the recurrence of the reductive peak was observed at *ca.* -0.5 V *vs* RHE but not for the dispersion using DMF. Even though the reductive processes were not fully removed after the first reductive sweep, bubbling was observed at the working electrode generally at *ca.* -0.35 V *vs* RHE, signifying the onset of HER.

Figure 4-2: (a) The Tafel plot and (b) the bar chart representation of the Tafel slope of the reduced-MoS₃ from various solvents after preparation for 2 weeks. (Data obtained from the second polarisation curves).

Figure 4-2 shows the Tafel plot and the corresponding Tafel slope of the reduced-MoS₃ after preparation for 2 weeks. The observed Tafel slopes for reduced-MoS₃ in the various solvents after preparation for 2 weeks, in this case, are all under 85 mV dec^{-1} and were obtained from the region (*ca.* $-0.15 - -0.45$ V *vs* RHE), close to the onset potential. The similar Tafel slope achieved by the different dispersion would hint at similar reaction kinetics and the choice of solvent has minimal impact on the electron transfer process. This Tafel slope, though not exceptional, is significant when compared to bulk MoS₂.³⁰⁻³² As in this case, the MoS₃ is used as per commercially available and no effort was made to enhance the material design. The lower Tafel slope of MoS₃ in general (compared to bulk MoS₂) could also be attributed to its amorphous nature.³⁻⁴ It was discussed by Chia *et al.*, that electrochemical process can result in the presence of higher amorphous phase of the material.³³ A detailed study by Li *et al.* exploring the relationship between crystallinity and Tafel slope also reported lower Tafel slopes for material with correspondingly lower crystallinity.²³

The superior HER activity of a-MoS_x (or MoS₃) after activation has been reported in the literature as introduced in **Chapter 1**. This chapter would not be a replication to report the lower overpotential that a-MoS_x can achieve but instead, to look into the different electrochemical response (in the form of voltammograms) when the same material (MoS₃) was dispersed in different solvents, (ACN, DMF, EtOH and water). What was discussed previously with regards to the first polarisation is exceptional especially when the choice of solvent for dispersion has always been something more intuitive in many instances especially in terms of electrocatalytic analysis. Given the increasing attention in a-MoS_x which includes MoS₃, certain differences across literature were discovered. According to the pioneering work of a-MoS_x by Hu's group, they mentioned the need for reductive activation of the as synthesized material.⁶ Such reductive activation was similarly reported by other groups.^{9, 13, 20-21} In coherence to our finding that the use of DMF obsolete the need for reductive activation (after a short time frame of 1.5 days), several groups whom did not mention this activation process utilises DMF in their synthesis process. Both Ge *et al.*¹⁴ and Chang *et al.*³⁴ uses DMF as a solvent for the synthesis of a-MoS_x where the MoS_x on nanoporous gold (MoS_{2.7}@NPG) and MoS_x on graphene-protected 3D Ni foam were synthesized respectively. Luxa *et al.* dispersed the as synthesised a-MoS_x/graphene composite in DMF;¹⁶ and similarly, Mohamad Latiff *et al.* also uses DMF as a dispersion medium for the study which involves MoS₃.³⁵ This aforementioned literature did not report any activation process and despite of that, the materials were also found to be highly catalytic for HER.

Attempt to Understand the Reductive Activation Process Through XPS

In an attempt to elucidate the structural differences, surface analysis with the use of XPS was done. The XPS data from the powder-MoS₃ was used as a reference for the fitting. The full width at half-maximum (fwhm) of the same Mo 3d and S 2p species were fixed within a ± 0.3 eV to that of the reference (Figure 4-3). This procedure is similar to Vrabel and Hu, whom fixed the fwhm of the Mo and S species.²⁹ The high resolution spectra for Mo 3d and S 2p were measured for the 4 solvents with the fresh and aged (2 weeks) dispersion, before and after the first reductive sweep. Aged and ‘2 weeks’ samples are used interchangeably throughout the text.

Figure 4-3: High resolution spectra of powder-MoS₃: (ai) Mo 3d, (aia) S 2p. The powder-MoS₃ sample is used as a reference for further deconvolution of the MoS₃ dispersion in various solvents. The binding energies are as follows: Mo⁴⁺ 3d_{5/2} (229.4 eV); Mo^(A) 3d_{5/2} (231.1 eV); Mo⁶⁺ 3d_{5/2} (232.6 eV); S 2s (227.5 eV); S^(B) 2p_{3/2} (162.2 eV); S^(C) 2p_{3/2} (163.5 eV).

In the Mo 3d spectra of the powder-MoS₃, 3 bonding types of Mo (Figure 4-3) were fitted. Mo 3d_{5/2} with the highest binding energy at *ca.* 232.6 eV were assigned to Mo⁶⁺. The lower binding energy (BE, in eV) Mo⁴⁺ at *ca.* 229.4 eV corresponding to 3d_{5/2} as in MoS₂ and the BE is similar to that of a-MoS_x by Lu *et al.*¹² While the Mo^(A) with an intermediate binding energy

between the two oxidation states at *ca.* 231.1 eV which can either be Mo⁵⁺ or Mo⁴⁺ as in MoO_xS_y.^{13, 36} The sulfur spectra which contain S either as S₂²⁻ or S²⁻ is consistent with other reports on MoS₃ and is markedly different from their MoS₂ counterparts. S^(B) corresponding to the lower BE is representative of terminal S₂²⁻ or unsaturated S²⁻ while S^(C) which have a higher BE can be due to bridging S₂²⁻ or apical S²⁻.^{13, 29}

Figure 4-4: High resolution spectra of MoS₃ dispersed in ACN. When the dispersions were freshly prepared: (a) as prepared, (b) after one reductive sweep. When the dispersions were prepared for 2 weeks: (c) as prepared, (d) after one reductive sweep. (i) Mo 3d; (ii) S 2p. Legend: ‘Fresh’ for freshly prepared dispersion; ‘aged’ for dispersion prepared for 2 weeks.

Figure 4-5: High resolution spectra of MoS₃ dispersed in DMF. When the dispersions were freshly prepared: (a) as prepared, (b) after one reductive sweep. When the dispersions were prepared for 2 weeks: (c) as prepared, (d) after one reductive sweep. (i) Mo 3d; (ii) S 2p. Legend: ‘Fresh’ for freshly prepared dispersion; ‘aged’ for dispersion prepared for 2 weeks.

Figure 4-6: High resolution spectra of MoS₃ dispersed in EtOH. When the dispersions were freshly prepared: (a) as prepared, (b) after one reductive sweep. When the dispersions were prepared for 2 weeks: (c) as prepared, (d) after one reductive sweep. (i) Mo 3d; (ii) S 2p. Legend: ‘Fresh’ for freshly prepared dispersion; ‘aged’ for dispersion prepared for 2 weeks.

Figure 4-7: High resolution spectra of MoS₃ dispersed in water. When the dispersions were freshly prepared: (a) as prepared, (b) after one reductive sweep. When the dispersions were prepared for 2 weeks: (c) as prepared, (d) after one reductive sweep. (i) Mo 3d; (ii) S 2p. Legend: ‘Fresh’ for freshly prepared dispersion; ‘aged’ for dispersion prepared for 2 weeks.

Figure 4-4 to Figure 4-7 shows the fitted XPS spectra of the investigated samples. Looking at the raw data (grey line in the spectra), it is identified that the lower energy peak of the doublet in the Mo 3d spectra has higher intensity (or similar) to the higher energy peak in the doublet after reduction. Before the application of cathodic potentials, the lower energy peak of the doublet is of lower intensity in general. This is a qualitative view of the spectra. Deconvolution was done and some general trends were observed across the samples in its XPS spectra. Firstly, proportion of Mo⁴⁺ shows an increase while Mo⁶⁺ decreases (Table 4-1 and Table 4-2) after reduction. Next, the proportion of S from the lower BE, S^(B), generally increases after reduction though exceptions were seen for dispersion in water (fresh) and in ACN (aged). Further inspection found a general trend such that the ratio of S^(B)/S^(C) is approximately 1 after reduction.

The electrochemical processes occurring during reductive activation is not yet well understood, with varying viewpoints presented. Hu's group has previously attributed it to the reduction of disulfide ligands, S_2^{2-} to S^{2-} , forming the active catalyst.⁶ Tran and co-workers proposed the formation of unsaturated Mo^{4+} sites during reduction as the catalytic sites for HER for their prepared a- MoS_x .²¹ Tang *et al.* also observed a photoreduction of their MoS_3 -coated CdS nanorods from Mo^{5+} to Mo^{4+} prior to photocatalysis of hydrogen reduction and the authors deemed the active specie to be an under-coordinated specie.⁸ The greater density of coordinatively unsaturated Mo and/or S sites in a- MoS_x are often offered as the reason for enhanced HER activity.^{2, 7, 11}

The presence of Mo^{6+} is commonly attributed to be due to the contamination by the presence of surface oxides in the form of MoO_3 .^{9, 29} The decrease in Mo^{6+} composition is likely to be due to the dissolution of the surface oxides in the electrolyte during the first reductive sweep. Benck *et al.* has found that the proportion of Mo^{6+} decreases after the catalyst film is rested in water or sulfuric acid even without the application of cathodic potentials.⁹ Though intuitive, the decrease in Mo^{6+} and a corresponding increase in Mo^{4+} proportion after reduction cannot be correlated simply. Instead, the composition of Mo 3d were normalized to look just at Mo^{4+} and $Mo^{(A)}$ as Mo^{6+} is contributed by the oxide contaminant and not part of the molybdenum sulfide component. The structure of MoS_3 is still debatable with literature citing either $Mo^{5+}(S_2^{2-})_{1/2}(S^{2-})_2$ or $Mo^{4+}(S_2^{2-})(S^{2-})$.^{4, 22, 24, 26, 28, 37} From Table 4-3 and Table 4-4, it is apparent that the increase in Mo^{4+} is likely due to a reduction of $Mo^{(A)}$. Less informative is the S spectra as it is hard to distinguish terminal S_2^{2-} from unsaturated S^{2-} at the lower BE; and between the bridging S_2^{2-} and apical S^{2-} at the higher BE due

to their similar BE.^{20, 34, 38} Their contribution to either S^(B) or S^(C) would very much depend on the actual chemical environment. But from the XPS data, a general increase in S^(B) proportion is observed with the exception of reduced-MoS₃-water (fresh) sample. This exception leads us to agree with Pham *et al.* whom caution against the exclusive use of the S 2p XPS spectra for the prediction of catalytic activity for MoS₃.¹³ Again, Li and co-workers have previously degraded MoS₃ by 50 cycles to MoS₂, but they observed that the catalytic activity was maintained even when the proportion of S at the higher BE was almost non-existence.²³ Herein, the increase in Mo⁴⁺ which is attributed to the reduction of Mo^(A); and a general increase in S^(B) proportion is observed. It is inferred that the reductive activation could be attributed to the reduction of Mo^(A) to Mo⁴⁺ as concluded from the XPS data. Instead of looking at the change in proportion of S composition, further inspection leads to the identification that the S^(B)/S^(C) ratio after reduction approaches close to 1 with the exception of reduced-MoS₃-DMF (fresh), whom have equally well catalytic activity. It is postulated that the reduced-MoS₃ specie in this study is likely to constitute mainly of Mo⁴⁺ with S^(B)/S^(C) ~ 1. The general increase in S^(B) coincides with the likelihood of a great proportion of terminal S₂²⁻. This terminal S₂²⁻ has been discussed to be involved in the catalytic process^{19, 23} for HER though opposing viewpoints exist.^{11, 20, 34} In this current study, a general increase in S^(B) is in tune with the involvement of terminal S₂²⁻.

The different solvents gave similar results where a significantly higher proportion of Mo⁴⁺ is observed with a S^(B)/S^(C) ratio close to 1 after reduction. Even without the application of cathodic potentials, MoS₃-DMF (aged) composition are highly similar to that of reduced-MoS₃-DMF. The application

of cathodic potentials did not lead to a significant change. This is in agreement with the LSV where the first reductive sweep was no longer required for MoS₃ when it was dispersed in DMF for a longer time period.

Table 4-1: Percentage composition as from XPS analysis. The samples were taken from the freshly-prepared dispersions. ‘Not Red’ – as prepared samples without the application of reductive potentials; ‘Red’ – refers to the samples after one reductive sweep.

Fresh %	ACN		DMF		EtOH		Water	
	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>
Mo ⁴⁺	53	64	54	75	43	56	40	66
Mo ^(A)	19	21	24	15	21	17	36	16
Mo ⁶⁺	28	15	22	10	36	27	24	18
S ^(B)	46	52	67	78	39	59	75	57
S ^(C)	54	48	33	22	61	41	25	43

Table 4-2: Percentage composition as from XPS analysis. The samples were taken from the dispersions prepared for 2 weeks (aged). ‘Not Red’ – as prepared samples without the application of reductive potentials; ‘Red’ – refers to the samples after one reductive sweep.

Aged %	ACN		DMF		EtOH		Water	
	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>
Mo ⁴⁺	35	61	61	63	29	52	44	62
Mo ^(A)	36	20	20	21	42	25	30	17
Mo ⁶⁺	29	19	19	16	29	23	26	21
S ^(B)	61	56	50	51	49	57	51	50
S ^(C)	39	44	50	49	51	43	49	50

Table 4-3: The percentage composition of Mo^{4+} and $\text{Mo}^{(\text{A})}$, normalized to exclude proportion of Mo^{6+} . The samples were taken from the freshly-prepared dispersions. ‘Not Red’ – as prepared samples without the application of reductive potentials; ‘Red’ – refers to the samples after one reductive sweep.

Fresh %	ACN		DMF		EtOH		Water	
	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>
Mo^{4+}	73	76	69	84	68	77	52	81
$\text{Mo}^{(\text{A})}$	27	24	31	16	32	23	48	19

Table 4-4: The percentage composition of Mo^{4+} and $\text{Mo}^{(\text{A})}$, normalized to exclude proportion of Mo^{6+} . The samples were taken from the dispersions prepared for 2 weeks (aged). ‘Not Red’ – as prepared samples without the application of reductive potentials; ‘Red’ – refers to the samples after one reductive sweep.

Aged %	ACN		DMF		EtOH		Water	
	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>	<i>Not Red</i>	<i>Red</i>
Mo^{4+}	49	76	76	75	41	67	59	79
$\text{Mo}^{(\text{A})}$	51	24	24	25	59	33	41	21

Testing the Catalytic Efficiencies of MoS₃/Solvents for ORR

Figure 4-8: LSV of MoS₃ dispersed in various solvents for investigation of its electrocatalytic performance for ORR. (a) ACN, (b) DMF, (c) EtOH, (d) water; (i) represents the polarisation curves in N₂-saturated electrolyte and (ii) in air-saturated electrolyte. Legend: ‘Solvent-2’ (lighter colour) refers to the second polarisation curve. Conditions: 0.1 M KOH; scan rate: 5 mV s⁻¹. Potentials are with respect to the Ag/AgCl reference electrode.

Most of the literature and effort has been focused on MoS₃ functionality as an effective HER electrocatalyst, much less is known about its efficiency towards oxygen reduction reaction (ORR). Similarly, a reductive sweep was run as in the experiments for HER but the electrolyte used in this case was 0.1 M KOH. A reductive peak occurs at a more negative potential compared to the ORR catalysed by bare GCE surface (Figure 4-9) is possibly due to the electrochemical reduction of the MoS₃ as observed in 0.5 M sulfuric acid (pH 0, for HER). The recurrence of the peak even when the experiments were replicated in N₂-saturated KOH further affirms this (Figure 4-8i). As noted in Figure 4-8i (N₂-saturated KOH), all of the second polarisation curve shows no obvious reduction peak. This would have meant two things. First, the first sweep has successfully rendered all the reducible moieties reduced and next, the reduced material is not able to be reduced further within the potential range. This irreversibly transformed the material after the applied cathodic potentials. Two reduction peaks were observed for the modified GCE in air-saturated KOH but not for N₂-saturated KOH. These reduction peaks are likely to constitute of ORR (*ca.* -0.5 V) and an inherent reduction of MoS₃ (*ca.* -0.8 V). The reductive peak at the more positive potential (*ca.* -0.5 V), is likely to be due to ORR as it is not present when the electrolyte is nitrogen saturated; while the inherent reduction peak persist at the more negative potential (*ca.* -0.8 V). This can serve as an important identification that ORR occurs even in the first polarisation, before MoS₃ is expected to be reduced in air-saturated electrolyte. From the various solvents, it is observed that MoS₃ dispersed in EtOH shows the most obvious ORR reduction peak in the first polarisation and its subsequent onset potential is the most positive as compared to the MoS₃ dispersed in other

solvents. An in-depth analysis of the onset potential of the reduced-MoS₃ material for ORR has shown no improvement from bare GCE (Figure 4-9). As such, MoS₃ does not seem to be highly active as an electrocatalyst for ORR since no significant enhancement is achieved with reduced-MoS₃-modified electrode surface as compared to bare GCE. Hence, effort was not taken to look into the aging effect of MoS₃ when the electrolyte used is 0.1 M KOH (pH 13), the conditions used for ORR. These experiments were conducted within 1 week of the preparation of the dispersions to ensure that it has reached a stable state in the particular solvent.

Figure 4-9: (a) The LSV plot for bare GCE; (b) the onset potential of the ORR using the potential at which 10% of the maximum current density is achieved. Data were obtained from the second polarisation curve; bare GC (N₂) refers to the N₂-saturated electrolyte. Conditions: 0.1 M KOH; scan rate: 5 mV s⁻¹. All potentials are with respect to the Ag/AgCl reference electrode. Error bars correspond to the standard deviation of three replicates.

Electrochemical Characterisation Through Studying its Inherent Electrochemistry

Figure 4-10: CVs of the prepared MoS₃ dispersion. (a) ACN, (b) DMF, (c) EtOH, (d) water; (i) represents the cathodic scan and (ii) anodic scan direction. Conditions: PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s⁻¹. Potentials are relative to the Ag/AgCl reference electrode.

Cathodic and anodic potentials were applied for the MoS₃ modified GCE surface in blank PBS. Figure 4-10 shows the electrochemical response when an initial (i) cathodic potential (ii) anodic is applied. This serves to investigate the electrochemistry of the materials when drop-casted on the GCE. At the two extreme ends of high cathodic and high anodic potentials, HER and oxygen evolution reaction (OER) occurs respectively. Therefore, the voltammogram will show a huge increase in current intensity. The region of interest would be between these two extreme potentials as any electrochemical reactions will not be masked by the exceedingly high current caused by HER and OER.

MoS₃ shows distinctively different inherent electrochemistry as compared to MoS₂ as presented in previous chapters and in literature.^{31, 33, 39} MoS₂ is commonly observed to give an oxidation peak at *ca.* +0.9 V, and is attributed to the oxidation of Mo⁴⁺ to Mo⁶⁺.^{33, 39} MoS₃, in this case does not exhibit such broad and obvious anodic peak as MoS₂. Instead, an anodic peak is observed at higher anodic potentials (*ca.* +1.60 to +1.65 V), obscured by the high current intensity of OER. The specie oxidised at the anodic potentials *ca.* +1.60 V is likely to be dependent on a prior reduction step at *ca.* -1.0 V. This is evident in the case where the second scan (plot in grey; in which the anodic potentials were first applied, Figure 4-10ii) produces a greater current intensity than the preceding scan. Thus, it seems that the specie produced during the reduction at *ca.* -1.0 V is being oxidised subsequently at the high anodic potential. It is likely that this would result in the formation of the same reduced moiety thereby causing the recurrence of the reductive peak at the second scan. Reductive peaks were similarly observed when cathodic potentials were applied to a-MoS_x at pH 7.²¹ The authors did not observe a recurrence of the reductive

peaks upon second cathodic polarisation. This further supports the proposition that the oxidative event at *ca.* +1.60 to +1.65 V is likely to produce the reducible specie. The reduction occurring is likely due to the reduction of Mo^{6+} as this was similarly observed for the cathodic scan of MoO_3 .³³ Similar behaviour was observed within all the samples with the current being less intense for the dispersion in water. This phenomenon was also observed in sulfuric acid where the first reductive sweep of MoS_3 dispersed in water yielded a less intense reductive current compared to the others (Figure 4-1d).

Heterogeneous Electron Transfer (HET) rate at MoS₃/Solvent-modified GCE for Ferro/ferricyanide Redox Probe

Figure 4-11: Results from which the various MoS₃-solvents dispersions were drop-casted on GCE are shown in (a) and (b); control experiments where the blank-solvents (no MoS₃) were drop-casted on bare GCE are presented in (c) and (d). CVs of the Fe(CN)₆^{4-/3-} redox probe for (a) MoS₃ dispersed in various solvents, (c) blank-solvents on bare GCE. Bar Chart representation of the peak separation between the anodic and cathodic peak current: (b) MoS₃ dispersed in various solvents, (c) control with only solvent on bare GCE. Conditions: 10 mM Fe(CN)₆^{3-/4-} in 50 mM PBS supporting electrolyte at pH 7.2; scan rate: 100 mV s⁻¹. Error bars correspond to standard deviations based on triplicate measurements. Potentials are with respect to the Ag/AgCl reference electrode. Only the second scans were used for data processing. (The materials were not electrochemically modified before the measurements).

Table 4-5: The k_{obs}^0 of MoS₃ dispersed in various solvents. Calculated based on the Nicholson's method.⁴⁰

MoS ₃ / Solvent	k_{obs}^0 (cm s ⁻¹)
ACN	9.18×10^{-4}
DMF	1.82×10^{-3}
EtOH	3.13×10^{-3}
Water	7.04×10^{-4}
Bare GCE	1.90×10^{-3}

The k_{obs}^0 is able to give an indication of the practically of the material for sensing applications. A small peak separation is indicative of a faster heterogeneous electron transfer (HET) rate and is favourable as it meant a lower overpotential for the electrochemical process. The calculated k_{obs}^0 is shown in Table 4-5 and Figure 4-11 shows the CV and the bar chart comparison of the peak separation. The ferro/ferricyanide redox probe is known to be surface sensitive⁴¹⁻⁴² and hence would allow us to evaluate the observed HET rate, k_{obs}^0 , of the prepared dispersions.

The as prepared dispersions were not electrochemically reduced before taking the measurement. Instead, the potential window of the CV run is kept small and within -0.4 to 0.6 V vs Ag/AgCl and the second scan was taken for the processing of data. Comparing with the control run, where solvents were drop-casted without any MoS₃ on the bare GCE, obvious contrast were observed despite the use of the same redox couple. In the control experiments, DMF resulted in the largest peak separation and it is hence expected to give the largest

peak separation for MoS₃ dispersed in DMF as well. However, MoS₃ dispersed in DMF did not give a peak separation much larger than that of bare GCE. Instead, MoS₃ dispersed in ACN or water gave a larger peak separation, even greater than bare GCE. Thus, the k_{obs}^0 is much slower for surface modified with MoS₃-ACN and MoS₃-water, giving k_{obs}^0 of 9.18×10^{-4} and 7.04×10^{-4} cm s⁻¹ respectively. A timed-study was not conducted for this redox couple; the results were collected within 1 week after the dispersions were prepared. Hence, the timed-electrochemical study of the various dispersion in the preceding section could have explained this differences. Previously it was observed that MoS₃ dispersed in DMF for a longer time period does not require any activation process. Thus, this same material (reduced-MoS₃ in DMF) could have been both the active catalyst for HER and also the material with enhanced HET rate as seen by the smaller peak separation. Following this same argument, MoS₃ in EtOH should have its peak separation similar to the dispersions in ACN or water since their electrochemical profiles are largely similar. The enhance catalytic efficiency of MoS₃ dispersed in EtOH is inferred to be due to the use of the solvent, which improved the catalytic efficiency on the bare GCE surface as observed in the control experiment. EtOH was previously studied as a dispersion medium for functionalized graphene sheets which the authors reported a larger porosity factor with a smaller peak to peak separation for EtOH suspension but not the deionised water suspension.⁴³ In addition, higher voltammetric response was recorded for multiwalled carbon nanotubes (MWCNT) dispersed in EtOH drop-casted on GCE.⁴⁴ Similar result was also obtained and discussed in **Chapter 3** where MoS₂ dispersed in EtOH achieved a smaller peak separation and highest current response. Although the interaction between the solvent and

the material would definitely differ for different materials, this serve as a supporting evidence where solvent can result in enhancement in certain responses rather than it being the intrinsic property of the material. The enhanced HET rate was achieved when MoS_3 was dispersed in DMF, where DMF itself was shown to detrimentally affect the sensitivity of the modified-GCE. Thus, this illustrates that the reduced- MoS_3 is highly functional, not just for HER but also in terms of HET for this redox probe. This is in direct contrast to TMDs which have consistently shown to have a slower HET rate as compared to bare GCE, especially when in bulk.⁴⁵⁻⁴⁸

4.3 Conclusion

The different solvents used in this case have been seen to have varying impact on the reductive activation of the MoS_3 used in this study. DMF has shown to be able to preferentially stabilise the specie after one reductive sweep, which has been named as reduced- MoS_3 , during a longer time period even without the application of any reductive potential. The proposed composition of the reduced- MoS_3 in this study is thought to be Mo^{4+} and with a $S^{(\text{B})}/S^{(\text{C})}$ ratio close to 1 through XPS analysis. Reduced- MoS_3 (as in the DMF solvent without application of reductive potential) has shown to be able to exhibit a much faster k_{obs}^0 despite that the use of blank-DMF (without MoS_3) can detrimentally affect the k_{obs}^0 on bare GCE. Thus, future applications in sensing can be envisaged for reduced- MoS_3 materials with its faster k_{obs}^0 . This demonstrates that the choice of solvents can indeed have a pronounced impact on the material in question.

4.4 Experimental

Materials.

The Molybdenum sulphide (MoS_3) used is commercially available as Molybdenum(VI) sulfide dihydrate, obtained from Alfa Aesar (Germany). Acetonitrile (HPLC/SPECTRO) was obtained from Fulltime (assay (by GC): 99.9% min; water: 100 ppm); ethanol (absolute) is of analytical reagent grade, obtained from Fisher Scientific UK; *N,N*-dimethyl formamide (purity (GC) $\geq$ 99.8%, water $\leq$ 0.1%) was obtained from Merck specialities; Milli-Q water with a resistivity of 18.2 $\text{M}\Omega$ cm was used.

Equipment.

A μ Autolab type III electrochemical analyser (Eco Chemie, Utrecht, The Netherlands) controlled using the NOVA 1.10 software was used to conduct the cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements. A standard three-electrode configuration consisting of the working electrode, reference electrode (Ag/AgCl) and the Platinum counter electrode was used for all voltammetry experiments. Measurements were performed relative to Ag/AgCl reference electrode. X-ray photoelectron spectroscopy (XPS) was conducted by utilizing a Phoibos 100 spectrometer with a Mg $\text{K}\alpha$ radiation source (SPECS, Germany) at 1254 eV.

Procedures.

MoS_3 was prepared in suspensions of concentration of 1 mg mL^{-1} in Milli-Q water, while for organic solvents (ACN, DMF, EtOH), a higher concentration of 5 mg mL^{-1} was used. The suspensions were sonicated for 20

minutes to ensure it is well dispersed. The materials were then immobilized on the glassy carbon electrode (GCE, 3 mm diameter) by transferring a 5 μL of the suspended MoS_3 in Milli-Q water (1 mg mL^{-1}); while 1 μL of the suspended MoS_3 in other organic solvents (5 mg mL^{-1}), were transferred on the electrode surface by drop-casting with subsequent drying of the solvent. This ensured that the catalyst loading was kept constant at $70.7 \text{ } \mu\text{g cm}^{-2}$ per electrode. All voltammetry experiments were repeated 3 times to ensure the reproducibility of the results with random electrodes. Results of the electrochemical measurements which were conducted right after the 20 minutes of sonication were presented as ‘fresh’. The modified GCEs were first subjected to the application of cathodic potentials from (+0.2 to $-1.4 \text{ V vs Ag/AgCl}$). The XPS spectra are calibrated to adventitious carbon to 284.5 eV.

Electrochemical Measurements.

LSV was conducted in 0.5 M sulfuric acid with a low scan rate of 2 mV s^{-1} , while for measurements in 0.1 M KOH, a scan rate of 5 mV s^{-1} was used. CV measurements were performed in 50 mM phosphate buffer solution (PBS) at pH 7.2 as the supporting electrolyte for 10 mM using the ferro/ferricyanide redox probe at a fixed scan rate of 100 mV s^{-1} , taking only the second scan for data processing. The potentials *vs* RHE is calculated based on the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\text{Ag/AgCl}}^0$ where $E_{\text{Ag/AgCl}}$ is the measured potential and $E_{\text{Ag/AgCl}}^0 = 0.235 \text{ V}$ which is the standard potential of Ag/AgCl (1 M KCl) at 25°C .

4.5 Reference

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Chapter 5

Conclusion

This thesis has looked specifically into molybdenum sulfide for its applications in the field of electrocatalysis. Molybdenum sulfide has shown to have great potential as an abundant-metal electrocatalyst for energy applications but generally found to be more functional in the application of hydrogen evolution reaction (HER), though works into oxygen reduction reaction (ORR) and for energy storage were also presented here and in contemporary literature. This thesis presented works that contributes towards the understanding of the basic aspect of the materials' electrocatalytic performances. Such knowledge is essential to the progress of this field. It probed into the experimental aspect that are commonly taken for granted.

This thesis studied the fundamentals in the practical aspect of electrocatalysis. In **Section I**, the various origins of molybdenum disulfide were studied and extensive characterisation tools were employed to understand the variations. While in **Section II**, the effect of different solvents as a dispersion medium for molybdenum disulfide and molybdenum trisulfide were probed. Dispersions were commonly prepared for solid materials for use in the analysis of electrocatalytic performances using a standard base electrode as substrate and the choice of solvent has been something more intuitive in many cases. The variations in terms of catalytic performances were documented rigorously and has confronted what was commonly regarded as intuitive. This work provides insights into the effect of solvents on molybdenum sulfide materials for electrocatalysis as such works on this emerging class of materials are less common. In **Chapter 4**, amorphous molybdenum sulfide (MoS_3 in this case) was explored. This sub-class of molybdenum sulfide material is gaining attention in the community with its novel application in electrocatalysis for

HER. Upon further scrutiny, the chapter has looked into explaining the reductive activation process through the use of surface analysis. The various sources of the starting material and the choice of dispersion medium for electrocatalytic measurements are commonly taken for granted. It is also important to note that the implications of each particular factors on the catalytic performances of the molybdenum sulfide materials would varies with different redox systems.

While there has been a steady progress in various catalyst design which has enhanced performances, further works which probe into the fundamental aspects of molybdenum sulfide and its impact on electrocatalysis or electroanalytical measurements would have to be considered. The contributions of various research team globally, devoting to the understanding of the material in its theoretical and practical aspects is hoped to lead to its eventual use as a robust and functional electrocatalyst for HER and other emerging applications. A substantial amount of work would still be required in order to realise the goal of a hydrogen economy and a carbon-neutral future.

List of Publications

1. Chua, X. J.; Tan, S. M.; Chia, X.; Sofer, Z; Luxa, J; Pumera, M. Origin of MoS₂ Significantly Influences Its Performance for Hydrogen Evolution Reaction due to Differences in Phase Purity. *Chem. Eur. J.* **2017**, *23*, 3169-3177.
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