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vulnerability of MoS₂, and direct correlation to Pt hydrogen
evolution reaction kinetics**

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ARTICLE

Sulfur poisoning of emergent and current electrocatalysts: vulnerability of MoS₂, and direct correlation to Pt hydrogen evolution reaction kinetics

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The recent surge in interest to utilise transition metal dichalcogenides for hydrogen evolution reaction (HER), as well as the long-standing problem of sulfur poisoning suffered by established Pt HER electrocatalyst, inspired the motivation to examine the impacts of sulfur poisoning on both emergent and current electrocatalysts. Through a comparative study between MoS₂ and Pt/C on the effects of sulfur poisoning, we demonstrate that MoS₂ is not invulnerable to poisoning. Additionally, using X-ray photoelectron spectroscopy, correlations have also been established between the atomic percentages of Pt–S bonds and normalised HER parameters *e.g.* Tafel slope and potential at –10 mA cm⁻². These findings are of high importance for potential hydrogen evolution catalysis.

Introduction

Hydrogen evolution reaction (HER) is an industrially important process for the sustainable production of hydrogen as an alternative energy fuel.¹ Currently, the biggest challenge yet to be solved is the development of a cost-effective and commercially-feasible method of hydrogen production. Furthermore, industrial HER is frequently plagued by high cost of noble metal catalyst or poisoning by trace amounts of catalyst poisons.^{2,3} As the best performing HER catalyst thus far, Pt is often condemned for its scarcity and high cost, as well as susceptibility to poisoning by various compounds.^{2,4} Amongst the poisons, of particular concern are sulfur-containing compounds such as H₂S and Na₂S, whose poisoning effects have been investigated to strongly lower the electrocatalytic activity of Pt towards HER.^{5,6}

Previously, it has been demonstrated that there are two types of H adsorption sites on Pt, namely underpotential (>0 V *vs.* RHE) hydrogen adsorption site (H_{UPD}) and overpotential (<0 V *vs.* RHE) hydrogen adsorption site (H_{OPD}), at which hydrogen is strongly and weakly adsorbed onto the Pt surface respectively.⁵ The latter adsorption sites are catalytically active sites towards HER due to the weak adsorption of hydrogen to the Pt surface which lowers the thermodynamic cost of

hydrogen desorption to form hydrogen gas.⁷ Protopopoff and co-worker studied the poisoning effects of sulfur on Pt (110) at various coverages of sulfur by H₂S, which was quantified through a radiotracer method in conjunction with various spectroscopic techniques.⁵ It was concluded that sulfur poisoning by blocking H_{UPD} is much more potent than poisoning by blocking H_{OPD}, as exemplified by the rapid decreasing exchange current density (at 0V *vs.* RHE), compared to the slight increase in Tafel slope. However, though the effects of sulfur poisoning were investigated, the sites of actual sulfur adsorption were neither studied nor correlated to the HER kinetics on Pt.

Given that the development of an inexpensive HER electrocatalyst that can match the efficiency of Pt is still in its nascent stage, it is imperative to study the problems facing the current Pt electrocatalyst. Herein, using NaHS as the poisoning agent, we report correlations between the atomic percentages of adsorbed sulfur species on Pt (at.%Pt–S), and trends in the corresponding HER Tafel slopes and potentials at –10 mA cm⁻². By exploiting X-ray photoelectron spectroscopy (XPS), the adsorbed sulfur species on Pt were identified and the atomic percentage of sulfur (at.%S2p) adsorbed onto the catalytic surface of Pt quantified. In addition, with the recent surge in

interest to employ various transition metal dichalcogenides (TMDs), especially MoS₂, for electrochemical hydrogen production,^{8–10} it is opportune to explore and compare the effects of sulfur poisoning on current and developing HER electrocatalysts. Such unprecedented comparisons of the impacts of poisoning between Pt and MoS₂, using three main parameters of comparison, namely normalised values of Tafel slope, exchange current density and potential at -10 mA cm^{-2} , are also presented in this study. These results reveal the susceptibility of MoS₂ to poisoning, and disclose correlations between poisoned Pt sites and its HER kinetics.

Experimental

Materials

Bulk MoS₂ powder (<2 μm) and *t*-butyllithium (1.7 M in pentane) were obtained from Sigma-Aldrich, Czech Republic while hexane was purchased from Lach-ner, Czech Republic. Argon (99.9999% purity) was obtained from SIAD, Czech Republic. Sulfuric acid (95–98%), sodium hydrogen sulfide (anhydrous) and 20 wt.% platinum on graphitised carbon (Pt/C) were purchased from Sigma Aldrich, Singapore. The glassy carbon (GC) working electrode, Ag/AgCl (1 M KCl) reference electrode and Pt auxiliary electrode were obtained from CH Instruments, USA.

Apparatus

X-ray photoelectron spectroscopy (XPS) was performed with a Phoibos 100 spectrometer with the Mg K α X-ray source (SPECS, Germany) at 1254 eV. XPS samples were prepared by dropcasting a uniform layer of the electrocatalyst onto a screen printed electrode (SPE) followed by a subsequent layer of NaHS of various concentrations. Excess NaHS was then rinsed off with deionised water and the SPEs were left to dry. The Cl2*p* peak originated from the SPEs.^{11,12} Survey and high-resolution core-level spectra were collected. The surface atomic compositions were obtained from the former spectra while the atomic percentages of Pt–S and SO₄²⁻ were acquired from the latter. Electrochemical analyses were conducted using an μ Autolab Type III electrochemical analyser (Eco Chemie, Utrecht, The Netherlands) operated by NOVA 1.8 software (Eco Chemie).

Procedures

FABRICATION OF *t*-BUTYLLITHIUM EXFOLIATED MoS₂. The bulk MoS₂ powder (3 g) was added to *t*-butyllithium in pentane (1.7 M, 20 mL) and stirred at 25 °C under argon atmosphere for 72 h. Suction filtration was subsequently used to isolate the Li-intercalated compound from excess intercalating agent, after which the isolated compound was washed repeatedly with hexane (dried over sodium). Water (100 mL) was used to disperse and exfoliate the Li-intercalated compound which was then centrifuged several times at 18000 g. The obtained material was subsequently dried in vacuum at 50 °C for 48 h prior to measurements.

PROCEDURE FOR PREPARATION OF ELECTROCATALYST-MODIFIED ELECTRODES. Prior to modification by the nanoparticles, the GC surface was renewed to a mirror finish using 0.05 μm alumina particles on a polishing pad. The Pt/C and MoS₂ nanoparticles (1.0 mg mL⁻¹) were individually dispersed in *N,N*-dimethylformamide (DMF) for 1 h before usage. After sonication for 5 min, 1 μL aliquot of the dispersed materials was dropcast onto the GC surface, which was then allowed to dry under a lamp.

PROCEDURE FOR POISONING OF ELECTROCATALYST SURFACE. Various concentrations of the poisoning agent, NaHS (0, 12.5, 25, 50, 100, 500 and 1000 mM), were prepared in Milli-Q water with resistivity of 18.2 M Ω cm. 3 μL of each solution was then dropcast onto a Pt/C or MoS₂ modified GC electrode. Upon drying, the poisoned electrodes were then rinsed with Milli-Q water to remove excess NaHS, followed by subsequent drying under a lamp. Prepared electrodes were then measured for their HER electrocatalytic performances.

ELECTROCHEMICAL CHARACTERISATION. Linear sweep voltammetric measurements were conducted at room temperature using a three-electrode configuration. The poisoned and modified GC served as the working electrode, while Ag/AgCl and Pt electrodes functioned as reference and counter electrodes respectively. All HER measurements were performed in a solution of 0.5 M sulfuric acid, purged with nitrogen gas prior to measurements, at a scan rate of 2 mV s⁻¹, and triplicate measurements were carried out for all materials. For both Pt/C and MoS₂, the values of Tafel slopes, exchange current densities and potentials at -10 mA cm^{-2} of the poisoned electrocatalysts were normalised to those of the unpoisoned electrocatalysts which were assigned the value of 1.

Results and Discussion

Glassy carbon (GC) electrodes modified with 1.0 mg mL⁻¹ of platinum on graphitised carbon (Pt/C) or MoS₂ nanoparticles were poisoned with varying concentrations of NaHS (0, 12.5, 25, 50, 100, 500 and 1000 mM) using the dropcast method, as described in the Experimental section. To examine the surface elemental composition of the poisoned electrocatalysts, XPS was employed and the corresponding wide scan spectra were plotted in Fig. S1 (see ESI). Analyses of the wide scan spectra afforded the surface atomic composition, some of which were tabulated in Table S1. From Table S1, S2*p* exhibited an increasing trend with concentration of NaHS for Pt/C, from 0 to 4.01 at.%; however, such trend was not observed for MoS₂, possibly due to the presence of sulfur in the electrocatalyst structure which accentuated the S2*p* signals for some of the poisoned samples.

S2*p* core-level XPS spectra were also obtained for Pt/C and MoS₂ and are exhibited in Fig. 1. Fig. 1A clearly shows no peaks in the S2*p* binding energy region for the unpoisoned Pt/C while a broad peak comprising of two peaks at *ca.* 162 and 163

eV, identified as $S2p_{3/2}$, and $S2p_{1/2}$, the spin orbit coupled peaks of MoS_2 ,¹³ was observed for the unpoisoned MoS_2 (Fig. 1B). However, upon poisoning with NaHS, both spectra report a new peak at *ca.* 169 eV and an additional peak at *ca.* 163 eV was obtained for Pt/C. The former peak was ascribed to SO_4^{2-} formed from the oxidation of HS^- ions by atmospheric oxygen^{14,15} while the latter was attributed to the Pt–S bond.^{16,17} These results ascertain the adsorption of sulfur poison onto the both Pt/C and MoS_2 , especially so for Pt/C where some of the sulfur poison directly forms a Pt–S bond with the electropositive Pt surface. Subsequently, we will correlate the at.%Pt–S with several parameters of HER electrocatalytic activities.

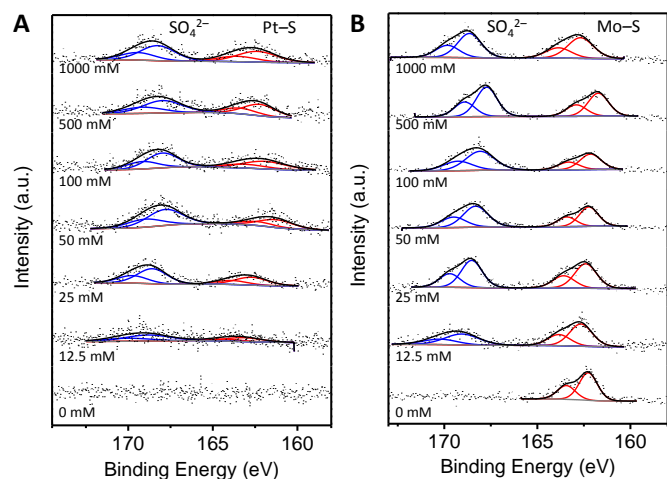


Figure 1. $S2p$ core-level XPS spectra of Pt/C (A) and MoS_2 (B) poisoned with increasing concentrations of NaHS, with the SO_4^{2-} (blue) and metal-sulfide (red) peaks deconvoluted to represent $S2p$ spin-orbit coupled doublets, $S2p_{3/2}$ and $S2p_{1/2}$. The concentrations of NaHS used were 0, 12.5, 25, 50, 100, 500 and 1000 mM, as indicated in the individual spectra.

Before the correlations can be constructed, the HER electrocatalytic activities of the poisoned electrocatalysts were first measured using linear sweep voltammetry (LSV). The LSV curves obtained, together with their corresponding Tafel plots, are shown in Fig. S2 (see ESI). The LSV curves for Pt/C clearly demonstrate the increasingly lower HER electrocatalytic activities of samples poisoned with higher concentration of NaHS. On the other hand, the MoS_2 samples simply display a wider spread of the LSV curves; no particular trend was observed with greater poisoning. Moreover, the Tafel plots show much larger increase in overpotential for HER on Pt/C than MoS_2 . Both LSV curves and Tafel plots exhibit a larger variance in HER performance for Pt/C compared to MoS_2 , upon poisoning.

To quantitatively compare between Pt/C and MoS_2 the impacts of poisoning on their HER activities, the normalised Tafel slopes, potentials at -10 mA cm^{-2} and exchange current densities obtained from the LSV curves were plotted against concentrations of NaHS in Fig. 2. The first two parameters provide information on the HER kinetics on the electrocatalysts¹⁸ while the third parameter offers insight into the intrinsic electrocatalytic activities of the electrocatalysts

towards HER.^{19,20} For poisoned Pt/C samples, substantial rise in the values of the Tafel slope and potential at -10 mA cm^{-2} (Fig. 2A and B) and fall in the exchange current density to near zero values were obtained (Fig. 2C), while fluctuating trends were observed across all three parameters of comparison for MoS_2 . These results reveal the superior tolerance of MoS_2 to poisoning by sulfur over that of Pt/C. The observed increase and plateau of Tafel slope values and decrease of exchange current densities of Pt with enhanced poisoning were achieved in a previous study which employed H_2S as the poisoning agent instead,⁵ indicating that poisoning effects of sulfur on Pt is irrespective of its physical state. It should be reiterated that such comparison between Pt and MoS_2 is unprecedented and provides fresh insight to the development of MoS_2 to substitute Pt as HER electrocatalyst.

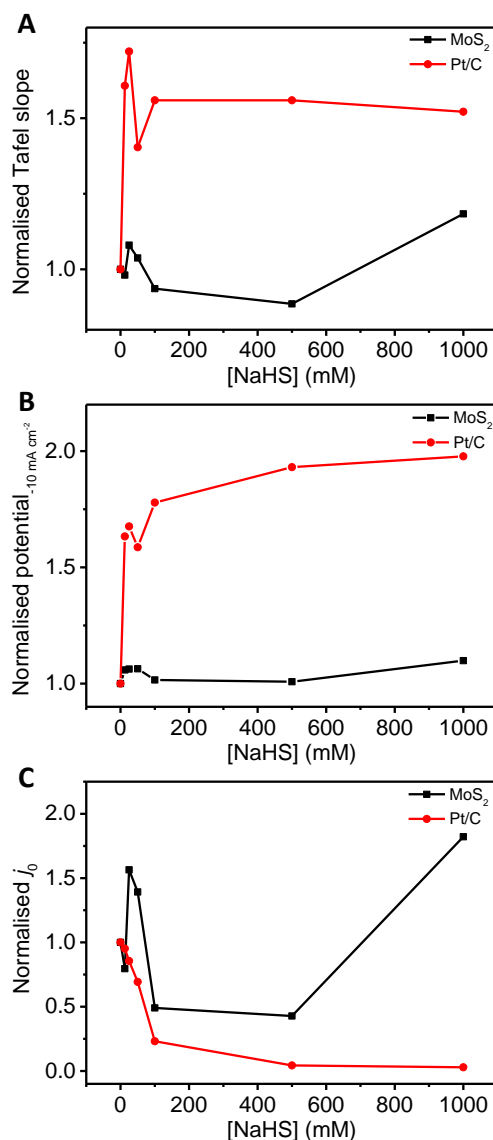


Figure 2. Plot of normalised Tafel slope (A), normalised potential at -10 mA cm^{-2} (B) and normalised exchange current density (j_0) (C) against increasing concentrations of NaHS for Pt/C and MoS_2 . The values of these HER parameters obtained for the poisoned electrocatalysts were normalised to those of the unpoisoned electrocatalysts which were assigned the value of 1.

The exchange current density is sensitive to factors such as bulk property of the electrocatalytic material, constituents of the electrolyte, and surface state of the modified electrode.¹⁹ By keeping the first two constant and varying the third factor *via* poisoning with NaHS, the exchange current density of Pt/C was observed to plateau towards the zero value (Fig. 2C). It is apparent that the poisoning decreases with greater concentration of NaHS, whereby the surface of the modified electrode becomes increasingly saturated with the sulfur poison and the effect weakens. This observation corroborates with previously reported poisoning effects, whereby the deactivating effect of sulfur atom diminished with increasing concentration of adsorbed sulfur.²¹

Despite its higher tolerance to sulfur poisoning, MoS₂ does not display total invulnerability, as observed from the variable values obtained for poisoned MoS₂ (Fig. 2). This contradicted expectations where sulfur was predicted to have negligible effects on MoS₂, stemming from it being integral to the structure of MoS₂. It is likely that the addition of adsorbed sulfur, present in the form of SO₄²⁻, sterically hindered the sulfur active sites on the Mo edges, leading to lower HER electrocatalytic activity.²²

Both Tafel slope and potential at -10 mA cm^{-2} are indicators of the kinetics of HER performances occurring on the catalytic surface.¹⁸ As such, it is anticipated that they are influenced to similar extents by the impacts of sulfur poisoning on the electrocatalyst, and correlations can be made between the amount of poisoned sites and these HER parameters. Thus for this purpose, Fig. 3 illustrates comparisons between the overlaid normalised parameters and the at.%Pt–S bond for various concentrations of the poisoning agent. From 0 mM to 25 mM of NaHS, an increase in the formation of direct platinum-sulfur bonds was accompanied by increases in the Tafel slope and potential values which indicate slower HER kinetics of Pt/C. At 50 mM, a dip in at.%Pt–S bond was again complemented with falls in the normalised values; thereafter, relatively stable trends were observed with increased poisoning.

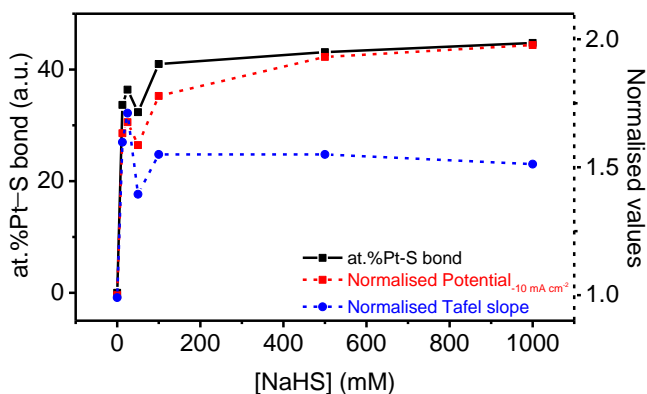


Figure 3. Plot of normalised potential at -10 mA cm^{-2} (red, dashed) and normalised Tafel slope (blue, dashed) against increasing concentrations of NaHS for Pt/C, compared against at.% Pt–S bond (black, solid) obtained from S2p core-level XPS spectra of Pt/C.

As aforementioned, the kinetics of HER are effectively governed by the HER active sites on an electrocatalyst and in the case for Pt/C, it is the H_{OPD} sites which are active towards HER. Hence, the results obtained through sulfur poisoning of the Pt/C surface gave strong evidence that the Pt–S bonds are namely those between sulfur and the H_{OPD} sites on Pt. Xiao *et al.* ascribed the poisoning of supported noble catalysts to the amount of SO₄²⁻, however no HER measurements were performed to support their claim.⁶ Here, SO₄²⁻ appears to be physically adsorbed onto the Pt surface with little influence on the electrocatalytic activity.

As highlighted before, poisoning at H_{UPD} and H_{OPD} affect the exchange current density and Tafel slope respectively.⁵ The observed slight deviations from the at.%Pt–S trend can then be attributed to the bonding between sulfur and H_{UPD} sites, which is likely to be present but in smaller percentages. From here, it can be concluded that the poisoning effect of sulfur on H_{OPD} is weaker than that on H_{UPD}, whereby a smaller extent of adsorption of sulfur to H_{UPD} sites led to a larger decrease in exchange current density. This is in line with the results obtained previously.⁵

Conclusion

In summary, we have demonstrated that both Pt/C and MoS₂ are vulnerable to sulfur poisoning, though the latter showed lower susceptibility. Additionally, strong correlations have been established between at.%Pt–S and the normalised values of Tafel slope and potential at -10 mA cm^{-2} , illustrating that the HER active sites were deactivated upon formation of direct Pt–S bonds. The results obtained contribute considerably to the development of MoS₂ as replacement for Pt and offer a deeper understanding towards sulfur poisoning which afflicts the performance of Pt. These findings have important implications for development of Pt- and MoS₂-based catalysts for hydrogen evolution.

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Notes and references

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Electronic Supplementary Information (ESI) available: survey scan XPS spectra, HER LSV curves and surface atomic compositions of poisoned and unpoisoned Pt/C and MoS₂ nanoparticles. See DOI: 10.1039/b000000x/

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