MoS₂-based materials as alternative cathode catalyst for PEM electrolysis

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Abstract

Pt and Ir are the popular catalysts for electrochemical water splitting, but their low abundance on Earth's crust and high price render them unsustainable for future use. In the quest for alternative catalyst materials, a popular hydro-treating catalyst, molybdenum disulphide (MoS₂), has been found to be promising for hydrogen evolution reaction (HER). Two types of MoS₂-carbon composites, (i) physical mixture of MoS₂ and carbon black (Vulcan[®]) and (ii) MoS₂ supported on reduced graphene oxide (RGO), were examined. Among the MoS₂-based materials tested, 47 wt% MoS₂/Vulcan[®] gave the best performance in terms of current density at an encouraging level for practical application. The poor performance of bare MoS₂ was attributed to its poor electrical conductivity. No indication of performance deterioration was observed for 18 h of continuous operation at 2.0 V cell voltage with 47 wt% MoS₂/Vulcan[®]. MoS₂/RGO hybrids showed HER activity, which was considerably higher than that of bare MoS₂.

1. Introduction

With increasing levels of global energy demand as well as climate changes suggested to be induced by CO₂ emission largely originating from burning fossil fuels, there is an imminent necessity to find chemical energy carrier alternatives to fossil fuels with a smaller carbon footprint. Hydrogen is one of the most promising candidates because it is an energetically rich molecule and only water is produced upon burning. Hydrogen can serve as raw material to synthesize more conveniently transportable liquid fuel such as methanol [1]. However, hydrogen does not naturally occur in nature and its production is one of the great challenges towards the so-called, hydrogen economy [2].

Hydrogen is widely produced by steam reforming of natural gas, but this technology is destined to be obsolete in a long run due to the depletion of fossil fuels and associated emission of CO₂. Therefore, environmentally and economically sustainable H₂ production technologies have been explored over the past decades. Among them, electrochemical water splitting (**Eq.1**) stands out as a cleaner and more advantageous approach in performance, reliability, and scalability

compared to other available technologies [3-5]. In the light of increasing installation of power plants sourced by renewable energy (e.g. sunlight and wind energy) as well as considering typical final energy form from such sources to be electric energy, generation of hydrogen by electric power is of primary importance for more sustainable development [6]. In proton exchange membrane (PEM) electrolyzers, high-purity hydrogen can be generated, promoted by heterogeneous metal catalysts with an energy conversion efficiency reaching around 57-69 % [7], and the efficiency keeps improving year by year. Furthermore, PEM electrolyser technology can overcome the drawbacks observed in alkaline electrolyzers, such as low partial load range, limited current density and low operating pressure [7]. Noble metals such as platinum (Pt black) and iridium (IrO₂ or Ir black) are widely chosen because of their high performance, but their low abundance on Earth's crust [8] as well as their high price make them unsustainable for future use and unfavoured on a large scale [7]. Moreover, Pt can be poisoned by chemical species adsorbed on its surface affecting the cathodic potential, resulting in decreased performance of hydrogen evolution reaction (HER) [9].

In the quest for non-precious metal alternatives, molybdenum disulphide (MoS₂) has been found to be a promising catalyst for HER [10-12]. MoS₂ is remarkably more economical than Pt and more importantly Mo is about 10⁴ times more abundant than Pt [8]. MoS₂-based catalysts have been used as hydrogenation catalysts in industrial processes like hydrodesulphurisation (HDS) of crude oil [13-15]. Thus, Mo-based materials are interesting alternatives, becoming a trending material for researchers during the last few years [12].

MoS₂ is classified as a metal dichalcogenide and it behaves as a semiconductor similar to silicon with good chemical stability and laminar structure, showing great benefits in the performance when used in electrochemical systems [9]. Electrocatalytic activity of MoS₂ catalysts correlates linearly with the number of edges in its substructure [10]. Amorphous MoS₂ is consequentially not as catalytically active as its nanoparticle-sized or hybrid-supported counterparts [16]. Recently, MoS₂ has been shown to exhibit competent performance in microbial electrolysis cells, outperforming stainless steel which is the leading low cost HER catalyst [9, 17]. Also, MoS₂ chemically bound to graphene oxide (GO) or reduced GO (RGO) was reported as a novel and advanced catalyst [16], exhibiting a high electrocatalytic activity in HER.

The aim of this work is to evaluate the performance of MoS₂-based materials as cathode catalyst in PEM electrolyzers. We have selected three different forms of MoS₂-based materials for this purpose: (1) bare pristine MoS₂, (2) MoS₂ physically mixed with an electrically conducting carbon material (Vulcan® XC72) [9] and (3) MoS₂ nanoparticles chemically bound to reduced graphene oxide (MoS₂/RGO). The performance of these materials was evaluated by means of polarization

curves and compared with that of Pt black, serving as a highly performing cathode reference catalyst in HER.

2. Experimental

2.1 Catalyst preparation

2.1.1 MoS₂ mixed with carbon material

Molybdenum(IV) sulphide (>99 %, powder, <2 µm, Sigma Aldrich) was physically mixed [9] with Vulcan®-XC72 (carbon black, Fuel Cell Store; for later occurrence it is denoted as “Vulcan”) during the preparation of the cathode catalyst inks. No further preparation was required prior to deposition over the polymer electrolyte membrane (see Section 2.2 for ink preparation). Four different weight percentages of MoS₂ in the mixture of MoS₂ with Vulcan, 9, 33, 47, and 70 wt% were examined.

2.1.2 MoS₂ nanoparticles deposited on reduced graphene oxide (MoS₂/RGO)

Graphene oxide (GO) was synthesized using the improved Hummers method [18] using graphite flakes (natural, 325 mesh, >99.8 % metals basis, Alfa Aesar) as the starting material. The hybrid MoS₂/RGO material was synthesized according to the method described by Li et al. [16]. In short, 10 mg of the obtained GO were suspended in *N,N*-dimethylformamide (DMF) by sonication for 30 min. 22 mg of ammonium tetrathiomolybdate ((NH₄)₂MoS₄, >99.97% trace metals basis, Sigma-Aldrich) was added and the solution was sonicated for 30 min. Then, 0.1 mL of hydrazine (N₂H₄ monohydrate, >99%, Alfa Aesar) was added to the solution, which was further sonicated for 30 min. The resultant solution was transferred to a 40 mL autoclave, heated at 200 °C for 10 h. During this solvothermal reaction, (NH₄)₂MoS₄ precursor was reduced to MoS₂ on GO surface and, at same time, the GO was transformed to RGO by hydrazine reduction, finally yielding MoS₂ dispersed on RGO (MoS₂/RGO).

The synthesised MoS₂/RGO materials were characterised by transmission electron microscopy (TEM) using a JEOL 1011 operated at 80 kV. The sample was dispersed in ethanol, and a drop of the suspension was poured onto carbon coated-copper grids. Furthermore, the starting and final materials were characterised by Raman spectroscopy (Renishaw InVia Raman) using a 633 nm excitation laser to confirm whether the desired materials (GO, RGO, and MoS₂) were properly synthesized. Moreover, energy dispersive X-ray (EDX) analysis was employed to quantify molybdenum to carbon and oxygen (Mo:C:O) ratio. EDX analysis was performed on an FEI Quanta 600 ESEM equipped with an Oxford Instruments EDS Detector.

2.2 Membrane electrode assembly (MEA) preparation

Nafion® 117 membrane (175 μm thick, Ion-Power) was used as the polymer electrolyte membrane (hereafter Nafion® is denoted as “Nafion”). The Nafion membrane was treated [19] before use by washing in 5 % H_2O_2 for 1 h at 80 °C to eliminate residual organic impurities [20], then in 0.5 M sulphuric acid for 1 h at 80 °C to incorporate water molecules and activate the membrane by hydration [21] and finally with boiling water for 1 h. The pre-treated membranes were stored in water at ambient temperature prior to deposition of the catalyst materials.

Iridium (IV) oxide (IrO_2 , >99 %, powder, Alfa Aesar) was used as the anode catalyst with a fixed loading of 2 mg/cm^2 . Pt black (≤ 20 μm powder, surface area ≥ 25 m^2/g , ≥ 99.97 % trace metal basis, Sigma Aldrich) was used as reference cathode catalyst with 0.6 mg/cm^2 loading.

Catalyst materials for anode or cathode were coated over the pre-treated Nafion membrane (2x2 cm^2 active area, 3.5x3.5 cm^2 total area) by spray deposition using a common airbrush ($\varnothing_{\text{nozzle}}$: 0.25mm, Ventus Titan). The inks were composed of a mixture of catalyst powder, 2 g of isopropanol (2-propanol, >99.7%, Panreac), and Nafion solution (Nafion D-521 dispersion, 5 % w/w in water and 1-propanol, ≥ 0.92 meq/g exchange capacity, Alfa Aesar) amounting to 15.4 wt% dry Nafion per total dry solid. The ink solutions were sonicated for 1 h using an ultrasonic bath (120W/60Hz, Bandelin SONOREX) prior to deposition. Deposition temperature was set to 85 °C so that the solvent evaporated upon deposition. This temperature control avoids membrane swelling and allows the formation of a homogeneous catalyst layer on both sides of the Nafion membrane.

2.3 PEM electrolyser setup

Electrolysis tests were performed using a home-made PEM-electrolyser cell (Figure 1), consisting of a membrane electrode assembly (MEA; Nafion membrane coated with electrode catalysts), porous Ti diffusion layers (2x2 cm^2 , 1 mm thick, $\varnothing_{\text{pores}}$: 50 μm , Sintered-Filter), and current collectors (2 mm thick) made of Ti (Grade 1) to avoid corrosion problems with a machined serpentine flow field of 0.5 cm^3 of total channel volume. These components were sandwiched together by the cell housing made of aluminium and the cell was properly sealed using PTFE gaskets. Figure 1 shows an illustrative view of the electrolyser setup: (1) electrochemical reaction cell, (2) peristaltic pump system and water reservoir, (3) temperature controller and (4) computer controlled potentiostat. Briefly, peristaltic pump (Ismatec Reglo Digital) was employed to supply water in the form of flow to the system. A temperature controller was used to set the desired working temperature (80 °C) inside the electrochemical reactor. Voltage (EMF, V) current (i, A) and current density (j, A/cm^2) values, obtained from polarization curves studies, were measured and recorded using a home-made power supply/potentiostat system (CPX400DP, 420 DC Power

Supply, 60 V max, 20 A max) controlled by LabVIEW. Evolved gases (O_2 from anode and H_2 from cathode) were released to the atmosphere through the outlets as shown in Figure 1.

Figure 1. PEM Electrolyser system: (1) electrochemical reaction cell, (2) peristaltic pump and water reservoir, (3) temperature controller and (4) computer controlled potentiostat.

Type-I ultrapure water (Milli-Q) was used and pumped into the anode compartment at a rate of 0.5 mL/min. Potential sweep experiments were performed starting at 1.20 V with increments of 0.05 V every 30 min up to 2.00 V. The average of the current values between 1 min after and 1 min before potential jump was taken.

3. Results and discussion

3.1 Hybrid MoS_2 /RGO characterization

Figure 2a shows the TEM images of the as-synthesized MoS_2 /RGO. From Figure 2a (top) we can recognize the characteristic folding of graphene oxide sheets and from Figure 2a (bottom) the MoS_2 (darker spots) deposited onto the graphene oxide sheet can be clearly observed. The Raman spectrum of MoS_2 /RGO (Figure 2b) confirms the co-presence of GO (two bands around 1500 cm^{-1}) and MoS_2 (bands in $100\text{-}1000\text{ cm}^{-1}$ with the prominent bands at 819 and 991 cm^{-1}), in agreement with the spectra of the respective reference materials (MoS_2 and GO, Figure 2b). Finally, Mo:C:O atomic ratio of the MoS_2 /RGO sample was determined by EDX analysis and found to be 1:13.5:2.7, corresponding to approximately 43.8 wt% MoS_2 in MoS_2 /RGO. The

characterization results were similar to those reported in literature [16]; therefore we concluded that the hybrid MoS₂/RGO material was successfully synthesized.

Figure 2. MoS₂/RGO characterization: (a) TEM images of as-synthesized MoS₂/RGO, (b) Raman spectra of MoS₂ (characteristic bands are highlighted in blue shadow), GO (characteristic bands are highlighted in red shadow), and chemically bound MoS₂ on reduced GO (MoS₂/RGO).

3.2 Performance of MoS₂/Carbon

First, the effect of mixing MoS₂ with electrically conducting carbon material (Vulcan) on PEM electrolysis performance was investigated by means of polarization curves. The physically-mixed materials with various amounts of MoS₂ namely 9, 33, 47, 70 and 100 wt%, with respect to the total weight of MoS₂/Vulcan were evaluated as the cathode catalyst. In the MoS₂/Vulcan composite, the amounts of Vulcan (5 mg·cm⁻²) and the Nafion binder were kept constant; therefore the amount of MoS₂ was changed to vary the loading of MoS₂.

Although the performance of MoS₂/Vulcan at 9 wt% MoS₂ is rather poor (Figure 3, curve a), increasing the amount of MoS₂ in the cathode catalyst remarkably improved the HER activity and electrolysis performance (Figure 3, curves b (33 wt%) and c (47 wt%)). However, further increase of MoS₂ in the catalyst (curve d (70 wt%)) resulted negatively, decreasing the HER activity. Pure MoS₂ without Vulcan (curve e) exhibited HER activity, but the performance was poor and lower than that of the sample where the least amount of MoS₂ was mixed with Vulcan (9 wt% MoS₂/Vulcan, curve a).

The results indicate the critical importance of the ratio between MoS₂ and carbon material (here Vulcan). The major role of the carbon material is the enhancement of catalyst conductivity, highly beneficial to efficiently utilize electrocatalytic sites distributed over the PEM. This was confirmed

by a simple 4-point measurement of the resistance through the cathode catalyst coated on the Nafion membrane using an Agilent 34401A digital multimeter. These measurements showed a much higher relative conductivity of the MoS₂/Vulcan membranes, which were between 14 and 20 S·m⁻¹, than that of the MoS₂ membrane, which showed conductivity values as low as 0.002 S·m⁻¹. The amount of MoS₂ is also critical because this is the active material of the reaction; therefore, there exists a well-balanced, optimum amount of MoS₂ in the MoS₂/Vulcan mixture. Following the trend observed in Figure 3, it can be concluded that the optimum lies around 47 wt% MoS₂ in MoS₂/Vulcan. This is exactly the value reported to be optimum for HER in microbial electrolysis cells and this study confirms that the specific amount of MoS₂ in MoS₂/Vulcan is also beneficial when used for PEM electrolysis.

Figure 3. Polarization curves (potential sweep from 1.2 to 2.0 V, $\Delta V = 0.05$ V) for PEM electrolysis using MoS₂/Vulcan as the cathode catalyst with varying amount of MoS₂ with respect to total amount of MoS₂/Vulcan: (a) 9 wt%, (b) 33 wt%, (c) 47 wt%, (d) 70 wt%, (e) 100 wt% (i.e. bare MoS₂ without Vulcan). As a reference, the performance of Pt black (f) is also shown. Anode: IrO₂ 2 mg/cm², cathode: Vulcan (5 mg/cm²) mixed with proper amount of MoS₂ or bare Pt black 0.6 mg/cm².

3.3 Performance of MoS₂/RGO

Furthermore, PEM electrolysis performance of the MoS₂/RGO nano-composite (Figure 2) as cathode catalyst was investigated to examine the effect of high dispersion of MoS₂ nanoparticles over the carbon support (RGO) and possible synergetic effects.

Figure 4 shows the PEM electrolysis performance of MoS₂/RGO with two different deposition loadings (1 and 3 mg/cm², curves a and b, respectively). It is compared with those of the optimum 47 wt% MoS₂/Vulcan (curve c), pure MoS₂ (curve d) and the reference Pt black cathode catalysts (curve e). Evidently, reasonable HER activities of MoS₂/RGO were observed. Increasing the amount of deposition loading (Figure 4, curves a and b) showed that the electrolysis performance was improved by increasing the amount, although the increase in current density was not fully proportional to the amount of the catalyst at higher cell voltage. Also, poorer performance (less prominent increase in current density) at higher cell voltage was noticed compared to the MoS₂/Vulcan composite catalysts prepared by physical mixing. This feature may be originated from the lower conductivity of RGO (according to a four point resistance measurement, the values were between 2 and 5 S·m⁻¹), being much lower than that of MoS₂/Vulcan composites. These can be attributed to the fact that reduced graphene oxide has lower electrical conductivity than that of graphene because of the lost uniformity in its structure after reduction, and also tends to agglomerate [22]. In fact, graphene oxide is known to be an electrical insulator [23], therefore the presence of remaining oxide groups could diminish conductivity.

This conductivity problem may be mitigated by the same approach as shown in Figure 3, i.e. physical mixing with carbon materials, or fine-tuning the reduction procedure of GO to increase the degree of reduction and thus the conductivity. This, together with the optimum loading of MoS₂ on RGO, are parameters promising to be optimized.

Figure 4. Polarization curves (potential sweep from 1.2 to 2.0 V, $\Delta V = 0.05$ V) for PEM electrolysis using two different catalyst loadings of MoS₂/RGO over the membrane (a) 1 mg/cm² and (b) 3 mg/cm². For the sake of better comparison, the performances of (c) 47 wt% and (d) 100 wt% MoS₂/Vulcan as well as (e) Pt black are shown. The loadings of these and the anode catalyst (IrO₂) are presented in the caption of Figure 3.

3.4 Effect of hot-press

Usually when preparing MEAs and before their usage, it is recommended to apply hot-press to properly embed the catalyst layer into the membrane [24], promoting good contact within the three-phase region [25] and alleviating ohmic losses [26], thus to achieve better PEM electrolysis performance and to avoid catalyst delamination [27]. We investigated the effects of hot-press on PEM electrolysis performance using 9 wt%, 33 wt% and 47 wt% MoS₂/Vulcan. Hot-press was performed at a constant pressure (140 bar) for 5 min at 85 °C. Figure 5 presents polarization curves obtained without hot-press (as obtained after spray deposition) and with hot-press. Surprisingly, the MEAs without hot-press gave better electrolysis performance at all cell voltages examined. At the cell voltage of ca. 1.6 V and above, the difference started to become prominent with increasing voltage and amount of MoS₂, even ca. 3 times higher for the MEA without hot-press at 47 wt% MoS₂ content. This suggests that hot-press strategy for MoS₂/Vulcan materials can be detrimental. Although the reason for the decreased performance of hot-pressed membranes is not known and further studies are needed to understand this phenomenon, it can be attributed to a reduction in the size of the pores of the Nafion membrane which diminishes proton conductivity and therefore performance [28]. This effect would become more apparent at higher current densities as observed in the polarization curves shown in Figure 5. It has been shown that the effect of hot-press varies depending on the thickness and tensile strength (among others) of the Nafion membrane [29, 30]. Thinner membranes with lower tensile strength such as Nafion 212 have shown more improvements by hot press than thicker membranes like Nafion 115 [29, 30]. Our data indicates that for Nafion 117 membranes water transport issues are surpassing the improved contact due to hot pressing.

Figure 5. Effects of hot-press on polarization curves in PEM electrolysis using the MEA with 9 wt%, 33 wt% and 47 wt% MoS₂/Vulcan. Hot press condition was 140 bar, 85 °C for 5 min.

3.5 Stability tests

The short-term and long-term stability of electrolyzers is of primary importance in practice, especially at a harsh condition such as at high cell voltage and consequently at higher current density. This point has been investigated using the best MoS₂-based cathode catalyst found in this work, 47 wt% MoS₂/Vulcan, at the highest cell voltage investigated in this study (2.0 V).

First, we investigated the reproducibility of polarization curves upon forward (1.2 to 2.0 V) and reverse (2.0 to 1.2 V) potential sweeps without an interval between the two experiments (Figure 6a). Almost identical current density values were observed at all the cell voltage points along the sweep, although a slight deviation was observed between 1.65 and 1.90 V. Actually, a performance improvement was detected upon reverse sweep due to improving stabilization period of the MEA (*vide infra*).

Secondly, we investigated the long-term stability of the MEA prepared without hot-press. Figure 6b shows the variation of current density profile over 18 h of continuous PEM electrolysis of 47 wt% MoS₂/Vulcan, which was performed immediately after the continuous voltage ramp from 1.2 to 2.0 V (potential sweep, Figure 3). A stable and relatively high current density (ca. 0.70 A/cm²) was reached after 15 h with no indication of performance deterioration over 18 h. The performance slightly increased overtime because of possible hydration effects as the proton and water transport occurred through the membrane [31]. Based on these results, we can conclude that MoS₂/Vulcan catalyst is a stable electrocatalyst for HER in PEM electrolysis.

Figure 6. Stability tests of 47 wt% MoS₂/Vulcan in PEM electrolysis. (a) polarization curves with forward and reverse potential sweeps and (b) long term stability test at a constant cell voltage of 2.0 V.

4. Conclusions

MoS₂ was found to be an efficient, inexpensive cathode catalyst in PEM electrolysis when its electrical conductivity is enhanced by simple physical mixing with highly conducting carbon materials (Vulcan XC-72) or by finely dispersing MoS₂ over RGO.

The ratio of MoS₂ to carbon highly influenced the performance of the physically mixed MoS₂/Vulcan composites. Best performance among all the materials evaluated in this study was observed with 47 wt% MoS₂/Vulcan, which also showed high long-term stability up to 18 h of continuous operation in a PEM electrolyser. This material's stability, facile preparation and

improved performance when compared to pristine MoS₂ are encouraging features for practical application.

MoS₂/RGO was successfully synthesized and characterized. This catalyst showed reasonable and promising activity in PEM electrolysis; however, further investigation is required to evaluate the real value of the nano-composite in HER, e.g. by increasing the conductivity of the material by physical mixing with carbon material and by tuning the reduction procedure of GO together with the amount of MoS₂ deposited on RGO.

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