



Molybdenum sulphides on carbon supports as electrocatalysts for hydrogen evolution in acidic industrial wastewater



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HIGHLIGHTS

- MoS_x is an efficient and durable catalyst for H₂ evolution in acidic wastewater.
- MoS_x outperformed Pt as H₂-catalyst in long term in acidic wastewater.
- Improved activity over time was likely due to changes in MoS_x structure.

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ABSTRACT

Microbial electrolysis cells (MECs) are an attractive future alternative technology to generate renewable hydrogen and simultaneously treat wastewaters. The thermodynamics of hydrogen evolution in MECs can be greatly improved by operating the cathode at acidic pH in combination with a neutral pH microbial anode. This can easily be achieved with acidic industrial wastewaters that have to be neutralised before discharge. For the hydrogen evolution reaction (HER) in acidic wastewater, efficient and inexpensive catalysts are required that are compatible with the often complex chemical composition of wastewaters. In this study, molybdenum sulphides (MoS_x) on different carbon supports were successfully used for hydrogen evolution in different acidic media. At first, the cathodes were screened by linear sweep voltammetry in sulphuric acid (pH 0) or phosphate buffer (pH 2.2). After this, the overpotentials for H₂ production of the best cathodes and their long term performances (≥ 1 week) were determined in acidic industrial wastewater (pH 2.4) obtained from a plant mainly producing cellulose acetate. For the most promising MoS_x cathodes, the overpotentials for HER (at 3 mA cm⁻²) were only ~ 40 mV higher than for a platinum electrode. Most importantly, the catalytic efficiency of the MoS_x electrodes improved in the wastewater over time (7–17 days), while Pt electrodes were found to be slowly deactivated. Thus, MoS_x emerges as an affordable, efficient and especially durable electrocatalyst for HER in real acidic wastewaters and this could be an important contribution to take energy production from wastewaters in the form of hydrogen towards practical applications.

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1. Introduction

Hydrogen, produced in a renewable way, is considered as a potential future energy carrier. While the majority of today's hydrogen is still generated from fossil fuels by steam reforming, water electrolysis using renewable electricity (e.g. solar or wind

power) is regarded as one of the key technologies for the sustainable production of hydrogen [1]. The energy required for hydrogen production through water electrolysis can be significantly lowered by choosing an alternative anode reaction that is thermodynamically more favorable than the oxygen evolution reaction. One such synergistic reaction is the bioelectrochemical oxidation of organic carbon (e.g. acetate) present in wastewaters by means of a microbial anode. Such systems with bacterial catalysts at the anode are called microbial electrolysis cells (MECs) and are currently being developed as an efficient technology to simultaneously treat wastewaters and produce hydrogen. In MECs, the biological oxida-

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tion of organic components at the anode (usually at neutral pH) produces the reducing equivalents used for H_2 evolution at the cathode, where the pH can range from 2 to 12.5 [2].

At neutral pH, the theoretical voltage difference required to drive the cathodic H_2 evolution reaction (HER) in combination with a microbial anode for acetate oxidation is only 0.11 V. This value is more than ten times lower compared to the theoretical minimum of 1.23 V required for the conventional electrolysis of water, where H_2 production at the cathode is coupled to anodic oxygen evolution. Furthermore, if an MEC is operated with a pH gradient between anode and cathode, the theoretically required voltage can be reduced by 59 mV for each pH unit that the acidic cathode deviates from neutral pH required at the microbial anode. While in theory a difference of two pH units between an acetate-oxidising anode and a hydrogen evolution cathode would be sufficient to drive the electrode reactions with zero voltage, irreversible losses occur and larger voltages are required partly due to overpotentials (η) at the cathode side.

Hydrogen production in an MEC with a pH difference between anode (pH 7) and cathode (pH 2) has previously been reported by Ruiz et al. [2]. However, their study was conducted with “laboratory electrolytes” that are not relevant to practical applications, where wastewater serves as electrolyte both at the anode and cathode chamber. The type and characteristics of the wastewater dictates the operational conditions at the cathode, and thus the overpotential of HER. The same applies to the emerging microbial electrosynthesis processes [3] and future “Power-to-X”-technologies, in which electrical energy is converted into valuable products such as e.g. CH_4 with the help of hydrogenotrophic microorganisms [4]. These require hydrogen evolution cathodes that are operational in a complex microbial environment. It is therefore essential to develop efficient, durable, and affordable catalysts that decrease the overpotential of the HER under conditions of practical relevance. The high cost of efficient cathode materials for HER is regarded as one of the main limiting factors in the scaling-up of MECs [5].

In conventional water electrolysis cells, noble metals such as platinum are often used as HER catalysts. However, the excellent catalytic properties of platinum (η 's close to 0 mV at some conditions [6,7]) come with a high cost of currently ~ 6800 US\$ $\cdot(\text{mol Pt})^{-1}$ (<http://www.lme.com>, accessed on 22.07.2016). In addition, the poisoning of Pt-based HER catalysts in MECs has been reported and might be caused by sulphide [8] or due to the adsorption of phosphate on the electrode surfaces [9]. In MECs, some alternative HER catalyst materials have been tested with real wastewaters as electrolytes, including stainless steel [10,11] and nickel [12,13]. However, stainless steel electrodes have high overpotentials and can also encounter poisoning [14] or corrosion [15]. Nickel catalysts have shown promising results for H_2 evolution at near neutral pH [16,17] but are not suitable for acidic pH values. There are no studies addressing HER in real wastewaters with acidic pH values.

Molybdenum sulphides (MoS_x) have recently gained attention due to their high catalytic activity for HER, their excellent chemical stability [18–20] and the very low cost of ~ 1.5 US\$ $\cdot(\text{mol Mo})^{-1}$ (<http://www.lme.com>, accessed on 22.07.2016). Molybdenum sulphides can be generally described as ionic compounds containing Mo^{4+} cations and sulphide (S^{2-}) as well as disulphide (S_2^{2-}) anions. A simplified general formula $Mo^{IV}(S^{2-})_a(S_2^{2-})_b$ can be formulated for these materials, for example, with $a = b = 1$ in the case of amorphous MoS_3 , i.e. $Mo^{IV}(S^{2-})(S_2^{2-})$ [21]. Additionally, the structural motif of Mo cations embedded in a sulphide-rich coordination sphere can also be found in the active site of the FeMoco-nitrogenase enzyme, where the FeMoco active site produces H_2 as a side-reaction while converting N_2 to NH_3 (for a review, see Laursen et al. [22]). For molybdenum sulphides, it has been shown

that hydrogen atoms bind easily to sulphur anions at the edges of MoS_x -layers, where the HER reaction is thought to take place [7]. In MECs, electrodes with MoS_2 catalyst have been reported to have H_2 production rates comparable to Pt electrodes at neutral pH in synthetic medium, thus making molybdenum sulphides promising catalysts for H_2 evolution [23].

However, MoS_x has two major limitations: (1) a low electric conductivity of the material and (2) a rather low number of active sites for HER catalysis [22–24]. To overcome these drawbacks, small MoS_x particles are often deposited on electrically conductive support materials by electrochemical deposition [25,26] or with the help of Nafion [27,28]. For MECs, MoS_x electrodes have been mainly prepared by mixing MoS_2 with Nafion and carbon black and the mixtures were then used to coat carbon cloth [14,29]. Nafion is, however, expensive, which might prevent its use in practical applications. Regarding the scaling-up of MECs, carbon based support materials such as carbon cloth are particularly attractive due to their low cost, sufficient electrical conductivity, and large specific surface area. Xia et al. [30] reported that the conductivity and current production capability of MoS_2 catalysts were affected by the concentration of MoS_2 on the electrode. In this way, the number of active sites and the material's conductivity could be improved, e.g., by increasing the number of electrodeposition cycles [31] or by using suitable support materials, such as carbon nanotubes (CNTs) [32]. Thus, the electrode preparation process appears to be a very important step as it affects the composition, particle morphology and distribution of the MoS_x deposited on the electrode surface. In addition, it influences the cost of the manufactured MoS_x electrodes. Thus, novel ways to prepare MoS_x electrodes are required. MoS_x electrodes have already been widely studied for possible applications in conventional water electrolysis [7,30,32]. However, the requirements for MEC cathodes to operate in real wastewaters are different due to generally lower conductivities of the electrolytes and pH values deviating from the extremes commonly used in alkaline or acidic electrolyzers. This difference in operation is compounded by the presence of various organic and sulphur-containing compounds that can compete for the electrons at the cathode or cause electrode poisoning.

The purpose of this study is to evaluate the use of MoS_x -based HER cathodes under application-relevant conditions in an acidic industrial wastewater. The major research question addressed is whether MoS_x -cathodes can sustain their high catalytic activity towards HER also in real acidic industrial wastewaters over extended periods of time. Furthermore, we investigated whether the H_2 production potentials under these conditions are affected by the electrode preparation method, since this will influence both cost and usability. Thereof different preparation methods for HER-cathodes composed of MoS_x as electrocatalyst and carbon materials as conducting supports were evaluated and their potential for HER was determined. Electrochemical hydrogen evolution by these MoS_x electrodes was first studied in sulphuric acid and phosphate buffer to screen for the most efficient cathodes and to compare their performances with earlier studies carried out under similar conditions. The best HER-cathodes from these screenings were then investigated in real acidic industrial wastewater obtained from a plant producing to a large part cellulose acetate. This cellulose derivative is produced worldwide on a large scale (especially for filter applications) by the reaction of acetic acid with cellulose, often in the presence of sulphuric acid acting as acetylation catalyst [33]. As a result, large amounts of acidic waste streams rich in acetic acid are available, which have to be neutralised at the industrial site before they can be discharged into a sewage system or wastewater treatment plant. Thus, a near neutral wastewater fraction, rich in acetic acid is available for the anodic oxidation in a MEC, while the acidic wastewater could be used directly as electrolyte at the cathode to provide more thermodynamically favor-

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