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Review Article

Towards the application of 2D metal dichalcogenides as hydrogen evolution electrocatalysts in proton exchange membrane electrolyzers

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Abstract

The electrolysis of water using renewable power inputs has tremendous potential for storing renewable energy in the form of hydrogen fuel. Proton exchange membrane electrolyzers are amongst the more promising classes of electrolyzer for renewables-driven hydrogen production, but these devices require expensive and scarce precious metal electrocatalysts (such as platinum) that add considerably to device costs and lifecycle carbon footprints. Replacing platinum in proton exchange membrane electrolyzers with cheaper and more abundant alternatives will thus make renewables-to-hydrogen devices more viable. Two-dimensional metal dichalcogenides have the required stability, electronic and catalytic properties to challenge platinum's position as the electrocatalyst of choice in proton exchange membrane electrolyzers. In this minireview, we give an overview of recent progress in the development of two dimensional metal dichalcogenides as hydrogen evolution electrocatalysts, with a particular focus on studies from the last two years.

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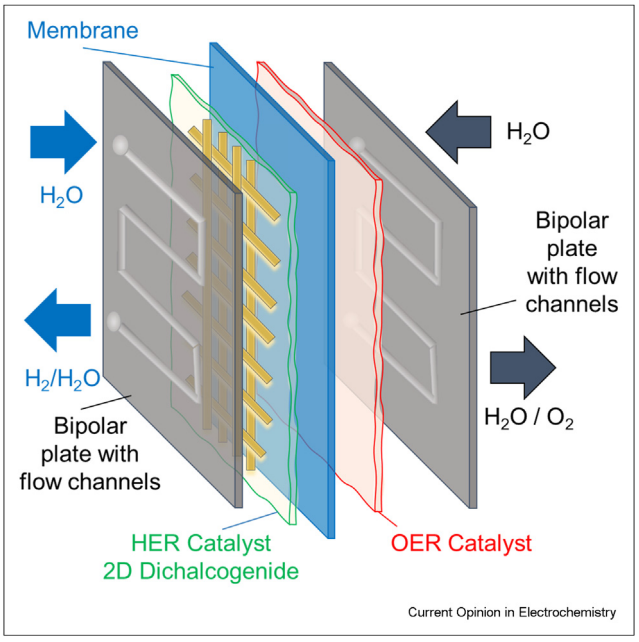
Water splitting, Metal dichalcogenide, Hydrogen evolution reaction, Electrolysis, 2D materials.

Introduction to metal dichalcogenides as hydrogen evolution electrocatalysts

Electrochemical devices will play a central role in facilitating a future powered by renewable energy sources, by allowing this energy to be stored to mitigate for the peaks and troughs in supply that characterize renewables [1]. Electrolyzers that split water into hydrogen and oxygen constitute one class of electrochemical technology that will be especially important in this regard, as hydrogen is an excellent fuel [2]. Moreover, if the required electricity comes from a renewable energy source, H_2 can be generated at minimal cost to the environment and practically carbon-neutrally [3,4]. Of the various electrolyzer technologies that currently exist, proton exchange membrane electrolyzers (see Figure 1) are generally viewed as the most promising for integration with renewable power sources due to their fast start-up and shut-down times, which should give these devices a certain tolerance to intermittent renewable power inputs [5,6]. However, the proton exchange membrane in such electrolyzers imposes a very acidic environment on the cell components, in turn requiring electrocatalysts that are stable at low pH. Typically, precious metals are the catalysts of choice: IrO_2 and RuO_2 at the anode and dispersed Pt at the cathode [7]. However, although highly catalytically active, such precious metal catalysts are rare, expensive and add considerably to the lifecycle carbon assessment of the electrolyzer; for example, producing 1 g of Pt produces ~33 kg of CO_2 equivalents [8].

For these reasons, minimizing the amount of Pt used in electrolyzers, or indeed replacing Pt entirely, is a major area of study at the current time [9,10]. In this regard, two-dimensional (2D) transition metal chalcogenides are exciting candidates for the role of hydrogen evolution electrocatalysts in proton exchange membrane electrolyzers for a number of reasons. Firstly, recent evidence suggests that the stability of these materials as hydrogen evolution electrocatalysts in acidic solution is similar to that of Pt, thus allowing them to compete with Pt in terms of durability [11]. Secondly, they can be deposited as continuous and robust thin films directly onto gas diffusion layers (or other suitable supports) in proton exchange membrane electrolyzers, potentially negating the need to deposit catalysts onto the membrane itself [12–14]. Finally, 2D dichalcogenides are fascinating from a fundamental point of view because, unlike nanoparticles (where the catalytic processes may happen at a range of surfaces, faces and edges), the orientation of

Figure 1



A schematic of a single cell proton exchange membrane electrolyzer. Dichalcogenide electrocatalysts can be deposited directly onto the porous gas diffusion layer (yellow grid in the figure) to maximize catalytic surface area. A typical device operates with a rapid flow of water and at temperatures ≈60–70 °C, requiring extremely robust materials. OER = oxygen evolution reaction; HER = hydrogen evolution reaction.

a 2D transition metal chalcogenide (film) is always precisely defined with respect to the substrate (Figure 2). Since the (001) lattice plane (commonly referred to as the basal plane) is the only interface participating in the hydrogen evolution reaction, there is no possibility for complications or ambiguity regarding selection of the optimal surface for hydrogen evolution [15].

In this minireview, we aim to give an overview of metallically-conductive 2D dichalcogenides reported since 2019 which show catalytic activity for the hydrogen evolution reaction from their basal plane sites, on account of these materials being the most promising for applications in proton exchange membrane electrolyzers. In doing so, we have intentionally selected reports which specified their materials' sizes and morphologies in order to make sure that any catalytic activity from edge sites can be neglected (recent work has indicated that the degradation of 2D dichalcogenides proceeds rapidly on the edge sites [16]). We have also chosen to avoid discussion of nanostructured materials due to the complexity of this subject (which would require significantly more space than available in this minireview to cover in adequate detail). Readers interested in nanostructured metal dichalcogenides for electrochemical energy conversion are directed to a number of excellent review articles on this subject [17–19].

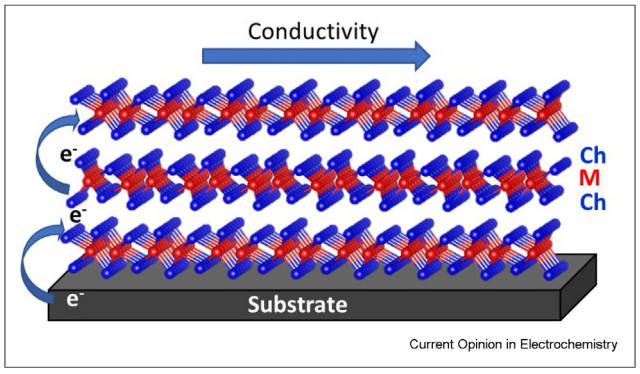
In choosing the examples we discuss below, we operate under the notion that continuous and defect-free films of dichalcogenides with intrinsically high electrical conductivity have the best prospects for withstanding interaction with the required water flow under the extremely reducing conditions prevailing at the cathode of a proton exchange membrane electrolyzer, and therefore, the best prospects for competing with Pt in a practical device. Table 1 summarizes data from research articles published since 2019 in which predominantly defect-free samples (with mainly the basal plane exposed) were studied for the electrochemical hydrogen evolution reaction, and which we will discuss further below. For comparison, Table 1 also includes entries for Pt and Ni_2P as alternative hydrogen evolution electrocatalysts.

The hydrogen evolution reaction on the basal plane of group 5 dichalcogenides

The Group 5 dichalcogenides (VTe_2, TaS_2, $TaSe_2$, NbS_2) might seem to be obvious choices as electrocatalysts for the hydrogen evolution reaction as they tend to show metallic conductivity in their stable crystal forms. Highly crystalline hexagonal TaS_2 flakes produced by exfoliation of single crystals (shown to be phase-pure by X-ray and electron diffraction studies, and with a nearly perfect Ta: S ratio of 1 : 2 according to XPS (X-ray photoelectron spectroscopy)) exhibits a relatively high overpotential requirement to achieve a current density of 10 mA cm^{-2} for hydrogen evolution of 575 mV [20]. As the flakes had sufficiently large lateral sizes (Table 1, entry 1) this suggested that the activity stemmed from the basal planes. However, the authors noted the presence of up to 40% of a surface oxide (Ta_2O_5) based on the presence of Ta^{5+} peaks in the XPS spectrum. This observation poses the question as to whether the formation of Ta nanoparticles is possible due to reduction of Ta_2O_5. The challenge of keeping crystals free from oxides was further confirmed by recent electrochemical studies on TaS_2 and $TaSe_2$ crystals which showed a significant presence of Ta_2O_5 (Table 1, entries 2 and 3) [21]. The identical overpotentials (390 mV) required to deliver current densities of 10 mA cm^{-2} for hydrogen evolution for TaS_2 and $TaSe_2$ indicate that oxides may play a determining role in electrochemical performance, further suggesting that TaS_2 is unlikely to be an ideal material for the hydrogen evolution reaction.

NbS_2 is an interesting target since the flakes can be grown directly on carbon cloth by chemical vapor deposition (CVD) from $NbCl_5$ and sulfur sources. The resulting NbS_2 flakes with lateral sizes of 1 × 1 μm^2 oriented in-plane with the carbon cloth fibres delivered hydrogen evolution at 10 mA cm^{-2} with η = 453 mV [14] (Table 1, entry 4). These results are however in stark contrast with a recent report on NbS_2 showing a respectable overpotential demand of only ≈290 mV in

Figure 2



A typical three-layer structural motif in a metallic 2D-dichalcogenide consisting of edge-sharing distorted {MCh_6} octahedra with the layers parallel to the substrate. The top (001) layer is often referred to as the basal plane. The conductivity is greater in-plane than perpendicular to the plane. A reduced number of planes may lead to lower Ohmic losses in an electrochemical cell. Usual performance criteria are based on electronic conductivity, structural integrity, and abundance of active sites. M = metal; Ch = chalcogenide.

order to achieve 10 mA cm^{-2} [22]. In addition, Yang et al. reported a significant decrease in the required overpotential for non-stoichiometric $Nb_{1.35}S_2$ from *ca.* 290 mV to 123 mV and a Tafel slope of just 43 mV/decade. Current densities of more than 5000 mA cm^{-2} were observed as well, contradicting earlier reports that showed that non-stoichiometric $NbS_{1.6}$ ($Nb_{1.25}S_2$) could not reach current densities even as low as 10 mA cm^{-2} [31]. A possible explanation could be differences in material morphology. It appears that the utilization of atomically thin (< 20 nm) flakes may play an important role due to improved electron transfer from the substrate (Figure 2) [22]; reducing the layer thickness may be a way to challenge the poor catalytic ability of Group 5 dichalcogenides [31].

The role of layer thickness seems to be further confirmed by recent work on 1T′-VTe_2 flakes with ≈30 nm thickness, which required η = 220 mV at 10 mA cm^{-2} (with a Tafel slope of 40 mV/decade) [24]. In comparison, a significantly higher overpotential requirement to reach 10 mA cm^{-2} (441 mV) and a higher Tafel slope (70 mV/decade) were previously reported on bulk VTe_2 crystals [23] (Table 1, entries 6 and 7).

The hydrogen evolution reaction on the basal plane of group 6 dichalcogenides

Arguably, no review is complete without mentioning metallic 1T-MoS_2 and 1T-WS_2 phases, which to-date are probably the most explored 2D dichalcogenides for the hydrogen evolution reaction following on from their first reports almost a decade ago [32–34]. Despite complex synthesis procedures which involve butyllithium-aided exfoliation, they appear as very competent hydrogen evolution electrocatalysts, with η for 1T-MoS_2 as low as 250 mV at 10 mA cm^{-2} reported (Table 1, entry 8) [22]. However, there is an important underlying issue with both of these dichalcogenides: they are metastable and tend to revert rapidly into semiconducting and

Table 1

An overview of 2D transition metal dichalcogenides tested in acidic conditions for the hydrogen evolution reaction reported since 2019. η = overpotential. All electrolytes are 0.5 M H_2SO_4 except entry 4 (0.05 M H_2SO_4).

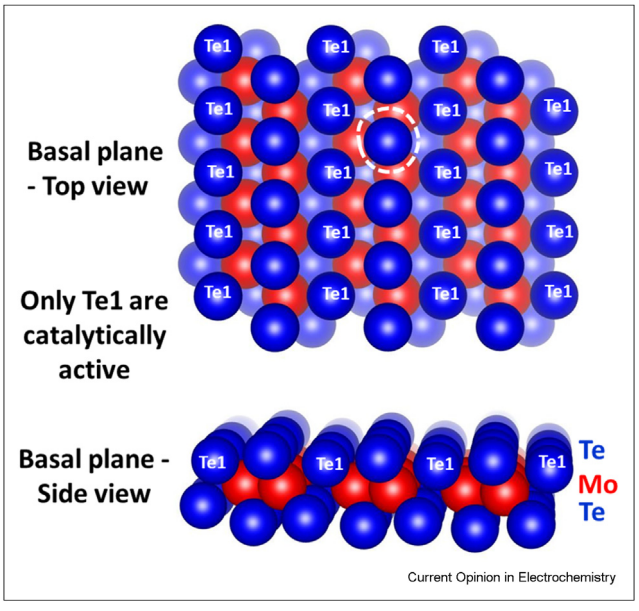
Entry	Electrode	Basal plane surface dimensions	η (mV) at 10 mA cm^{-2}	Tafel slope (mV/dec)	Substrate	Reference
1	2H–TaS_2	0.3 × 0.4 μm^2 flakes	575	>100	Glassy carbon button	[20]
2	2H–TaS_2	0.1 × 0.1 μm^2 flakes	390	–	Glassy carbon	[21]
3	2H–$TaSe_2$	0.1 × 0.1 μm^2 flakes	390	–	Glassy carbon	[21]
4	2H–NbS_2	1 × 1 μm^2 flakes	453	125	Carbon paper	[14]
5	2H–NbS_2	1 × 2 μm^2 flakes	≈290	140	Glassy carbon button	[22]
6	1T-VTe_2	Single crystal	441	70	Au covered Si/SiO_2	[23]
7	1T-VTe_2	50 × 40 μm^2 flakes	220	≈40	Glassy carbon	[24]
8	1T-MoS_2	1 × 1 μm^2 flakes	≈250	50	Glassy carbon button	[22]
9	1T-MoS_2	0.1 × 0.1 μm^2 flakes	352	72	Carbon paper	[25]
10	1T-WS_2	1 × 1 μm^2 flakes	≈210	48	Glassy carbon button	[22]
11	1T′-$MoTe_2$	1 × 2 μm^2 flakes	340	78	Glassy carbon button	[26]
12	1T′-$MoTe_2$	Thin films	481	67	1 cm^2 pyrolytic carbon	[12]
13	1T′-$MoTe_2$	Thin films	> 900[a]	392	0.3 × 0.5 cm^2 on Cu	[27]
14	1T′-$MoTe_2$	Single crystal	480	–	0.01 cm^2 crystal on Cu wire	[28]
15	1T′-$MoTe_2$	Single crystal	668	137	Au covered Si/SiO_2	[23]
16	1T′-WTe_2	10 × 10 μm^2 flakes	450	238	Au covered Si/SiO_2	[29]
17	1T′-WTe_2	Single crystal	692	169	Au covered Si/SiO_2	[23]
18	Pt	N/A	~30	30	N/A	[30]
19	Ni_2P	N/A	150	46	Ti foil	[30]

[a] At a current density of 4 mA cm^{-2}.

effectively non-catalytic materials over time, with this conversion rapidly accelerated at temperatures as low as 80 °C [25]. Given that typical proton exchange membrane electrolyzers operate at ≈60−70 °C [35], both 1T-MoS_2 and WS_2 probably make poor choices as electrode materials in practical devices. Intercalation of phenanthroline into layered 1T-MoS_2 has been shown to slow the transformation with only moderate increase in the overpotential requirement, from 352 to 383 mV at 10 mA cm^{-2} [25]. Furthermore, computational studies also suggest that intercalation of small molecules into 1T′-MoS_2 may improve its stability [36]. However, this could prove complex to implement at large scale, and so the practicality of such an approach for electrocatalysts in real-world devices remains to be established.

Given the challenges associated with MoS_2 and WS_2, metallic 1T′-$MoTe_2$ has become a rather popular alternative (Figure 3). Despite the fact that only 50% of the Te centres at the surface have sufficiently low hydrogen adsorption energies, single crystals (*ca.* 1 × 2 μm^2 in size) displayed η for 10 mA cm^{-2} as low as 340 mV (Table 1, entry 11), which suggests that the catalytic activity originates from the basal plane [26]. A key advantage of $MoTe_2$ is the simplicity with which thin films of this material can be grown selectively on various substrates [37]. However, the evaluation of metallic 1T′-$MoTe_2$ films deposited and measured directly on the 1 cm^2 scale revealed a much higher overpotential requirement of 481 mV at 10 mA cm^{-2} [12]. These high overpotential values are in line with work by Zhuang et al. [27], which showed that a film of $MoTe_2$ transferred onto Cu foil could only achieve a current density of 4 mA cm^{-2} at η > 900 mV (Table 1, entry 13). However, as the initial film was grown by a CVD process and later transferred onto the Cu-substrate, the oxidation of the film surface during this transfer could not be completely excluded. In addition, the hydrophobic nature of 1T′-$MoTe_2$ films [38] could also be a factor inhibiting catalysis. This highlights the challenges associated with implementation of chalcogenides in practical applications, especially as they seem to be quite prone to surface oxidation. This hypothesis is borne out by recent work on a high-quality single crystal of 1T′-$MoTe_2$ [28], which reported an overpotential value of 480 mV at 10 mA cm^{-2} (more in line with the values founds by McManus et al. in films of this material [12]).

Figure 3



The basal plane of 1T′-$MoTe_2$ (a typical metallic dichalcogenide). Only 50% of the Te atoms are active. The white dashed circle highlights the Te atom that could be removed to drive the improvement in catalytic ability.

The already mentioned low energy of adsorption seems to be quite evident from the Tafel slopes of the majority of the 1T′-$MoTe_2$ samples, which tend to gravitate towards 120 mV/decade, suggesting that the effective adsorption of protons at the surface (the Volmer process) is the reaction limiting step [39]. Inducing vacancies in the material has been suggested as effective way of reducing of the energy of adsorption to 0.21 eV [23]. This may give some clue as to why there is such variation in electrochemical performance observed for the metallic $MoTe_2$ samples across the literature. If there are a small number of vacancies, especially on non-catalytic sites (highlighted as the white dashed circle in Figure 3), this may lead to improved performance, and this may in turn provide an explanation for the observation that, upon prolonged cycling, 1T′-$MoTe_2$ shows a gradual reduction of the overpotential requirement to achieve 10 mA cm^{-2} from 320 to 170 mV [40] (or 340 to 261 mV at the same current density in single crystals [26]). However, the presence of vacancies is not necessarily the only explanation. It has been suggested that this improvement in performance could be a purely electronic phenomenon due to doping of electrons into the topological structure [26,28]. The change in Tafel slope from 68 to 117 mV/decade does, however, indicate that prolonged cycling may lead to the elimination of the surface oxide and that the lower overpotentials may in fact be displayed by pure 1T′-$MoTe_2$. As mentioned above, DFT simulations have shown a relatively high energy of adsorption of H^+ on the surface of $MoTe_2$. Therefore, the change to a higher Tafel slope, alongside decreased overpotential, seem to support this hypothesis. Still, whether it is electron doping, removal of an oxide layer, or the presence of vacancies that drives this activation process, it is currently unclear as to the effects of any of these on the integrity of the films. Careful experiments under inert conditions are required in order to undercover the full details of this reduction in overpotential. More investigation in practical conditions (*e.g.* flow-cells) would also be useful; studies so far have shown that $MoTe_2$ remains stable (up to current

densities of 250 mA cm^{-2}) during prolonged bulk electrolysis and cycling for at least 1000 scans, as confirmed by analysis of the electrolyte [26].

Finally, WTe_2 is the only Group 6 dichalcogenide for which the metallic state is always stable and so there is no ambiguity as to whether a tiny impurity of the semiconducting phase may have been the cause for any deterioration in performance. The study of 10×10 μm^2 flakes (identified as single phase by X-ray diffraction and Raman spectroscopy) on Au electrodes revealed $\eta = 450$ mV at a current density of 10 mA cm^{-2} [29]. This is around 250 mV lower than similar studies on larger single crystals (Table 1, entries 16 and 17), indicating that non-stoichiometry and the possible presence of edge sites plays an important role in catalytic performance in the WTe_2 system [23].

Conclusions and outlook

In this minireview, we have given a short overview of some of the more recent developments in the field of 2D metal dichalcogenides as hydrogen evolution electrocatalysts, especially in the context of applying these materials in proton exchange membrane electrolyzers. Although their overpotential metrics for hydrogen production are worse than those of Pt, 2D metal dichalcogenides are generally less scarce than Pt and production of their metallic components incurs considerably lower global warming potential (*e.g.* ~12 kg of CO_2 equivalents per kg of Nb and 260 kg of CO_2 equivalents per kg of Ta, both of which values are several orders of magnitude lower than for Pt [41]). 2D metal dichalcogenides and their components are also considerably cheaper and more abundant than Pt [42]. These factors will be important in the context of powering electrolyzers at low current densities using renewable energy sources [43]. Such low current density conditions can tolerate less effective electrocatalysts and it may well make sense to employ higher loadings of cheaper materials in such contexts, rather than Pt. Finding materials that can be deployed at high loading and which form continuous, robust thin films on high surface area substrates is therefore a very attractive target for facilitating electrochemical renewables-to-hydrogen conversion. 2D metal dichalcogenides fit this profile very well, and recent theoretical work indicates that the nature of the substrate may have a distinct effect on the electronic and catalytic properties of various 2D metal dichalcogenides [44], with implications for how these materials might be deployed (direct deposition on gas diffusion layers in a "catalyst-coated substrate" approach [45] being a possibility [37]).

In terms of the immediate opportunities and challenges in the field, exact information about the nature of the surface offers exciting prospects for computational research, allowing rapid screening of the properties of a broad range of chalcogenides and predictions of catalytic performance [46,47]. Being able to predict with confidence whether a particular 2D chalcogenide is catalytically active or not would be a major boon to innovation. Meanwhile, finding the right balance between the durability of 2D metal dichalcogenide films and the number of induced defects will be crucial for real-world applications; in this regard applying high-throughput flow cells and bespoke micro-reactors for in-depth analysis of these materials *in operando* will be essential [48,49]. Finally, these materials must then be incorporated into scaled-up electrolyzer devices and their performance monitored over extended time periods. Through efforts such as these, the tremendous potential of 2D metal dichalcogenides to act as low-cost electrocatalysts for the production of hydrogen from water driven by renewable energy will come closer to being realized.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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