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Molybdenum carbide nanoparticles as a catalyst for hydrogen evolution reaction and the effect of pH

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Abstract

Molybdenum carbide nanoparticles supported on carbon catalysts have been prepared with a modified carbothermal reduction method. The soft carburization conditions of this method allows the preparation of a nanoparticulate Mo₂C even with high Mo loading (50 wt%). The catalytic activity towards hydrogen evolution reaction was analyzed both in an electrochemical cell at various pHs and in a laboratory-scale electrolyser. These nanoparticles were found to be very active for catalyzing hydrogen evolution reaction in acidic media and appeared to promote kinetics leaning towards the Volmer-Heyrovský mechanism at low pH. Moreover, the Mo₂C/C catalyst was shown to be suitable for hydrogen production in the laboratory-scale electrolysis cell retaining its performance during the four week durability experiment. Thus this study implies that the investigated Mo₂C/C electrocatalyst is a promising alternative for platinum as a

cathode material for electrolytic hydrogen production because of favorable kinetics and stability.

Keywords: molybdenum carbide, carbothermal reduction, hydrogen evolution, electrolysis

1 Introduction

Hydrogen has proven its potential as an energy carrier for future electrical devices due to its high energy density and environmentally friendly production possibilities. The rise of the fuel cell powered electrical machines and vehicles is creating a demand for new on-site hydrogen production methods. On the other hand, increased share of renewable energy production based on solar and wind creates a need for chemical energy storage when the energy production and consumption peaks do not coincide. Electrolytic production of hydrogen by splitting water is already commercially utilized but is mainly based on alkaline techniques. Electrolyzers utilizing polymer electrolyte membranes (PEM) are promising alternatives for alkaline electrolyzers, e.g. because of superior hydrogen evolution reaction (HER) kinetics. Thus the former has sparked interest in researching novel materials and methods to enhance the performance and to decrease the price of the electrolysis cell [1-11].

Because of its high activity, platinum is widely used as an electrocatalyst for the HER but its relatively low abundance renders it too expensive to be utilized in mass produced devices. This has led to investigation and the introduction of potentially less costly alternatives. Among other materials different sizes and shapes of molybdenum sulphide particles and films have been studied during the last two decades [12-18]. Molybdenum sulfide edge sites where sulfur atoms can mediate HER have similar properties as platinum and hydrogenase enzymes found in nature [19, 20]. Nevertheless, catalytic activity of the molybdenum sulfide catalysts is limited by the amount of the edge sites on the surface [20]. Molybdenum carbides (Mo_2C) are emerging alternatives for molybdenum sulfides as non-noble metal catalysts for the HER as their catalytic activity depends on the surface orientation [21] instead of edge sites suggesting that materials with higher content of active sites can be synthesized. This has resulted in synthesis and investigation of different Mo_2C structures from nanoparticles to nanorods [22-36] revealing that the method and conditions used for molybdenum carbide preparation determines the chemical nature of the obtained phases and the structures. Soft conditions in the carbothermal reduction method, reduction of Mo^{6+} precursor using reduction agent and a carbonaceous support as carbon source of the carbide, allows the preparation of nanoparticles of Mo_2C crystalline phase even with high Mo loading [37].

Though molybdenum carbides with different surfaces have been synthesised the underlying HER mechanism has not been investigated in detail. Therefore, in this research the electrocatalytic activity of $\text{Mo}_2\text{C}/\text{C}$ nanoparticles towards the HER was analyzed in an electrochemical cell at various pHs to gain understanding of the reaction mechanism. In addition to the Tafel slope analysis, impedance spectroscopy was used to

investigate the kinetic of the HER. Finally, to show the potential of the investigated Mo₂C/C electrocatalyst for a real application electrolysis cell measurements, including long-term stability measurements, were performed in a laboratory-scale test cell.

2 Experimental

2.1 Synthesis of the catalysts

The catalysts were prepared using a modification of the carbothermal reduction carburization method [37]. This modification includes four stages in the preparation of Mo₂C nanoparticles supported on carbon carrier (Mo₂C/C). The control of the preparation conditions of each stage guarantees the production of molybdenum carbide nanoparticles. In stage (i) a Mo salt precursor ((NH₄)₆Mo₇O₂₄·4H₂O from *Sigma-Aldrich*) is deposited on the surface of *Vulcan* carbon black (C) from *Cabot* by wet impregnation. Selected quantity of Mo salt was chosen for the process to obtain Mo loadings of 10, 20 and 50 wt%. In stage (ii) the Mo salt/C precursor is reduced from Mo⁶⁺ to Mo⁴⁺ under N₂ flow (50 mL·min⁻¹) at 550 °C for 2 h to form partially reduced MoO₂/C oxide. In stage (iii) the carburization process is carried out where the previous the Mo⁴⁺ is reduced to Mo⁰. The carbothermal carburization of 400 mg of Mo-precursor was carried with a 50 mL·min⁻¹ of a mixture of 10 vol% H₂/Ar at a low GHSV ≈ 1500 h⁻¹ at 840 °C for 1 h in a Micromeritics 2900 TPD/TPR instrument monitoring the H₂ consumption taking place during the carburization process. The sample with 50 wt%

Mo was subjected to the same treatment but using temperature of 870 °C to guarantee the formation of only Mo₂C phases. In stage (iv) the formed molybdenum carbide particles were passivated with pulses of air/helium mixture to form a stable product by oxidation of a really fine superficial layer (less than 4 nm) of the carbide support in order to avoid bulk oxidation when the particles are exposed to air. This synthesis yielded carbon supported molybdenum carbide nanoparticles. The catalysts nomenclature and their main characteristics are summarized in Table 1.

2.2 Characterization of the catalysts

Mo loading was determined by chemical analysis using an ICP-AES Perkin-Elmer Optima 3300 DV spectrometer. Quantitative Mo determination was also provided by thermogravimetric analysis through recording the loss of weight during carbon support combustion with an air flow (100 mL·min⁻¹) using a Mettler Toledo TGA/SDTA 851 thermal analyser.

XRD patterns of the powdered Mo₂C/C samples were recorded at room temperature on a Seifert XRD 3000P diffractometer using Cu K α radiation ($\lambda = 1.54056$ Å). XRD patterns were collected in the range of 2θ from 5° to 70°, (0.04°/step, integration time of 50 s/step). Identification of the phases was achieved by reference to the JCPDS diffraction data file. Mean particle size of Mo₂C phases were calculated from the

experimental line broadening of their characteristic reflections using the Debye-Scherrer equation.

X-ray photoelectron spectroscopy (XPS) was used to verify the passivation step by determination of the nature and thickness (in combination with XRD) of the molybdenum oxide layer. The XPS spectra was acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a MgK ($h\nu=1253.6$ eV) X-ray source. The peaks were fitted by a non-linear least square fitting program using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley. The constant charging of the samples was corrected by referencing all energies to the C1s peak at 284.6 eV.

The synthesised electrocatalysts were examined using a Tecnai 12 transmission electron microscopy (TEM) operating at an accelerating voltage of 120 kV. The samples were prepared by dispersing the catalyst in ethanol and dropping a small amount onto holey carbon film grids (*Electron Microscopy Sciences*, 300 meshes).

2.3 Electrochemical measurements

The electrocatalytic HER activities of the Mo₂C/C catalysts were investigated with rotating disc electrode (RDE) experiments using glassy carbon (GC) electrodes with a radius of 5 mm (Pine Instruments). Commercial Mo₂C bulk (*Sigma-Aldrich*) and 60

wt% Pt/C (*Alfa Aesar*) catalysts were used as reference materials. The catalyst was mixed with 5 wt-% Nafion solution (*Aldrich*) and ethanol to form an ink which was deposited on the electrode to yield a catalyst loading of 0.56-0.60 mg·cm⁻² and Nafion content of 0.42-0.46 mg·cm⁻². The experiments were carried out in 0.5 M H₂SO₄ solution with N₂ bubbling at 30 °C temperature. A sweep rate of 10 mV·s⁻¹ was used. A platinum mesh was used as a counter electrode and a reversible hydrogen electrode (RHE) as a reference electrode. The measurement equipment consisted of an Autolab PGSTAT100 potentiostat and a Pine Instruments MSR rotator. All the potentials are given against RHE. Currents are normalized against the geometrical area of the GC electrode. The electrochemical impedance spectroscopy analysis was carried out from 10 000 Hz to 1 Hz with overpotentials of 100 mV, 200 mV, 300 mV and 400 mV using 5 mV amplitude.

The electrocatalysts performance for HER was measures in the pH range 0.11 to 7. The electrolyte solutions were made by mixing appropriate amount of 1 M sulfuric acid with 1 M sodium sulfate to obtain the desired pH while maintaining electrical conductivity.

2.4 Electrolyzer cell measurements

As an alternative to the conventional water electrolyzers a methanol based electrolysis systems was used to produce hydrogen at lower voltage. This allowed a more gentle reaction environment resulting in improved material durability on the anode side [38-

43]. The electrolyzer cell consisted of a membrane electrode assembly (MEA), diffusion layers, polytetrafluoroethylene gaskets, graphite blocks with serpentine flow channels (*Fuel Cell Technologies*) and current collector plates. The cell was clamped together with 8 bolts that were tightened with a torque of 10 Nm. The MEA was made by spraying catalyst ink onto both the sides of the Nafion[®] 115 membrane (*Ion Power*), where the ink was made by mixing the catalyst powder (50 wt% Mo₂C/C for the cathode, 60 wt% Pt-Ru on carbon support (*Alfa Aesar*) for the anode) with appropriate amount of solvent (isopropanol and water) to form a homogeneous slurry. After painting, the MEA was dried in a vacuum oven at 80 °C for 60 min and subsequently hot pressed for 120 s at 30 MPa and 130 °C. The MEA with geometric area of 5.29 cm² had metal (Pt, Pt-Ru or Mo) loadings of 4.8 mg·cm⁻² for the cathode and 3.2 mg·cm⁻² for the anode.

The cell was stabilized overnight before starting the measurements and for 30 minutes after each temperature change. The anode was fed with 2 M MeOH solution at a rate of 2 ml·min⁻¹ and the cathode was fed with a hydrogen flow of 50 ml·min⁻¹. Potential sweeps were performed with a low sweep rate, 1 mV·s⁻¹, to ensure stable conditions through the potential scale.

3 Results

3.1 Characterization of the catalysts

Composition and properties of the synthesised Mo₂C/C catalysts were investigated and analyzed using ICP chemical analysis, thermogravimetry, XRD, XPS and TEM. Mo loadings obtained by ICP chemical analysis and by thermogravimetry analyses were similar and they are close to the nominal ones. Thus, we can conclude that no Mo losses occurred during synthesis steps.

Table 1. Main properties and characteristic of the Mo₂C/C catalysts.

Samples	Experimental Mo-loading (wt% Mo)	XRD Results		
		Main phase*	Secondary phase*	t _{Mo₂C} (nm)
10 Mo ₂ C /C	9	C	Mo ₂ C	12
20 Mo ₂ C /C	21	Mo ₂ C	C	15
50 Mo ₂ C /C	52	Mo ₂ C	-	29

*Mo₂C (JCPDF: 01-079-0744; C-graphite (JCPDF: 00-023-0064).

Fig. 1a shows the H₂ consumption profile during the carburization process (stage iii) of each of three samples with the different Mo loadings. The main peak for the three samples arises at temperatures higher than 600 °C. This main peak is linked to reduction of Mo⁴⁺ to Mo metal and the immediate formation of carbide. The temperature for the reduction is dependent on the Mo particle size and the interaction between the Mo particles and the C support [37, 44]. The higher particle size of the 50 wt% Mo catalyst

results in a higher reduction temperature. For the 10 wt% Mo catalyst smaller particle size results in a higher interaction between the particles and the support which explains the slightly higher reduction temperature compared to 20 wt% Mo catalyst. The reduction of Mo^{4+} to Mo metal was completed with 10 and 20 wt% Mo catalyst but the 50 wt% Mo catalysts reduction seemed to continue until the end of the carburization process. The additional peaks in the samples with higher Mo loading (20 and 50 wt% of Mo) are related to the reduction of residuary Mo^{6+} species to Mo^{4+} which were not reduced during the stage (ii).

207

208 Fig. 1. H₂ consumption profile during the carburization process (stage iii) of the
 209 Mo₂C/C samples with the different Mo loadings (a) and the XRD patterns of the three
 210 Mo₂C/C samples with the different Mo-loadings (b).

211

212 The XRD diffraction patterns of the three Mo₂C/C samples are displayed in Fig. 1b. The
 213 only Mo crystalline phase detected in all the samples was the most stable Mo₂C phase.
 214 The samples with the lower Mo loading (10 and 20 wt% Mo) show an additional phase

of C-graphite from the support. The C-graphite phase is also detected in the 50 wt% sample but it is outweighed by the Mo₂C peaks. Detection of this phase from the amorphous carbon black Vulcan support is indicative of high dispersion of the Mo₂C particles on the C support surface. The controlled preparation conditions allow the synthesis of molybdenum carbide nanoparticles with an average diameter of 12, 15 and 29 nm for the 10, 20 and 50 wt% Mo loadings, respectively.

Passivation of the carburized samples was carried out with the aim of developing a few atomic layers shell close to the surface of the carburized Mo-phases to stabilize the carburized core and to minimize further oxidation when the samples are exposed to ambient conditions. The XPS measurements were carried out in addition to XRD to further investigate the nature of the catalysts surface after the passivation (stage iv): Although the XRD patterns (*vide supra*) of the carburized samples showed formation of only a crystalline Mo₂C carbide phase, it is expected that a thin layer of oxidized phases would be developed on the topmost few atomic layers of the crystallite particles after exposure to air during the passivation step. All the samples showed the major Mo3d_{5/2} component of the Mo3d doublet at 233.0 eV which is typical of MoO₃ phase. However, no diffraction lines of MoO₃ phases were detected for the samples, even though MoO₃ species were dominant in their corresponding photoelectron spectra. The explanation for this discrepancy lies in the fact that the passivation layer is very thin, in the order of the electron mean free path of the Mo3d photoelectrons (ca. 3 nm) which, in turn, is still below the detection limit of the XRD technique. These results suggest successful synthesis of the desired thin passivation layer.

238

239 TEM images (Fig. S1-3) show that the Mo₂C catalysts (the scattered small particles) are
240 dispersed on the carbon support (the big flakes) evenly and no agglomerates are
241 observed. The structure of the Mo₂C/C assemblies are similar with 10, 20 and 50 wt%
242 Mo loadings. However, the low contrast between the Mo₂C particles and carbon support
243 makes it difficult to analyze the particle sizes from the TEM images and thus the
244 analysis is only made using the XRD data.

245

246 **3.2 Electrochemical measurements**

247

248 The Mo₂C/C catalyst with 50 wt% Mo loading showed the lowest onset overpotential of
249 69 mV at 1 mA cm⁻² while the corresponding onset overpotentials for the 20 and 10
250 wt% catalysts were 156 mV and 131 mV, respectively (Fig 2). The higher onset
251 overpotential with the 10 wt% catalyst is assumed to result from smaller particle size
252 which has been shown to affect the catalytic behavior of other types of electrocatalyst
253 materials for a wide range of reactions [44-53]. Even the shape of the current voltage
254 curve of 10 % wt carbide is clearly different from those of the others suggesting a
255 different mechanism. The lower onset overpotential of the 50 wt% catalyst can be
256 explained with the higher amount of molybdenum carbide resulting in a higher amount
257 of HER active surface area and consequently higher currents at lower overpotentials. To
258 obtain 50 mA·cm⁻² current the required overpotentials were 264 mV, 348 mV and 389
259 mV for the 50, 20 and 10 wt% catalysts, respectively. These results indicate that at
260 higher overpotentials currents reflect the amount of molybdenum carbide in the catalyst

and the effect of the observed lower overpotential with smaller particle size diminishes. The currents obtained with these catalysts are much higher than those with Mo₂C bulk catalyst which required overpotential of 290 mV to achieve 1 mA·cm⁻² current and the electrolysis current was only 3 mA·cm⁻² with 400 mV overpotential. This clearly shows the benefit of nanosizing and thus increasing the amount of the active sites on the catalyst materials.

Fig. 2. The polarization curves for the Mo₂C/C catalysts with 10, 20 and 50 wt% Mo loadings, bulk Mo₂C and the commercial Pt catalyst.

It is generally accepted that hydrogen evolution under acidic conditions consist of the following steps [54-56]:

1. Proton adsorption with charge transfer (Volmer reaction):

2. Combination of surface hydrogen atoms (Tafel reaction):

3. Combination of a surface hydrogen atom and a solvated proton (Heyrovský reaction):

In the equations 1-3 S denotes the active free surface sites of the catalyst while SH_{ads} is adsorbed hydrogen atom on the catalyst site. The HER begins with electrochemical adsorption of protons (the Volmer reaction) and is continued either with the combination of two adsorbed hydrogen atoms (the Tafel reaction) or with the combination of an adsorbed hydrogen atom and a solvated proton (the Heyrovský reaction) thus resulting in a molecular hydrogen. The mechanism depends on the kinetics of the reaction on the selected catalyst material.

294

295 According to previous measurements and modelling of the kinetics [54, 56], the Tafel
296 slope for the HER is $30 \text{ mV} \cdot \text{dec}^{-1}$ at low overpotentials if the reaction proceeds through
297 the Volmer reaction followed by the Tafel reaction. At high overpotentials the reaction
298 is kinetically limited by the Tafel reaction and thus, is independent of the potential. If
299 the reaction proceeds through the Volmer reaction followed by the Heyrovský reaction
300 then a Tafel slope is $40 \text{ mV} \cdot \text{dec}^{-1}$ at low overpotentials. For this Volmer-Tafel
301 mechanism, at high overpotentials Tafel slope of $120 \text{ mV} \cdot \text{dec}^{-1}$ is observed. The
302 obtained Tafel slopes of 82, 92 and $110 \text{ mV} \cdot \text{dec}^{-1}$ for the 50, 20 and 10 wt% catalysts,
303 respectively, are not representative for a single reaction mechanism with very low or
304 high proton coverage. The values for the Tafel slopes are remarkably higher than the
305 expected values at low overpotentials when the surface coverage in respect to protons is
306 close to zero, but not high enough to be representative for the Volmer-Heyrovský
307 mechanism with high surface coverage.

308

309 Based on the results presented above the 50 wt% molybdenum carbide catalyst was
310 chosen for further studies. The Bode plot (Fig. 3a) reveals typical single time constant
311 behavior related to smooth surfaces with one dominant reaction while multiple time
312 constants would suggest a porous and rough electrode surface [57]. The equivalent
313 circuit model for the single time constant is described as a series resistance (R_s) in series
314 with a charge transfer process containing parallel double layer capacitance (C_{dl}) and
315 charge transfer resistance (R_{ct}). The Nyquist plot of the measured data (Fig. 3b) was
316 fitted to this model circuit, using a constant phase element instead of C_{dl} to better mimic

a real system, which yielded values for R_s and R_{ct} with acceptable error estimates (Table 2). R_s was slightly less than 5 Ohm while R_{ct} continuously decreases with the increasing overpotential. The decrease in the R_{ct} is representative as the hydrogen evolution reaction becomes more facile with the increasing overpotential. The obtained values are in agreement with the currents and corresponding resistances that have been earlier reported for molybdenum carbide [22, 25-27].

Fig. 3. The Bode plots of the impedance analysis of the 50 wt% Mo₂C/C catalyst with 100, 200, 300 and 400 mV overpotentials (a) and the Nyquist plots of the impedance analysis of the 50 wt% Mo₂C/C catalyst with 100, 200, 300 and 400 mV overpotentials (b).

Table 2. Series resistance (R_s) and charge transfer resistance (R_{ct}) values with their error estimates for 50 wt% Mo₂C/C in 0.5 M H₂SO₄ at 30 °C.

Overpotential (mV)	R_s (Ohm)	R_s Error Estimate (%)	R_{ct} (Ohm)	R_{ct} Error Estimate (%)
100	4.9	0.2	500	2.3

200	5.0	0.3	13	0.5
300	5.0	0.2	2.8	0.8
400	5.0	0.1	1.5	0.8

The reaction mechanism of the HER was also investigated by analyzing the rate of the reaction at various pHs. According to the derivation of the reaction rates (see Supporting Information) the slope of $\log i$ vs. pH is around 2 for both the mechanisms at low overpotentials but at high overpotentials the slope is 1 or 0 for the the Volmer-Heyrovský or Volmer-Tafel mechanism, respectively.

The currents at the high pHs of 2.3 - 7.0 (Fig. 4a) showed very little dependency on the proton concentration but there is a significant change in the behavior at pH 2 corresponding to the value where sulfate ion is protonated. At pH 2 and lower (Fig. 4b) there is an evident dependency of the proton concentration on the HER current. The background current (Fig. S4) significantly increases while the pH decreases and approaches pH 2 but immediately disappears after that point. The background current originates from the reaction of sulfate ion with protons to form sulfur dioxide and water. The formed sulfur dioxide is observed as bubble formation on the electrode surface. When the sulfate ion is protonated at pH 2 the reaction is inhibited to an insignificant level. When the background corrected logarithm of the electrolysis current is plotted as a function of pH, linear dependency is observed in the pH range 0.11 to 0.66 (Fig. S5). Our results show slope of 2 at low overpotentials for both the mechanisms with overpotentials up to 50 mV in the pH range 0.11 - 0.66 (Fig. 5). No linear relation is observed at pHs higher than 0.66. When the overpotential is increased the slope begins to decrease as expected for both the mechanisms. The change in the slope value

between 50 and 200 mV is attributed to the change from zero surface coverage to full surface coverage. The slope reaches a value of 0.67 before it begins to slowly increase after the overpotential of 200 mV. This behavior suggests that the reaction proceeds with mixed reaction mechanisms or intermediate surface coverages at the high overpotentials as the slope is between 0 and 1, which are the expected values for the Volmer-Tafel and Volmer-Heyrovský mechanisms at high overpotentials, respectively. The values of the slope rises closer to 1 which implies leaning towards the Volmer-Heyrovský mechanism when the potential is increased.

Fig. 4. The polarization curves for the 50 wt% Mo₂C/C catalyst with the high pH sulfuric acid buffer solutions (a) and with the low pH sulfuric acid buffer solutions (b).

Fig. 5. The $\log i / \text{pH}$ slopes vs. chosen overpotentials for the 50 wt% $\text{Mo}_2\text{C}/\text{C}$ catalyst at the low pH sulfuric acid buffer solutions.

Change in the behavior of the Tafel slopes at the low pHs can also be readily observed (Fig. 6). First, the HER is activated at overpotentials lower than 100 mV and a second change is around an overpotential of 150 mV. The values of the Tafel slopes (Table 3) in the lower overpotential region are in the range of 59 - 78 $\text{mV} \cdot \text{dec}^{-1}$ with pH 0.39 - 1.84. The slopes increase to 111 and 117 $\text{mV} \cdot \text{dec}^{-1}$ for pH 0.11 and 0.23, respectively. These results indicate that already overpotential of 100 mV is high

379 enough to obtain features of a proton covered surface as the values close to 120
380 $\text{mV}\cdot\text{dec}^{-1}$ are representative for the Volmer-Heyrovský reaction at high surface
381 coverage *e.g.* at high overpotential. This result is also in agreement with the previous
382 findings that there is no clearly predominant reaction mechanism close to 100 mV
383 overpotential as the mechanism is dependent on pH in that overpotential region. For
384 the higher overpotential region the Tafel slopes are 60 - 71 $\text{mV}\cdot\text{dec}^{-1}$ with pH 0.39 -
385 1.84 while rising only to 86 $\text{mV}\cdot\text{dec}^{-1}$ for pH 0.11 and 0.23. These results support the
386 previous conclusion that the reaction proceeds with mixed reaction mechanisms or
387 intermediate coverages at high overpotentials. The increase of the Tafel slopes with
388 the decreasing pH is suggested to result from increased proton coverage at higher
389 proton concentration which is typical behavior for adsorbing species. In other words,
390 the proton surface coverage changes with pH resulting in different Tafel slopes.
391 Differences in the Tafel slope curvatures observed at low overpotentials of less than
392 some 100 mV are attributed to the formation of sulphur dioxide (discussed above in
393 the context of Figs. 4 and 5) as this reaction also depends on the proton
394 concentration.

Fig. 6. The Tafel slopes for the HER on the 50 wt% Mo₂C/C catalyst at the low pH sulfuric acid buffer solutions.

Table 3. The Tafel slope values for the HER on the 50 wt% Mo₂C/C catalyst.

	Low overpotential		High overpotential	
pH	Tafel region (mV)	Slope (mV·dec ⁻¹)	Tafel region (mV)	Slope (mV·dec ⁻¹)
1.87	80-120	59	130-150	60
1.44	80-120	61	130-150	60
1.01	80-120	68	130-150	60
0.66	80-120	66	130-150	62
0.39	80-120	78	130-150	71
0.23	80-120	117	150-170	86
0.11	80-120	111	150-170	86

The currents and Tafel slopes obtained in this research are comparable to previously measured ones for Mo₂C catalysts (Table 4). As previously shown HER is strongly

dependent on the measurement conditions and for this reason great care must be taken when comparing the results. The electrolyte has strong impact on the current obtained and the Tafel slopes while also the catalyst loading affects the results.

Table 4. Performance of Mo₂C based catalysts for HER in acidic media.

Mo ₂ C Catalyst	Ref.	Electrolyte	Loading (mg·cm ⁻²)	<i>i</i> ₂₀₀ (mA·cm ⁻²)	<i>η</i> ₁₀ (mV)	Tafel (mV·dec ⁻¹)
Nanoparticles/C	-	0.5 M H ₂ SO ₄	0.6	16	180	82
Nanowires	[31]	0.5 M H ₂ SO ₄	1.3	20	180	56
Nanoparticles	[30]	0.5 M H ₂ SO ₄	0.1	10	198	56
Micro-islands/CC	[29]	0.5 M H ₂ SO ₄	1.5	28	140	124
Nano-octahedrons	[32]	0.5 M H ₂ SO ₄	0.8	50	140	53
Nanoparticles/C	[33]	0.1 M HClO ₄	6.3	13	170	251
Nanoparticles/CNT	[22]	0.1 M HClO ₄	2	-	150	55
Nanowires	[25]	0.5 M H ₂ SO ₄	0.2	60	140	53
Nanocomposites	[26]	0.05 M H ₂ SO ₄	0.3	1.5	-	110-235
Nano-rods	[27]	0.5 M H ₂ SO ₄	0.4	32	160	58
Nanocrystals/NCNT	[35]	0.5 M H ₂ SO ₄	-	73	150	71
Nanocrystals/CNT-GN	[34]	0.5 M H ₂ SO ₄	0.7	-	130	58

*i*₂₀₀ – approximate current density at 200 mV overpotential, *η*₁₀ – approximate overpotential for 10 mA·cm⁻² current density.

3.3 Electrolyzer cell measurements

The suitability of the most promising 50 wt% Mo₂C/C catalyst for a real electrolysis system was analyzed with a laboratory-scale aqueous methanol electrolysis cell. The electrochemical reactions in the cell are as follows:

The electrolyzer cell results (Fig. 7a) confirm that this molybdenum carbide catalyst is efficient in a realistic hydrogen production system. The performance of the cell increases with increasing temperature as the onset potential with $5 \text{ mA} \cdot \text{cm}^{-2}$ current decrease from 544 mV to 386 mV and the current density at 1 V increases from 130 to 422 mA cm^{-2} (Table 5). The current at 1 V with 70 °C temperature is about 80 % of the current ($515 \text{ mA} \cdot \text{cm}^{-2}$) obtained with a similar MEA (Fig. 7b) with platinum cathode ($1.43 \text{ mg} \cdot \text{cm}^{-2}$ loading).

Fig. 7. The polarization curves of the methanol electrolyzer cell with the 50 wt% Mo₂C/C catalyst at chosen temperatures (a) and comparison of the 50 wt% Mo₂C/C catalyst and platinum as the cathode catalyst for the electrolyzer cell at 70 °C.

Table 5. The onset potentials and maximum current densities of the electrolyzer cell with the 50 wt% Mo₂C/C cathode at chosen temperatures.

Temperature (°C)	η_5 (mV)	i_1 (mA·cm ⁻²)
30	544	130
40	503	188
50	455	267
60	427	345
70	386	422

η_5 – overpotential for 5 mA·cm⁻² current density, i_1 – current density at 1 V overpotential.

The long term measurements at a constant potential of 0.8 V and at the temperature of 30 °C were performed in one week periods so that the whole duration of the experiment was four weeks. A potential scan was measured after each week to observe any difference in the polarization curves. During the first week the constant potential measurement shows some activation during the first days but is relatively stable from there onwards (Fig. 8a). The short period of downtime and a potential sweep seems to result in a temporal activation of the cell which can be seen in higher currents at the beginning of the weeks 2-4. The current densities stabilize to the level of 56-58 mA·cm⁻², though slight variation can be seen at the end of the measurement weeks. The scans performed before the first week and after each week (Fig. 8b) confirm the previous observation of the cells stability. There is an increase in the current from the initial scan

to the following ones but no significant change can be seen thereafter suggesting that the 50 wt% Mo₂C/C catalyst is stable under conditions prevailing in the electrolyser cathode.

Fig. 8. Constant potential electrolyzer cell measurement with the 50 wt% Mo₂C/C catalyst at 0.8 V and 30 °C (a) and polarization curves of the electrolyzer cell before the long term measurements and after each measurement week at 30 °C.

4 Conclusions

Molybdenum carbide nanoparticles are a promising alternative to replace platinum as a hydrogen evolution catalyst. While the catalytic activity is high, the abundance of the material and the low price of the catalyst are also important factors when considering mass production. The measurements at different pHs yield valuable information regarding the reaction mechanism of the HER and gives us a new tool to analyze the

performance of this catalyst. The finding of strong correlation of pH to the performance of the catalyst verifies that comparison between catalysts can be done only when they are measured under identical conditions.

The results suggest that the HER proceeds with mixed reaction mechanisms. This is the first time the reaction mechanism on Mo_2C have been studied with advanced methods. The catalyst was proved to be effective by electrochemical analysis and in a realistic electrolysis system, and the long term stability has been verified. The synthesis route of the catalyst is simple and thus is scalable for industrial applications which is relevant in the search for new catalyst materials for real applications. The comparison of different loadings of molybdenum reveals that there are a lot of opportunities for further improvements by optimizing the composition of the catalyst. Due to the low cost of the catalyst an interesting future research area is an optimization of the electrode layer in the electrolyzer cell which would result in a higher catalyst loadings thus enabling performance comparable to the platinum cathode but for a fraction of the price.

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596 **Supporting information**

597 Depending on the reaction mechanism the electrolysis current has different behavior
598 with changes in pH.

599

600 For the Volmer-Heyrovský reaction can be written:

$$601 \quad v_1 = k_1[\text{H}^+](1 - \theta)e^{(\alpha-1)f\eta}$$

602

$$v_{-1} = k_{-1}\theta e^{\alpha f\eta}$$

$$v_2 = k_2[\text{H}^+]\theta e^{(\alpha-1)f\eta}$$

where v_1 , v_{-1} and v_2 are the reaction rates of the forward Volmer reaction, backward Volmer reaction and forward Heyrovský reactions, respectively; k_1 , k_{-1} and k_2 are the respective reaction rate constants; θ is the hydrogen surface coverage; $f = RT/F$ and η is the overpotential.

If it assumed the proton coverage is constant at a given overpotential:

$$\frac{d\theta}{dt} = v_1 - v_{-1} - v_2 = 0$$

$$k_1[\text{H}^+](1 - \theta)e^{(\alpha-1)f\eta} - k_{-1}\theta e^{\alpha f\eta} - k_2[\text{H}^+]\theta e^{(\alpha-1)f\eta} = 0$$

Solving θ from the equation results in:

$$\theta = \frac{k_1[\text{H}^+]}{(k_1 + k_2)[\text{H}^+] + k_{-1}e^{f\eta}}$$

In the case of $\theta \approx 0$ which is achieved with low overpotential when $k_{-1} \gg k_1, k_2$, the surface coverage can be written as:

$$\theta \approx \frac{k_1[\text{H}^+]}{k_{-1}}e^{-f\eta}$$

As the system is a steady state the net rate of the Volmer reactions equals to the rate of the Heyrovský reaction. This leads to:

$$\frac{i}{F} = 2v_2 = 2 \frac{k_2 k_1 [\text{H}^+]^2}{k_{-1}} e^{(\alpha-2)f\eta}$$

And further to:

$$\frac{\partial \log i}{\partial \log [\text{H}^+]} = 2$$

This implies that the current increases hundredfold when the pH is decreased by one unit.

In similar fashion the current behavior can be calculated for the case $\theta \approx 1$ which is achieved with high overpotentials when $k_1 \gg k_{-1}, k_2$:

$$\frac{i}{F} = 2k_2 [\text{H}^+] e^{(\alpha-1)f\eta}$$

$$\frac{\partial \log i}{\partial \log [\text{H}^+]} = 1$$

The current increases tenfold when pH is decreased by one unit.

For the Volmer-Tafel mechanism the Volmer reactions are as previously and for the Tafel reaction:

$$v_3 = k_3 \theta^2$$

655

656 The steady state assumption in this case is

657

$$\frac{d\theta}{dt} = v_1 - v_{-1} - 2v_3 = 0$$

659

$$k_1[\text{H}^+](1 - \theta)e^{(\alpha-1)f\eta} - k_{-1}\theta e^{\alpha f\eta} - 2k_3\theta^2 = 0$$

661

662 Considering the situation when $\theta \approx 0$ which is obtained at low overpotentials as $k_{-1} \gg$
 663 k_1 the surface coverage is approximately:

664

$$\theta \approx \frac{k_1[\text{H}^+]}{k_{-1}} e^{-f\eta}$$

666

667 Thus the current is:

668

$$\frac{i}{F} = k_3 \frac{k_1}{k_{-1}} [\text{H}^+]^2 e^{-2f\eta}$$

670

$$\frac{\partial \log i}{\partial \log [\text{H}^+]} = 2$$

672

673 So again the current increases hundredfold when pH is decreased by one unit.

674

675 In the case of $\theta \approx 1$ which is obtained with high overpotentials as $k_1 \gg k_{-1}, k_2$:

676

677
$$\frac{i}{F} = k_3 = \text{constant}$$

678

679 Thus the current is independent of overpotential or pH, and is kinetically limited.

680

681 The previous analyses assumes steady state for the surface coverage of protons. This
682 condition is met only when the second reaction is the rate determining.

683

684

685 Fig. S1. TEM image of the 10 wt% Mo₂C/C catalyst.

686
687 Fig. S2. TEM image of the 20 wt% Mo₂C/C catalyst.

Fig. S3. TEM image of the 50 wt% Mo₂C/C catalyst.

692

693 Fig. S4. The background current at 0 V on the 50 wt% Mo₂C/C catalyst.

Fig. S5. The linear slopes of the $\log i$ vs. chosen overpotentials for the 50 wt% Mo₂C/C catalyst at the low pH sulfuric acid buffer solutions.