Malaysian Journal of Analytical Sciences, Vol 28 No 6 (2024): 1482 - 1508

Malaysian Journal of Analytical Sciences
(MJAS)
Published by Malaysian Analytical Sciences Society

TRANSITION METAL CARBIDES AS AN ELECTROCATALYST FOR THE HYDROGEN EVOLUTION REACTION: A REVIEW

(Karbida Logam Peralihan Sebagai Elektrokatalis Untuk Tindak Balas Evolusi Hidrogen: Satu Kajian)

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Received: 7 April 2024; Accepted: 7 October 2024; Published: 29 December 2024

Abstract

Transition metal carbides (TMCs) have recently garnered attention as electrocatalysts with significant potential for hydrogen evolution reaction (HER) due to their exceptional activity, cost-effectiveness, and abundance. This comprehensive review provides an extensive examination of the synthesis, electrocatalytic activity and transition metal carbides application in HER. Several synthesis techniques and important parameters affecting the structure and behaviour of transition metal carbides are discussed in this article. Additionally, the transition metal carbides' electrocatalytic performance in HER is reviewed and compared with other electrocatalysts. This article also provides mechanistic insights into HER catalysis by transition metal carbides, and recent advancements in understanding the HER mechanism on these materials. Furthermore, the potential applications of transition metal carbides as HER electrocatalysts are highlighted, and the advantages and disadvantages for utilising these materials in practical applications are discussed. Overall, this review provides a critical evaluation of the current status of transition metal carbides as electrocatalysts for the hydrogen evolution reaction (HER), highlighting major challenges and opportunities for additional research in this domain.

Keywords: transition metal carbides, electrocatalyst, hydrogen evolution reaction

Abstrak

Karbida logam peralihan baru-baru ini menarik perhatian sebagai elektrokatalis dengan potensi yang besar untuk tindak balas evolusi hidrogen disebabkan oleh aktiviti yang luar biasa, kos-efektif, dan kelimpahan yang tinggi. Kajian menyeluruh ini menyediakan tinjauan yang meluas mengenai sintesis, aktiviti elektrokatalisis dan aplikasi karbida logam peralihan dalam tindak balas evolusi hidrogen. Beberapa teknik sintesis dan parameter penting yang mempengaruhi struktur dan tingkah laku karbida logam peralihan dibincangkan. Selain itu, prestasi elektrokatalisis karbida logam peralihan dalam tindak balas evolusi hidrogen disemak semula dan dibandingkan dengan elektrokatalisis lain. Pandangan mekanisme ke atas katalisis HER oleh karbida logam peralihan disediakan, dan kemajuan terkini dalam pemahaman mengenai mekanisme tindak balas evolusi hidrogen pada bahan-bahan ini disemak semula. Selanjutnya, aplikasi karbida logam peralihan yang berpotensi sebagai elektrokatalis HER ditekankan, dan kelebihan dan kekurangan untuk menggunakan bahan-bahan ini dalam aplikasi praktikal dibincangkan. Secara keseluruhan, kajian ini menyediakan penilaian kritis terhadap status semasa karbida logam peralihan sebagai elektrokatalis untuk tindak balas evolusi hidrogen, menekankan cabaran utama dan peluang untuk penyelidikan tambahan dalam bidang ini.

Kata kunci: karbida logam peralihan, elektrokatalis, tindak balas evolusi hidrogen

Introduction

The hydrogen evolution reaction (HER) refers to the electrochemical reaction where hydrogen gas (H_2) is produced from the electrolysis of water. The The use of HER has a significant impact on several domains, including energy conversion, chemical synthesis, and remediation of the environment. The utilisation of several clean energy technologies, including fuel cells, electrolysers, and photoelectrochemical cells, represents a pivotal stage with the potential to supplant conventional fossil fuel sources. Hydrogen is well recognised as an environmentally friendly and adaptable energy carrier that is expected to have a pivotal position within the forthcoming sustainable energy framework. The mechanism of HER involves the reduction of protons to produce hydrogen gas [1]. It is facilitated by a catalyst which is frequently composed of transition metals or metal alloys that help minimise the activation energy necessary for the reaction to occur efficiently [2,3].

In the context of HER, electrocatalysts play a vital part in facilitating the reduction of the activation energy needed for the reaction to take place [4]. These surfaces facilitate the process of adsorption and dissociation of water molecules, resulting in an intermediate state that enhances the production of hydrogen gas. Electrocatalysts act as molecular intermediaries, facilitating the transfer of charge between reactants — in this case, protons and electrons. They lower the activation energy and aid in the desorption of hydrogen, thereby expediting the rate of the chemical reaction [5]. HER is a crucial occurrence that holds substantial importance in various critical technological and environmental contexts, such as energy storage, corrosion prevention, sustainable chemistry, and electrochemical sensing. Boosting the efficacy of hydrogen production technologies demands the development of efficient and economical electrocatalysts. Researchers are exploring various materials for electrocatalysts, including transition metals, metal chalcogenides, and carbon-based materials. Additionally, researchers also focus on improving the stability and durability of electrocatalysts to increase their lifespan. The importance of HER lies in producing sustainable hydrogen to produce clean energy sources. Electrochemistry and electrocatalysis play a vital role in HER and developing efficient and durable electrocatalysts is critical to maximise energy efficiency and reduce costs associated with hydrogen production [6,7]. Platinum has been recognised as a highly efficient electrocatalyst for water splitting [8]. However, its expensive cost and limited availability render it unsuitable for implementation on a large scale. Hence, the need for a cost-effective alternative metal to platinum arises to facilitate the mass production of hydrogen gas in the future.

Transition metal carbides (TMCs) are emerging as potential electrocatalysts for HER owing to their distinctive electrical and catalytic efficiency. As a result, there has been significant research interest in studying the performance and mechanism of these materials as HER electrocatalysts. TMCs are materials that contain transition metals bonded to carbon atoms, and they exhibit unique d-band electronic structure and catalytic properties that make them highly efficient at catalysing HER [9,10]. Consequently, TMCs have garnered considerable interest in the field of HER catalysis. In the relevant research, it is found that the group VIB elements molybdenum (Mo), chromium (Cr), and tungsten (W) and their derivatives exhibit outstanding catalytic activities toward HER and serve a crucial role in the advancement of sustainable hydrogen energy products [11,12]. TMCs have notable benefits such as exceptional electrochemical stability, and favourable conductivity and can be easily synthesised using simple and low-cost methods [13,14]. Recent studies have demonstrated that TMCs including molybdenum carbide (Mo_2C) and tungsten carbide (WC) can exhibit excellent HER activity. Consequently, they can serve as viable alternatives to platinum catalysts. This makes TMCs a highly attractive option for enhancing the efficiency and sustainability of hydrogen production via water splitting. Zang and colleagues synthesised molybdenum carbide, which demonstrated excellent electrocatalytic performance with high electrical conductivity and significant surface area in alkaline conditions, nearly matching the catalytic efficiency of commercially available platinum catalysts [15,16]. With regards to the previous study, TMCs have shown some promising catalytic activity in HER and should be extensively studied in many areas.

The primary aim of this review is to offer a comprehensive summary of the latest advancements in this domain, including the synthesis and performance of various transition metal carbides as HER electrocatalysts. Specifically, the review will also focus on discussing the application of TMCs to explore their potential for practical applications in converting renewable energy and water splitting.

Synthesis Method of Transitition Metal Carbides

Carbothermal reduction

Carbothermal reduction is a facile technique that can be employed to produce diverse materials, particularly nanostructures that have been functionalised with transition metals. Metal materials including Mo, Cr and Fe have been extensively synthesised in combination with various carbon nanostructures through carbothermal reduction. The utilisation of inexpensive starting materials has contributed to the widespread acceptance of this method in the industrial sector. Furthermore, a diverse range of carbon types can be used as economically feasible carbon precursors in the production of carbon-based functional nanomaterials. The materials consist of carbon ferromagnetic nanoparticles, such as FeC_3@C, Fe_3O_4@C, and Co_3O_4@C [17]. Functional nanomaterials hold great promise for applications in the energy and environment sectors. Carbothermal reduction techniques have notable benefits, such as their user-friendly nature, relatively low expenses, and exceptional reproducibility, rendering them highly suitable for industrial applications. In addition, there has been a recent surge in interest regarding the exploration of alternative pathways to produce carbon-based materials using sustainable resources.

The carbothermal reaction involves heating a mixture of metal powders and carbon sources at elevated temperatures (>1000 °C) in an inert atmosphere [18]. This method is widely used for synthesising TMCs, where the carbon source can be graphite, carbon black or amorphous carbon. Mu's group synthesised Mo_2C nanoparticles incorporated within porous carbon nanosheets using a solid-state reaction method. In this technique, cornstalk was utilised as a cost-effective carbon source. The cornstalk exhibited a high level of porosity, which facilitated its interaction with the electrolyte and resulted in a greater number of exposed active sites. The nanomaterial Mo_2C/C-900 exhibited remarkable electrocatalytic performance, characterised by a low overpotential of 114 mV and a small Tafel slope of 52 mV dec^{-1}, enabling the attainment of a current density of 10 mA cm^{-2} in 0.5M H_2SO_4 acid solution [19]. In a recent study by Hussain et al. showed that by subjecting tungsten carbide (W_2C) and molybdenum carbide (Mo_2C) materials to annealing at a temperature of 850°C in a tube furnace for several hours, these materials can demonstrate exceptional electrocatalytic properties. Specifically, exhibiting an overpotential of 134 mV in an acid medium and 116 mV in an alkaline medium. In comparison, W_2C nanoparticles require an overpotential of 173 mV in an acidic medium and 130 mV in an alkaline medium. The experimental findings demonstrate that W_2C and Mo_2C nanoparticles, which possess high- and low-pH activity, respectively, exhibit significant efficacy as electrocatalysts in the process of hydrogen synthesis through water electrolysis, specifically in facilitating the hydrogen evolution reaction (HER) [20]. Figure 1(a) below depicts the method employed by Hussain et al., to produce the potential electrocatalyst for water splitting.

In another study by Lui and co-researchers, MoC-Mo_2C hetero-nanowires were created by accurately forming nanoparticles by controlled carbonisation. The hetero-nanowires exhibited significant efficacy in HER, displaying rapid kinetic characteristics and exceptional durability in both basic and acidic electrolyte conditions. A composition containing 31.4 wt% MoC. was found to be the one that demonstrated the highest level of efficiency. The composition exhibited a minimal overpotential of 120 mV, enabling the attainment of a 10 mA cm^{-2} current density. Additionally, it displayed a narrow Tafel slope with 42 mV dec^{-1} and a low onset overpotential of 33 mV in a 1.0 M KOH solution [21]. Yu et al. fabricated a catalyst consisting of porous carbon-supported Ni/Mo_2C. This was achieved by subjecting nickel molybdate 60 nanorods coated with polydopamine to thermal treatment. The current research presents the efficacy of the composite catalyst in facilitating the catalytic activity of both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) in an alkaline medium. Significantly, the material demonstrates advantageous kinetic characteristics, including a low onset potential of 60 mV for HER and 270 mV for OER, in addition to minimal overpotentials (η) of 179 mV for HER and 368 mV for OER, enabling the achievement of a current density of 10 mA cm^{-2}. The exceptional catalytic activity is attributed to the synergistic interaction between Mo_2C and Ni nanoparticles, as well as their robust chemical bonding with highly conductive carbon. The utilisation of a bifunctional catalyst, specifically Ni/Mo_2C -PC, in the alkaline electrolyser, has been found to provide a current density of 10 mA cm^{-2} at a low cell voltage of 1.66 V. Furthermore, this catalyst has demonstrated reliable and consistent performance [22].

Meanwhile, Kim et al. successfully synthesised Mo_2C/rGO, as depicted in Figure 1(b). Notably, this electrocatalyst demonstrated a significantly higher capacitance-normalised current density in comparison to the other electrocatalysts utilised in the experiment. According to calculations using density functional theory, it has been determined that the distinctive reactivity of Mo_2C can be ascribed to the structure-dependent binding energies of hydrogen atoms. Specifically, it has been observed that hydrogen atoms exhibit weaker binding on the stepped surface of Mo_2C compared to the flat surface [23]. The carbothermal hydrogen reduction method circumvents the utilisation of carbon-containing gases, Hence, this process resulted in a reduction of the amount of carbon in the surface polymer of the TMCs, as compared to the carburisation method including carbon-containing gases. Nevertheless, it is crucial to acknowledge that despite the advancements achieved in the reaction, the emission of carbon species persists, leading to an inevitable contamination of the product's surface to a certain degree with polymeric carbon.

Chemical vapor deposition (CVD)

Chemical vapour deposition (CVD) is a widely employed technique for the fabrication of solid films characterised by their exceptional quality, conformality, uniformity, and precise thickness. In CVD, a reactive gas or vapour is deposited onto the substrate, where it undergoes a chemical reaction on the surface to form a solid film. The basic mechanism of CVD involves the reaction of a gas-phase reactant with a solid surface at a high temperature, typically between 500 and 1200 °C [24,25]. The gas-phase reactant is transported to the surface by diffusion and then undergoes a chemical reaction on the surface to form a solid product [26]. Then, the solid product is deposited onto the surface, resulting in the creation and growth of a thin layer of film. Ultimately, the targeted metal carbide films or nanostructures are acquired by carefully regulating the parameters of temperature, pressure, flow rate, and duration. CVD is used extensively in microelectronics, optics, and material science applications. Zhao et al. have devised a technique for the synthesis of molybdenum carbides through the application of microwave plasma treatment involving hydrogen and methane gases They utilised a microwave-plasma chemical vapor deposition system (MPCVD) for this purpose. The direct synthesis of two-dimensional α -Mo_2C was achieved by utilising a plate-to-plate substrate holder structure, by employing a partial pressure of 20 kPa and microwave energy of 920W [27]. Furthermore, the production of α-Mo2C can be achieved through the utilisation of a CVD approach, whereby methane is employed as the carbon precursor. This procedure involves placing a copper (Cu) foil on top of a molybdenum (Mo) foil, which serves as the substrate. The temperature required for this manufacturing process is set above 1085°C. The nanocrystals have a significant thickness of 100m and have been documented to possess stability under ambient circumstances. The nucleation density can be readily adjusted by manipulating the experimental parameters, such as temperature, where an elevation in temperature results in a corresponding increase in nucleation density. Similarly, the lateral size of the nucleation can be increased by extending the duration of the experiment [28]. Zhang et al. effectively synthesised a composite material composed of WC-nitrogen-doped carbon in a recent work. The hybrid M-

N-C material was created via the impregnation and subsequent pyrolysis of a solution including ammonium meta tungstate (AMT), melamine and carbon precursor. The combination consists of hydrated forms of $Fe(NO_3)_3$, $Co(NO_3)_2$, and $Fe(NO_3)_3$. The resorcinol-formaldehyde resin, which was utilised in the polycondensation polymerisation process, served as the carbon source in this investigation and silica was employed as the hard material for the template. Initially, a solution was formulated by AMT, melamine and a fixed quantity of silica iron nitrate and cobalt nitrate in distilled water.

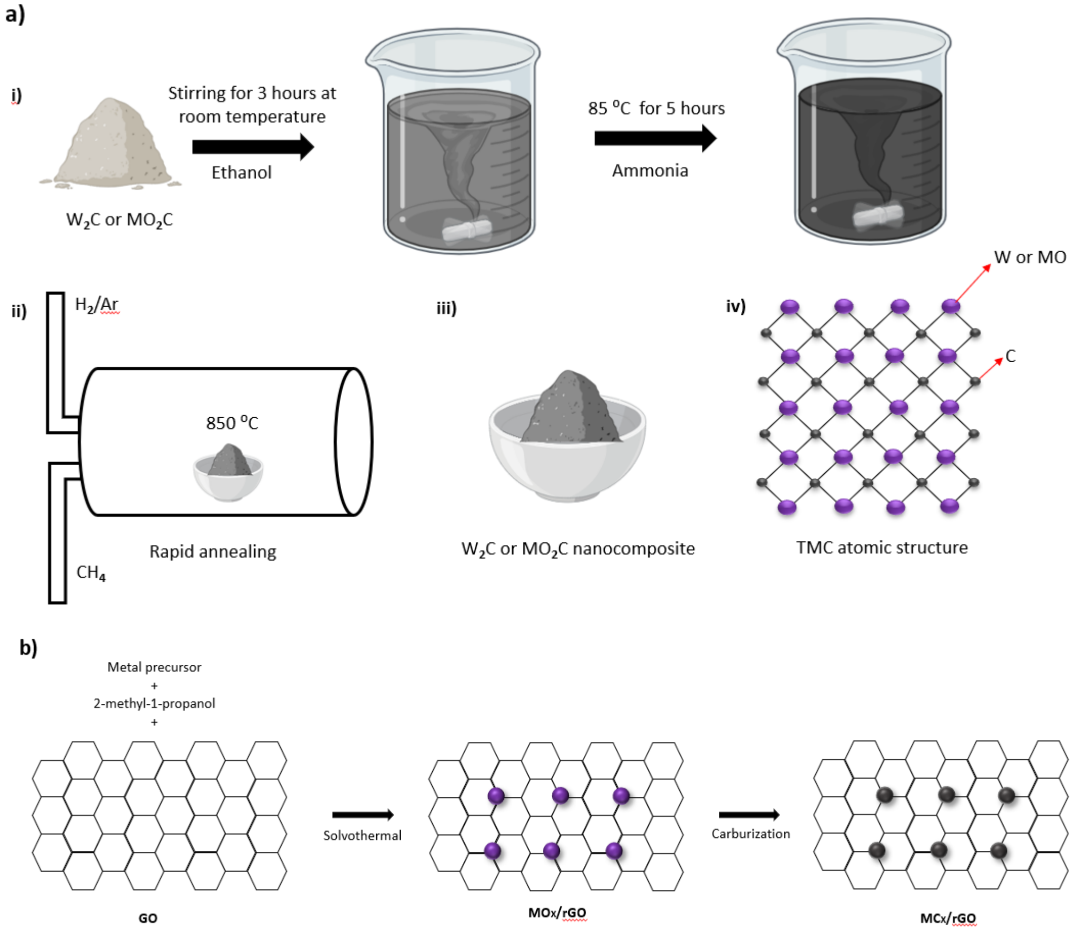


Figure 1. a) (i) Schematic illustration the material chemically reduction, (ii) thermal annealing using tube furnace, (iii) prepared powder, (iv) atomic structure of MO_2C and W_2C nanoparticles. b) Schematic illustration of synthesis method of TMC/rGO nanomaterial. GO, rGO, TMC denoted graphene oxide, reduced graphene oxide and transition metal carbide, respectively.

Subsequently, a total of 0.550 grams of resorcinol and 0.95 ml of formaldehyde, which had been diluted to a concentration of 37% in water, were vigorously mixed into the aqueous mixture. Following the completion of the reaction, the liquid was subsequently transferred into a beaker and subjected to heating at a temperature of 85°C for three hours. Following the reaction, the solution mixture was subjected to a temperature of 80°C for a prolonged duration to aid in the vaporisation process of the solvent. Afterwards, the material obtained was exposed to calcination at temperatures varying between 700°C and 900°C for three hours. The silica particles were eliminated from the produced composites using an initial rinse process at a temperature of 120°C for 3 hours, using a solution of 30 mmol/L of 1 M KOH. Subsequently, the composites were subjected to a rinse procedure utilising distilled water until the solution achieved a pH level that was neither acidic nor alkaline. After undergoing a single overnight curing in a vacuum oven, the end product was designated as Fe/Co/WC@NC [29]. Ko et al. successfully produced a hybrid material consisting of WC nanoparticles integrated with a nano wall structure. The fabrication process involved the use of a tungsten cathode that underwent surface carburisation, followed by direct current plasma-assisted chemical vapour deposition (DC-PACD) to create a tungsten carbide nano walls layer. This film was deposited onto a silicon wafer coated with nanocrystalline diamond (NCD). The construction of WC nano walls normally follows this established procedure. The substrate had exposure to hydrogen plasma within the chemical vapour deposition (CVD) chamber. The volumetric flow rate of hydrogen gas through the chamber was measured to be 150 SCCM, while the pressure within the chamber was recorded as 100 Torr [30].

Next, Fan et al., utilised the chemical vapour deposition (CVD) method to synthesise molybdenum carbide-graphene nanoribbons (Mo_2C-GNR). The researchers prepared molybdenum carbide by applying a layer of metallic Mo, approximately 75 nm in thickness, onto graphene nanoribbons (Figure 2 (a)). This was done through atomic hydrogen treatment at a temperature of 850°C [31]. In their study, Huang et al., grew Mo_2C nanoparticles uniformly on carbon fibre paper, known as Mo_2C/CF. The synthesis time can be reduced to just 10 seconds by using graphene powder to cover the surface, which acts as a self-heating high-temperature reactor during microwave irradiation CVD as depicted in Figure 2(b). The Mo_2C/CF electrode showed superior catalytic performance for the HER compared to commercial Pt foil in alkaline conditions, specifically at applied potentials below -0.2 V (vs RHE) [32]. The chemical vapour deposition method offers several advantages, including the production of high-purity products with consistent structural properties. However, it is crucial to note that this technique requires a high vacuum environment, which can be costly and limit scalability [27]. Table 1 shows the summary of the synthesised catalyst TMC using the highlighted method for hydrogen evolution reaction.

Sol-gel

The sol-gel method involves the formation of a metal-organic gel that is subsequently heated to form TMCs. The starting materials are metal alkoxides, which are hydrolysed and polycondensed to form a gel. The gel is then heated at high temperatures to form TMCs. One of the advantages of sol-gel chemistry is its relative simplicity, which applies to both the precursors used and the processing techniques employed [33]. Typically, the sol-gel method is employed to synthesise Fe_3N or Fe_3C nanoparticles by combining aqueous iron salts (such as nitrate and acetate) with organic compounds like urea or gelatine, along with melamine and CTAB [34,35]. The resulting gel subsequently undergoes a drying process and then pyrolysed under an inert atmosphere, resulting in the formation of nanoparticles of the desired product. Although sol-gel chemistry is a basic and expandable method, it presents challenges in attaining substantial regulation of particle size. Obtaining pure carbide phases is a challenging task due to the inherent difficulties in isolation [35]. Additionally, slight variations in experimental parameters can significantly impact the resulting product composition.

Zhao et al. prepared metallic cobalt molybdenum carbide@graphtitic carbon through the -sol-gel method where the precursors were mixed with ethylene glycol and citric acid to fabricate the product. Later, the solution undergoes rotary evaporation to obtain the gel as illustrated in Figure 3. The nanomaterials CoMo(0.5:0.5)-800@GC demonstrate the enhanced performance of catalytic for HER as evidenced by their ability to achieve a current density of 10 mA cm^{-2} with the lowest overpotential of approximately 165 mV in 0.1 M KOH solution [36]. Another form of synthesis using the sol-gel method by Simonenko et al. uses silicon carbide (SiC) as the precursor with the use of silicon alkoxides (TEOS) as sol-gel approaches. The TEOS hydrolysis was conducted in a solution of phenolic resin, catalysed by either hydrochloric acid or sodium hydroxide. Subsequently, the resulting mixture underwent a carbonisation procedure at a temperature of 700°C [37].

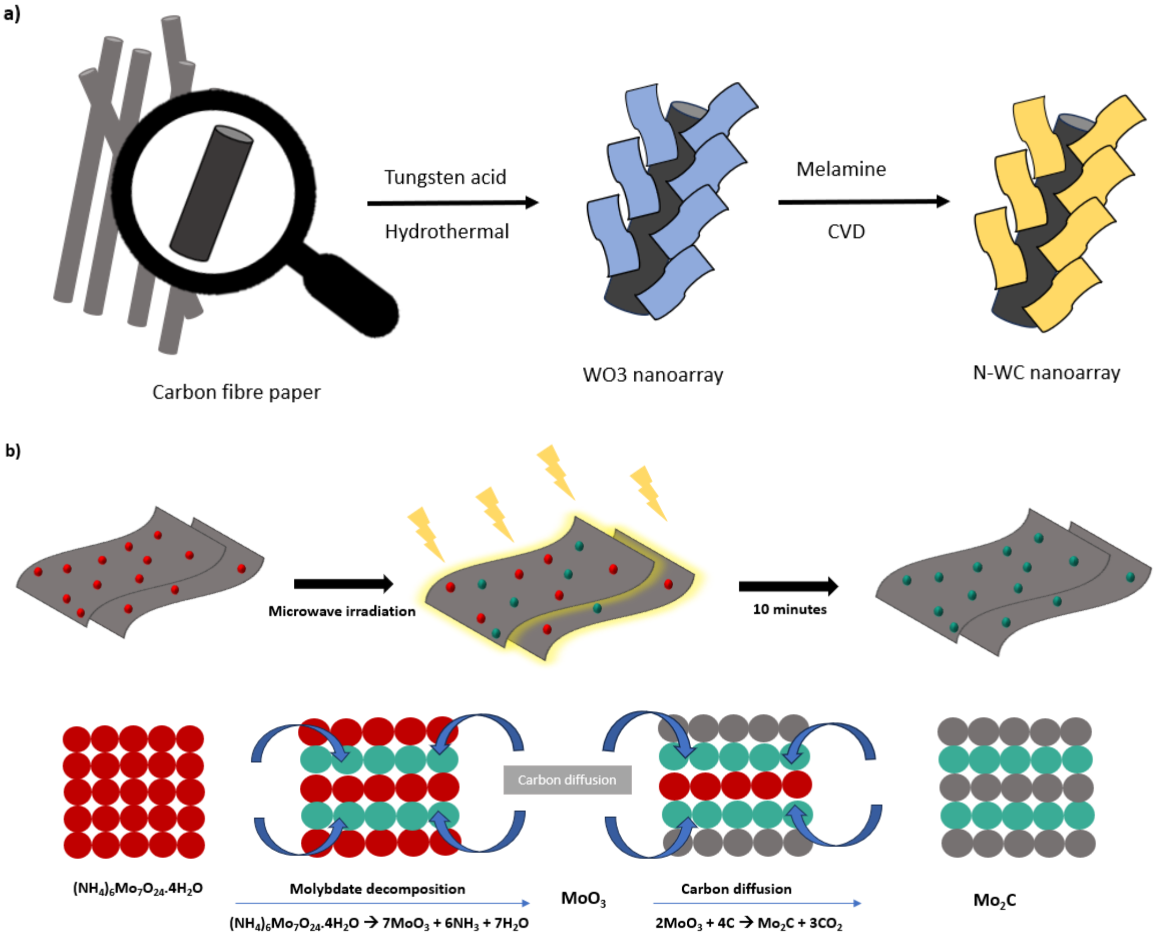


Figure 2. Scheme illustration of the fabrication of (a) molybdenum carbide-graphene nanoribbons (Mo_2C-GNR) (b) Mo_2C/CF [31, 32]

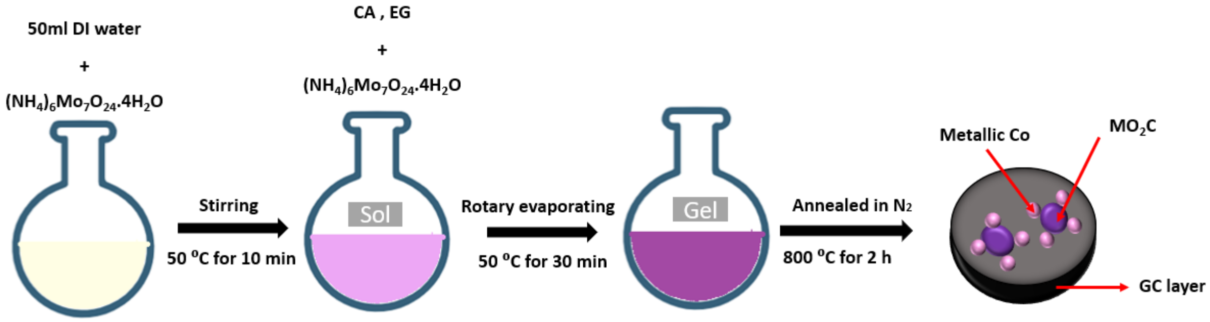


Figure 3. Schematic illustration of the synthesis of CoMo (0.5:0.5)- 800@GC [36]

Table 1. Summary of TMCs catalyst using different methods for water splitting.

Catalyst	Method	Tafel slope (mV dec^{-1})	Over potential (mV)	Current density (mA/cm^2)	Electrolyte	Ref.
MO_2C/C-900	Carbothermal	52	-	10	0.5M H_2SO_4	[19]
Mo_2C/NC	Carbothermal	104	-	10	0.5M H_2SO_4	[38]
α-Mo_2C	CVD	68	-	10	0.5M H_2SO_4	[38]
CoMo(0.5:0.5) - 800@GC	Sol-gel	-	165	10	0.1 M KOH	[39]
Mo_2C	Carbothermal	83	134	10	0.5M H_2SO_4	[20]
Mo_2C-GNR	CVD	65	39	10	0.5M H_2SO_4	[31]
Mo_2C-GNR	CVD	54	53	10	0.1 M KOH	[31]
Mo_2C/CF	CVD	80	166	10	0.5M H_2SO_4	[32]
Ni/MO_2C-PC	Carbothermal	-	179	10	1.0 M KOH	[22]
N-WC nanoarray	CVD	75	89	10	0.5M H_2SO_4	[40]
$Ti_3C_2T_x$	Carbothermal	222	-	10	0.5M H_2SO_4	[41]
$NiSe_2/Ti_3C_2T_x$	Carbothermal	37.7	200	10	0.5M H_2SO_4	[41]
Mo_2C/N-C	Carbothermal	58	189	10	1.0M KOH	[42]
Mo_2C@MCS	Carbothermal	51	134	10	1.0M KOH	[43]

Electrocatalytic Performance of Transition Metal Carbides (TMCs) in Hydrogen Evolution Reaction

Numerous research has been conducted to investigate the electrocatalytic efficiency of transition metal carbides in HER activity. The remarkable effects observed can be attributed to the strong intrinsic behaviour, low cost, and exceptional stability exhibited by these materials molybdenum carbide (Mo_2C), tungsten carbide (WC), and titanium carbide (TiC) have been found to have low overpotential values, which suggests that they require less energy to catalyse HER than other types of transition metals. TMCs have been observed to exhibit a low Tafel slope, which is a measure of the pace of electrode reaction. This shows that they are effective HER catalysts that can speed up the reaction. In addition, the exchange current density, which has been reported to be high for transition metal carbides, serves as an indicator of the rate of electron transport between the electrode and the electrolyte. This indicates that these materials can transmit electrons effectively, which is essential for HER. The overall electrocatalytic performance of transition metal carbides in HER has shown excellent catalytic activity making them a potential class of materials for applications in renewable energy.

Tafel slope and exchange current density

The relationship between the current density (i) and the overpotential (η) of the water-splitting process is described by the Butler-Volmer equation, represented as Equation (1).

$$j=j0[\exp(\alpha AnF/RT\times \eta) - \exp(-\alpha CnF/RT \times \eta)] \qquad (1)$$

The symbol j0 is frequently used to indicate the exchange current density, whereas the variable T denotes the temperature expressed in units of Kelvin. The value n denotes the quantity of electrons participating in the electrode reaction. The Faraday constant is commonly represented by the symbol F, while the gas constant is typically denoted by the symbol R. The electron transfer coefficient associated with the anode reaction is denoted as A, whereas the electron transfer coefficient associated with the cathode reaction is denoted as C. It is important to note that the sum of A and C is equal to 1. With the Butler-Volmer equation, both the anode and cathode processes are taken into consideration simultaneously. When the electrode experiences a higher overpotential and only when the cathode reaction is taken into account, the rate of the anode reaction is insignificant and can be disregarded. Its equation can then be reformulated as the Tafel equation, denoted as Equation (2):

$$\ln(j)=\ln(j0)+(\alpha nF/RT)\times\eta \tag{2}$$

The determination of the relationship between current density and overpotential can be achieved by simplifying the preceding equation, denoted as Equation (3).

$$\eta = a + b \ln(j) \tag{3}$$

If $a=2.303RT/nF \ln(j0)$, then $b=2.303RT/nF$.

The equation illustrates the linear correlation between the overpotential and the logarithm of the current density. The parameter "b" denotes the Tafel slope, which is analogous to the gradient of the equation. The variable "a" denotes the intercept in the given context. The Tafel slope is utilised to ascertain the rate-determining phases of a process. Photoelectrochemical tests are commonly conducted to analyse the effectiveness of working electrodes, particularly those engaged in HER and OER. The term "it" denotes the variable representing the slope, a fundamental quantity in this context. This slope is determined by applying the graphical representation of the current density logarithm about the overpotential. Tafel slope is a crucial parameter in electrochemical systems analysis due to its substantial significance. It functions as a beneficial tool for assessing reaction kinetics and enables the measurement of exchange current density, which is a metric used to quantify the reactivity of the electrochemical system. When a reaction is at its equilibrium potential, the current density is referred to as the exchange current density, which is indicated by the symbol j0 when the current densities at the cathode and the anode are equal [44,45]. It is important to note that the exchange current density is a crucial factor in determining the intrinsic function of the catalytic process when equilibrium circumstances are present [46]. The determination of the value of j0 is frequently performed by extrapolating the linear portion of the Tafel plot to the point when the equilibrium potential is reached, specifically when it equalszero.

Overpotential

The term "overpotential" (η) refers to the excess potential that is required, beyond the thermodynamic requirement, to attain a specific current density or activity in a half-cell process. The calculation of overpotential involves the subtraction of the applied potential (E_{app}) from the thermodynamic potential, which is also referred to as the equilibrium potential, for the catalysed half-reaction. In the context of oxidation reactions, it is customary to interchange the two words, resulting in the subtraction of the standard reduction potential (EA/B) from the apparent potential (E_{app}) [47,48].

$$\eta= E_{A/B} - E_{app} \tag{4}$$

The assessment of electrocatalytic performance in HER heavily relies on the crucial parameter known as overpotential. The term "overpotential" refers to the discrepancy between the applied voltage and the thermodynamic potential necessary for the conversion of protons to hydrogen. The assessment of a catalyst's activity can be inferred from the overpotential value seen at a specific current density. A lower overpotential value corresponds to a higher level of electrocatalytic performance exhibited by the catalyst. Typically, three overpotentials, denoted as η1, η10, and η100, are utilised at current densities of 1, 10, and 100 mA cm^{-2}, respectively, in order to conduct an assessment and evaluation of the electrocatalytic activity of several catalysts [48]. The parameter η1 is widely acknowledged as the point at which the reaction begins, generally referred to as the onset overpotential. A current density of 10 mA cm^{-2} is employed as a benchmark to establish the parity of a 12.3% efficiency in the process of photoelectrochemical water separation. As a result, the parameter η10 is frequently employed to assess the catalytic efficacy of diverse catalysts. Nevertheless, it is important to note that the parameter η10 should not be regarded as the sole criterion for evaluating activity, as it exerts a substantial influence on the load mass, even in cases when the geometric area remains consistent. Furthermore, in real-world scenarios, it is necessary to achieve a larger current density, rendering the η10 unsuitable as a benchmark. Therefore, the η100 is suggested for evaluating practical applications.

The greatest hindrance to the effective implementation of water splitting is the sluggish reaction rate exhibited by the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), which are characterised by high overpotentials indicating significant kinetic energy barriers. The importance of catalysts in both HER and OER cannot be overstated. To enhance the efficiency of hydrogen and oxygen generation through OER and HER, it is imperative to employ catalysts that exhibit minimal overpotentials. Transition metal carbides have been reported to have low overpotential values for the HER. An illustrative instance may be found in a recent investigation conducted by Zhang et al. in which it was observed that the overpotential value of single-layer molybdenum carbide (Mo_2C) stood at a mere 0.17 V when subjected to a current density of 10 mA cm^{-2}. This value is notably lower than that of numerous other catalysts employed for the hydrogen evolution reaction (HER) [17]. In a similar vein, it has been documented that tungsten carbide (WC) and titanium carbide (TiC) exhibit notable reductions in overpotential values when utilised in HER. In a study conducted by Yin et al. it was observed that the overpotential for WC was measured to be 0.21 V when a current density of 10 mA cm^{-2} was applied [49] Similarly, Yuan et al. stated that TiC attained an overpotential value of 0.24 V with the same current density of 10 mA cm^{-2} [43]. The results of this study indicated that transition metal carbides exhibited potential as catalysts for HER, displaying low overpotential values. This characteristic is significant as it contributes to the reduction of energy utilisation during hydrogen production.

Faradic efficiency

The concept of faradic efficiency also called coulombic efficiency applies to the proportion of electrons utilised in a particular electrochemical process compared to the overall quantity of electrons that were available for the process [50]. Regarding the hydrogen evolution reaction (HER), the faradaic efficiency refers to the proportion of electrons utilised in the generation of hydrogen gas via water. Several factors can influence the faradic efficiency of HER, including the type of electrode material, pH level, temperature, and the existence of impurities within the electrolyte. A higher faradic efficiency is preferable as it signifies that a greater proportion of the accessible electrons are being employed for the generation of hydrogen gas, thereby enhancing the efficiency and cost-effectiveness of the process. According to a study published in the journal ACS Energy Letters, a high faradic efficiency of up to 97% was achieved for HER using a nickel carbide catalyst on a carbon cloth electrode in an alkaline electrolyte. The study also found that the faradic efficiency was dependent on the pH of the electrolyte, with the highest efficiency being achieved at an alkaline pH of 13. This demonstrates that the selection of appropriate catalysts and optimisation of the reaction conditions can greatly improve the faradic efficiency of HER.

Durability

The durability and electrocatalytic performance of TMCs in HER is an area of significant interest due to the potential of these materials to serve as cost-effective alternatives to noble metal catalysts. Long-term stability is a critical factor, influenced by the intrinsic properties of TMCs, the operating conditions, and their interaction with electrolytes. For instance, molybdenum carbide (Mo_2C) and tungsten carbide (WC) have shown considerable stability under acidic and alkaline conditions, respectively, due to their robust crystal structures [51]. Mo_2C has been noted for its stability in acidic media, maintaining catalytic performance over extended periods despite potential challenges such as surface oxidation at high potentials, which can lead to the formation of MoOx species that may reduce catalytic efficiency [52,53]. The interaction between the TMC surface and the electrolyte is crucial in determining the material’s long-term stability. In particular, the stability of TMCs in harsh acidic environments, such as 0.5 M H_2SO_4, is often a benchmark for their durability in HER [54]. Some studies have shown that TMCs can maintain their catalytic performance over extended periods in acidic environments, with minimal degradation. However, the formation of passive layers, such as oxides, during prolonged operation can impact their effectiveness.

In addition, cycling stability is critical for evaluating the practical applicability of TMCs in HER. Studies have shown that TMCs like Mo_2C and WC can retain a significant portion of their initial catalytic activity even after extensive electrochemical cycling [55]. For example, Mo_2C has demonstrated over 90% retention of its initial activity after 1000 HER cycles in acidic media, underscoring its potential as a durable HER catalyst [56]. Table 2 highlights the durability of TMCs in water splitting. The structural integrity of TMCs during cycling is essential for maintaining long-term performance, and this is often enhanced by incorporating TMCs into carbon-based supports or using nanostructured forms of TMCs to provide additional stability and prevent the collapse of active material. The inclusion of stabilising agents or co-catalysts, such as platinum or ruthenium, can further enhance cycling stability by facilitating efficient hydrogen evolution and preventing degradation of the TMC structure [57]. Hence, the durability of TMCs in HER is influenced by multiple factors and addressing these factors through various strategies and understanding their underlying mechanisms are crucial for the development of effective and durable TMC-based catalysts for hydrogen production.

Table 2. Durability of TMCs catalyst in Hydrogen Evolution Reaction (HER)

Catalyst	**Electrolyte**	**Number of Cycles**	**Retention (%)**	**Stability Test Duration (hrs)**	**Remarks**	**Ref.**
Mo_2C/Ni	0.5M H_2SO_4	10000	90	24	Maintain remarkable stability	[58]
TiC	0.5M H_2SO_4	2000	93	12	Minor catalyst poisoning	[59]
WC	1.0 M KOH	1000	90	36	Good mechanical stability	[60]
NbC/Nitrogen doped graphene	1.0 M KOH	5000	90	48	Minor catalyst oxidation	[61]

Mechanistic Insights into the HER Catalysis by Transition Metal Carbides (TMCs)

Mechanistic of hydrogen evolution reaction

The electrochemical process of water splitting often occurs within an electrolyser, which consists of a cathode and an anode. These elements support the oxidation and reduction processes of water. Charges and ions are transferred between the electrodes via the reactions, which take place in suitable electrolytes. In order to induce acidic and alkaline environments, potassium hydroxide and sulphuric acid are commonly employed as electrolytes, respectively. The anode separation of water into oxygen and hydrogen occurs via the electrochemical process of water splitting when the electrodes are supplied with an appropriate voltage. This reaction is represented as follows:

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (5)$$

The entire reaction comprises two half-reactions, namely the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), as depicted in Figure 4. HER proceeds via the Volmer-Herovsky, and Tafel mechanisms, resulting in the production of hydrogen gas [62] [63]. Within an acidic solution, the initial stage entails the interaction between a proton and an electron, leading to the creation of an adsorbed hydrogen atom (H*) on the surface of the electrode. The approach is generally known as the Volmer step. Subsequently, the subsequent stage in the process involves the Heyrovsky step which is also referred to as the electrochemical desorption step or the Tafel step. The Heyrovsky step comprises the reaction of an adsorbed hydrogen atom (H*) with a hydrogen ion (H^+) and an electron, resulting in the formation of a hydrogen molecule. In contrast, during the Tafel step, two hydrogen atoms that are adsorbed (H*) undergo a reaction with one another, leading to the production of hydrogen gas.

The mechanism in alkaline solution differs from that in acidic solution due to the absence of hydrogen ions (H^+) in the former. The HER initiates with the dissociation of water (H_2O) molecules, resulting in the release of protons. These protons participate in the Heyrovsky step and Volmer step of the reaction. The Tafel step in alkaline solutions is similar to the one observed in acid solutions. The phenomenon of water dissociation during a chemical reaction creates an additional energy barrier, leading to greater overpotentials under alkaline conditions compared to acidic conditions. The HER route is depicted as follows:

In acidic electrolyte:

Overall reaction:

$2H^+ + 2e- \rightarrow H_2$ (6)

Reaction pathway:

$H^+ + e- + * \rightarrow H^*$ (Volmer reaction) (7)

$H^+ + e- + H^* \rightarrow H_2$ (Heyrovsky reaction) (8)

$2H^* \rightarrow H_2$ (Tafel reaction) (9)

In alkaline electrolyte:

Overall reaction:

$2H_2O + 2e- \rightarrow H_2 + 2OH-$ (10)

Reaction pathway:

$H_2O + e- \rightarrow H^* + OH-$ (Volmer reaction) (11)

$H_2O + e- + H^* \rightarrow H_2 + OH-$ (Heyrovsky reaction) (12)

$2H^* \rightarrow H_2$ (Tafel reaction) (13)

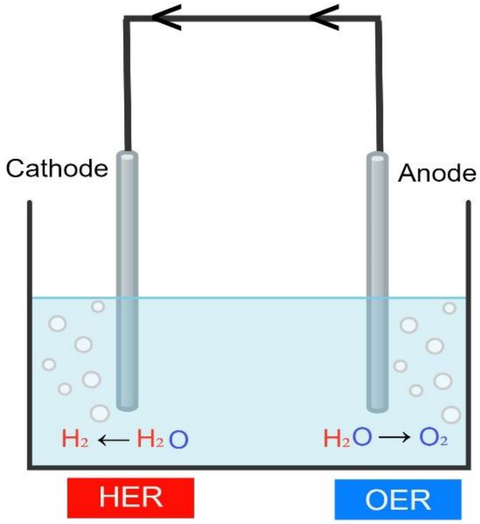


Figure 4. Schematic diagram of an electrochemical hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)

The process of HER involves the direct adsorption of hydrogen molecules onto the electrode surface. As soon as gas molecules adhere to the electrode surface, followed by their dissociation into hydrogen atoms, which then participate in the subsequent electrochemical reactions to produce hydrogen gas. Figure 5 illustrates the detailed mechanism of the proposed model as developed by TMC, highlighting the key processes and interactions involved.

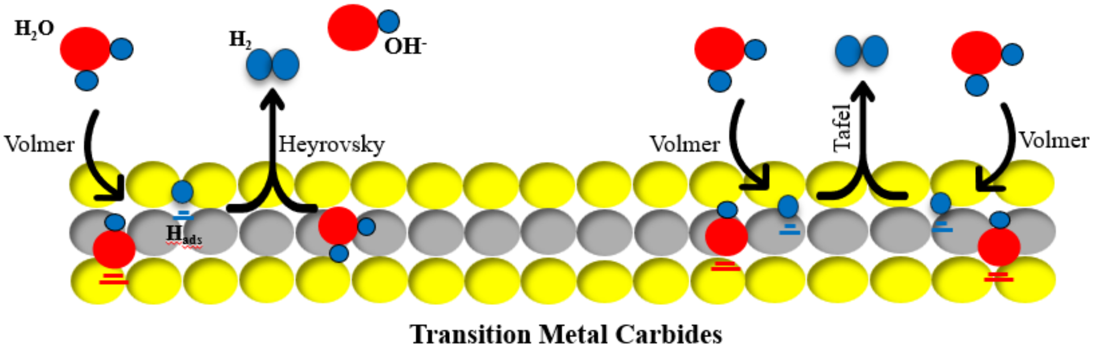


Figure 5. HER mechanism reaction by Transition Metal Carbides (TMCs)

Proposed reaction mechanism of transition metal carbides

The process of carbothermal synthesis of metal carbides entails the direct conversion of metal into carbides through carburisation, which is achieved by subjecting the metal to high temperatures in the presence of a carbon source [64]. Typically, the process of incorporating carbon into metal structures from a variety of carbon sources has been carried out under conditions of high temperature, specifically beyond 600 °C. Equations 14 and 15 represent the overall reaction that takes place throughout the diffusion process of carbon from the carbon source into the metal framework.

$$M_{(s)} + C_{(s)} \rightarrow MC_{x(s)} \quad (14)$$

$$M_{(s)} + C_mH_{n(g)} \rightarrow MC_{x(s)} + H_{2(g)} \quad (15)$$

The utilisation of a gaseous carbon source in carburisation has several notable benefits. Firstly, it allows for carburisation to occur at relatively low temperatures, specifically at or above 750 °C. Additionally, this method surpasses carburisation with a solid-phase carbon source by generating well-defined composites that exhibit stability and reproducibility [34]. Metal carbides can be tailored in terms of their dimensions and properties by employing a precisely defined carbon source, such as graphene. Furthermore, it should be noted that graphene was utilised as a growth substrate [64].

In their study, Fan et al. detailed the process used to create a hybrid electrocatalyst free of precious metals. The catalyst is composed of Mo_2C nanocrystals that are supported on vertically aligned graphene nanoribbons (VAGNRs). The researchers demonstrate that this synthesised catalyst exhibited exceptional activity and stability. The synthesis of VA-GNR-supported-Mo_2C (Mo_2CGNR) involved the direct application of atomic hydrogen treatment on metallic molybdenum with a carbon source, by employing the hot filament chemical vapour deposition (HFCVD) method [31]. The presented reaction mechanism is depicted in the following manner:

$$H_2 \rightarrow H^* \quad (16)$$

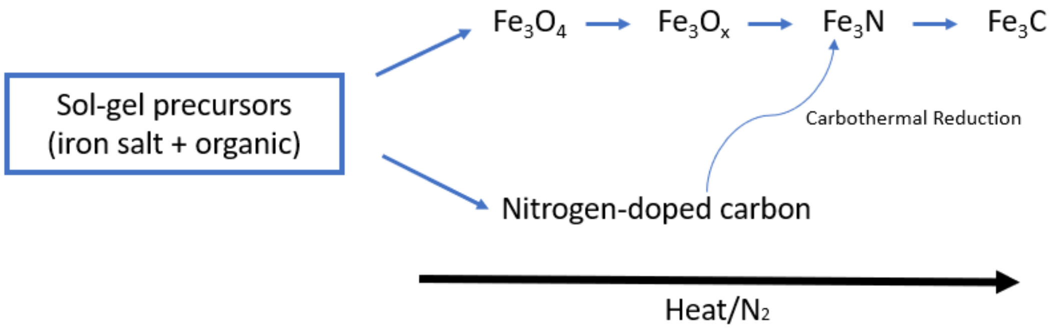
$$CH_4 \rightarrow C + H \quad (17)$$

$$MoO_3 + H^* \rightarrow Mo + H_2O \quad (18)$$

$$Mo + C^* \xrightarrow[H^*]{} Mo_2C \quad (19)$$

Equations 16-19 elucidate the mechanisms behind the interaction between Mo_2C and atomic hydrogen, facilitated through the employment of the HF-CVD technique. The HF-CVD system produces activated gas compositions comprising atomic hydrogen (H*, as described in Equation 16) and carbon-containing species (as described in Equation 17) at a filament temperature higher than 2000 °C. In equation 18, the conversion of MoO_3 to metallic Mo is facilitated by the presence of hydrogen gas (H*). At elevated temperatures, the resulting C* exhibits significant reactivity, leading to a direct reaction with metallic Mo and subsequent formation of Mo_2C (as shown in Equation 19). The process by which MoO_3 is transformed into Mo_2C involves the substitution of oxygen with carbon inside the MoO_3 structure while ensuring minimum displacement of the Mo atoms [65]. Nevertheless, it is important to mention that during the HF-CVD process, the system's heat is considerably greater than the heat range in which MoO3 is susceptible to instability, leading to its breakdown into MoO_2 and subsequent decomposition of MoO_2 into Mo metal [66]. Consequently, the formation of Mo_2C nanocrystals takes place by directly converting Mo metal into Mo2C through carburization, without the formation of intermediary compounds such as MoO_2.

Thus, the main chemical pathway involves the reduction of MoO_3 to Mo using hydrogen, driven by the incorporation of carbon at elevated temperatures. The addition of the heated filament stage in the synthesis procedure is essential for the formation of Mo_2C nanocrystals. The process not only facilitates the production of active carbon, which then diffuses into the surface of Mo and undergoes a reaction with Mo, but it also generates an excessive amount of atomic hydrogen. The atomic hydrogen initiates the activation of the Mo surface by chemically reducing MoO_3 and facilitates the process of crystallizing Mo_2C [31]. Furthermore, iron carbide (Fe_3C), similar to other metal carbides, is a readily available catalyst that exhibits stability in both acidic and alkaline environments, displaying catalytic properties comparable to platinum (Pt). Chamber et al. have proposed a reaction mechanism for iron carbide utilising a sol-gel chemistry reaction, as depicted in Scheme 1 below. The hypothesis stated that the transition from Fe_3N to Fe_3C took place through the process of carbon diffusion into the nitride, resulting in the formation of a carbonitride intermediate. This hypothesis was formulated based on the observed peak shift in the Fe_3N phase. The synthesis was conducted using the sol-gel method, whereby gelatine was employed as the precursor along with aqueous iron nitrate [35].



Scheme 1. Proposed Reaction mechanism for Fe_3C formation. [35]

Key Factors Influencing Mechanism of HER by Transition Metal Carbides (TMCs)

Electronic structure of TMCs

The catalytic performance of TMCs for HER is significantly influenced by their electrical structure [67]. The d-band centre theory is extensively employed to comprehend the correlation between the electronic configuration of transition metal carbides (TMCs) and their catalytic performance [68]. Based on this theoretical framework, the adsorption strength of hydrogen intermediates on the catalyst's surface is influenced by the d-band centre of the transition metal in the TMC [69]. Ensuring an ideal equilibrium between the adsorption and desorption of hydrogen is essential for an effective hydrogen evolution reaction (HER). Transition metal carbides (TMCs) with d-band centres positioned nearer to the Fermi level demonstrate improved hydrogen adsorption, thereby enhancing reaction kinetics at the active sites [69,70]. Notably, TMCs such as molybdenum carbide (Mo_2C) and tungsten carbide (WC) possess favourable electronic configurations that enhance the activity of the hydrogen evolution reaction. Research conducted by Liu et al. showed that the electrical characteristics of Mo_2C enabled it to outperform conventional metal catalysts in hydrogen evolution reaction (HER) by reducing the reaction overpotential [21]. The inherent conductivity of TMCs further enhances their catalytic effectiveness by facilitating electron transfer during the hydrogen evolution reaction process.

The benefit renders TMCs a viable substitute for costly and limited noble metal catalysts such as platinum. Moreover, the capacity to alter the electrical configuration of transition metal catalysts (TMCs) by doping or alloying has created novel opportunities to adjust their catalytic performance [68]. Doping transition metal carbides (TMCs) with nitrogen, sulphur, or boron can modify the d-band centre, therefore enhancing the catalyst's interaction with hydrogen intermediates [71]. The previously mentioned alterations are essential for optimising the performance of the HER. Recent research by He et al. had demonstrated that nitrogen-doped TMCs have increased hydrogen evolution reaction (HER) activity as a result of higher charge distribution and electron density at the catalytic sites [72]. In general, the electrical configuration of TMCs plays a crucial role in determining their efficiency in the hydrogen evolution reaction (HER). Through precise manipulation and optimisation of the d-band centre, scientists can greatly improve the efficiency of electrocatalysts based on TMC. The capacity to precisely adjust electronic characteristics by alteration of composition and structural design emphasises the potential of TMCs in hybrid electrochemical HER applications.

Surface properties and catalytic active sites

The surface characteristics of transition metal carbides (TMCs), such as surface roughness, shape, and the existence of visible active sites, play a crucial role in determining the performance of hydrogen evolution reaction (HER). TMCs are directly proportional to the population of catalytic sites accessible for hydrogen adsorption and reaction, thereby influencing the total reaction rate [55]. Transition metal carbides that have a large surface area and a large number of active sites exhibit enhanced hydrogen evolution reaction (HER) activity because of the heightened contact between the catalyst surface and the reactants [73]. Surface imperfections, step edges, and grain boundaries function as catalytic active sites, facilitating the adsorption and dissociation of hydrogen intermediates [74]. The catalytic efficiency of transition metal carbides (TMCs) can be improved by manipulating their surface characteristics to generate additional defect sites. Yang et al. found that increasing the number of grain boundaries in Mo_2C resulted in improved hydrogen evolution reaction (HER) performance by offering more locations for hydrogen bonding [75].

Furthermore, the formation of nanoporous morphologies on the TMC surface has been shown to greatly enhance the active surface area, hence enhancing the kinetics of the hydrogen evolution reaction (HER). The chemical stability of TMC surfaces in acidic or alkaline conditions is an essential determinant. Transition metal carbides (TMCs) are renowned for their exceptional corrosion resistance, which makes them very appropriate for extended catalytic processes in challenging electrochemical environments. Nevertheless, it is possible to adjust the surface characteristics of TMCs to maximise their chemical stability. Application of surface passivation or coating with protective layers can effectively inhibit the oxidation and deterioration of the catalyst in the hydrogen evolution reaction approach. This guarantees the sustained action of the catalyst throughout prolonged periods of operation. Finally, the surface characteristics of TMCs can be further enhanced by surface changes achieved by functionalisation with heteroatoms or small molecules. Functionalising the surface of TMCs with oxygen or nitrogen can modify the electrical environment surrounding the active sites, thereby enhancing the energy required for hydrogen adsorption. These surface treatments have been shown to improve the hydrogen evolution reaction (HER) activity of transition metal carbides (TMCs) by increasing the concentration of catalytic sites and optimising the surface reactivity.

Temperature

The temperature of the hydrogen evolution reaction (HER) greatly affects the catalytic activity of transition metal carbides (TMCs). Elevated temperatures generally amplify reaction kinetics by supplying more energy to overcome activation barriers, resulting in higher rates of hydrogen evolution reaction (HER) [76].

Elevated temperatures can enhance the hydrogen adsorption and desorption processes in TMCs, which are crucial stages in the HER mechanism. Elevated temperatures drive an accelerated electron transfer rate, therefore augmenting the efficacy of the catalytic process [77]. The impact of temperature on thermomechanical coefficients TMCs has been thoroughly investigated. Research conducted by Ling et al. demonstrated that Mo_2C and WC catalysts display enhanced hydrogen evolution reaction (HER) activity at elevated temperatures [78]. This is attributed to the enhanced mobility of surface atoms, resulting in the exposure of more catalytic active sites. Furthermore, at high temperatures, TMCs retain their structural integrity more effectively than most other catalysts, therefore guaranteeing prolonged stability in electrochemical systems. This is especially crucial for industrial application characterised by potential fluctuations in reaction temperature.

Nevertheless, there exists a maximum threshold for the advantageous impacts of temperature on the performance of HER. At elevated temperatures, some TMCs may undergo structural deterioration or phase changes, therefore adversely affecting their catalytic performance. For instance, Mo_2C undergoes oxidation at temperatures exceeding 500°C, resulting in a decrease in the performance of the hydrogen evolution reaction (HER) [79]. Hence, it is essential to optimise the working temperature in order to maximise the efficiency and longevity of TMC catalysts. Furthermore, the chemical mechanism itself can be influenced by temperature. The Volmer, Heyrovsky, and Tafel stages of the hydrogen evolution reaction (HER) process are all constrained by temperature, and the step that determines the rate may vary depending on the temperature. Specifically, the Volmer step, which entails the process of hydrogen adsorption, is more advantageous at lower temperatures, but the Tafel step (hydrogen desorption) becomes more prominent at higher temperatures [80]. Overall, temperature is a crucial determinant in affecting the HER activity of transition metal carbides (TMCs). Although elevated temperatures can improve the speed of reactions and maximise the accessibility of catalytic sites, caution should be exercised to prevent circumstances that may result in catalyst deterioration.

Applications of Transition Metal Carbides in Hydrogen Evolution Reaction

Electrochemical water splitting

Hydrogen (H_2) production is a potential renewable sustainable energy production method. It is produced industrially through the reforming of natural gas, a process that requires a considerable amount of non-renewable energy and generates carbon dioxide, thereby contributing to environmental degradation. In contrast, electrochemical water splitting exhibits considerable potential as an environmentally friendly and pollutant-free approach to hydrogen generation. This method, which involves separating water into hydrogen (H_2) and oxygen (O_2), has been known for over two centuries. The hydrogen produced can be used in power generation, transportation, and fuel cells, making it a versatile pure fuel. The oxygen can be utilised in industrial processes or released safely into the atmosphere. Large-scale production of H_2 in an economical and environmentally favourable manner must be achieved immediately [81]. Water electrolysis (Figure 4) offers a straightforward, effective, and auspicious mechanism by which the hydrogen evolution reaction can be implemented as a cutting-edge energy conversion technology. Therefore, the development of technologies for electrochemical water separation that are both efficient and economical has been a global scientific priority.

Tungsten carbide (WC) shares similarities with Mo_2C as an acid-stabilised catalyst that exhibits catalytic characteristics comparable to platinum (Pt), while also being abundant and cost-effective. Fe-WCN electrocatalysts were synthesised by Hashimoto et al. wherein the authors proposed that the addition of nitrogen to the catalyst structure decreases the electron density of the tungsten atoms, leading to an increase in catalytic performance for HER [82]. Subsequently, Yang et al. published a study on an electrocatalyst comprising tungsten carbide-nitride and graphene nanosheets. Their findings revealed that the collaborative interaction between the W_2C and WN phases enhances the efficiency of catalysing water-splitting reactions. Nevertheless, the impact cannot be solely ascribed to elevated current densities [83].

In a recent study conducted by Zhao et al., eutectoid-structured WC/W_2C heterostructures were successfully constructed, exhibiting remarkable long-term stability. The weakened H–O–H bond rupture, resulting in an accompanying energy barrier, and the pronounced attraction of tungsten carbide towards OH* intermediates, resulting in the phenomenon of poisoning, are the underlying factors contributing to the limited alkaline reactivity observed in tungsten carbide. The creation of the WC and W_2C phases is a consequence of the regulation of carbon diffusion rates, where high and low diffusion rates correspond to the respective phases. The W_2C phase has a higher concentration of active sites for the hydrogen evolution reaction (HER), whereas the WC phase demonstrates greater stability. The combined influence of W_2C and WC results in an increased catalytic activity of the hydrogen evolution reaction (HER) in alkaline solutions. This enhanced activity is characterised by an exceptionally low onset potential of 17 mV, a relatively small overpotential of 75 mV at a current density of 10 mA cm^{-2}, and a Tafel slope of 59 mV dec^{-1}. During a twenty-day duration, the durability tests demonstrate an absence of noticeable degradation, a characteristic that is more desirable compared to most catalysts derived from tungsten carbide. Leveraging the synergistic effects of heterostructures composed of diverse phases to harness their complementary benefits represents a very successful approach for augmenting electrocatalytic activity.

Table 3. Electrochemical water splitting performance and its hybrid for HER

Catalyst	Overpotential (mV)	Tafel slope (mV/dec)	Current density (mA/cm^2)	Electrolyte	Ref.
W_xC/NG	77.82	45.95	10	0.5M H_2SO_4	[84]
WC/W_2C	75	59	10	0.1 M KOH	[84]
WC/W_2N	148.5	47.4	10	1.0 M KOH	[85]
MoC-Mo_2C	43	38	10	0.5M H_2SO_4	[86]
Mo_2C	46	61	10	0.5M H_2SO_4	[86]
WC_X/C	264	85	10	0.5M H_2SO_4	[87]
N-WCnano array	89	75	10	0.5M H_2SO_4	[40]

Photoelectrochemical water splitting

Moving beyond traditional electrochemical methods, photoelectrochemical (PEC) water splitting emerges as another innovation. This process utilises specialised semiconductors, known as photoelectrochemical materials, to create hydrogen from water using sunlight. These materials harness light energy to directly separate molecules of water into hydrogen and oxygen [88,89]. The core principle involves harnessing solar energy to drive water-splitting reactions, where semiconductors act as photocatalysts, capturing light and providing the necessary energy for the reactions. This is accomplished by applying an external force on photovoltaic materials that are submerged in an electrolyte solution containing a redox couple. One component of this redox couple is a semiconductor that is capable of absorbing light when exposed to it [90,91]. Subsequently, the generated electricity is employed in the process of water electrolysis. Semiconductors possess a distinctive capability to serve as photocatalysts. Transition metal carbides (TMCs), when combined with other semiconductor materials to form heterojunctions, can enhance performance by expanding the light absorption range and facilitating charge separation. Molybdenum carbide (Mo_2C), for example, has demonstrated resilience in both alkali and acidic environments, making it suitable for PEC water splitting. Mo_2C-based photoelectrodes have shown high photocurrents and efficient charge separation, further highlighting the versatility and potential of TMCs in hydrogen generation applications. The presence of light has a substantial impact on the activation of the chemical reduction and oxidation process. The photocatalyst electrodes could capture light, hence supplying energy for the reactions. The externally supplied electric/chemical bias is responsible for supplying the additional voltage necessary to facilitate the reaction [92,93]. TMCs can be combined with other semiconductor materials to form heterojunction enhancing its performance by expanding the light absorption range and facilitating charge separation.

Molybdenum carbide (Mo_2C) was ascertained to be resilient in both alkali and acidic environments for PEC water splitting. Owing to their good electrical conductivity and the appropriate band structure of these materials, Mo_2C-based photoelectrodes have demonstrated high photocurrents and efficient charge separation. Liang et al. incorporated Mo_2C catalysts with amorphous silicon (a-Si) via direct sputtering of magnetron. This involved the utilisation of a Mo target and a carbon target. It has a high photovoltage making it suitable for hydrogen production [94]. Table 4 below highlights the performance of TMCs in photoelectrochemical water-splitting applications.

Table 4. The performance of photoelectrochemical water splitting and its hybrid for HER

Electrocatalyst	**J @ 0 V (mA cm^{-2})**	**Overpotential (V)**	**Electrolyte**	**Light Source**	**Ref.**
W2C/MWNT	0.16	0.2	0.5 M H_2SO_4	300 W Xe lamp	[95]
MoC@NC-900	-	160	1.0 M KOH	300 W Xe lamp	[93]
CdS@Mo_2C–C	0.4	283	0.5 M H_2SO_4	300 W Xe lamp	[96]
CdS/MoC	-	70	0.5 M Na_2SO_4	300 W Xe lamp	[97]
a-Si/Mo_2C	0.9	270	0.1 M H_2SO_4	300 W Xe lamp	[98]
Mo_2C/CNT	3.8	152	0.1 M $HClO_4$	300 W Xe lamp	[98]

Fuel cells

Lastly, fuel cells represent a well-established method of energy production, serving as a sustainable alternative to conventional fossil fuels. Fuel cells have served as the fundamental source of energy production for numerous decades. It is an electrochemical cell that transforms fuel into electrical energy through an electrochemical reaction involving an oxidant and fuel, bypassing the need for combustion [99]. Fuel cells convert fuel into electrical energy through an electrochemical reaction involving an oxidant and fuel, with water as the only byproduct. While fuel cells are recognised for their exceptional performance and potential as a primary energy source in the future, large-scale production remains impractical due to the high costs and lack of reliability associated with platinum (Pt)-based electrocatalysts. The need for durable and cost-effective catalysts has led to significant interest in TMCs as potential substitutes for carbon-based catalytic supports in fuel cells. Recent studies, such as those by Pineiro Garcia et al., have demonstrated the potential of cobalt molybdenum (Co-Mo) carbides as effective anodic electrooxidation catalysts in fuel cells, further underscoring the importance of TMCs in advancing sustainable energy technologies. It is a sustainable energy option compared to conventional fossil fuel because water is the only by-product emitted [100]. Nowadays, fuel cells have been utilised in diverse fields such as transportation, stationary power generation and portable power as energy storage.

Currently, energy storage and conversion are mostly dominated by two distinct groups of devices. There are two types of energy storage technologies: fuel cells and electrochemical energy storage (EES) devices, which encompass a range of supercapacitors (SCs) and batteries. The generation of power in a fuel cell is attributed to the electrochemical reactions that take place between hydrogen and oxygen. The reactions are facilitated through the utilisation of water-splitting technology, which is powered by solar energy [101,102]. The fuel cell has been recognised as the main source of energy in the future, owing to its exceptional performance and inexhaustible nature. Nevertheless, the current impracticality of large-scale production is mostly attributed to the exorbitant expenses and the lack of reliability associated with Pt-based electrocatalysts. The fuel cell electrodes are commonly composed of active electrocatalysts and a support matrix. The active electrocatalyst is of the utmost significance in influencing the overall performance of the fuel cells [103,104].

The lifespan of catalysts employed in proton exchange membrane fuel cells (PEMFCs) now poses a considerable obstacle, which hinders their widespread adoption in both consumer and industrial sectors. Platinum group metals (PGMs) remain the predominant catalysts employed in PEMFCs because of their outstanding enduring durability and catalytic performance. One potential strategy for reducing Pt loading involves implementing a support material that can improve both the dispersion and durability of Pt [105]. The primary cause of performance loss in carbon-based supports has been determined to be corrosion, resulting from parasitic oxidation to CO_2 at the cathode. Hence, there exists a notable inclination towards investigating stable alternatives that can serve as substitutes for carbon support in proton exchange membrane fuel cells (PEMFCs). In recent years, TMCs have attracted significant interest as a possible substitute for carbon-based catalytic support in fuel cells.

Numerous works on transition metal carbide as a support catalyst fuel cell have been published throughout recent years. One of the works demonstrated by Izhar & Nagai et al. where they synthesized cobalt molybdenum (Co-Mo) carbides and further carburizing Co-Mo oxides in a CH_4 and H_2 gas stream at temperatures ranging from 723 to 973 K. The carburized catalysts were assessed by conducting experiments using both a single-stack fuel cell and a three-electrode system cell. The results indicated that the Co-Mo catalysts carburised at temperatures of 873K and 923K exhibited significant activity for the anodic electrooxidation of hydrogen. The carburized Co-Mo catalyst, with a temperature of 873 K, exhibited the highest activity among the catalysts tested. It achieved a performance level of 10.9% compared to a commercial Pt/C catalyst in a single-stack fuel cell [107]. The X-ray diffraction (XRD) analysis revealed the existence of the CoMo oxycarbide within the bulk material, which served as a crucial component in facilitating the anodic electrooxidation process.

Conclusion

The pursuit of an environmentally sustainable pure energy substitute for conventional fossil fuels propels the enthusiasm surrounding hydrogen energy. Hydrogen production necessitates the creation of electrochemical water-splitting catalysts that are both efficient and economical. Recent advancements in water splitting utilising TMCs and their composites are summarised in this article. The exceptional water electrolysis efficiency of these transition metal-based materials can be attributed to their notable attributes, including elevated conductivity, durability, and distinct electronic structure. An additional avenue for improving catalyst performance would be to implement a diverse range of synthesis strategies and modification techniques. Despite notable advancements in contemporary research, disparities remain in comparison to benchmark catalysts composed of noble metals (e.g., materials based on Pt, Ru, and Ir), especially regarding lethargic kinetic properties. Research has shown that carbides composed of Mo and W possess significant catalytic activity when it comes to water splitting application. Nevertheless, the enduring stability of these catalysts remains an undesirable attribute.

Further endeavours ought to be devoted to the development of novel approaches that rival the performance of catalysts composed of noble metals. Numerous strategies may be employed to effectuate enhancement. In order to enhance the surface area and surface-active site exposure of the catalysts, it is imperative to decrease their dimensions and establish a porous, hierarchical structure. Furthermore, the electronic structure is optimised through heteroatom modification, which enables the manipulation of the hydrogen adsorption and desorption energy on the catalyst surface. Thirdly, the catalytic activity and stability can be enhanced by forming a heterostructure, thereby harnessing a synergistic effect. Increase intrinsic conductivity or combine with conductive substrates to accelerate electron transport and reduce kinetic barriers.

Table 5. Advantages and disadvantages between each application of TMCs for HER

Applications	**Advantages**	**Disadvantages**	**Refs.**
Electrochemical water splitting	By adjusting their composition, surface modifications, and nanostructure, transition metal carbides can have their properties modified. Researchers can optimize these materials for specific applications, thereby improving their overall performance, due to their tunability. Additionally, it can be combined with other substances, such as carbon-based supports or catalysts, to produce composites with increased catalytic activity.	The utilization of transition metal carbides is hindered primarily by the challenge of maintaining their stability under operational settings. Numerous transition metal carbides are susceptible to oxidation at high temperatures and in reactive environments. This can cause their catalytic activity and structural integrity to degrade over time, thereby limiting their long-term performance.	[4,108]
Photoelectrochemical water splitting	Metal carbides are a highly promising material for use as photocathodes. This is mostly due to their low-cost synthetic pathways and their superior stability when compared to other semiconductor materials.	In general, TMCs are metallic conductors instead of semiconductors materials in which this characteristic can restrict their use as photo absorbers in PEC cells, as semiconductors are typically utilized to generate electron-hole pairs when exposed to light. Modification of TMCs with other materials can increase the efficiency of charge separation.	[109,110]
Fuel Cells	TMCs relatively is abundant and less costly and noble metal for instance, platinum. This cost effectiveness makes it an attractive alternative. The catalyst's durability and longevity are increased by its good stability under fuel cell operating conditions.	Undesirable species may be adsorbed onto the catalyst surface which can reduce its catalytic activity	[100,111]

In addition, the subsequent factors must be considered to develop and acquire electrocatalysts that are efficient. Large-scale preparation comes first. Although numerous advancements have been documented, the synthesis of electrocatalysts remains confined to laboratory settings. Constraints on energy and time imposed by the intricate synthetic procedure generally result in a diminished yield. It is critical to develop a synthetic method that is both scalable and cost-effective to facilitate practical applications. Unpretentious and environmentally sustainable large-scale fabrication of components and morphology that is also environmentally friendly will continue to be a competition in the years to come.

Second, the long-term durability. Catalysts are prone to degradation when exposed under strong acidic and basic conditions, which leads to their instability and reduced lifespan. The exploration of efficient electrocatalysts in solutions that are either neutral or close to neutral is of utmost importance. However, there are still significant tasks to be achieved in the sector of electrochemical water separation, particularly in the context of neutral or nearly neutral conditions. In contrast, the OER poses a significant impediment to the overall efficacy of the water-splitting reaction, which is higher in conductivity under alkaline conditions as opposed to acidic ones. As a result, enhancing the reactivity and stability of catalysts in alkaline environments ought to be an ongoing area of investigation. Lastly, research into mechanisms. To construct and rationally design electrocatalysts, it is vital to possess a comprehensive understanding of the mechanisms underlying HER. While the underlying principles of electrochemical hydrogen production may appear simple, there is still limited knowledge regarding the precise reaction mechanism occurring on the two electrodes. Furthermore, the electrode materials stability was documented in most studies, discussions regarding the mechanism of functional degradation were infrequent. Further comprehensive and methodical investigation into the mechanism would be advantageous to enhance understanding and ascertain the reaction process.

Declaration of Competing Interest

The authors hereby disclose any personal relationships or financial interests that may have appeared to exert an influence on the research presented in this article.

Acknowledgements

The research conducted in this study received funding from the Ministry of Higher Education (MOHE) Fundamental Research Grant Scheme (FRGS/1/2021/STG04/UMT/02/1). The author expresses gratitude to Universiti Malaysia Terengganu for their financial assistance and provision of research facilities.

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