

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/377337167>

Molybdenum–Based Electrocatalysts for Direct Alcohol Fuel Cells: A Critical Review

Article in *Journal of Electrochemical Science and Technology* · January 2024

DOI: 10.33961/jecst.2023.00528

CITATIONS

0

READS

261

6 authors, including:



Gaurav Kumar Yogesh

King Mongkut University of Technology North Bangkok

21 PUBLICATIONS 306 CITATIONS

SEE PROFILE



Rungsima Yeetsorn

King Mongkut's University of Technology North Bangkok

22 PUBLICATIONS 142 CITATIONS

SEE PROFILE



Waritnan Wanchan

King Mongkut's University of Technology North Bangkok

10 PUBLICATIONS 39 CITATIONS

SEE PROFILE



Michael Fowler

University of Waterloo

369 PUBLICATIONS 23,220 CITATIONS

SEE PROFILE

Molybdenum–Based Electrocatalysts for Direct Alcohol Fuel Cells: A Critical Review

Gaurav Kumar Yogesh¹, Rungsima Yeetsorn^{2*}, Waritnan Wanchan², Michael Fowler³, Kamlesh Yadav⁴, and Pankaj Koinkar⁵

¹Department of Physics and Astrophysics, Central University of Haryana, Mahendergarh, 123031, India

²Materials and Production Engineering, The Sirindhorn International Thai–German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok– 10800, Thailand

³Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

⁴Department of Physics, University of Allahabad, Uttar Pradesh– 211002, India

⁵Department of Optical Science, Tokushima University, Tokushima– 7708501, Japan

ABSTRACT

Direct alcohol fuel cells (DAFCs) have gained much attention as promising energy conversion devices due to their ability to utilize alcohol as a fuel source. In this regard, Molybdenum-based electrocatalysts (Mo-ECs) have emerged as a substitution for expensive Pt and Ru-based co-catalyst electrode materials in DAFCs, owing to their unique electrochemical properties useful for alcohol oxidation. The catalytic activity of Mo-ECs displays an increase in alcohol oxidation current density by several folds to 1000–2000 mA mg_{Pt}^{−1}, compared to commercial Pt and PtRu catalysts of 10–100 mA mg_{Pt}^{−1}. In addition, the methanol oxidation peak and onset potential have been significantly reduced by 100–200 mV and 0.5–0.6 V, respectively. The performance of Mo-ECs in both acidic and alkaline media has shown the potential to significantly reduce the Pt loading. This review aims to provide a comprehensive overview of the bifunctional mechanism involved in the oxidation of alcohols and factors affecting the electrocatalytic oxidation of alcohol, such as synthesis method, structural properties, and catalytic support materials. Furthermore, the challenges and prospects of Mo-ECs for DAFCs anode materials are discussed. This in-depth review serves as valuable insight toward enhancing the performance and efficiency of DAFC by employing Mo-ECs.

Keywords : Alcohol oxidation reaction, Cyclic voltammogram, Electrocatalysts, Direct alcohol fuel cells, Molybdenum

Received : 19 June 2023, Accepted : 16 October 2023

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have gained interest as a viable alternative energy source due to their temperature operation and suitability for powering electronic devices and vehicles [1–4]. Among the various types of PEMFCs, direct alcohol fuel cells (DAFCs) utilize alcohol as a fuel source, offering advantages such as high energy density, a low environmental impact, and the use of renewable fuels. DAFCs are a modified version of

PEMFCs that primarily employ ethanol and methanol instead of hydrogen gas. Alcohol is obtained through various methods and is a promising candidate for power generation. With the DAFC technology, producing electricity using alcohol as a fuel could become more accessible and efficient [5,6]. DAFCs employ electrodes coated with electrocatalysts, facilitating alcohol oxidation at the anode and oxygen reduction at the cathode. The convenience and cost-effectiveness of PEMFCs make them appealing for replacing internal combustion engines in various applications.

In DAFCs, co-catalysts are necessary to enhance the sluggish kinetics of alcohol oxidation at the anode. Nevertheless, the electrocatalysts utilized in DAFCs must exhibit high reactivity, long-term stability, and cost-effectiveness [7,8]. Carbon-supported

*E-mail address: rungsima.y@tggs.kmutnb.ac.th

DOI: <https://doi.org/10.33961/jecst.2023.00528>

This is an open-access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/4.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

platinum (Pt/C) is a common electrocatalyst in DAFCs but is susceptible to fuel impurities and corrosion, which necessitate high platinum loading and resulting in high costs [1,9,10]. Researchers have explored alternative approaches to address these challenges, including alloying with multi-metallic Pt and PtRu-based composites electrocatalysts with non-noble transition metals such as Ni, Co, Fe, Cu, W, Sn, and Mo. These non-noble transition metal-based electrocatalysts have been demonstrated to improve catalytic activity and stability, offering a potential solution to the limitations of Pt/C electrocatalysts [11–13].

Transition metals have been extensively studied as support electrocatalysts in DAFCs due to their ability to resist CO poisoning and reduce the cost of Pt loading. Incorporating a second or third oxophilic metal, such as Mo, can improve CO tolerance through a bifunctional process [14–18]. Molybdenum (Mo) is a new type of advanced electrocatalyst (EC) that has shown promise for use in fuel cells, metal-air batteries, and supercapacitors. Molybdenum has an oxyphilic nature and can exist in multiple oxidation states, making it a desirable candidate for co-catalyst materials that promote CO oxidation at a lower potential. Mo-based electrocatalysts (Mo-ECs) exhibit remarkable catalytic activity, durability, tunability, and reduced potential for water dissociation. These properties make Mo-ECs superior to pure catalysts while being cost-effective [1,2].

Interestingly, Mo alloyed with Pt exhibits more accessible water dissociation abilities than pure Pt [19]. Multi-metallic composite nanostructures have gained interest due to their improved electrocatalytic performance compared to commercial Pt/C [20,21]. Molybdenum-based electrocatalyst nanomaterials, collectively referred to as Mo-ECs, including Pt–Mo alloys, Molybdenum oxide (MoO_x), Molybdenum carbide (MoC or Mo_2C), Molybdenum nitride (MoN), molybdenum sulfide (MoS_2), and graphene/CNTs supported Mo nanostructures (Graphene/CNTs/Mo). It significantly reduces the onset potential and dramatically increases the power and current densities. This study aims to investigate various Mo-ECs used as support catalysts in DAFCs,

Over the past two decades (1998–2022), extensive research has been conducted on various Mo-ECs as co-catalysts for potential use in DAFCs. These investigations have led to significant advancements in syn-

thesis techniques and resulted in notable scientific breakthroughs, particularly in the development of highly stable enriched Pt and Pt-free Mo-ECs for DAFCs. This report critically evaluates the design and development of Mo-ECs for their specific application in direct alcohol fuel cells (DAFCs). Our investigation focuses on the electrocatalytic processes of Mo-ECs, particularly methanol oxidation and ethanol oxidation, aiming to understand their importance within the context of DAFCs comprehensively. This report does not cover electrocatalytic reactions such as the hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), and oxygen evolution reaction, as they are not directly involved in DAFCs. Furthermore, this report includes a comprehensive analysis of the structural, spectroscopic, and electronic properties of Mo-ECs electrocatalysts utilizing advanced characterization techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy.

2. Components of direct alcohol fuel cells

The basic components of DAFCs include the membrane electrode assembly (MEA), bipolar plate, gasket, and current collector and end plate. A schematic diagram of DAFCs component is presented in Fig. 1. The heart of a DAFCs is MEA, which comprises three primary components including membrane and gas diffusion layer (GDL) and catalyst layer. Typically, these components are compacted into 5-layers sandwich as follows:

GDL | Catalyst layer (anode) | Membrane
| Catalyst layer (cathode) | GDL

The membrane, placed at the core of MEA sandwich, acts as the selective passage of protons (H^+) and facilitates electrochemical reactions between hydrogen and oxygen. The gas diffusion layer (GDL) is a porous material that assists in transporting reactants and products, prevents direct contact between the electrodes and reactants, and manages water during electrochemical reactions. The catalyst layers consist of two electrodes: (i) the anode catalyst, which is the negative electrode, initiates the alcohol oxidation reaction. (i) the cathode catalyst, which is a

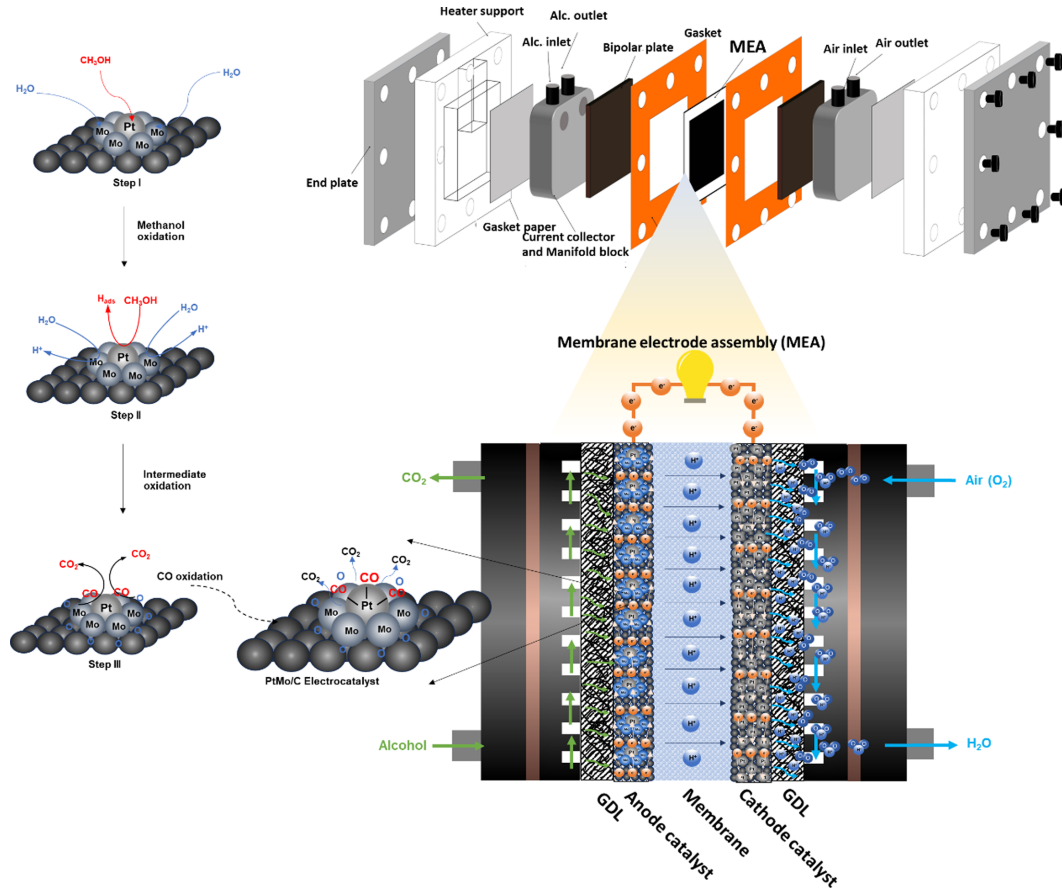
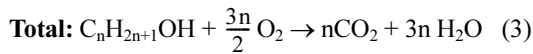
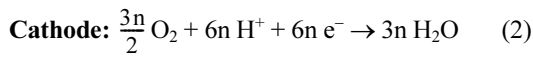
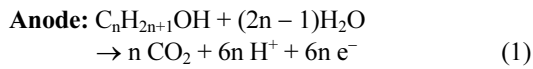


Fig. 1. The schematic diagram of DAFCs component.

positive electrode, serves an oxygen reduction reaction. The direction of a half and total redox reaction of alcohol in a DAFCs is as follows:



In addition, other components are critical for achieving maximum potential. Bipolar plates, placed on both sides, serve to separate individual cells in a fuel cell, provide a conductive path for electrons, and include flow fields for reactants as well as coolant channels to maintain stack integrity. A current collects the electrons generated by the electrochemical

reaction and transfers them efficiently to the external circuit, which requires excellent electrical conductivity and durability. The endplate is a crucial component that is placed at the end of the cell. The key function is providing uniform pressure distribution, reducing contact resistance, and providing structural support.

3. Bifunctional mechanism

The bifunctional mechanism in electrochemistry refers to a phenomenon where catalytic reactions occur simultaneously at the same electrode but involve different catalytic sites with distinct electrochemical properties. These processes are interdependent, meaning the rate of one reaction can impact the other. In DAFCs, two electrochemical processes occur during the alcohol oxidation reaction (AOR):

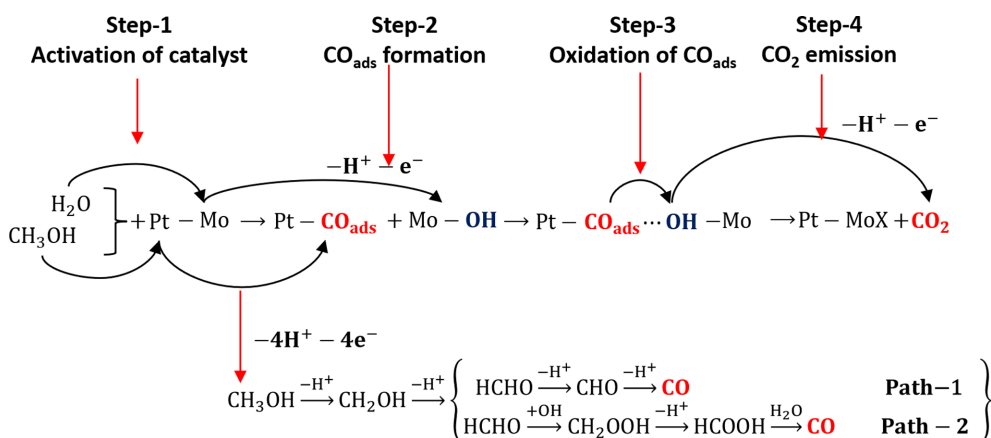


Fig. 2. Bifunctional electrochemical reaction process for methanol oxidation.

the adsorption/desorption of intermediate species and water at one active site and the alcohol oxidation at different active sites on the same electrocatalyst surface. For example, in the case of methanol oxidation with Mo-ECs (as illustrated in Fig. 2), the process involves the conversion of reactants (methanol) into intermediates (such as CO) and ultimately into products (such as CO₂). This complex reaction pathway gives rise to various intermediates formed through different pathways [2,5]. During alcohol oxidation, full oxidation can occur through deprotonation or the absorption of hydroxyl groups by the intermediate species. These processes involve the interplay of different active sites on the electrocatalyst surface.

Fig. 2 presents a summary of the oxidation reaction of methanol by Mo-ECs in DAFCs. The deprotonation of methanol (path 1) is a six-electron process in which six pairs of protons and electrons are released during the conversion of methanol to CO₂. As in path 2, different complex species are formed by the abstraction of proton H⁺ and the adsorption of OH⁻ ions [6]. Typically, methanol molecules can be activated via hydrogen abstraction from either carbon or oxygen atoms at the catalyst surface. Continuous abstraction of hydrogen/protons can create a large number of intermediate species, including formaldehyde (HCHO), formyl (CHO), formic acid (HCOOH), and carbon monoxide (CO).

Typically, methanol oxidation can be described in four steps. In the first step, methanol molecules adsorb onto the catalyst surface through the carbon atom, facilitated by Pt sites and water molecules by

Mo-sites. The second step involves the oxidation of the adsorbed methanol and water molecules at their respective sites. The Pt-Mo electrocatalyst breaks water molecules into hydroxyl groups (OH⁻) and hydrogen ions (H⁺), which are then adsorbed on the Mo and Pt surfaces. During the reaction, partially oxidized methanol intermediates, mainly CO, are adsorbed on the Pt surface. However, the strong affinity of CO towards the Pt surface decreases the active surface area for further oxidation of methanol. In step three, the Pt and Mo active sites nearby bind the CO and OH species. Finally, in the fourth step, CO is oxidized by the OH species, forming CO₂ and water as the final products of methanol oxidation. The hydrogen ions from water dissociation react with the electrons from methanol oxidation to form water. In this bifunctional mechanism, the Pt sites serve as methanol adsorption sites, while the Mo sites facilitate water dissociation and promote the reaction between hydroxyl groups and methanol. These two active sites work together to improve the efficiency and selectivity of the methanol oxidation reaction (MOR). The Mo sites are crucial in minimizing the formation of undesired intermediate products, such as formaldehyde and formic acid, during methanol oxidation.

The overall reaction for ethanol oxidation using a Pt-Mo electrocatalyst based on a bifunctional mechanism is shown in Fig 3. The typical electrochemical conversion of ethanol to CO₂ involves five steps. Firstly, the Pt facilitates the breaking of the C-C bond in ethanol, which is the rate-limiting step in the reaction, whereas the activation of H₂O oxidized to OH⁻

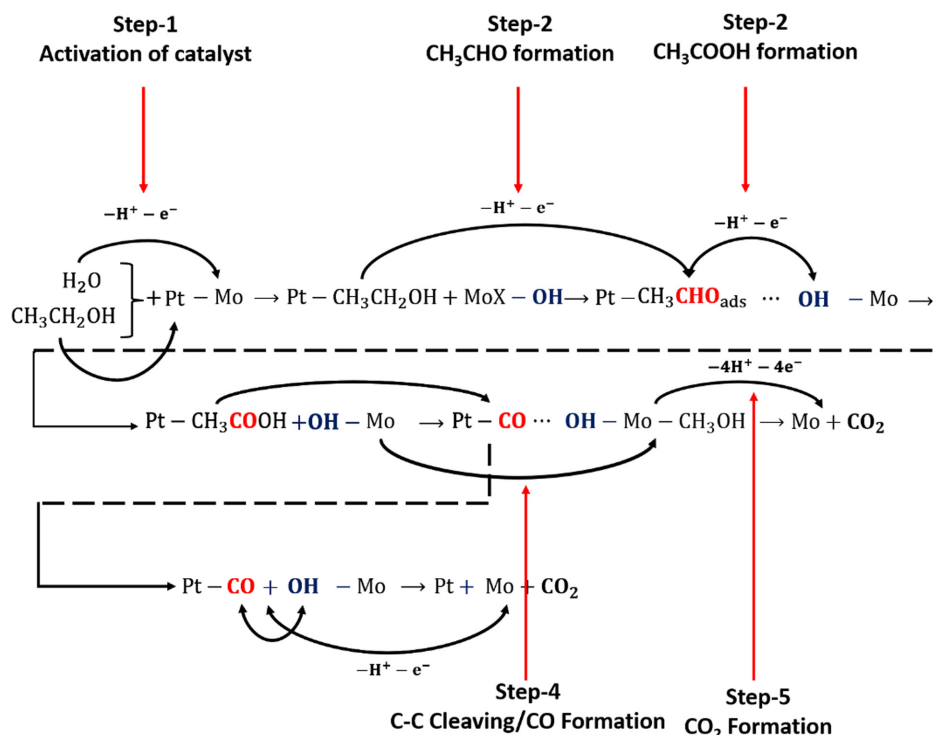
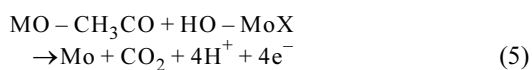
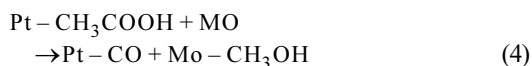


Fig. 3. Bifunctional electrochemical reaction process for ethanol.

species on the Mo-site is the rate-determining step [7]. In the first step, ethanol is adsorbed dissociative on the Pt surface, which is observed at a low potential [8]. In step 2, dissociative adsorbed ethanol molecules are transformed into intermediate species, such as acetaldehyde, by abstracting proton/electron pairs from the ethanol molecules. In step 3, OH species at the active Mo sites facilitated the oxidation of acetaldehyde to acetic acid (Eq. 4). In step 4, the partially dehydrogenated ethanolic species undergo C-C bond cleavage with the formation of Pt-CO and a methoxy linkage (Mo-CH₃OH) (Eq. 5) [9]. The Pt-sites initiate the cleavage of the C-C bond and the formation of CO species from the intermediate species, as shown in the following reaction [10]:



In the final step, the Pt-Mo alloy can suppress CO

poisoning, a common issue with other electrocatalysts. CO poisoning occurs when CO molecules adsorb onto the catalyst surface and block the Pt active sites (Pt-CO), thereby reducing electrocatalytic activity. The active sites (Mo-OH and Pt-OH) on the Pt-Mo electrocatalysts effectively oxidized CO molecules and CH₃OH via the abstraction of proton/electron pairs, preventing the accumulation of CO species on the catalyst surface.

According to existing research, in monometallic Pt/C catalysts, CO is produced as an intermediate species that blocks the active site and restricts the rate of methanol oxidation in the anode because of its relatively high stability [11,12,22]. Mo-based electrocatalysts serve as sites for the oxidation of methanol and water. A key aspect of their bifunctional mechanism is the presence of numerous active sites on their surfaces capable of adsorbing methanol and facilitating its oxidation. These active sites typically consist of Mo-OH [8,13-15], MoO_x(OH) [15-18], H_xMoO_x [16,20,23,24], Mo-O-Mo, Mo₂C-OH, MoS₂-OH [21] groups that can form strong chemical bonds with methanol [17]. The oxidation process commences

when a methanol molecule adsorbs onto an active site on the surface of Mo nanoparticles. It is also worth noting that the spectroscopic data suggest that the Mo surface atoms have multiple O and OH ligands at all potentials, which effectively oxidize CO on neighboring Pt sites. This results in a bifunctional mechanism similar to that observed for Pt–Ru alloys. However, the O/OH ligands on the surface are insufficient for CO oxidation. They must react with CO and quickly regenerate via extraction from H₂O. Another mechanism that may contribute to CO oxidation is the reactivity of CO adsorbed on the Pt sites, possibly through an electronic interaction between Pt and Mo. It is probable that both mechanisms play a role or are interconnected. In the case of Mo-based electrocatalysts, methanol oxidation occurs through a bifunctional mechanism, which can be expressed as follows [14,15,25,26].

4. CV analysis of alcohol electrooxidation reaction

Cyclic voltammetry (CV) is a crucial tool for investigating the electrooxidation of alcohols and is widely employed in fuel cell testing to evaluate catalyst efficiency in promoting fuel oxidation or oxygen reduction. This technique involves applying voltage cycles to an electrochemical cell containing the electrocatalyst and fuel cell electrolyte and recording the resulting current response as a function of voltage, referred to as a CV curve. By comparing the CV curves of different catalysts, researchers can gain

insight into the electrochemical behavior of the catalysts and identify the most effective catalysts for fuel cell applications. This section presents a detailed discussion of factors influencing the electrooxidation performance of alcohols, including Mo content/composition, carbon support, scan rate, electrolyte/alcohol concentration, and ageing.

A typical CV curve of alcohol oxidation exhibits a large background current because of the double-layer capacitance caused by the high surface area of the carbonaceous materials such as (graphene/CNTs structure) [17]. The redox peaks between 0.3 V and 0.5 V correspond to the redox behavior of carboxylic acid groups such as –COOH and –OH. Furthermore, no current peak for alcohol oxidation is observed. Fig. 4(a) indicates that the CNT/graphene electrode did not possess significant electrocatalytic activity [17]. Fig. 4(b) represented the CV curve for methanol oxidation using the Pt/MWCNTs. Adding Mo in Pt/MWCNTs significantly improved the alcohol oxidation activity by the bifunctional mechanism [18].

In contrast, the CV curve of the Pt/Mo-ECs shows an intense peak in both forward and backward scans positioned at 0.7–0.9 V and 0.3–0.5 V, respectively, within the potential window of 0.0–1.2 V, as for reference from the previous studies [27–29]. The alcohol oxidation region can be divided into four peaks in forward and backward scans at around 0.0–0.3 V, 0.3–0.6 V, 0.6–0.9 V, and 0.6–0.3 V, respectively. As the potential scans in the forward direction of 0.0–

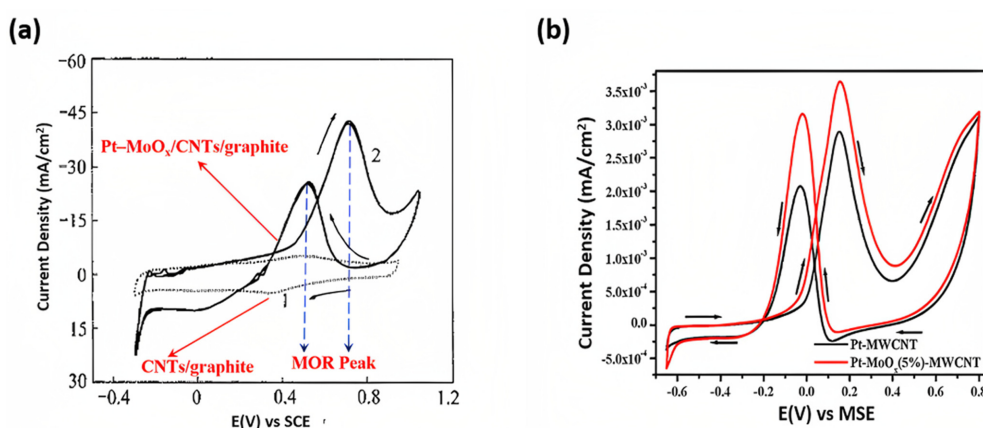


Fig. 4. Cyclic voltammograms of methanol oxidation in 0.5 M H₂SO₄ electrolyte (a) CNTs/graphite electrode and Pt–MoO_x/CNTs/graphite electrodes in 1 M CH₃OH, at a scan rate of 20 mV s^{−1} (Reproduced with permission from Ref. [17] Copyright © 2007 Elsevier) and (b) Pt–MoO_x (5%)–MWCNT and Pt–MWCNT in 0.5 M CH₃OH at 10 mV s^{−1} scan rate (Reproduced with permission from Ref. [18] Copyright © 2010 Elsevier).

0.3 V, the electrocatalyst is in a metallic state and is active for methanol, ethanol, and hydrogen adsorption, corresponding to the minimal non-zero current density [27]. At 0.3 V, water molecules dissociate on the electrocatalyst surface to form the active oxidant “-OH”, which species is responsible for oxidizing the adsorbed methanol or intermediate carbonaceous species such as CH_3OH , CO, HCHO, and CHO, leading to an increase in current until the potential reaches the peak current. At the peak current, the electrocatalyst surface is fully oxidized, and it is no longer active for the oxidation of carbonaceous species, resulting in a decrease in current until 0.9 V. Beyond this potential, the current gradually increased because of the oxidation of carbonaceous species on the oxide form of the catalyst (PtO , PdO , PtMoO_x , and PtRuO) at a high potential. As the potential was scanned back, the re-adsorption of the carbonaceous species increased the current in the backward scan until it reached a peak. Beyond this potential, the surface was recovered to the metallic surface, supplying more active sites for methanol/carbon species oxidation (0.6–0.4 V). However, this potential is too low to allow the dissociation of the water molecules into active oxidants. The small oxidation peak in the backward scan implies that the backward oxidation peak during the MOR was not due to the oxidation of the CO residue. However, the shape and nature of alcohol oxidation in the CV curve are highly affected by various factors such as morphological/ structural properties of the catalyst, concentration of alcohol/ electrolytic solution, Pt/Mo ratio, scan rate, and carbon support. In this section, important pioneering results are discussed. Table 1 presents the alcohol oxidation results of Mo-ECs for DAFCs used in the past two decades.

4.1 Mo content

Grgur *et al.* [30] found that the characteristics of the $\text{Pt}_{75}\text{Mo}_{25}$ surface in terms of oxidation of H_2/CO mixtures are surprisingly similar to those of $\text{Pt}_{50}\text{Ru}_{50}$ alloy. These intriguing characteristics arise from the distinct electrochemistry of ruthenium (Ru) and molybdenum (Mo) [30]. The investigation of CO tolerance of PtMo alloys in the presence of reformat gas (H_2/CO : 100 ppm) showed two CO stripping peaks at 0.45 V and 0.65 V, indicating that CO adsorbed on Pt sites was oxidized by oxygenated species activated at neighboring Mo atoms. However,

complete stripping can only be achieved at a high overpotential, $E > 0.55$ V, on the Pt sites between CO and Pt-OH [31]. In a typical AOR process, Mo mediates oxygen transfer to CO, reducing alcohol oxidation peak and onset potential [28]. The onset potential of CO oxidation on Mo-modified Pt(332) was observed at 0.15 V and the main peak at 0.3 V [23]. Mo causes a shift in the onset potential for the oxidation of adsorbed CO to lower potentials (around 0.15 to 0.2 V) compared to Sn [32]. However, at these low potentials, only approximately 10% of the adsorbate is oxidized, and the main oxidation peak remains largely unaffected [32]. In contrast, Ru competes with CO oxidation and oxygen transfer to Pt via a bifunctional mechanism. To improve the performance of Mo as co-catalysts, researchers tried to optimize the Mo content in different chemical compositions with Pt. Anjos *et al.* [8] prepared PtMo (80:20 and 50:50) bimetallic electrodes using an arc-melting furnace technique. Ethanol was detected during the positive CV scan. The onset potential for the oxidation of the alcohol was approximately 0.3 V vs. RHE, with a decrease in the hydrogen region attributed to the adsorption of organic species. Adding Mo causes a shift in ethanol oxidation toward less positive potentials, with Mo-modified electrodes exhibiting higher activities of up to 0.75 V vs. RHE. In comparison, Pt-Mo (50:50) electrocatalysts had lower current densities than Pt-alone after this potential, likely due to fewer Pt-OH sites for the oxidative removal of adsorbed CO. The enhanced activity of Pt-Mo (80:20) is possibly due to an increase in the electrode surface roughness caused by the dissolution of Mo surface atoms or the modification of the electronic structure of Pt. The high catalytic activity of PtMo (80:20) may be attributed to the enhanced roughness of the electrode surface caused by the dissolution of Mo in the solution. The presence of the Mo a modified electrode led to a shift in the ethanol oxidation peak positions to lower positive potential [8].

Lima *et al.* [33] initially categorically investigated methanol oxidation using PtRu-X (X = Au, Co, Cu, Fe, Mo, Ni, Sn, and W) ternary metallic electrocatalysts. Comparative studies showed that polyaniline PtRuMo is the most efficient anode co-catalyst with electrooxidation potential under 0.5 V vs. RHE under stationary conditions. The current density of PANi/PtRuMo was ten times higher than that of the PANi/PtRu counterpart in the same potential window [33].

The encouraging results demonstrate that Mo atoms as a ternary catalyst at a weight ratio close to 5% have achieved a single cell potential of 0.55 V after 5 min of 1.0 M methanol oxidation. CV results were used to compare the performance of the PAni/PtRuMo anodes with that of other electrocatalysts, specifically PAni/PtRu.

The results indicated that the PAni/PtRuMo ternary system exhibits superior catalytic performance, producing higher current densities across the potential range of 0.0–0.65 V vs. RHE [33]. The impact of Mo introduction on PtRu/C electrocatalysts for the oxidation of ethanol and methanol was further studied by Neto *et al.* [34]. Researchers synthesized two PtRuMo catalysts with the composition of PtRuMo (1:1:0.5) and PtRuMo (1:1:1), respectively. They found that adding Mo to the catalyst improved its performance, especially for ethanol oxidation. In addition, the amount of Mo is important, as the catalyst's performance is much poorer when the amount of Mo is 0.5 compared to Mo at 1. Because Mo is a good promoter for ethanol oxidation, and a higher amount of Mo leads to better catalyst performance.

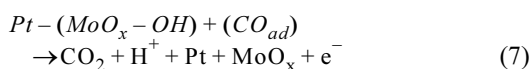
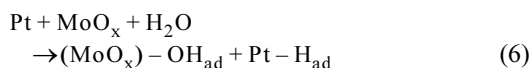
Adding Mo with the thermal treatment at 300°C in a hydrogen atmosphere leads to improve the catalyst performance. This is because thermal treatment can activate the catalyst and improve its surface properties [34]. Adding Mo to the Pt–Ru electrocatalyst enhanced the oxidation of 1.0 M ethanol and methanol and facilitated the breaking of the C–C bonds. An increase in the oxidation current above 0.5 V was observed as the concentrations of methanol and ethanol increased, but this increase was not proportional. It indicates the adsorption of alcohol on the catalyst surface, which leads to catalyst poisoning [34]. Jaksic *et al.* [35,36] reported that electrocatalytic activity depends on Mo oxidation; lower oxidation states, such as MoO₂ or Mo(IV) and MoO₂(OH) or Mo(V), tend to exhibit higher conductivities and higher electrocatalytic activities than higher oxidation states, such as MoO₃. The latter can significantly reduce the number of active catalytic sites and decrease the catalytic activity under methanol oxidation [32,33,35,36]. Guillén–Villafuerte *et al.* [19] found that increasing the Pt content in Pt/Mo₂C@MoO₃/C catalysts shifts the maximum current density generated during methanol oxidation towards less positive potentials. The impact of Pt loading (5, 20, and 30 wt.%) on the electrocatalytic oxidation of adsorbed CO for Pt/

X@MoO₃/C and Pt/C catalysts. The increase in Pt loading while keeping the Pt particle sizes consistent. As a result, the number of exposed Pt atoms increases in active sites for alcohol oxidation proportionally with the Pt loading [19].

The inclusive behavior of the third metal promoted the generation of a more electroactive surface and conductive pathways on the rGO sheets. The synergistic effect of conductive rGO and well-dispersed third metal (Ru, W, Sn, Cu, Co, Ni, and conducting polymer) involves a faradic process of inserting hydrogen at neighboring Mo sites H_yW(Mo)O₃: 0 < y < 1 [15,38,39], excellent electrically conductive for charge transfer during the oxidation [37]. The strong oxidation peaks attributed to the anchoring of hydrogen-terminated from the Pt surface by the rGO-supported metal nanoparticles increased both active sites and electrical conductivity. The synergistic effect of Mo⁴⁺ and Co⁴⁺ ions, active edge sites of MoS₂/CoS₂, and the conductivity and structure of rGO facilitated charge transfer, leading to a maximum power density of 19 mW cm⁻² at 60°C for MoS₂/CoS₂/rGO [40]. Padmini *et al.* [41] investigated a conductivity-tailored PtNi/MoS₂ 3D nanoflower catalyst prepared via Sc doping. It was found that electrocatalytic activity toward the EOR using PtSc_{0.5}Ni/MoS₂@graphene exhibited a mass activity of 3579 mA mg⁻¹. This mass activity value is notably higher, 1.73 times greater than PtNi/MoS₂@graphene, 2.98 times greater than Pt@graphene, and 4.68 times greater than commercial Pt/C. The enhanced electrocatalytic performance of PtSc_{0.5}Ni/MoS₂@graphene can be attributed to the relatively slower reduction kinetics of Sc³⁺ ions compared to Pt²⁺. This difference in reduction kinetics results in a more uniform distribution of catalyst components, ultimately enhancing the electrocatalytic activity of PtNi for the EOR. Moreover, in practical application, PtSc_{0.5}Ni/MoS₂@graphene demonstrated an impressive power density of 51.70 mW cm⁻² in an ethanol fuel cell operating at 50°C. This power density surpassed previous reported values, highlighting its exceptional performance. In contrast, the commercial Pt/C catalyst exhibited a significantly lower power density, approximately 3.7 times less than that of PtSc_{0.5}Ni/MoS₂@graphene [41].

Wang *et al.* [13] investigated the impact of different Pt/Mo ratios on the methanol oxidation of PtMoO_x/C. They claimed the best Pt/Mo atomic ratio

of 1.5 to 2.0 yields better methanol oxidation results. The methanol oxidation CV curve for Pt/Mo (atomic 1.5–2.0) demonstrates one oxidation peak in the forward scan at 0.18 V (scan range –0.8 to 0.4 V), and an oxidation peak at approximately 0.02 V was observed.



The oxidation peak observed at about 0.18 V on the Pt/MoO_x/GC electrode indicates that methanol oxidation is controlled by diffusion. Dissociative adsorption occurred during methanol oxidation, forming adsorbed intermediates (CH_xO_{ad}; x = 1–3) and strongly bound adsorbed CO species. When converting intermediates into CO₂ as the final product, the adsorbate must react with adjacent adsorbed oxygen-containing species such as OH_{ad} or water in aqueous solutions (Eq. 6 and 7). This study suggests that Pt/MoO_x/GC electrodes possess bifunctional characteristics, making them excellent methanol electrooxidation catalysts [15].

Lee *et al.* [14] examined the effect of adding Mo to PtSn using Pt/C prepared via a conventional chemical reduction method. It indicates that the mass and specific activity of the EOR decreased in the following order: PtSnMo_{0.6}/C > PtSnMo_{0.4}/C > PtSn/C > Pt/C. Moreover, the study investigated methanol electrooxidation under a 0.5 M NaOH electrolyte solution, which exhibited two peaks: the oxidation of methanol (0.45 V, forward) and the oxidation of carbonaceous species formed during the forward oxidation scan, as well as the removal of oxide catalyst (0.4 V, backward) [42,43]. Dai *et al.* [44] suggested that the reduction in the peak intensity indicates a weaker interaction between the oxygen species and the Pt surface [44,45]. The single-cell performance of PtSn/ and PtSnMo_{0.6}/C was evaluated at 65 and 90°C. The open circuit voltage was 0.50 and 0.70 V, respectively. The cell exhibited the maximum output power density values of 14.3 and 25.7 mW cm^{–2}, respectively, at 65 and 90°C compared to 6.7 and 17.8 mW cm^{–2}, since the Sn and Mo are in an unalloyed phase, where enhancement of EOR activity is attributed from the bifunctional mechanism (Pt–SnO₂ and Pt–

MoO_x) on the oxidation of alcohol [14]. Another study by Jeon *et al.* [25] demonstrated that the Pt₄₅–Ru₄₅Mo₁₀/C had the lowest mass loading and specific activity for methanol electrooxidation compared to other catalysts. However, this particular catalyst displayed a 56% improvement in the specific ethanol electrooxidation activity. This finding is consistent with previous research suggesting that adding Mo to PtRu/C can enhance EOR catalytic activity but contradicts the results obtained for MOR.

4.2 Mo composition

Fathirad *et al.* [46] found that Pd–Mo supported on Vulcan carbon showed higher catalytic activity than pure Pd, whereas Pd₃Mo supported on Vulcan carbon demonstrated superior electrocatalytic activity compared to pure Pd/C and Pd–Mo/C and PdMo₃/C. Fig. 5(a) shows the Pd₃Mo/VC catalyst activity for 0.1 M ethylene glycol methanol oxidation, indicating significantly higher activity than that of monometallic Pd/VC and PdMo/VC. The reduced activity of Pd–Mo/C compared to PdMo₃/C may stem from the depletion of the active surface area during alloy formation and a downshift of the Pd d-center, which weakens the binding energy of the adatoms [46]. In Fig. 5(b), the current densities of the Pd₃Mo/VC catalyst initially declined quite rapidly for all the different alcohols and then reached a steady state. A higher current density signifies greater electroactivity. Despite the initial drop in performance, the catalyst's activity stabilized, maintaining a consistently high current density for all the alcohols tested [46]. Even the morphological and structural compositions of Mo-ECs control the electrocatalytic behavior of the electrode. Typically, the 2H phase of transition metal dichalcogenides (TMD: MoS₂) has a tunable band-gap and poor electrocatalytic properties [47].

In contrast, Gopalakrishnan *et al.* [48] found that defect-induced MoS₂/NF-5 exhibited the highest current density of 73 mA cm^{–2} at the peak potential (0.7 V) for methanol electrooxidation compared with the control samples (MoS₂/NF-2, MoS₂/NF-5, and MoS₂/NF-12). The improved charge transportation and oxidation processes can be attributed to the effect of the hybrid few-layer crumpled nanostructure on the nickel foam substrate. The crumpled MoS₂ hybrid nanostructure demonstrated high electrocatalytic activity and increased active sites, making it suitable for MOR [48]. Similarly, Tang *et al.* [49] developed

an exceptional catalyst, Pt/MoS₂/Ni₃S₂-NRs/NF, by growing single crystal Ni₃S₂ nanorods with exposed {110} high-index facets on Ni foam and coating them with MoS₂. The forward peak current density observed in CV between +0.14 and +0.23 V (potential range -0.8 to 0.4 V) in the positive scan direction is considered a reliable indicator of the electrocatalytic performance of the catalyst, while the oxidation peak between -0.46 and -0.33 V in the negative scan direction corresponds to the oxidation of residual intermediates, such as CO_{ads} and CHO_{ads}. The catalyst had low Pt loading (0.5 wt.%), significantly enhancing its structural stability and resistance to CO_{ads} poisoning. The Pt/MoS₂/Ni₃S₂-NRs/NF catalyst exhibited a mass activity of 805.4 mA mg_{Pt}⁻¹, which was 1.97 times higher than that of commercial Pt/C (10 wt.%), and excellent cyclic durability with only a 4.6% decline (compared to 40.2% for Pt/C) after 28 hours of use [49]. The uniform dispersion of Pt on the surface of Mo structures benefits the interaction between Pt and Mo, which prevents the fast inactivation of Pt active sites during MOR. Moreover, the hierarchical nanostructure (MoS₂/Ni₃S₂-NRs/NF) hindered Pt nanoparticle aggregation and significantly increased charge-transfer ability. Even the dangling bonds at the edges facilitate charge transfer through the non-vertical transition and MoS₂ layers [49]. The synergistic effect of Mo, Pt, and carbon support collectively empowered the MOR activity.

Even the synthesis temperature of the electrocatalyst influences the surface electronic structure, which usually follows the material crystallinity [50]. Consequently, the synthesis temperature increased electrocatalytic activity at 1000°C for 10 wt.% of Mo, using two different concentrations of urea solutions: 1.0 M and 2.0 M. The results indicate that preparing the nanofibers at a high temperature (1000°C) significantly improves the electrocatalytic performance of the functional material in two ways: by achieving a high current density and a distinct urea oxidation peak. However, raising the treatment temperature from 700 to 850°C did not demonstrate a significant variation in the electrocatalytic activity [50]. In contradiction, Izhar *et al.* [51] observed that Mo-based electrocatalysts carburized at 773, 873, and 973 K showed higher activity for the MOR and current density between 10–20 mA cm⁻², respectively, for Mo₂C-based electrocatalyst [51]. However, Mo carburized at 1073 K displayed a current density of

9 mA cm⁻², while the non-carburized catalyst showed activity below 1 mA cm⁻². Thus, the carburization temperature helps produce active sites for MOR activity, and the critical temperature limits MOR activity. The carburized Mo catalyst at 773 and 873 K demonstrated better catalytic activity than non-carburized MoO₃/KB. Active carbides, such as oxy-carbides and β-Mo₂C species, facilitate methanol oxidation [51].

Zhang *et al.* [52] compared the Mo₂C deposited nanotubes (ALD600_{Pt}/Mo₂C) catalyst with commercial PtRu/C, Pt/C, and Pt-black catalysts for the MOR. The nanotube catalyst exhibited higher catalytic activity MOR than commercial PtRu/C, Pt/C, and Pt-black catalysts [53]. In particular, the I_f/I_b (1.71) ratio, which indicates the CO tolerance of the catalyst, was significantly higher for the ALD600_{Pt}/Mo₂C nanotube catalyst than for commercial catalysts, suggesting better CO tolerance and more efficient oxidation of methanol. The strong affinity for MOR arose from the significant amount of sp²-C, facilitating the easy adsorption of methanol on the Pt and MoO_x layers on the surface of Mo₂C nanotubes favors the adsorption of OH in solution and acting as a nanostructured OH reservoir for the MOR. Thus, the Mo₂C nanotube-based catalyst exhibits enhanced CO tolerance [52]. While varying the Mo₂C concentration (0.1, 0.2, and 0.5) compared to Pt/C, Pt/C-Mo₂C (0.02) exhibited the highest catalytic activity because of its higher surface area, displayed in Fig. 5(c) [53]. All Pt/C-Mo₂C electrocatalysts had a more negative onset potential than Pt/C, and the peak current density of Pt/C-Mo₂C (0.02) was 1.7 times that of Pt/C. The onset potential for methanol oxidation on Pt/C-Mo₂C (0.02) was also negatively shifted by 0.1 V compared to that of Pt/C, whereas the lower surface areas of C-Mo₂C (0.50) and C-Mo₂C (0.10) were less effective in promoting the synergistic effect on Pt [53].

Kakati *et al.* [54] investigated the effects of pH and Mo/Pd composition on the electrochemical performance of methanol oxidation using Mo@Pt/MWCNT nanoparticles anchored to MWCNTs. The particles synthesized at pH 9 exhibit a core-shell-like behavior due to the predominant role of Mo or MoO_x in creating a ligand effect. This ligand effect, coupled with a larger electrochemically active surface area, surpasses the bifunctional effect seen in nanoparticles produced at pH 7 with MoO_x. However, excessive

OH adsorption on the catalyst surface impairs performance. Therefore, the precise amount of Mo in these catalysts is essential for optimal performance, as indicated in Fig. 5(d). The increasing PdO content enhances the methanol oxidation current because it requires the presence of surface oxygen-containing species for the oxidative removal of CO. Surprisingly, despite having a higher PdO content compared to Mo@Pd/MWCNT (pH 5) and Pd@MoMWCNT (pH 7), Pd/MWCNT exhibits a lower oxidation current. This suggests that the coexistence of Mo with Pd is the key factor for achieving a higher methanol oxidation current in Mo@Pd/MWCNT (pH 9) [54].

Abhishek and his group investigated the role of polypyrrole–MoO₃ composites in EOR. The con-

ducting polymer network facilitates the conduction of electron/proton pairs generated at the active site – Mo–O–Mo– [10]. The notable increase in the oxidation current density may be due to the mixed valence states of Mo (Mo⁶⁺, Mo⁵⁺, and Mo⁴⁺), as MoO₃/H_xMoO₃ and MoO₂. Typically, the lower oxidation state of MoO_x results in higher CO tolerance and excellent MOR/EOR activity [10]. The direct methanol fuel cell (DMFC) performance revealed that the PtPd/MOPC catalyst showed the highest power density of 27.3 mW cm⁻² among all the catalysts, which is 88% higher than the Pt/C catalyst [10]. The catalytic oxidation of reactant molecules using the Mo₄O₁₁ Magnéli phase of molybdenum oxides involves dissociation, oxidation, and hydrogen spillover

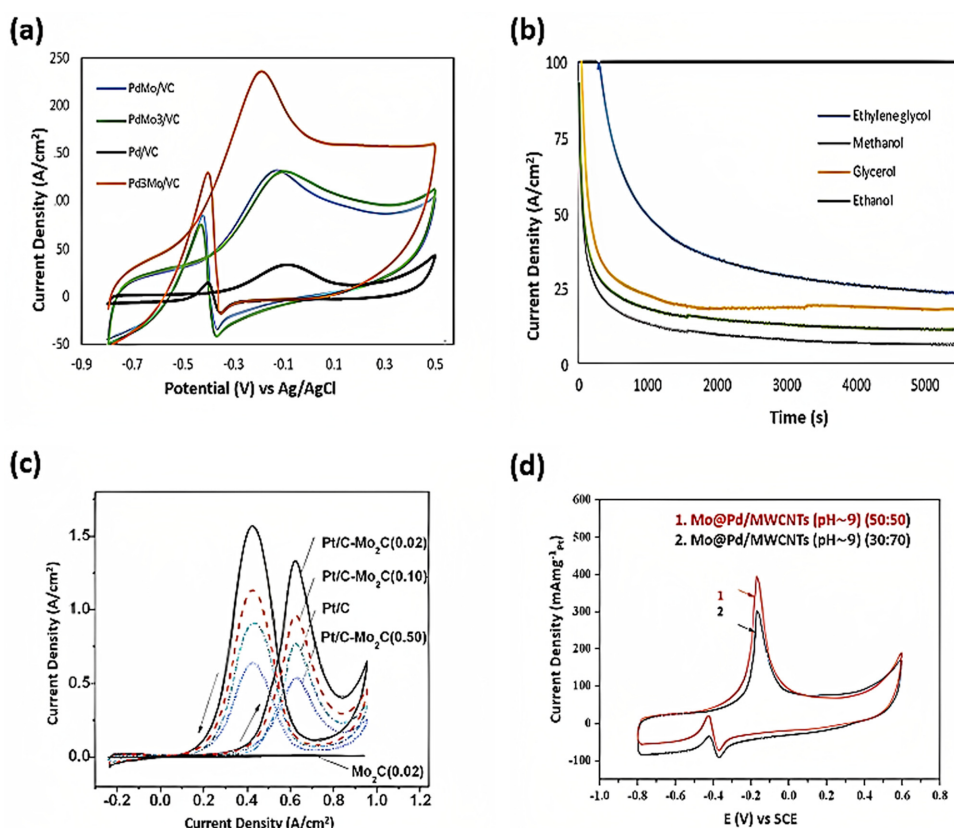
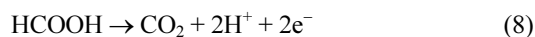


Fig. 5. Effect of different Mo content electrooxidation of different alcohols (a) CV curves of Pd/VC and PdMo/VC in 1.0 M ethylene glycol + 1 M KOH at scan rate of 10 mV s⁻¹ (Reproduced with permission from Ref. [46] Copyright © 2017 Elsevier). (b) Chronoamperometric curves of Pd₃Mo/VC catalyst in electrooxidation of different alcohols (Reproduced with permission from Ref. [46] Copyright © 2017 Elsevier). (c) Pt/C–Mo₂C (0.50), Pt/C–Mo₂C (0.10), Pt/C–Mo₂C (0.02) and Pt/C electrodes in 0.5 M H₂SO₄ + 1.0 M CH₃OH at scan rate of 50 mV s⁻¹ (Reproduced with permission from Ref. [53] Copyright © 2013 Elsevier), and (d) Mo@Pd/MWCNT (pH = 9) with different composition in 1 M KOH + 1 M CH₃OH at scan rate of 50 mV s⁻¹ (Reproduced with permission from Ref. [54] Copyright © 2012 Elsevier).

[24]. The improvement of active sites accompanied by the dispersion of Pt in Pt/Mo₄O₁₁ catalyst sites creates the hydrogen spillover, resulting in improved ECSA from 356.1 mA mg_{Pt}⁻¹ to 722 mA mg_{Pt}⁻¹ and negative anodic peak from 0.93 V to 0.87 V. However, the forward and backward anodic peaks are unexpectedly still higher than many published previous reports. Thus, mixed oxidation showed a much higher CO tolerance than the pure Pt/C electrocatalyst.

Song *et al.* [20] investigated formic acid oxidation using a PtMoO_x/C catalyst. The oxidation of formic acid on Pt occurs through a direct pathway (Eq. 8) that does not involve the generation of CO_{ad}, whereas an indirect pathway involves the generation of CO_{ad}. The bifunctional mechanism of MoO_x only affects the indirect pathway, which is less significant in formic acid cells than in formaldehyde cells (Eq. 9 and 10). Thus, the impact of the CO pathway on formic acid oxidation was significantly decreased [20].



4.3 pH and Scan Rate

Kakati *et al.* [54] studied the effect of pH on the electrocatalytic activity of Mo@Pd/MWCNTs on methanol. Researchers observed that the Mo@Pd/MWCNT catalyst, synthesized under pH = 9 conditions, displayed the highest forward peak current density at 395.61 mA cm⁻²mg_{Pd}⁻¹, surpassing other catalysts produced at various pH levels (Fig. 6(a)) [54]. A trend emerged as the pH of the precursor solution increased, with catalysts generally exhibiting higher forward peak currents. Specifically, Pd@Mo/MWCNT (pH = 7) outperformed Mo@Pd/MWCNT (pH 5) in peak current density. They intriguingly examined the Pd@Mo nanoparticles synthesized at pH = 7 revealing surface segregation of Mo towards the exteriors of nanoparticles. Despite reducing the electrochemically active surface area, this configuration demonstrated superior activity to nanoparticles synthesized at pH 5, where Mo's presence on the surface was minimal. This indicated that the presence of MoO_x on the catalyst surface, synthesized at pH 7, contributed to a bifunctional effect due to its oxophilic nature, which could overcome core-based

ligand effects and the limited bifunctional effect of MoO_x in pH = 5-synthesized nanoparticles.

In contrast, pH 9-synthesized particles exhibited a core-shell-like structure, where Mo or MoO_x primarily contributed to a ligand effect. This resulted in a higher electrochemically active surface area, and the ligand effect of Mo or MoO_x predominated over the bifunctional effect of MoO_x in pH 7-synthesized nanoparticles. However, excessive OH adsorption on the catalyst surface impaired performance, underscoring the critical role of controlling Mo content for optimal catalyst performance [54]. An increase in the scan rate from a slower scan rate (1–10 mV) to a higher scan rate (70–100 mV s⁻¹) resulted in an initial increase in the alcohol oxidation current density and a decrease in the onset potential until the critical scan rate was between the higher and lower scan rates. At higher scan rates, the electrolytes do not have sufficient time to penetrate the electrode surface, and only the electrode surface undergoes electrooxidation. Askari *et al.* [40] comprehensively studied the MOR activity using MoS₂/CoS₂/rGO catalyst. Fig. 6(b) displays the CV curves of the MoS₂/CoS₂/rGO catalyst in 1 M KOH and at the optimal methanol concentration of 0.3 M, measured at various scan rates ranging from 10 to 100 mV s⁻¹. As the scan rate increased, the anodic current density increased, reaching a maximum value of 1.7 mA cm⁻² at a scan rate of 60 mV s⁻¹. However, the current density slightly decreased for scan rates above 60 mV s⁻¹. This decrease is attributed to the insufficient time to oxidize certain active compounds.

Consequently, the optimal scan rate for the catalyst was determined to be 60 mV s⁻¹. Researchers discovered that at a constant concentration of 1 M methanol/1 M KOH, the current density increases, and the onset potential decreases for a scan rate of 10–70 mV s⁻¹ for MoS₂/Ni₃S₂/rGO ECs [13]. From 80 mV s⁻¹, the peak current density decreased as anticipated. A gradual increase in the area under the curve with increasing scan rate and anodic/cathodic peak shift, is attributed to excellent electrochemical redox activity [48]. In contrast, Padmini *et al.* [41] suggested an increase in the forward anodic peak alongside a positive shift in the peak potential owing to the ohmic drop generated by the high current density [41]. The oxidation peak current density obtained from the positive-scan is proportional to the square root of the scan rate, suggesting a diffusion-controlled process.

These findings indicate that the methanol oxidation occurred via diffusion in the Pt–Mo/CNT/rGO/graphite electrode. While a pair of broad redox peaks between 0.3 V and 0.5 V is visible, which could be linked to the redox behavior of carboxylic acid groups such as –COOH and –OH, no current peak for methanol oxidation is detected, indicating that the CNT/graphite electrode lacks significant electrocatalytic activity [17]. The linear relationship between the anodic peak current density versus the square root of the scan rate proves that electrooxidation is a diffusion-controlled process [17,48,54,55].

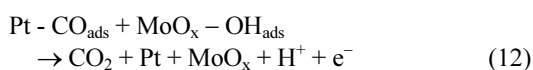
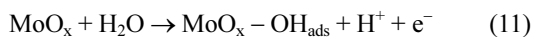
4.4 Concentration of alcohol and temperature

The alcohol oxidation current is increased proportionately with increasing concentration of the alcohol solution. After attaining the critical concentration, the methanol alcohol oxidation current density decreased as the electrolyte concentration increased. The significant decrease in alcohol oxidation results from the formation of methanol byproduct, which affects the electrocatalytic activity of Pt-based electrocatalysts [13]. As methanol concentration increased from 0.1 to 0.5 M at a scan rate of 30 mV s^{−1}, the polarization current started to increase from 0.0 to 0.7 V in the positive direction and followed the reverse in the cathodic direction [48]. The optimal concentration of MoS₂/NF is 0.5 M methanol in 0.1 M NaOH electrolytic solution [48]. Chen *et al.* [16] presented a study utilizing PtRuMo/CNTs as anode catalysts to optimize the performance of DMFC performance. The researchers stabilized the optimal operating conditions by using a methanol concentration of 2.0–2.5 M, a 1.0–2.0 mL min^{−1} flow rate for methanol, and an oxygen flow rate of 100–150 mL min^{−1}. This results in open circuit voltages and power densities of 0.571 V (23.54 mW cm^{−2}), 0.591 V (38.24 mW cm^{−2}), and 0.570 V (61.32 mW cm^{−2}) at different operating temperatures 20, 40, and 60°C, respectively [16]. The performance of DMFC is significantly affected by the methanol concentration (0.5–2.5 M). A higher methanol concentration increases the reaction rate of the anode, which also results in more methanol crossing over to the cathode. This crossover of methanol to the cathode causes oxidation over the Pt catalyst, generating a mixed potential and decreasing DMFC performance [16]. Parisa *et al.* observed an upward trend in methanol oxidation current density for MoS₂/Ni₃S₂/rGO ECs from 0.1 to 1.0 M methanol/1 M

KOH solution [13]. As the methanol concentration increased from 1.5 to 2.0 M methanol/1 M KOH, methanol oxidation, and current density exhibited a downward trend. This decrease resulted from byproduct formation after passing the critical current density of 1 M methanol, inhibiting charge transfer and decreasing the current density. Thus, researchers claim that 1 M methanol is a critical concentration in the alkaline medium for the best performance using MoS₂/Ni₃S₂/rGO ECs [13].

Askari *et al.* [40] comprehensively studied the MOR activity using MoS₂/CoS₂/rGO catalyst in 1 M KOH/ 0.05–0.7 M methanol concentration at a sweep rate of 20 mV s^{−1}, represented in Fig. 6(c). The peak current density increased from 0.4 to 0.9 mA cm^{−2} with an increase in methanol concentration from 0.05 to 0.3 M. However, for concentrations above 0.3 M, the current density did not exhibit an increasing trend, and for 0.7 M, the current density reached 0.6 mA cm^{−2} due to the byproducts of methanol that restrict the charge transfer process [40]. The oxidation current density increased from 1.68 to 2.71 mA cm^{−2} as the temperature increased from 290 to 310 K (Fig. 6(d)). The oxidation current density significantly increases due to reduced charge transfer resistance at the electrolyte-electrocatalyst interface [40]. Ramakrishnan *et al.* [21] studied the electrochemical activity Pt@MoS₂/NrGO in different alcohols (1.0 M methanol/ethylene glycol/glycerol in 0.5 M H₂SO₄) at a scan rate of 50 mV s^{−1} [21]. The electrooxidation activity in methanol, ethylene glycol, and glycerol, with mass activities of 448.0, 158.0, and 147.0 mA mg_{Pt}^{−1}, respectively, which is approximately 4.14, 2.82, and 3.34 times higher than that of the commercial Pt–C (20%) catalyst. Moreover, the electrocatalytic activity loss was higher in methanol (19%) and the least in glycerol activity loss of 14.76%. The forward and backward peaks of alcohol oxidation, positioned at 0.65–0.72 V and 0.39–0.49 V, correspond to the oxidation of methanol, ethylene glycol, and glycerol into intermediate carbonaceous species such as HCOOH, HCOOCH₃, and CO. Additionally, the reduction of Pt–O to Pt or oxidation of chemisorbed carbonaceous species occurs at lower potentials [19,46–48]. These observations provided insights into the electrochemical behavior and mechanisms of oxidizing methanol, ethylene glycol, and glycerol on the catalyst surface [21]. Further research is required to elucidate the potential mechanism of CO oxidation

based on these effects. The electron density of Mo can be transferred to Pt, thereby increasing the coverage sites and reducing the Pt–CO binding energies [16]. It has also been shown that Mo present in the MoO_x species on the surface of CNTs favors the activation of water to generate OH_{ads} through Eq. 11 and 12, aiding in the oxidation of CO and enhancing the catalytic activity of PtRuMo/CNTs for methanol oxidation [16].



Muira *et al.* [56] evaluated platinum–based nitride,

$\text{Pt}_2\text{Mo}_3\text{N}$, using a composition spread thin–film deposition technique. Researchers analyzed Pt–Mo–N films energy, stability, and catalytic activities and concluded that $\text{Pt}_2\text{Mo}_3\text{N}$ is more stable in acidic media than $\text{Pt}_{0.45}\text{Mo}_{0.55}$ and MoN_y because of its high formation energy. Although $\text{Pt}_2\text{Mo}_3\text{N}$ did not exhibit higher activity for methanol oxidation or oxygen reduction than Pt, it showed higher activity toward formic acid oxidation–based nitrides are promising fuel cell catalysts because of their high electrochemical stability at low platinum concentrations [56]. Comparative analysis of the activities of Pt– $\text{Mo}_2\text{N}/\text{C}$ and Pt/C catalysts for methanol and formic acid oxidation using linear sweep voltammetry revealed that the double–layer capacitance of Pt– $\text{Mo}_2\text{N}/\text{C}$ was larger than that of Pt/C, indicating better capacitance

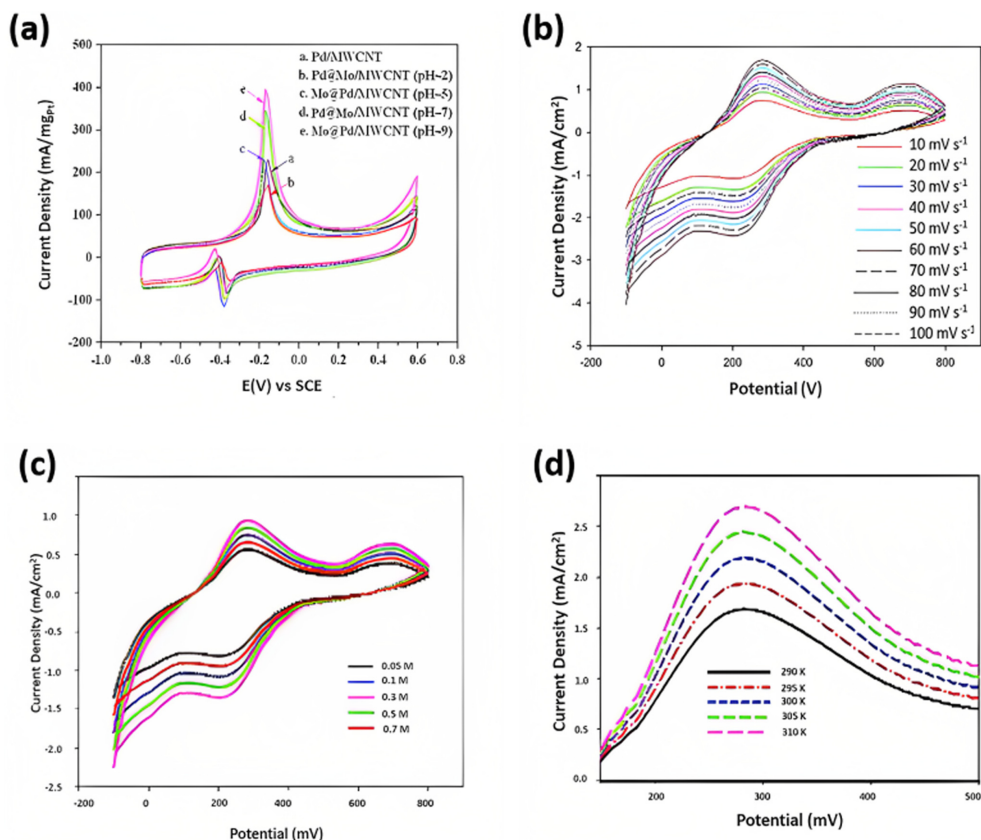


Fig. 6. Cyclic voltammograms of the Mo-ECs of methanol at different (a) at different pH concentration with a scan rate of 50 mV s^{-1} (Reproduced with permission from Ref. [54] Copyright © 2012 Elsevier), (b) $\text{MoS}_2/\text{CoS}_2/\text{rGO}$ catalyst at different scan rate (at $0.3 \text{ M CH}_3\text{OH}$) (Reproduced with permission from Ref. [40] Copyright © 2019 Elsevier), (c) methanol concentration (at 60 mV s^{-1}) (Reproduced with permission from Ref. [40] Copyright © 2019 Elsevier), and (d) temperature (at $0.3 \text{ M CH}_3\text{OH}$ and scan rate 60 mV s^{-1}) (Reproduced with permission from Ref. [40] Copyright © 2019 Elsevier).

behavior. For methanol electrooxidation, the onset potential on Pt–Mo₂N/C was 0.2 V, which is lower than that on Pt/C (0.28 V), and the current density at 0.4 V was 31 mA mg_{Pt}^{−1} on Pt–Mo₂N/C, 2.2 times higher than that on Pt/C (14 mA mg_{Pt}^{−1}). For formic acid oxidation, the first peak current density at 0.35 V on Pt–Mo₂N/C was 86 mA mg_{Pt}^{−1}, approximately 50% higher than that on Pt/C (59 mA mg_{Pt}^{−1}) [56]. Varying the Mo concentration (0.0, 5.0, 10.0, 25.0, 35.0%), the maximum performance of urea oxidation (1.0 M Urea in 1.0 KOH, scan rate 50 mV s^{−1}) was achieved for 25 wt.% Mo, mimicking the alcohol oxidation process [50]. Even varying the urea concentration (0.0, 0.33, 1.00, 2.00, and 3.00 M) resulted in a sharp increase in the current density [50]. Thus, increasing the reactant concentration enhances the reaction rate and improves the mass transfer process. However, the rate-limiting step for the entire process can be the mass transfer of the reactant or the mass transfer rate of the product [50].

4.5 Carbon support

Previously, Mo-ECs employing commercial carbon black as a supported catalyst for alcohol and CO electrooxidation exhibited instability in acidic/alkaline media [57–60]. This instability led to the loss of Pt and Mo surface area, particle leaching, dissolution, and aggregation from the carbon support. On the contrary, catalysts supported on graphene-based materials offer superior attributes such as high stability, conductivity, and easy availability for catalyst fabrication. Notably, nitrogen-doped graphene [57], carbon nanotubes [61], and carbon nanofibers [62] enhance the localized binding energy around Pt particles, effectively preventing aggregation and dissolution of the catalysts [63–66]. Consequently, this leads to a substantial increase in catalytic activity and improved durability and longevity of the catalyst's lifespan. Carbon supports, such as rGO, CNTs, and carbon nanofibers, play a positive role in the electrooxidation of alcohols. The well-organized morphology of carbon support materials facilitates alcohol adsorption because of their increased surface area and excellent electrical conductivity [13]. Zhai *et al.* [64] prepared a 2D–MoS₂/graphene composite for methanol oxidation [67].

Fig. 7(a) demonstrated the CV result of the methanol electrooxidation pattern of over (i) Pt–MoS₂, (ii) Pt–MoS₂/RGO, and (iii) commercial Pt/C. The elec-

trooxidation results exhibited peaks between 0.3 V and 0.9 V. The two distinct oxidation peaks are around 0.7 V (forward peak) and 0.49 V (backward peak). These peaks are characteristic of methanol oxidation on Pt catalysts. The forward peak (0.6–0.9 V) is associated with removing adsorbed/dehydrogenated methanol fractions by Pt–OH, resulting in CO, CO₂, HCOOH, HCOH, and HCOOCH₃ formation. The reverse peak (*ca.* 0.5 V) is linked to the reoxidation of CO and other incompletely oxidized carbonaceous species that formed during the forward scan. The electrocatalytic performance of the materials was evaluated based on the intensity of the forward peak current density. The forward peak current density on PtMoS₂/RGO electrodes was found to be 7.35 mA cm^{−2}, which is 1.73 and 5.65 times higher than that of Pt–MoS₂ (4.26 mA cm^{−2}) and commercial Pt/C (1.30 mA cm^{−2}) electrodes, respectively. The enhanced charge transfer efficiency within the MoS₂/RGO composite is crucial in enhancing the overall electrocatalytic performance [67]. The presence of rGO can dramatically enhance the specific areas of the carriers and contribute to the dispersion of Pt nanoparticles, which may favor exposing more active sites and enhancing the synergy between Pt and the carbon supports [37]. Researchers have studied the porous/starfish morphology of MoS₂/Ni₂S₂/rGO nanostructures for DAFCs (Fig. 7(b)). The study revealed that in 0.1 M methanol/0.1 M ethanol/1 M KOH, MoS₂/Ni₃S₂/rGO nanocatalysts exhibited a higher current density (15.0 mA cm^{−2}, 27.19 mA cm^{−2}) and lower potential peak (0.42 V, 0.41 V) than MoS₂/Ni₃S₂ (10.36 mA cm^{−2} and 0.42 V, 18.13 mA cm^{−2} and 0.42 V), which can be attributed to the positive role of rGO. The I_f/I_b ratio was higher in MoS₂/Ni₃S₂/rGO (1.06, 1.21) than in MoS₂/Ni₃S₂ (1.04, 1.05), indicating the higher electrocatalytic activity and tolerance of the former. These findings were revealed by comparing the CV curves of the MoS₂/Ni₃S₂ and MoS₂/Ni₃S₂/rGO nanocatalysts, confirming that rGO played a positive role in increasing the absorption of methanol because of its increased active surface area, which resulted in increased absorption. Finally, the fuel cell test reveals that anode catalyst MoS₂/Ni₃S₂/rGO resulted in an OCV of 0.59 V/0.48 V and peak power density of 4.42 mW cm^{−2}/3.5 mW cm^{−2}, indicating promising performance [13]. Li *et al.* [37] investigated the MOR activity of Pt/MoWC/rGO electrocatalysts in two electrolytes, *i.e.*, 0.1 M HClO₄

and 0.1 M KOH.

Fig. 7(c,d) shows that the specific activity of the Pt/MoWC/rGO electrocatalyst was as high as 60.11 mA cm^{-2} in an acidic electrolyte, which was superior to that of other catalysts, including Pt/Mo₂C/rGO, Pt/WC/rGO, Pt/MoWC, Pt/rGO, and Pt/C. In alkaline electrolytes, the Pt/MoWC/rGO catalyst also exhibited superior mass and specific activity toward the MOR compared to the other catalysts in the order of Pt/MoWC/rGO > Pt/WC/rGO > Pt/Mo₂C/rGO > Pt/rGO > Pt/MoWC > Pt/C. The improved MOR activity of Pt/MoWC/rGO was attributed to the compositional effect of binary MoWC solid solution and the mesoporous structure of MoWC loaded onto the rGO surface, which exposes more active sites and contributes to their accessibility [37]. The interaction of

MoS₂-to- paved the way for efficient charge transfer in rGO in the Pt-MoS₂/rGO electrocatalyst, which resulted in the electrooxidation of 1 M methanol and HCOOH in 0.5 M H₂SO₄ by 1.73 and 5.63 times the Pt/C catalysts [67]. Vellacheri *et al.* [18] investigated the use of MWCNT-supported Pt-MoO_x ($2 \leq x \leq 3$) electrocatalysts for PEMFC applications. Researchers successfully controlled the effective surface interface between Pt-MoO_x, and adding 5%, MoO_x resulted in excellent performance for the oxygen reduction reaction in the presence of methanol, as depicted in Fig. 4(b). Contrarily, the deposition of 10% MoO_x led to a significant reduction in the active surface area by approximately 80% compared to the Pt-MWCNTs. However, an increase in the number of active sites was observed due to the forming of a Pt-

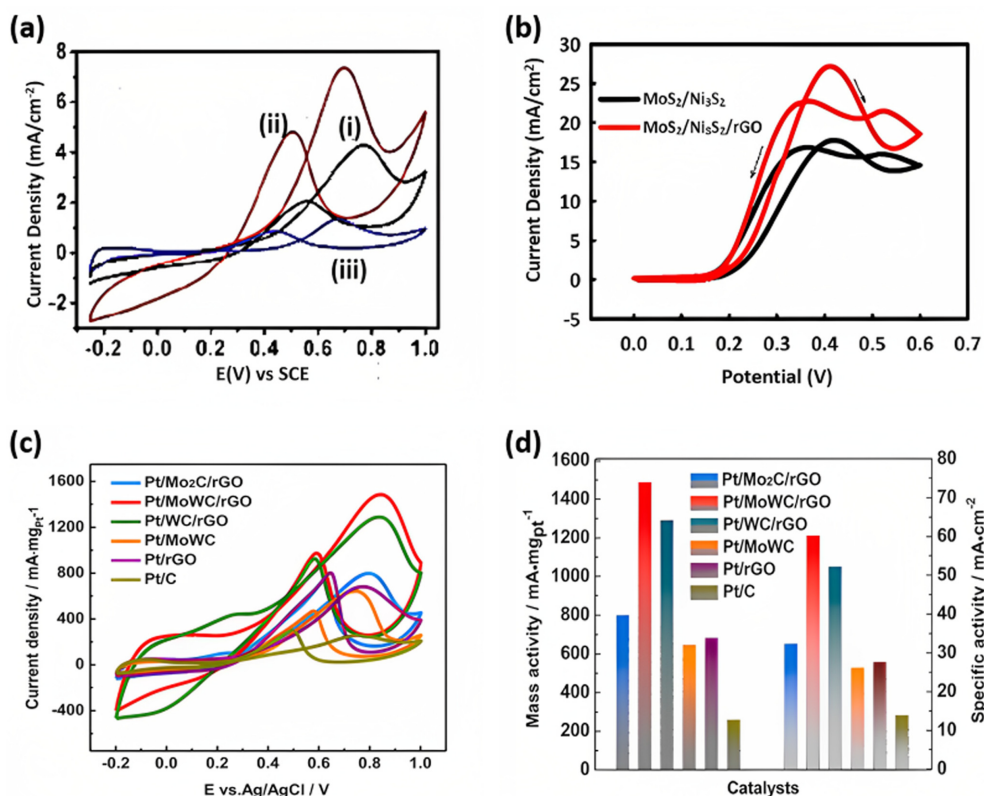


Fig. 7. Effect of carbon support materials on CV curve of methanol oxidation in (a) i-Pt-MoS₂, ii-Pt-MoS₂/rGO, and iii-Pt/C in 0.5 M H₂SO₄ + 1.0 M CH₃OH solution (Reproduced with permission from Ref. [67] Copyright © 2015 Elsevier), (b) MoS₂/Ni₃S₂ and MoS₂/Ni₃S₂/rGO at 0.1 M CH₃OH + 1 M KOH (Reproduced with permission from Ref. [13] Copyright © 2022 American Chemical Society), (c) CVs of the catalysts of different electrocatalysts (Reproduced with permission from Ref. [37] Copyright © 2022 Elsevier), and (d) mass and area-specific activities at 0.84 V and -0.14 V vs. Ag/AgCl in 0.1 M HClO₄ + 1.0 M CH₃OH (Reproduced with permission from Ref. [37] Copyright © 2022 Elsevier).

MoO_x interface. The presence of MoO_x promoted the adsorption of OH species on Pt–MoO_x (5%)–MWCNTs at a lower potential compared to Pd–MWCNTs. This facilitated methanol oxidation, indicating an enhanced catalytic activity [18].

4.6 Stability Test

Gopalakrishnan *et al.* [48] studied electrode durability (MoS₂/NF-5) under varying methanol molarity. The results indicated that MoS₂/NF-5 started to oxidize methanol without any decay and retain 80% of the initial current after 5000 s under methanol for durability test. This may be due to the strong interfacial bonding between the nickel foam (NF) and MoS₂ sheet providing rapid and facile electron transport path and synergic effect between the substrate and MoS₂ for strong structural integrity under the increasing scan rate and methanol molarity [48]. The electrocatalyst stability was confirmed by repeated cycling at the constant scan rate and electrolyte solution. After 200 consecutive cycles of MoS₂/Ni₃S₂/rGO ECs (70 mV s^{−1} and 1.0 M Methanol/1.0 M KOH), there was an increase in the current density by 6% due to gradual penetration of electrolyte solution (methanol) within the MoS₂/Ni₃S₂/rGO ECs. Thus, researchers claim that after several cycles (200 cycles), the active materials are exposed to contact with the electrolyte, and as a result, more electroactive sites are available for the MOR process [13]. Barakat and group demonstrated that an increase in the sweeping cycle leads to a progressive increase in

the current density of the cathodic peak due to the entry of OH[−] into the Ni(OH)₂ surface layer, which results in a thicker layer of NiOOH and gradual increase in the current density [50]. Yan *et al.* [53] analyzed the stability of Pt/C–Mo₂C (0.02) and Pt/C against the ageing of the catalyst under 5000 cycles (Fig. 8(a)). The activity of commercial electrocatalyst Pt/C decreased from 767.8 mA mg_{Pt}^{−1} to 601.1 mA mg_{Pt}^{−1} for MOR. In contrast, the activity of Pt/C–Mo₂C reduced by 8.9% from 1327.6 mA mg_{Pt}^{−1} to 1209.5 mA mg_{Pt}^{−1}. The enhanced electrochemical activity and stability may be due to the strong electronic interaction between Pt and M₂C compared to Pt and C, primarily supported by the XPS and XANES results [53].

Zhou *et al.* [69] explored the importance of dynamic stability in practical use, and an expedited test was conducted to evaluate methanol oxidation's stability. This involved running 1000 cyclic voltammetry (CV) cycles at 150 mV s^{−1}. The results demonstrate that the peak current density of the PtCuMo₂C-2 electrode gradually declines as the number of scans increases (Fig. 8(b)). This decline in performance is linked to the buildup of detrimental intermediates on the electrode surface, which act as poisons. Ultimately, after the completion of the 1000 cycles, the peak current density is diminished for all tested samples [69].

4.7 Electronic effect

The catalytic activity of Pt–Mo ECs can be explained by either the electronic effect or the d-band

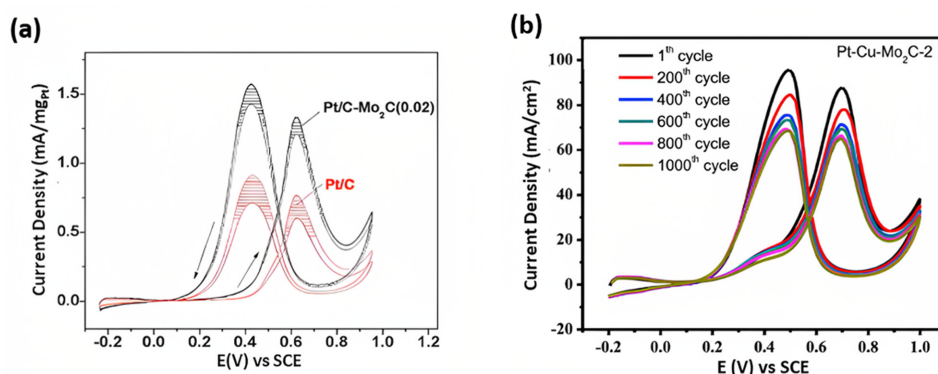


Fig. 8. (a) The cyclic voltammograms of methanol oxidation on Pt/C–Mo₂C (0.02) and Pt/C electrodes in 0.5 M H₂SO₄ + 1.0 M CH₃OH solution, scan rate: 50 mV s^{−1}. The shadow shows the difference between the 1st cycle and the 5000th cycle (Reproduced with permission from Ref. [53] Copyright © 2013 Elsevier). (b) Cyclic voltammograms of PtCuMo₂C-2 catalyst for 0.5 M H₂SO₄ + 1 M CH₃OH solution at 150 mV s^{−1} in an accelerated stability test for 1000th cycles (Reproduced with permission from Ref. [68] Copyright © 2021 Elsevier).

center model [19,69]. The d-band center represents the energy level of the d-orbital of Pt. The position of the d-band determines the strength of the interaction between Pt and C_1 species, such as CO, CHO, and HCHO. The manipulation of the particle size and the chemical environment surrounding Pt atoms effectively alters the d-band center. Due to the smaller particle size of Pt, the d-band orbital becomes more localized closer to the Fermi energy, which is the energy level at which electrons are more likely to be found. Typically, the energy of the antibonding orbital of CO or C_1 species has higher energy than the d-band center of Pt. A higher position of the d-band center relative to the Fermi energy (in Pt metal) indicates that more vacant antibonding states are available for CO poisoning. Consequently, stronger adsorption of CO on the Pt surface results in poor performance of fuel cells.

However, when Pt is combined with Mo through alloy or composite formation, the energy of the Pt d-band center decreases due to the hybridization of d-orbitals, strain effects, contraction or expansion of lattice parameters, and surface defects. This decrease

in the d-band center weakens the CO bond, facilitating CO desorption and promoting CO oxidation through a bifunctional mechanism using the oxyphilic species of Mo. X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) spectra were used to study the changes in the electronic structure of Pt-Mo ECs. The electronic effect can be observed by comparing the binding energies to those of the Pt/C catalyst. For instance, the metallic state of Pt $4f_{7/2}$ of Pt-Mo was observed at 71.4 or 71.6 eV, which is lower than that of the Pt/C catalyst (71.8 eV)—indicating a negative shift of 0.2 eV compared to Pt/C. The variations in the negative shifts of Pt binding energies are likely due to the complex interactions among multiple components. It is widely acknowledged that the decrease in Pt binding energy can alter the electronic structure and reduce the d-band center of Pt atoms relative to the Fermi level. As a result, the adsorption of harmful intermediates on Pt active sites during alcohol fuel oxidation is weakened [68]. XPS analysis provides insight into electronic transitions. The strong interaction of d-electrons from hyper-d-electrons (antibond-

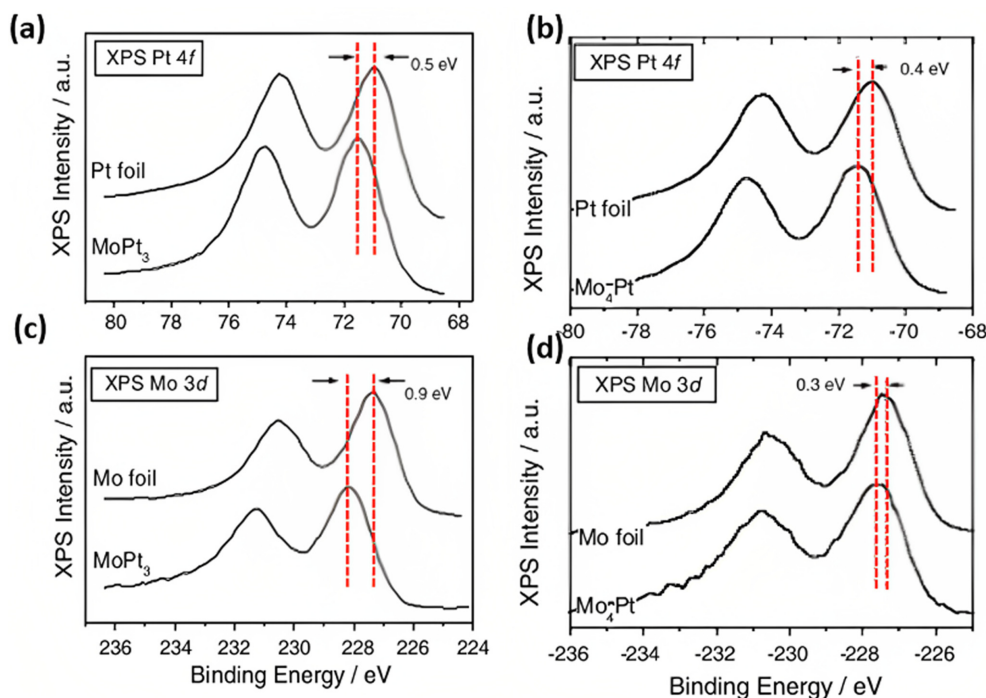


Fig. 9. Comparative XPS spectrum of the Pt(4f) and Mo(3d) region of (a,c) MoPt₃ and (b,d) Mo₄Pt along with pure individual Mo and Pt foil samples (Reproduced with permission from Ref. [36] Copyright © 2005 Elsevier).

ing electrons) to the hypo-d-electron Mo (bonding electrons) was observed in PtMo nanoalloys catalysts (Fig. 9(a,c)) [36]. Though at the higher Mo content (PtMo₃ and PtMo₄), reversed hyper-hypo-d-d electron transfer was also observed (Fig. 9(b,d)). This hypo-hyper-d-d electronic transition is primarily based on the d-electron delocalization. Similar characteristics in PdMo nanoalloys were observed by Fathirad *et al.* [46]. Researchers explained the lower

catalytic activity of PdMo/VC than Pd₃Mo/VC [46]. PdMo alloys undergo phase segregation, in which Pd migrates to the surface, forming an overlayer over the PdMo alloy. Similarly, the change in the electronic structure modifies the catalytic properties of alloying Pd with Mo, and this d-band position of Pd is lowered by inducing strain or electron redistribution of the substrate and overlayer [46].

Table 1. Experimental parameters for anode oxidation using Mo-based nanocatalysts

Electrocatalysts	Electrolyte Solution		Onset Potential (V)	Peak Potential (V)	Current density (mA cm ⁻²) /Scan rate (mV s ⁻¹)	Ref.
	Alcohol	Electrolyte				
PANI/Pt–Ru–Mo	1.0 M MeOH	0.5 M H ₂ SO ₄	–	0.5	7 mA mg ⁻¹ /5	[33]
PtMo/C (3:1)	0.3 M MeOH	1.0 M HClO ₄	–	–	/50	[70]
Pt–Ru–Mo/C	2.0 M MeOH	0.5 M H ₂ SO ₄	0.03	0.43	–	[71]
Pt/X@MoO ₃ /C	2.0 M MeOH	0.5 M H ₂ SO ₄	0.61	0.73	–/20	[19]
Pt–Mo ₄ O ₁₁	0.1 M MeOH	0.1 M HClO ₄	–	0.87	722 mA mg ⁻¹ /100	[24]
Mo ₂ C	1.0 M MeOH	0.5 M H ₂ SO ₄	0.30	0.60	/50	[53]
β–Mo ₂ C	1.5 M MeOH	1.0 N H ₂ SO ₄	–	0.50	20/100	[53]
Pt–Mo ₂ C	0.5 M MeOH	0.5 M H ₂ SO ₄	–0.15	60	–/100	[52]
Pt–Mo–N Thin	1.0 M MeOH	0.1 M H ₂ SO ₄	0.4	–	–/50	[56]
Mo ₂ N/C	1.0 M MeOH	0.5 M H ₂ SO ₄	0.2	0.35	86 mA mg ⁻¹ /–	[72]
Pt/MoO _x /CNTs/Graphite	1.0 M MeOH	0.5 M H ₂ SO ₄	0.4	0.75	264.8 mA mg ⁻¹ /20	[17]
PtRuMo/CNTs	2.0 M MeOH	0.5 M H ₂ SO ₄	–	–	240/–	[14]
Pt–MoO _x /MWCNTs	1.0 M MeOH	0.5 M H ₂ SO ₄	–0.20	0.15	0.00364/10	[17]
PdMo/ECNTs	1.0 M MeOH	1.0 M KOH	–0.172	–0.55	395.61 mA mg ⁻¹ /50	[54]
Pt@MoS ₂ /NrGO	1.0 M MeOH	0.5 M H ₂ SO ₄	–	0.69	448 mA mg ⁻¹ /50	[21]
MoWC–rGO	1.0 M MeOH	0.1 M HClO ₄	0.47	0.835	60.11/5	[37]
Pt/MoS ₂ /Ni ₃ S ₂ –NRs/NF	1.0 M MeOH	1.0 M KOH	–0.184	0.1	805 mA mg ⁻¹ /50	[49]
MoS ₂ /NF	0.5 M MeOH	0.1 M KOH	–	0.70	73/30	[44]
Pt/MoS ₂ /rGO	1.0 M MeOH	0.5 M H ₂ SO ₄	0.3	0.70	7.35/–	[67]
MoS ₂ /CoS ₂ /rGO	1.0 M MeOH	1.0 M KOH	0.09	0.30	2.10/20	[40]
MoS ₂ /Ni ₃ S ₂ /rGO	1.0 M MeOH	1.0 M KOH	0.18	0.40	80.4/70	[13]
MoS ₂ /Ni ₃ S ₂ /rGO	0.5 M EtOH	1.0 M KOH	0.20	0.42	42.9/50	[13]
Pd–Co–Mo	1.0 M EtOH	0.5 M H ₂ SO ₄	–	–	/25	[73]
Pt–Sn–Mo/C	1.0 M EtOH	0.5 M H ₂ SO ₄	0.30	–	–/50	[14]
Pt ₄₅ Ru ₄₅ Mo ₁₀	1.0 M EtOH	1.0 M H ₂ SO ₄	–	–	280 mA m ⁻² /15	[25]
Pt/MoO _x /Glassy carbon	1.0 M EtOH	0.5 M H ₂ SO ₄	–	0.18	–/200	[15]
PtNi/MoS ₂ /Graphene	0.5 M EtOH	0.5 M H ₂ SO ₄	0.18	0.47	2067 mA mg ⁻¹ /10	[41]
MoO _x	0.5 M MeOH	1.0 M HCHO	–	–	20/–	[20]

5. Characterization techniques

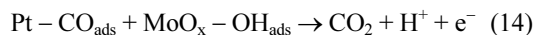
Investigation of various characterization techniques is crucial for understanding the electrochemical reactions involved in the catalytic oxidation of alcohol in direct alcohol fuel cells (DAFCs). In this section, Fourier transforms infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and absorption spectroscopy were comprehensively examined to elucidate the impact of physical, chemical, and structural modifications on the electrochemical performance of Mo-ECs in DAFCs. These characterization techniques provide valuable insights into the molecular, crystallographic, and surface changes, facilitating a deeper understanding of the catalyst's behavior and its role in alcohol oxidation reactions in DAFCs.

5.1 Spectroscopic technique

In-situ Fourier Transform infrared spectroscopy (FTIR) spectra of alcohol oxidation can provide insight into the chemical transformations that occur during the oxidation process and can be used to identify the specific chemical products that are formed. The FTIR spectra of alcohol oxidation can be categorized into three groups: high frequency, medium frequency, and low frequency. Tsouvaras *et al.* [71] comprehensively discussed methanol oxidation to CO and CO₂ over different catalysts, using in situ FTIR spectroscopy (Fig. 10). In the high-frequency region, the bands assigned to CO₂ and CO production are around 2343 cm⁻¹ and ~2040–2060 cm⁻¹ (Fig. 10(a)), are highlighted in the blue and yellow region of FTIR spectrum. The bridge CO band (weakly bonded) was also detected at ~1836 cm⁻¹ [74]. The vibration of the H–O–H bonds in the water molecule was observed at ~1647 cm⁻¹. The spectral band observed at 1200 cm⁻¹ was attributed to CHO species, whereas the characteristic bands of formaldehyde and carbonyls, typically located at 1450 cm⁻¹ and 1280 cm⁻¹, were not identified, which means lesser intermediate formed under the alcohol oxidation. Fig. 10(b,c) presented the integrated intensity of CO₂ and CO₂/CO species observed in FTIR spectrum during the methanol oxidation using binary and ternary catalysts (PtRuMo) with/without heat treatment in H₂ and He atmosphere.

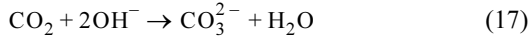
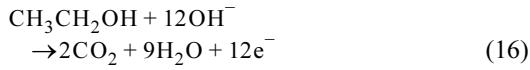
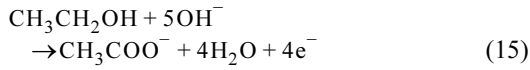
The CO₂ production band was smaller than the CO band in the binary catalyst, whereas all ternary cata-

lysts presented a larger CO₂ production band than the CO band [71,74,76]. The PR₅Mo₃₀₀H₂ catalyst exhibits the largest difference between the CO and CO₂ bands. This means that the CO band in FTIR measures the CO coverage and catalyst tolerance, while the CO₂ band signals the amount of methanol completely oxidized to CO₂ and is used as an activity indicator [71]. The role of Mo in PtMo-ECs to facilitate the –OH species to the Pt. Mo is the form of oxyhydroxides –O(OH) at low potentials that can promote CO oxidation, resulting in higher CO tolerance and alcohol activity. The CO oxidation steps are presented in Eq. 13 and 14.



In the case of the ethanol oxidation reaction, FTIR spectra resemble the methanol oxidation reaction except for identifying carbonate and larger intermediate product species. The high-frequency region shows an upward band appears between ~2340–2050 and ~2010–2050 cm⁻¹ corresponds to the generation of CO₂ and CO species from ethanol oxidation [8,77,78], and the absorption bands at approximately 2800–2900 cm⁻¹, which can be attributed to the asymmetrical stretching of the C–H bonds [34]. The generation of CO₂ has been observed in most of the previous studies. The mid-frequency region ranges from ~1710–1280 cm⁻¹, attributed to the vibration caused by the intermediate species of acetate and acetaldehyde. The absorption bands at 1716, 1410, and 1284 cm⁻¹, related to the formation of intermediates containing the carbonyl C=O stretching mode of carboxylic (COOH) or aldehyde (–CHO), C–O stretching vibrational mode of CH₃COOH and C–O and –OH deformation bands of –COOH [8,77]. The carbonate (CO₃²⁻) band was previously reported at 1370 cm⁻¹ in the spectrum, suggesting the oxidation of CO₂ by the OH⁻ species. Various researchers claim that the suppression of the carbonated band (~1350 cm⁻¹) is due to overlap with the C–O band of acetate ions (–COO⁻) at ~1410 cm⁻¹ [78,79]. The low-frequency region displays peaks around ~1080, ~1036, ~926, and ~874 cm⁻¹ associated with bands of ethanol; the increase in intensity signifies ethanol consumption [77–79]. The acetic acid deformation band at 1350 cm⁻¹ shifted to a higher frequency at 1390 cm⁻¹, sug-

gesting ethanol consumption [80]. Methanol and ethanol exhibited broad peaks in the 3200–3600 cm^{-1} range, corresponding to the stretching vibration of the O–H bond. The main difference between the FTIR spectra of ethanol oxidation and oxidation is that the –OH band is stronger and wider in ethanol because of the two –OH groups. The following reaction is anticipated during ethanol oxidation based on the In-situ FTIR spectroscopy results (Eq. 13–15) [78]:



5.2 Structural properties

Researchers observed that intermixing of Mo in Pt

either existed in the form of Pt–Mo alloy [8,14,56,70,81–83] or a solid solution along with Mo oxide clusters [8,36,84,85]. The lattice parameters of Pt–Mo ECs are so close to pure Pt that the composition of the nanocrystalline phase could not be determined accurately [82,84,86]. It has commonly been observed that Pt/Mo–ECs exhibit minimal peaks of complete absence or Mo peaks other than Pt indicate the successful alloying of PtMo. Fig. 11 shows the peak positions in the Pt–Mo alloys that mainly reflect the (111) crystal plane of Pt/Mo–ECs. This peak is often used as a reference peak to determine the size of nanoparticles using the Debye–Scherrer equation [87]. The Pt {111} facet is the most active and stable, providing optimal binding energy between the Pt atoms and the adsorbed species AOR, because it does not undergo surface reconstruction, unlike Pt {100} and Pt {110} surfaces [88]. The position of the (111) peak in the XRD spectra of Pt nanoparticles is typically around $2\theta = 39\text{--}40^\circ$, with other observable peaks appearing at $2\theta = 46\text{--}48^\circ$, $67\text{--}69^\circ$, and $81\text{--}82^\circ$,

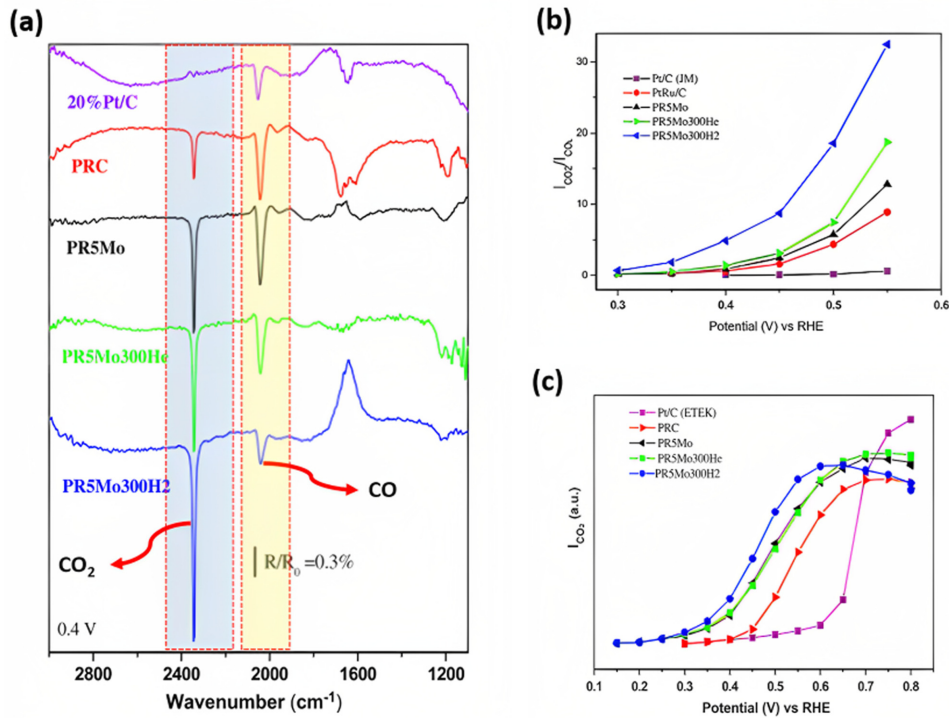


Fig. 10. (a) In-situ FTIR spectra for the ternary in a 2 M CH_3OH + 0.5 M H_2SO_4 electrolyte and the potential was maintained at 0.4 V. Integrated intensities of the (b) CO_2 and (c) CO_2 versus CO during methanol oxidation in 2 M CH_3OH + 0.5 M H_2SO_4 (Reproduced with permission from Ref. [71] Copyright © 2010 Elsevier).

that are related to the (200), (220), and (311) fcc crystal planes of Pt [16,44,53,83,89,90]. Alloying Pt with Mo atoms can result in a contraction of the Pt crystal structure lattice parameter, revealing the same diffraction peak as Pt/C, and a shift in the XRD peak position to a higher diffraction angle, suggesting the formation of a PtMo alloy [10,36,57]. Hernandez *et al.* [57] observed that the XRD reflection of PtMo/C alloys is the same as Pt/C, with lattice parameters $a = 3.92 \pm 0.02 \text{ \AA}$, similar to $3.92 \text{ \AA}$ fcc cell of Pt due to nearly similar elemental radii of Mo and Pt [81,85]. No noteworthy diffraction peaks of Mo were detected, suggesting that a low degree of Mo alloyed with Pt or Mo exists in an unalloyed oxide with poor crystallinity of Mo [46,82,91]. The lower degree of alloying between Pt and Mo corresponds to increased lattice parameters compared to the solution. De *et al.* [10] suggested that the diffraction peaks of MoO_3 did not appear in the XRD pattern because the MoO_3 phase was converted to an amorphous state during the Pt reduction process. The XRD position shifted to a higher angle of diffraction contraction of the lattice parameter owing to alloy formation with dissimilar atomic radii between the Mo and Pt/Pd atoms [46]. The extent of the shift in the peak position and lattice parameters increased with increasing temperature, suggesting an increase in alloying in PtMo [91,92]. The heat treatment temperature of PtMo-ECs, between 400 and 700 degrees Celsius, enables the restoration of the single-phase Face-centered (fcc) structure [82]. The less intense peak around $2\theta = 25^\circ$ corresponds to the (002) diffraction peak of crystalline graphitic carbon [57,66,73].

Similarly, Rao and Viswanathan [73] observed that the diffraction peak shifted to a higher value of the diffraction angle as the heat treatment temperature for Pd-Co-Mo/CDX975 increased from 973 to 1173 K corresponding to the contraction of the lattice due to alloy formation [73] (Fig. 11). Even, several reports suggested that diffraction peaks of the ternary PtRuMo catalyst showed a lower shift in the diffraction angle than those of the binary PtRu/C catalyst. Incorporating Ru (atomic no. 44) in Pt (atomic no. 78) results in a peak shift to a higher diffraction angle. Alloying with Pt, Ru, and Mo resulted in higher stability and, thus, a lower shift to diffraction angle [25]. Tsiouvaras *et al.* [71] demonstrated the effect of He and H_2 gases on the heat treatment of a PtRuMo/C catalyst. When He was used for treatment, there was only a

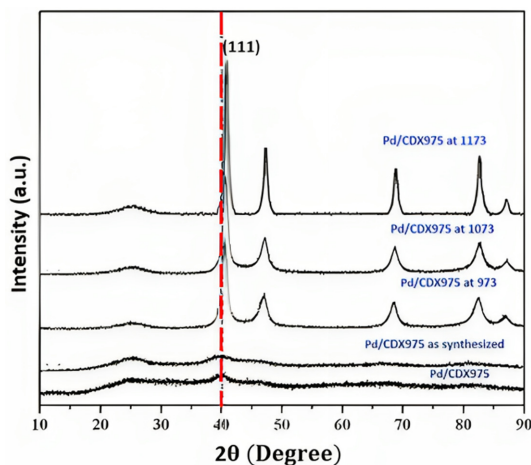


Fig. 11. Powder X-ray diffraction patterns of Pd/CDX975, as-synthesized Pd/CDX975; heat-treated Pd/CDX975 at 973, 1073, and 1173 K, respectively (Reproduced with permission from Ref. [73] Copyright © 2010 Elsevier [73].

minor increase in the particle grain size. However, treatment with H_2 resulted in a more significant change. Adding Mo to the PtRu catalyst produced a noticeable shift in the Pt (111) peak towards a higher diffraction angle, particularly in the PR5Mo300H2 sample. This shift often indicates the formation of a PtRu alloy and suggests that Mo incorporation enhances the interaction between Pt and Ru [71]. Similar diffraction peaks were observed in Pd–Mo and Mo–Pd nanoparticles for PtMo/C. The diffraction slightly shifted towards higher 2θ values, indicating the compression of the Pd lattice. This compression can be attributed to the partial incorporation of Mo into the Pd structure. Additionally, previous research suggests that the deformation of lattice planes due to the small size and support materials can cause changes in lattice parameters [54]. It is evident from previous studies that alloying of Pt/Pd with Mo nanoparticle not only contract the lattice parameter, it also changes in electronic structure, which relatively down-shift the d-band center of Pt/Pd involved in the adsorption of the adsorbate for methanol/CO oxidation [46,54].

5.3 X-ray photoelectron spectroscopy

Table 2 presents the peak positions of XPS for different electrocatalysts for fuel cells. The various research articles summarize the XPS data for inter-

preparing Mo-based electrocatalysts' structural chemical and chemical properties. The electronic effect can be observed by comparing the binding energy of Pt(4f) and Mo(3d) bands of Pt/Mo-ECs XPS spectra. The XPS spectra of the Pt–Mo alloy, MoO₃, Mo₂C, MoS₂, and MoN nanoparticles can provide information about these materials' chemical composition, electronic structure, and surface properties at the nanoscale. The peak positions in the XPS spectra correspond to the binding energy, which helps to understand the charge transfer mechanism from the metallic surface of the catalyst to support the catalyst and vice-versa. The XPS spectrum of the Pt–Mo alloy nanoparticles depended on the alloy composition, size, and shape of the nanoparticles. The peaks combined the individual metals (Pt and Mo) and any new chemical states that formed in the alloy. The chemical composition of the PtMo alloy revealed two distinct peaks for Pt and Mo at ~72 eV and ~230 eV, respectively. The Pt 4f signal is also broken down into three pairs of doublets: 71.13 and 74.51 eV, 71.94 and 75.23 eV, and 74.40 and 77.50 eV. These doublets correspond to metallic Pt, Pt–O or Pt–(OH)₂, and PtO₂, respectively. At the same time, the Mo 3d doublet level spectra peak appears at around 228.6, 229.1, and 230.1 eV for Mo⁰, Mo⁴⁺, and Mo⁶⁺ oxidation states. Molybdenum oxide MoO_x usually exists in two stable states, MoO₂ and MoO₃. Mo in MoO₂ exists in the +4-oxidation state, whereas MoO₃ is in the +6-oxidation state. The XPS spectra of these two compounds show differences in the energy levels of the Mo 3d and O 1s peaks. In the case of MoO₂,

the Mo 3d_{5/2} peak appeared at approximately 229 eV, whereas the Mo 3d_{3/2} peaks were typically observed at approximately 232 eV. These peaks are shifted to higher energies than the corresponding peaks in MoO₃ owing to the lower oxidation state of Mo in MoO₂. The O 1s peak of MoO₂ is typically observed at approximately 530 eV, which is also shifted to a higher energy than that of MoO₃. The XPS spectra of MoO₃, the Mo 3d_{5/2} peak, were expected to appear at approximately 233 eV, whereas the Mo 3d_{3/2} peak is observed at around 236 eV. The O 1s peak of MoO₃ is typically observed at approximately 530 eV, which is lower in energy than that of MoO₂. The energy separation between the Mo 3d_{5/2} and Mo 3d_{3/2} peaks is also expected to be slightly larger in MoO₃ than in MoO₂, reflecting the higher oxidation state of Mo in MoO₃. The spin energy separation between the Mo 3d_{3/2} and Mo 3d_{5/2} lies close to 3.1±0.1 eV, related to either the Mo²⁺ [48], Mo⁴⁺ [93], or Mo⁶⁺ [94] oxidation state of Mo.

During the survey scan of Mo-ECs (MoN, Mo₂C, and MoS₂) nanomaterials, MoO_x phases (MoO₂ and MoO₃) were also detected, which suggests that Mo species were either oxidized during the synthesis process or absorbed or contaminated by atmospheric oxygen [32,50,56,95,96]. Bayati *et al.* [97] suggested that various oxidation states, such as Mo²⁺, Mo³⁺, Mo⁵⁺, and Mo⁶⁺ as in a single Mo, can be linked to the presence of carbide, nitride, and oxide species, respectively [97,98]. A positive shift of 0.2 eV compared to the Pt 4f_{7/2} of pure Pt can be attributed to an induced positive charge on the dis-

Table 2. XPS peak position of Mo-based electrocatalyst

Element	Binding Energy (eV)	Peak	Oxidation state/level	References
Pt	~71.1–74.4	Pt 4f	~71.0 Pt ⁰ (Pt 4f _{7/2}) ~74.5 Pt ⁰ (Pt 4f _{5/2}) ~72.5 Pt ²⁺ (Pt 4f _{7/2}) ~75.7 Pt ²⁺ (Pt 4f _{5/2}) ~74.5 Pt ⁴⁺ (Pt 4f _{7/2}) ~77.6 Pt ⁴⁺ (Pt 4f _{5/2})	[10,16,18,21,41,49,53,56,57,67,72,97,100]
Pd	~220–224	Pd 3d	~335.8 Pd ⁰ (Pd 3d) ~341.0 Pd ⁰ (Pd 3d)	[98]
Mo	~228–236	Mo3d	~228.6 (Mo ⁰ 3d _{5/2}) ~229.1 (Mo ⁴⁺ 3d _{5/2}) ~232.1 (Mo ⁴⁺ 3d _{3/2}) ~230.1 (Mo ⁶⁺ 3d _{5/2}) ~235.6 (Mo ⁶⁺ 3d _{3/2})	[10,13,16,18,19,24,21,37,41,48–50,53,54,57,67,93,94,96–105]

persed Pt particles interacting with the support and suggesting that Mo atoms were not alloyed with Pt in the Pt–molybdenum carbide–derived composites [97]. Yan *et al.* [53] discovered that a positive shift in XPS spectra occurred after the introduction of Mo₂C. These results indicate an increased interaction force between Pt and Mo₂C compared to that between Pt and C, which might result in the increased electrochemical stability of Pt/C–Mo₂C.

5.4 X-ray absorption spectroscopy

XAS is an important analytical technique to investigate the electronic and structural changes in Mo-ECs during electrochemical reactions [106]. XANES spectra analysis has revealed a shift in the pre-edge and white line peaks to higher energy, indicating a higher oxidation state of Mo in the electrocatalysts used in DAFCs [84]. This suggests that the electronic properties of Mo atoms in the electrocatalysts are altered, which could affect their catalytic activity [80–82]. XAS analysis has been used to investigate the coordination environment of Mo atoms in the electrocatalysts, indicating that Mo atoms in the electrocatalysts are well dispersed in the nanomaterials, leading to higher catalytic performance. EXAFS spectra analysis provides further insights into the local atomic structure around Mo atoms in the electrocatalysts, showing a greater degree of Mo–O coordination and the presence of both Mo oxide and Mo metal clusters. Overall, XAS and XANES spectra analysis have provided valuable insights into the electronic and structural properties of Mo–based nanomaterials in DAFCs, aiding in optimizing their composition and structure to enhance their catalytic activity.

X-ray absorption at the Pt L₃ edge for Pt/C (0.54 V) is used to measure the occupancy of Pt 5d electronic states, with the white line intensity being proportional to the occupancy of 5d states [70,82,107]. Mukerjee *et al.* [70] investigated methanol oxidation using PtMo/C electrocatalyst in 1 M HClO₄ solution. XANES spectra revealed an increase in white line intensity and broadening at a potential of 0.54 V, suggesting a buildup of CO on the Pt surface during methanol oxidation. At 0.84 V, adsorption by oxygenated species becomes evident, resulting in two peaks (Pt/Pt and Pt/C interactions) below 2 Å, similar to those observed for Pt/C with adsorbed CO. The XANES spectra of the PtMo/C

catalyst shows an increase in Pt d-band vacancies with increasing potential up to 0.6 V, indicating that oxyhydroxides of Mo are not removing C1 oxide species. However, beyond 0.7 V, the d-band vacancies show a lowering trend, which could be due to the formation of Pt/OH on the surface resulting from the activation of water in the aqueous acid on the Pt surface. This suggests that the removal of CO species in PtMo/C beyond 0.7 V is due to the formation of oxides on Pt due to water activation [70].

Fig. 12(a–d) represented the X-ray absorption profiles (XANES) at the Pt L₃ edge (11,564 eV) for Pt/C and PtMo/C materials under different conditions: 0.1 V vs. RHE in two different gas environments, H₂ and H₂/CO, both at 80°C [108]. The key focus was on the “white-line” intensity, a peak near the edge energy directly related to the electron density in Pt’s 5d band. In an H₂ atmosphere (Fig. 12(a,c)), the presence of Mo near Pt atoms slightly altered the Pt chemical environment, resulting in a minor increase in the Pt 5d band vacancy, indicated by a slightly higher absorption intensity. Analysis of XPS data revealed that the Mo species predominantly existed as Mo (VI) oxide, consistent with prior literature suggesting that metal oxides near Pt atoms can withdraw electrons, reducing Pt–CO adsorption energy. In an H₂/CO atmosphere (Fig. 12(b,d)), Pt/C and PtMo/C exhibited increased Pt 5d band vacancies due to CO adsorption compared to hydrogen alone. This was attributed to Pt transferring electrons to CO through electron back-donation. However, the Pt/C electrocatalyst displayed a more significant increase in electron vacancy, indicating that the presence of Mo oxide near Pt atoms reduced the spillover of electrons from Pt to CO, consequently weakening CO adsorption strength [109].

Hassan *et al.* [82] observed that heat-treated PtMo/C electrocatalysts exhibit a slight increase in the white line intensity compared to prepared catalysts when exposed to H₂ and H₂/CO atmospheres, indicating a slight increase in the occupancy of the Pt 5d band, possibly due to changes in particle size. It is evident in various studies that the white line intensity increases more with increasing potential for catalysts with smaller particle sizes and the effect of heat treatment indicating a modification of the average Pt oxidation state [31,109]. The white line intensity of PtMo/C is slightly higher than Pt/C, indicating an increase in the number of Pt 5d band vacancies due to

alloying [70]. CO adsorption affects the electronic properties of Pt, with the white line intensity of Pt/C significantly increasing after CO exposure, indicating an increase in the number of Pt 5d band vacancies due to electron back-donation from Pt to CO. A similar but smaller effect was observed for PtMo/C. The increase in the white line intensity suggests that CO adsorption alters the electronic structure of Pt, and this effect is more pronounced in Pt/C than in PtMo/C [82]. According to the Mo K-edge XANES spectra at 0.0V, Mo is present in the form of a hydrated oxide species with an estimated oxidation state of

Mo⁵⁺. There is a noticeable change in the oxidation state of Mo from Mo⁵⁺ to Mo⁶⁺ at 0.54 V, which remains constant until 0.85 V. The redox couple observed at approximately 0.2V and 0.45V in the voltammogram results corresponds to the presence of Mo in an oxidation state between Mo⁵⁺ and Mo⁶⁺ [85]. In another work, Hassan *et al.* [109] investigated the XANES spectra of PtMo/Mo₂C/C, PtMo/C, and Pt/C electrocatalysts were recorded before and after CO adsorption at 50 mV *vs.* RHE. The spectra showed a slight increase in the white line intensity of PtMo/Mo₂C/C and PtMo/C compared to Pt/C in the

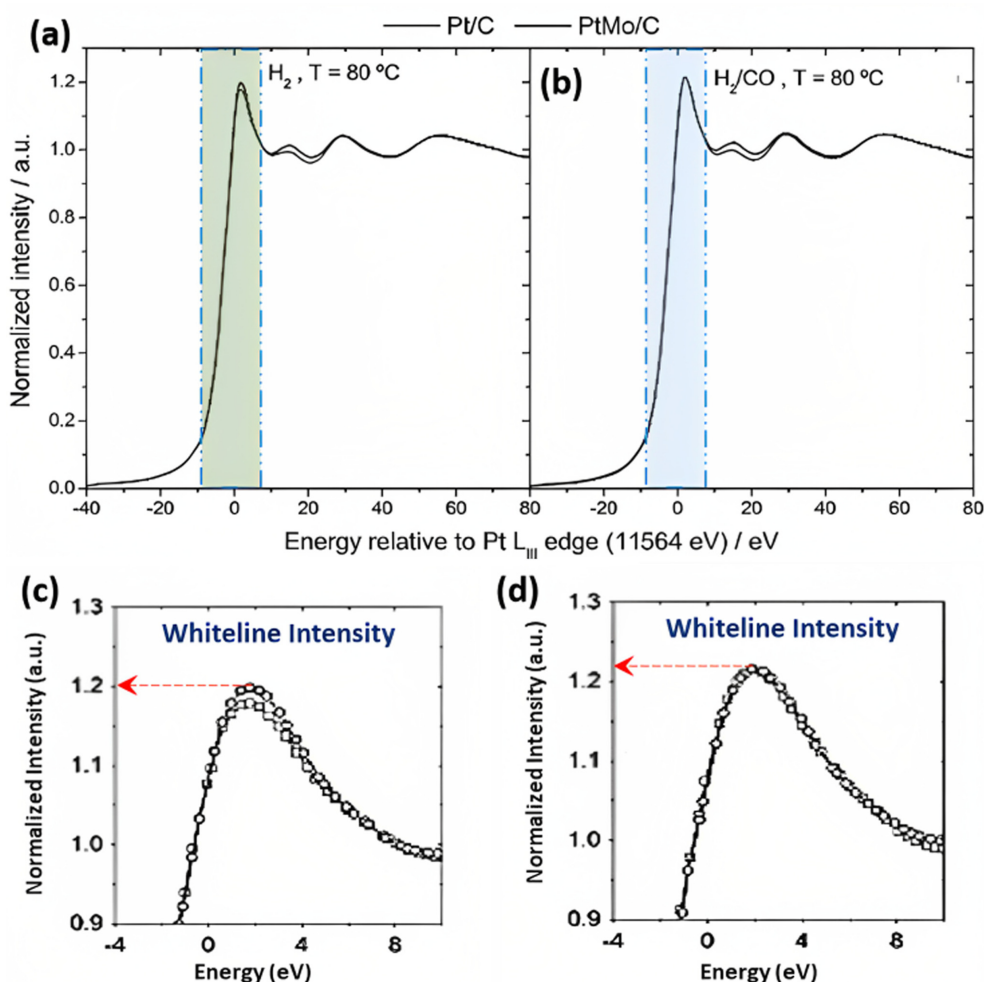


Fig. 12. (a,b) XANES spectra for Pt/C and PtMo/C electrocatalysts at two distinct atmospheres at 80°C, H₂ and H₂/CO atmosphere (Reproduced with permission from Ref. [108] Copyright © 2013 Elsevier), (c,d) enlarge section of Whiteline intensity of XANES spectra environments at 80°C in H₂ and H₂/CO (Reproduced with permission from Ref. [108] Copyright © 2013 Elsevier).

H₂ atmosphere, indicating a change in the chemical environment of Pt due to the presence of Mo or Mo₂C. The intensity of the white line increased noticeably in all three electrocatalysts after CO adsorption, indicating electron back donation from Pt to CO, and this effect was greater in Pt/C than in PtMo/Mo₂C/C and PtMo/C catalysts [109].

In conclusion, White line intensity in X-ray absorption at the Pt L₃ edge can be used to measure the occupancy of Pt 5d electronic states, which increases with the number of Pt 5d band vacancies caused by CO adsorption or particle size. XANES spectra studies on PtMo/Mo₂C/C, PtMo/C and Pt/C electrocatalysts reveal a slight increase in PtMo/Mo₂C/C and PtMo/C white line intensity after CO adsorption, indicating a change in the chemical environment of Pt due to Mo, while Pt/C shows a greater effect of CO adsorption compared to PtMo/Mo₂C/C and PtMo/C. Investigating the structural, electrical, and spectroscopic results is crucial for understanding the chemical and electronic state change in Mo with its surroundings, which is essential for developing efficient Mo-ECs for DAFC.

6. Challenges and Opportunities in Mo-ECs

Molybdenum-based electrocatalysts have been widely studied in DAFCs owing to their unique properties, such as high electrocatalytic activity towards alcohol oxidation reactions, low cost, and abundant availability. Despite these advantages, several challenges must be addressed to improve the performance of DAFCs. Herein, we discuss some key challenges associated with Mo-based electrocatalysts for DAFCs.

6.1 Low durability

One of the main challenges associated with Mo-based electrocatalysts for DAFCs is their low durability [21]. During the electrochemical reaction, Mo-based catalysts are subjected to harsh conditions that can cause surface oxidation [37,50,56,95,96], corrosion, and Mo dissolution, leading to loss of catalytic activity over time [8,71,82,83,86,100,109–111]. Several studies have been conducted to improve the durability of Mo-based catalysts, including carbon-based supports, such as graphene and carbon nanotubes, to enhance the stability of the catalyst [54,56,72,112,113].

6.2 Limited activity towards CO oxidation

Another significant challenge with Mo-based electrocatalysts in DAFCs is their limited activity towards CO oxidation. CO is a common intermediate formed during alcohol oxidation and can poison the catalyst surface, reducing activity and efficiency. Several strategies have been proposed to address this issue, such as modifying Mo-based catalysts with other transition metals, such as Pt and Pd, to enhance their activity for CO oxidation [114].

6.3 Synthesis complexity

The synthesis of Mo-based electrocatalysts for DAFCs is complex and challenging. The synthesis conditions, such as precursor concentration [83], temperature [48,49,71,80,89,90], and pH [52,54], must be carefully controlled to achieve the desired morphology, crystal structure, and composition of the catalyst [94]. Several studies have focused on developing new synthesis methods for Mo-based electrocatalysts, such as hydrothermal and solvothermal methods, to improve the reproducibility and scalability of the synthesis process [46,115].

6.4 Poor electrochemical stability

Mo-based electrocatalysts can also suffer from poor electrochemical stability, particularly under high current densities and low alcohol concentrations [56,72,112,113]. This instability can reduce the catalyst's performance and durability, limiting its practical application. Several strategies have been proposed to improve the electrochemical stability of Mo-based catalysts, such as using carbon-based supports, such as graphene, reduced graphene oxide, and carbon nanotubes, to enhance the mechanical and electrochemical stability of the catalyst [16–18,21,37,54,57,93,94,101].

7. Conclusions

In contrast to Pt and Pt–Ru electrocatalysts, the catalytic response of Mo-ECs against different alcohols in both acidic and alkaline fuel cells shows superior performance. However, determining the optimal Mo content in an electrocatalyst remains poorly understood and depends on various factors, including the ratio of alloyed or non-alloyed Mo and preparation conditions such as pH, temperature, precursor nature, and composition. Mo-ECs and their species exhibit

unusual oxyphilic behavior, significantly lowering the onset potential for CO oxidation, methanol, and ethanol oxidation. By incorporating Mo into noble metals like Pt and Pd, the onset/peak potential for alcohol or CO oxidation decreases due to forming a complex oxidation state inherent to Mo. Consequently, the catalytic oxidation current density for methanol or ethanol oxidation in DAFCs can be substantially improved from 1–10 mA mg⁻¹ to 1000–2000 mA mg⁻¹. However, the susceptibility of Mo-EC catalysts to oxidation and dissolution poses a significant challenge. To address this issue, researchers are exploring methods to modify the surfaces of molybdenum-based materials by applying protective coatings or using alloying agents to enhance their stability and durability. Another research focus is the development of novel synthetic approaches for preparing additional support materials, including graphene, carbon nanotubes (CNTs), conducting polymers, and various metal or metal oxides. These materials can impart unique morphologies and structures to molybdenum-based materials, enhancing their catalytic activity and performance. Researchers have employed facile and expensive techniques to fabricate nanoscale structures of molybdenum-based materials, thereby increasing their surface areas and electrocatalytic activities. These advancements can yield more efficient and stable molybdenum-based electrode materials for implementation in DAFCs.

Acknowledgement

The authors sincerely thank King Mongkut's University of Technology North Bangkok, Thailand, for funding this research work under the Postdoctoral Program (Grant No. KMUTNB-POST-66-09, KMUTNB-64-KNOW-08).

Conflict of Interest

The authors declare that they have no conflicts of interest regarding this manuscript.

References

- [1] S. Basri, S. K. Kamarudin, W. R. W. Daud, and Z. Yaakub, *Int. J. Hydrogen Energy*, **2010**, 35(15), 7957–7970.
- [2] A. B. Anderson, E. Grantscharova, and S. Seong, *J. Electrochem. Soc.*, **1996**, 143(6), 2075–2082.
- [3] R. Yeetsorn, W. P. Ouajai, and K. Onyu, *RSC Adv.*, **2020**, 10, 24330–24342.
- [4] R. Yeetsorn, Y. Maiket, and W. Kaewmanee, *RSC Adv.*, **2020**, 10, 13100–13111.
- [5] D. M. Fadzillah, S. K. Kamarudin, M. A. Zainoodin, and M. S. Masdar, *Int. J. Hydrogen Energy*, **2019**, 44(5), 3031–3054.
- [6] M. Bowker, A. F. Carley, and M. House, *Catal. Lett.*, **2008**, 120(1–2), 34–39.
- [7] C.-W. Liu, Y.-W. Chang, Y.-C. Wei, and K.-W. Wang, *Electrochim. Acta.*, **2011**, 56(1), 2574–2581.
- [8] D. M. dos Anjos, K. B. Kokoh, J. M. Léger, A. R. D. Andrade, P. Olivi, and G. Tremiliosi-Filho, *J. Appl. Electrochem.*, **2006**, 36, 1391–1397.
- [9] B. Beden, C. Lamy, N. R. de Tacconi, and A. J. Arvia, *Electrochim. Acta.*, **1990**, 35(4), 691–704.
- [10] A. De, J. Datta, I. Haldar, and M. Biswas, *ACS Appl. Mater. Interfaces*, **2016**, 8(42), 28574–28584.
- [11] A. Yuda, A. Ashok, and A. Kumar, *Catal. Rev.*, **2022**, 64(1), 126–228.
- [12] P. Ferrin, A. U. Nilekar, J. Greeley, M. Mavrikakis, and J. Rossmeisl, *Surf. Sci.*, **2008**, 602, 3424–3431.
- [13] P. Salarizadeh, M. B. Askari, and A. D. Bartolomeo, *ACS Appl. Nano Mater.*, **2022**, 5(3), 3361–3373.
- [14] E. Lee, A. Murthy, and A. Manthiram, *Electrochim. Acta*, **2011**, 56, 1611–1618.
- [15] Y. Wang, E. R. Fachini, G. Cruz, Y. Zhu, Y. Ishikawa, J. A. Colucci, and C. R. Cabrera, *J. Electrochem. Soc.*, **2001**, 148, C222.
- [16] S. Chen, F. Ye, and W. Lin, *Int. J. Hydrogen Energy*, **2010**, 35(15), 8225–8233.
- [17] Y. Gan, H. Huang, and W. Zhang, *Trans. Nonferrous Met. Soc. China*, **2007**, 17(1), 214–219.
- [18] R. Vellacheri, S. M. Unni, S. Nahire, U. K. Kharul, and S. Kurungot, *Electrochim. Acta*, **2010**, 55(8), 2878–2887.
- [19] O. Guillén-Villafuerte, G. García, J. L. Rodríguez, E. Pastor, R. Guil-López, E. Nieto, and J. L. G. Fierro, *Int. J. Hydrogen Energy*, **2013**, 38(19), 7811–7821.
- [20] C. Song, M. Khanfar, and P. G. Pickup, *J. Appl. Electrochem.*, **2006**, 36, 339–345.
- [21] S. Ramakrishnan, M. Karuppannan, M. Vinokannan, K. Ramachandran, O. J. Kwon, and D. J. Yoo, *ACS Appl. Mater. Interfaces*, **2019**, 11(13), 12504–12515.
- [22] R. Parsons and T. VanderNoot, *J. Electroanal. Chem. Interfacial Electrochem.*, **1988**, 257(1–2), 9–45.
- [23] G. Samjeské, H. Wang, T. Löffler, and H. Baltruschat, *Electrochim. Acta*, **2002**, 47(22–23), 3681–3692.
- [24] F. Yang, F. Li, Y. Wang, X. Chen, D. Xia, and J. Liu, *J. Mol. Catal. A Chem.*, **2015**, 400, 7–13.
- [25] M. K. Jeon, K. R. Lee, and S. I. Woo, *Korean J. Chem. Eng.*, **2009**, 26, 1028–1033.
- [26] B. N. Grgur, N. M. Markovic, and P. N. Ross, *J. Phys. Chem. B*, **1998**, 102(14), 2494–2501.
- [27] A. B. Kashyout, A. B. A. A. Nassr, L. Giorgi, T. Maiyalagan, and B. A. B. Youssef, *Int. J. Electrochem.*

- Sci.*, **2011**, 6, 379–393.
- [28] S. Wu, J. Liu, Z. Tian, Y. Cai, Y. Ye, Q. Yuan, and C. Liang, *ACS Appl. Mater. Interfaces*, **2015**, 7, 22935–22940.
- [29] L. Lai, G. Yang, Q. Zhang, H. Yu, and F. Peng, *J. Power Sources*, **2021**, 509, 230397.
- [30] B. N. Grgur, G. Zhuang, N. M. Markovic, and P. N. Ross, *J. Phys. Chem. B*, **1997**, 101, 3910–3913.
- [31] S. Mukerjee, S. J. Lee, E. A. Ticianelli, J. McBreen, B. N. Grgur, N. M. Markovic, P. N. Ross, J. R. Giallombardo, and E. S. De Castro, *Electrochem. Solid-State Lett.*, **1999**, 2(1), 12–15.
- [32] H. Massong, H. Wang, G. Samjeské, and H. Baltruschat, *Electrochim. Acta*, **2001**, 46(5), 701–707.
- [33] A. Lima, C. Coutanceau, J. M. Léger, and C. Lamy, *J. Appl. Electrochem.*, **2001**, 31, 379–386.
- [34] A. Oliveira Neto, E. G. Franco, E. Aricó, M. Linardi, and E. R. Gonzalez, *J. Eur. Ceram. Soc.*, **2003**, 23(15), 2987–2992.
- [35] J. M. Jakšić, L. M. Vračar, S. G. Neophytides, and N. V. Krstajić, *Chem. Ind. Chem. Eng. Q.*, **2005**, 11(3), 129–136.
- [36] J. M. Jaksic, L. Vracar, S. G. Neophytides, S. Zafeiratos, G. Papakonstantinou, N. V. Krstajic, and M. M. Jaksic, *Surf. Sci.*, **2005**, 598(1–3), 156–173.
- [37] S. Li, Y. Zhang, Y. Han, F. Lv, B. Liu, and L. Huo, *Appl. Surf. Sci.*, **2022**, 600, 154134.
- [38] C. V. Ramana, A. Mauger, and C. M. Julien, *Prog. Cryst. Growth Charact. Mater.*, **2021**, 67(3), 100533.
- [39] N. R. Elezović, L. M. Gajić-Krstajić, L. M. Vračar, and N. V. Krstajić, *Int. J. Hydrogen Energy*, **2010**, 35(23), 12878–12887.
- [40] M. B. Askari, P. Salarizadeh, M. Seifi, and S. M. Rozati, *J. Phys. Chem. Solids*, **2019**, 135, 109103.
- [41] P. Basumatary, D. Konwar, and Y. S. Yoon, *Appl. Catal. B Environ.*, **2020**, 267, 118724.
- [42] A. Sharma, S. K. Mehta, S. Singh, and S. Gupta, *J. Appl. Electrochem.*, **2016**, 46(1), 27–38.
- [43] J. Huang, Z. Liu, C. He, and L. M. Gan, *J. Phys. Chem. B*, **2005**, 109(35), 16644–16649.
- [44] Y. Dai, K. Sun, and Y. Li, *J. Electroanal. Chem.*, **2015**, 757, 94–99.
- [45] L. Ou and S. Chen, *J. Electrochem.*, **2013**, 19(1), 10.
- [46] F. Fathirad, A. Mostafavi, and D. Afzali, *Int. J. Hydrogen Energy*, **2017**, 42, 3215–3221.
- [47] K. Chang, X. Hai, H. Pang, H. Zhang, L. Shi, G. Liu, H. Liu, G. Zhao, M. Li, and J. Ye, *Adv. Mater.*, **2016**, 28(45), 10033–10041.
- [48] A. Gopalakrishnan, L. Durai, J. Ma, C. Y. Kong, and S. Badhulika, *Energy Fuels*, **2021**, 35(12), 10169–10180.
- [49] B. Tang, Y. Lv, J. Du, Y. Dai, S. Pan, Y. Xie, and J. Zou, *ACS Sustain. Chem. Eng.*, **2019**, 7(13), 11101–11109.
- [50] N. A. M. Barakat and M. A. Ali, *Sci. Rep.*, **2022**, 12, 22574.
- [51] S. Izhar and M. Nagai, *Open Catal. J.*, **2013**, 6, 37–40.
- [52] K. Zhang, W. Yang, C. Ma, Y. Wang, C. Sun, Y. Chen, P. Duchesne, J. Zhou, J. Wang, Y. Hu, M. N. Banis, P. Zhang, F. Li, J. Li, and L. Chen, *NPG Asia Mater.*, **2015**, 7, e153.
- [53] Z. Yan, H. Wang, M. Zhang, Z. Jiang, T. Jiang, and J. Xie, *Electrochim. Acta*, **2013**, 95, 218–224.
- [54] N. Kakati, J. Maiti, S. H. Lee, and Y. S. Yoon, *Int. J. Hydrogen Energy*, **2012**, 37(24), 19055–19064.
- [55] Z.-P. Sun, X.-G. Zhang, Y.-Y. Liang, and H.-L. Li, *Electrochem. Commun.*, **2009**, 11(3), 557–561.
- [56] A. Miura, M. E. Tague, J. M. Gregoire, X.-D. Wen, R. B. van Dover, H. D. Abruña, and F. J. Disalvo, *Mater. Chem.*, **2010**, 22(11), 3451–3456.
- [57] M. González-Hernández, E. Antolini, and J. Perez, *Int. J. Hydrogen Energy*, **2020**, 45(8), 5276–5284.
- [58] S. Maass, F. Finsterwalder, G. Frank, R. Hartmann, and C. Merten, *J. Power Sources*, **2008**, 176(2), 444–451.
- [59] K. H. Kangasniemi, D. A. Condit, and T. D. Jarvi, *J. Electrochem. Soc.*, **2004**, 151(4), E125.
- [60] M. Li, J. Shi, X. Guo, Y. Ying, Y. Wu, Y. Wen, and H. Yang, *J. Electroanal. Chem.*, **2023**, 928, 117038.
- [61] N. Tsiouvaras, M. V. Martínez-Huerta, R. Moliner, M. J. Lázaro, J. L. Rodríguez, E. Pastor, M. A. Peña, and J. L. G. Fierro, *J. Power Sources*, **2009**, 186(2), 299–304.
- [62] R. Yeetsorn, *The Journal of KMITNB*, **2004**, 14(4), 60–64.
- [63] M. N. Groves, A. S. W. Chan, C. Malardier-Jugroot, and M. Jugroot, *Chem. Phys. Lett.*, **2009**, 481(4–6), 214–219.
- [64] R. I. Jafri, N. Rajalakshmi, K. S. Dhathathreyan, and S. Ramaprabhu, *Int. J. Hydrogen Energy*, **2015**, 40(12), 4337–4348.
- [65] Q. Sun and S. Kim, *Electrochim. Acta*, **2015**, 153, 566–573.
- [66] A. Heydari and H. Gharibi, *J. Power Sources*, **2016**, 325, 808–815.
- [67] C. Zhai, M. Zhu, D. Bin, F. Ren, C. Wang, P. Yang, and Y. Du, *J. Power Sources*, **2015**, 275, 483–488.
- [68] Y. Zhou, D. Liu, W. Qiao, Z. Liu, J. Yang, and L. Feng, *Mater. Today Phys.*, **2021**, 17, 100357.
- [69] Y. Wang, G. Wang, G. Li, B. Huang, J. Pan, Q. Liu, J. Han, L. Xiao, J. Lu, and L. Zhuang, *Energy Environ. Sci.*, **2015**, 8(1), 177–181.
- [70] S. Mukerjee and R. C. Urian, *Electrochim. Acta*, **2002**, 47(19), 3219–3231.
- [71] N. Tsiouvaras, M. V. Martínez-Huerta, O. Paschos, U. Stimming, J. L. G. Fierro, and M. A. Peña, *Int. J. Hydrogen Energy*, **2010**, 35(20), 11478–11488.
- [72] Z. Cui, M. Yang, and F. J. Di Salvo, *Electrochem. Commun.*, **2013**, 33, 63–67.
- [73] C.V. Rao and B. Viswanathan, *Electrochim. Acta*, **2010**, 55(8), 3002–3007.
- [74] M. V. Martínez-Huerta, J. L. Rodríguez, N. Tsiouvaras, M. A. Peña, J. L. G. Fierro, and E. Pastor, *Chem. Mater.*, **2008**, 20(13), 4249–4259.
- [75] T. Iwasita and F. C. Nart, *J. Electroanal. Chem. Interfacial Electrochem.*, **1991**, 317(1–2), 291–298.

- [76] P. W. Faguy, N. Markovic, and P. N. Ross, *J. Electrochem. Soc.*, **1993**, *140*, 1638–1641.
- [77] E. H. Fontes, R. M. Piasentin, J. M. S. Ayoub, J. C. M. da Silva, M. H. M. T. Assumpção, E. V. Spinacé, A. O. Neto, and R. F. B. de Souza, *Mater. Renew. Sustain. Energy*, **2015**, *4*(1), 3.
- [78] Z.-Y. Zhou, Q. Wang, J.-L. Lin, N. Tian, and S.-G. Sun, *Electrochim. Acta*, **2010**, *55*(27), 7995–7999.
- [79] X. Fang, L. Wang, P. K. Shen, G. Cui, and C. Bianchini, *J. Power Sources*, **2010**, *195*(5), 1375–1378.
- [80] A. O. Neto, J. Nandenha, M. H. M. T. Assumpção, M. Linardi, E. V. Spinacé, and R. F. B. de Souza, *Int. J. Hydrogen Energy*, **2013**, *38*(25), 10585–10591.
- [81] Z. Liu, J. E. Hu, Q. Wang, K. Gaskell, A. I. Frenkel, G. S. Jackson, and B. Eichhorn, *J. Am. Chem. Soc.*, **2009**, *131*(20), 6924–6925.
- [82] A. Hassan, A. Carreras, J. Trincavelli, and E. A. Ticianelli, *J. Power Sources*, **2014**, *247*, 712–720.
- [83] S. Mukerjee, R. C. Urian, S. J. Lee, E. A. Ticianelli, and J. McBreen, *J. Electrochem. Soc.*, **2004**, *151*(7), A1094.
- [84] B. N. Grgur, N. M. Markovic, and P. N. Ross, *J. Electrochem. Soc.*, **1999**, *146*(5), 1613–1619.
- [85] N. Tsiouvaras, M. A. Peña, J. L. G. Fierro, E. Pastor, and M. V. Martínez-Huerta, *Catal. Today*, **2010**, *158*(1–2), 12–21.
- [86] S. Feng, J. Chen, G. Qian, Y. Mo, J. Lu, W. Chen, L. Luo, and S. Yin, *ACS Appl. Energy Mater.*, **2020**, *3*(12), 12246–12253.
- [87] D. K. Kang, C. S. Noh, N. H. Kim, S.-H. Cho, J. M. Sohn, T. J. Kim, and Y.-K. Park, *J. Ind. Eng. Chem.*, **2010**, *16*(3), 385–389.
- [88] R. A. M. Esfahani and E. B. Easton, *Appl. Catal. B Environ.*, **2020**, *268*, 118743.
- [89] R. C. Urian, A. F. Gullá, and S. Mukerjee, *J. Electroanal. Chem.*, **2003**, *554*–555, 307–324.
- [90] S. R. Pillai, S. H. Sonawane, S. P. Gumfekar, P. L. Suryawanshi, M. Ashokkumar, and I. Potoroko, *Mater. Chem. Phys.*, **2019**, *237*, 121854.
- [91] A. Sarkar, A. V. Murugan, and A. Manthiram, *J. Phys. Chem. C*, **2008**, *112*(31), 12037–12043.
- [92] V. Raghuveer, A. Manthiram, and A. J. Bard, *J. Phys. Chem. B*, **2005**, *109*, 22909–22912.
- [93] P. Li, X. Yin, Y. Yan, K. Zhan, J. Yang, B. Zhao, and J. Li, *J. Mater. Sci.*, **2018**, *53*, 6124–6134.
- [94] S. Chandrasekaran, E. J. Kim, J. S. Chung, C. R. Bowen, B. Rajagopalan, V. Adamaki, R. D. K. Misra, and S. H. Hur, *J. Mater. Chem. A*, **2016**, *4*, 13271–13279.
- [95] C. Tang, A. Sun, Y. Xu, Z. Wu, and D. Wang, *J. Power Sources*, **2015**, *296*, 18–22.
- [96] Y. Hu and D. H. C. Chua, *Sci. Rep.*, **2016**, *6*, 28088.
- [97] M. Bayati, X. Liu, P. Abellan, D. Pocock, M. Dixon, and K. Scott, *ACS Appl. Energy Mater.*, **2020**, *3*(1), 843–851.
- [98] T. Li, Z. Tang, K. Wang, W. Wu, S. Chen, and C. Wang, *Int. J. Hydrogen Energy*, **2018**, *43*, 4932–4941.
- [99] A. M. Gómez-Marín, J. L. Bott-Neto, J. B. Souza Jr., T. L. Silva, W. Beck Jr., L. C. Varanda, and E. A. Ticianelli, *ChemElectroChem*, **2016**, *3*(10), 1570–1579.
- [100] Á. Vass, I. Borbáth, I. Bakos, Z. Pászti, G. Sáfrán, and A. Tompos, *Reac. Kinet. Mech. Cat.*, **2019**, *126*, 679–699.
- [101] M. T. Anwar, X. Yan, M. R. Asghar, N. Husnain, S. Shen, L. Luo, X. Cheng, G. Wei, and J. Zhang, *Chinese J. Catal.*, **2019**, *40*(8), 1160–1167.
- [102] J. Qi, L. Jiang, Q. Jiang, S. Wang, and G. Sun, *J. Phys. Chem. C*, **2010**, *114*(42), 18159–18166.
- [102] M. Feng, J. Huang, Y. Peng, C. Huang, X. Yue, and S. Huang, *Chem. Eng. J.*, **2021**, *428*, 131206.
- [104] E. C. Weigert, D. V. Esposito, and J. G. Chen, *J. Power Sources*, **2009**, *193*(2), 501–506.
- [105] X. Liu, H. Wang, S. Chen, X. Qi, H. Gao, Y. Hui, Y. Bai, L. Guo, W. Ding, and Z. Wei, *J. Energy Chem.*, **2014**, *23*(3), 358–362.
- [106] L. G. S. Pereira, V. A. Paganin, and E. A. Ticianelli, *Electrochim. Acta*, **2009**, *54*(7), 1992–1998.
- [107] M.-K. Min, J. Cho, K. Cho, and H. Kim, *Electrochim. Acta*, **2000**, *45*(25–26), 4211–4217.
- [108] T. C. M. Nepel, P. P. Lopes, V. A. Paganin, and E. A. Ticianelli, *Electrochim. Acta*, **2013**, *88*, 217–224.
- [109] A. Hassan, V. A. Paganin, A. Carreras, and E. A. Ticianelli, *Electrochim. Acta*, **2014**, *142*, 307–316.
- [110] N. P. Lebedeva and G. J. M. Janssen, *Electrochim. Acta*, **2005**, *51*(1), 29–40.
- [111] G. Papakonstantinou, F. Paloukis, A. Siokou, and S. G. Neophytides, *J. Electrochem. Soc.*, **2007**, *154*, B989.
- [112] T.-C. Liu, W. G. Pell, B. E. Conway, and S. L. Roberson, *J. Electrochem. Soc.*, **1998**, *145*(6), 1882–1888.
- [113] S. L. Roberson, D. Finello, and R. F. Davis, *J. Appl. Electrochem.*, **1999**, *29*, 75–80.
- [114] J. Hu, Z. Liu, B. Eichhorn, and G. S. Jackson, *ECSS Trans.*, **2009**, *19*(31), 1–12.
- [115] B. Mendoza-Sánchez, T. Brousse, C. Ramirez-Castro, V. Nicolosi, and P. S. Grant, *Electrochim. Acta*, **2013**, *91*, 253–260.