ПРИЛОЗИ, Одделение за природно-математички и биотехнички науки, МАНУ, том **43**, бр. 1–2, стр. 47–57 (2022)
CONTRIBUTIONS, Section of Natural, Mathematical and Biotechnical Sciences, MASA, Vol. **43,** No. 1–2, pp. 47–57 (2022)

Received: November 09, 2023
Accepted: March 20, 2024

ISSN 1857–9027
e-ISSN 1857–9949
UDC: 669.243.7:544.47]:661.721
DOI: 10.20903/masa/nmbsci.2022.43.4

Original scientific paper

NICKEL BASED METAL CARBIDES AS ELECTROCATALYSTS FOR METHANOL OXIDATION REACTION

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Effective catalysts play a crucial role in enhancing methanol oxidation within in cells. In light of this, diverse catalysts have undergone examination; however, recently, significant research interest has turned towards Ni-based metal carbides. Their appeal lies in their cost-effectiveness, high activity, and notably, the presence of metal-carbon bonds. These bonds are formed due to carbon's *s*- and *p*-hybridization with the metal d orbitals. This combination heightens the *d*-band activity of the metal, akin to that of Pt, as suggested by density functional theory (DFT) approximations. The catalytic potential can be further augmented through the combination of metal carbides with other active materials. Furthermore, refining the catalyst's size and morphology has the potential to enhance its electrochemical application for methanol oxidation. This involves maximizing the active surface area by optimizing its morphology and increasing the availability of metal carbide atoms. The introduction of multiple metals to metal carbides or the incorporation of multi-metal-based electrocatalysts onto the metal carbide's surface is also an area of fervent exploration. Such endeavors hold the promise of enhancing activity and devising economically viable methods for methanol oxidation-based fuel cells.

Key words: Nickel; metal carbide; MOR; fuel cells; Energy; Zero carbon emission

INTRODUCTION

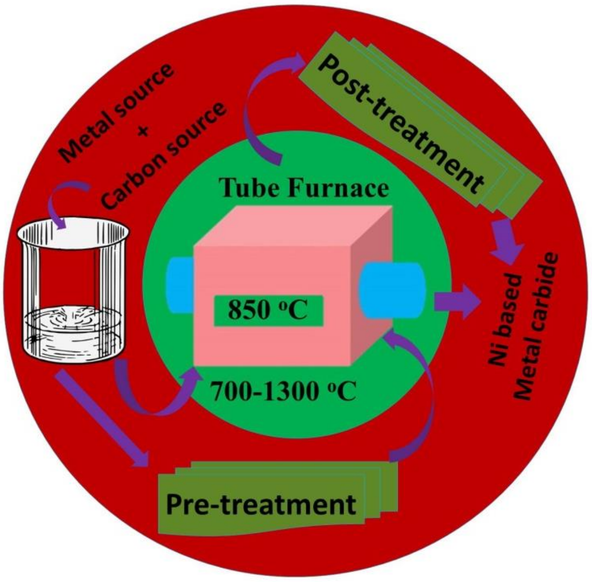
The primary energy source of current society is non-renewable fossil fuel, and its excessive consumption has led to energy and environmental problems. To mitigate these issues, an effective plan for environmentally friendly technology with renewable energy is needed [1–3]. Chemical energy conversion to electrical energy through fuel cells is the best possible option, considering its minimal or low environmental impact [4–6]. Among the available technologies, direct methanol fuel cells (DMFCs) are hailed as one of the most promising technologies, with methanol acting as the chemical fuel. Methanol offers various advantages, such as ease of transport and storage, low cost, low operating temperature, and high energy density [7–11]. However, DMFCs face two serious problems that limit their performance for practical applications: 1) the slow kinetics of electron transfer during the anodic oxidation of methanol, which affects the production rate of protons and consequently impacts power generation efficiency; 2) crossover of methanol, which is related to the electrolyte’s catharsis ability [12–14]. DMFCs require an electrocatalyst to reduce the activation energy of the methanol oxidation reaction (MOR). So far, platinum (Pt) is the state-of-the-art electrocatalyst for MOR, but its poisoning effect caused by CO chemisorption significantly restricts its practical application [15, 16]. Although extensive research has been conducted to overcome this issue by combining it with other elements like PtRu, PtZn [17, 18], or two or more elements like PtRuIr, PtRuIrSn [19, 20], unfortunately, high cost, low availability, and poor stability still hinder their practical application [20–22].

Therefore, extensive investigative studies have been conducted to develop non-precious metal-based electrocatalysts for MOR [23]. Among these non-precious metals, nickel (Ni) has gained special research attention due to its low price, environmental friendliness, and, most importantly, its excellent surface oxidation properties [24, 25]. However, the catalytic application of Ni-based electrocatalysts faces challenges due to their poor electrical conductivity, low surface area, and limited durability. Consequently, the study of Ni-based MOR still offers unexplored opportunities for investigation [26].

To enhance the electrocatalyst's performance, morphology plays a vital role. For instance, one-dimensional (1D) electrocatalysts have demonstrated excellence in fast electron transportation, remarkable durability, and a high exposure of active lattice planes compared to their bulk counterparts [27–30]. Similarly, three-dimensional (3D) morphology retains the fundamental characteristics of bulk materials while offering a large surface area, excellent mechanical and chemical strength, high flexibility, an open and porous structure, and resistance to aggregation [31–33]. Additionally, 3D morphology boasts advantages such as abundant active sites, a high ratio for utilization, excellent electron/mass transfer kinetics, and impressive MOR activity coupled with outstanding stability and durability [34, 35].

Furthermore, two-dimensional (2D) materials have attracted extensive research attention owing to their shortened charge migration pathways, large surface area, and rich diffusion channels for molecules and ions. Prominent examples of 2D materials include transition metal dichalcogenides, layered double hydroxides, and MXenes, where MXenes encompass metal nitrides and carbides [36–38]. Intriguingly, these materials can alleviate stress resulting from volume changes and bubble generation due to surface reactions, resulting in excellent stability and activity.

Additional engineering approaches that can enhance catalyst performance encompass factors like thickness, porosity, size, doping, defects, crystal phases, and the preferential growth of active lattice planes [39]. Electrochemical applications can be further enhanced through the incorporation of carbon as a carbide with Ni or the introduction of co-catalysts alongside Ni. The incorporation of carbon with nickel enhances its catalytic performance due to improved conductivity, altered electronic configurations, and the presence of a large electronic cloud, particularly at their junction points. Co-catalysts like tungsten carbide (WC) can also enhance performance by providing excellent stability under thermal and electrochemical oxidation [40]. These co-catalysts serve both as catalysts for MOR oxidation and as supports to prevent the agglomeration of active materials, thus offering ample active sites for reactions [41, 42].



Scheme 1. A general diagram for the synthesis of Ni based metal carbide

The primary focus of this review article is to explore Ni carbides and other Ni-based metal carbides employed for methanol electrooxidation reactions. The study concludes that the incorporation of multi-metal concepts with synergistic effects has led to performance improvements. Additionally, the utilization of conductive supports has also enhanced performance. Morphology has played a significant role in boosting performance by offering a large surface area and active sites for reactions. A crucial consideration that merits further investigation is that Ni-based metal carbides possess the ability to facilitate MOR and produce formate instead of carbon dioxide/monoxide. The formate produced could find applications in various industries, and the superiority of these carbides over hydrogen oxidation has even been confirmed in some studies.

SYNTHETIC PROTOCOL

The synthetic route commonly employed for the synthesis of metal carbides involves the annealing method, as demonstrated in Scheme 1, with polyvinyl alcohol (PVA) being the most frequently utilized carbon source. In the annealing process, temperatures ranging from 700°C to 1300°C have been applied in various studies (Fig. 1). The primary rationale behind employing such high temperatures is the inherent stability of carbon bonds within the precursor materials. These bonds are notably robust and not easily broken under typical temperature conditions. Consequently, elevated temperatures are necessary to disrupt these sturdy bonds, initiating the desired reaction between carbon and metal. While the energy consumption associated with high temperatures is not ideal, the preparation of metal carbides often demands these conditions. Nevertheless, there are advantages to this method that can mitigate its drawbacks. The elevated temperature contributes to the formation of highly crystalline products and provides surface modifications that enhance the catalytic properties of the materials. Additionally, the high temperature facilitates the creation of a porous structure by releasing carbon dioxide and monoxide during the decomposition of reactants [43-45].

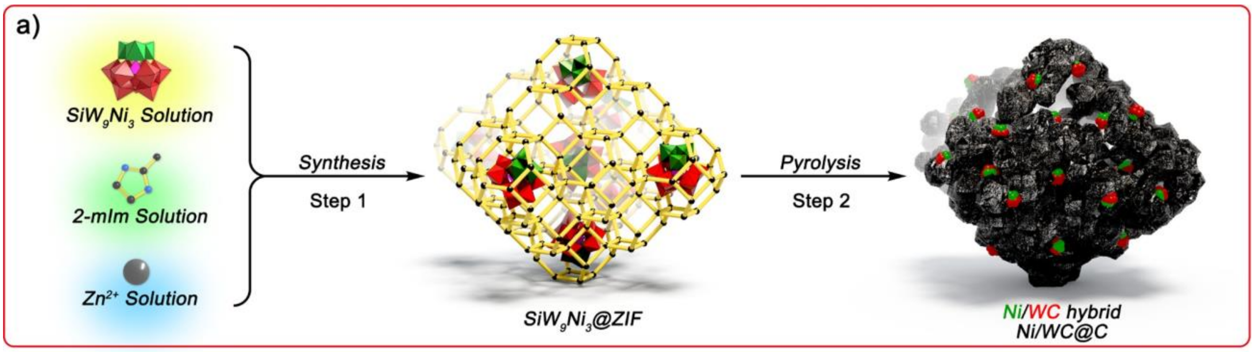


Fig. 1. Scheme for the synthesis of (a) Ni/WC Hybrid NPs (Ni/WC@C). Reprinted with permission from [45]. Copyright (2022) American Chemical Society

In tandem with the annealing method, some researchers have employed pre-treatments for materials. These pre-treatments can influence the composition or morphology of the final catalyst product. Notably, an intriguing procedure involves a one-pot solution-based strategy for synthesizing nickel carbide. In this approach, researchers dissolved nickel acetate in a mixture of oleylamine and Octadecene solvents. The solution was then subjected to a flux and reflux setup equipped with a magnetic stirrer. Employing a vacuum pump, low-boiling-point organic compounds, water, and air were removed from the solution at 80°C for 1 hour. Subsequently, the system was purged with argon gas and heated to 240°C at a rate of 5°C per minute. Heating was halted when a change in solution color was observed. The flask was then removed from the heating setup and allowed to cool to room temperature in a water bath. The resulting catalyst was collected and washed with ethanol to remove any unreacted reactants [46].

Electrochemical application

Fuel cells have demonstrated their potential as a promising energy source capable of addressing both energy and environmental concerns. Methanol serves as the primary fuel for these cells, with the oxidation of methanol yielding high energy output due to its remarkable energy density. Nevertheless, this process of methanol oxidation necessitates a catalyst to lower the activation energy required for oxidation. In this regard, numerous catalysts have undergone extensive study in pursuit of optimal performance. Among these catalysts, Ni-based metal carbides have garnered special research attention for various reasons, which will be extensively explained in the following lines. A comparative analysis for better understanding is presented in Table 1.

Among the array of catalysts investigated, Pt/Ni-WC was synthesized by Wang et al. [44] using a microwave-assisted annealing method. This catalyst exhibited a nanoparticle morphology and showcased catalytic performance of 0.51 mA/cm^2 at 0.4 V vs Ag/AgCl in an electrolyte comprising 1.0 M CH_3OH and 0.5 M H_2SO_4. Notably, this catalyst exhibited superior stability compared to Pt/C, attributed to the robust interaction between Pt and Ni-WC, resulting in sustained durability over a span of 7000 seconds. Although this catalyst demonstrated activity in the methanol oxidation reaction, its response remained modest, falling short of meeting the societal energy demands. The intrinsic value of Pt, being a precious metal, further raises concerns among scientists regarding its practical application in fuel cells. Consequently, the pursuit of precious metal-free electrocatalysts with efficient performance has become a paramount objective. Urgent attention is required to enhance the efficiency of the methanol oxidation reaction, addressing the pressing need for higher energy output.

Comparatively, good work in this direction was achieved by Wang et al. [43], who introduced PtNiPb/WC in an electrolyte comprising 0.5 M CH_3OH and 0.5 M H_2SO_4. This catalyst exhibited a remarkable current density of 2.67 mA/cm^2 at an overpotential of 0.85 V vs RHE. This enhanced performance, surpassing the capabilities of previously discussed materials, can be attributed to the presence of multiple metals in the sample. The synergistic effects resulting from these multimetals within the catalyst contributed to its heightened performance. Impressively, the catalyst also demonstrated excellent stability over a prolonged duration of approximately 1.5 h. Despite this improvement, the achieved performance still falls short of effectively addressing the energy crisis. The inclusion of Pt within the catalyst remains a drawback due to its associated cost and availability limitations.

In a similar vein, Zhang et al. [48] utilized a microwave-assisted reduction approach to craft a Ni-MoC_x/C-supported Pt (10 wt%) electrocatalyst (10Pt/Ni-MoC_x/C), which exhibited pronounced electrocatalytic proficiency in methanol oxidation. The outcomes underscored the superior electrocatalytic activity and stability of the 10Pt/Ni-MoC_x/C electrocatalyst in comparison to the 20 wt% Pt/C (20Pt/C) alternative. Notably, the electrochemical surface area of 10Pt/Ni-MoC_x/C attained 68.4 m^2/g, surpassing 20Pt/C's 63.2 m^2/g. This heightened stability and activity within the 10Pt/Ni-MoC_x/C electrocatalyst can be ascribed to two key factors: firstly, the anchoring effect stemming from Ni and MoC_x formation during the carbonthermal reduction process; and secondly, the synergistic interplay among Pt, Ni, MoOx, and MoCx. These findings underscored the promise of 10Pt/Ni-MoC_x/C as an effective electrocatalyst for direct methanol fuel cells.

Remarkably, the catalyst 10Pt/Ni-MoC_x/C exhibited a current density of 260.5 mA/mg at an overpotential of 0.9 V vs RHE in an electrolyte comprising 1.0 M CH_3OH and 0.5 M H_2SO_4. This exceptional performance can be attributed to the presence of Pt, along with the extensive surface area where nanoparticles are uniformly dispersed, preventing agglomeration and ensuring maximum active sites for reactions. The inclusion of Mo in the composition notably heightened the responsiveness to methanol oxidation. The synergistic interaction among multiple atoms (Ni, Mo, Pt) facilitated heightened electronic cloud density, particularly at their junctions, thus proving immensely effective in methanol oxidation reactions. Additionally, the presence of carbon as a support accelerated rapid electron transport, further amplifying this catalytic activity. While the material exhibits excellence and holds potential for practical applications, the presence of precious metals might impede industrialization due to their elevated costs and limited availability. Consequently, it is highly advisable to focus on developing electrocatalysts based on transition metals and their carbides, excluding precious metals, to overcome these limitations.

In recent times, non-precious catalysts with efficient performance have been extensively investigated. For instance, Hou et al. [49] developed a Ni-WC based catalyst on the surface of a carbon aerogel derived from bacterial cellulose. The catalyst exhibited a current density of 105.7 mA/cm^2 at an overpotential of 0.8 V vs SCE. The optimal reaction medium was found to be 0.5 M CH_3OH and 1.0 M KOH, showcasing excellent stability over 3600 s. Moreover, with the introduction of a novel electrolyte, the peak current density rebounds to 88.42% of the initial value, highlighting notable stability. The synergy between Ni and WC produces a collaborative effect that facilitates the formation of NiOOH, subsequently diminishing the surface adsorption of CO. This effect effectively mitigates the temporary blockage of active catalytic sites. The achieved W_1Ni_{10}/CA composite in this study, known for its affordability, substantial specific surface area, elevated catalytic efficiency, and impressive resistance to CO-induced inhibition, emerges as a promising catalyst for application in DMFC scenarios. The response is promising but still requires performance improvement, leaving room for further advancements in catalytic applications that require research.

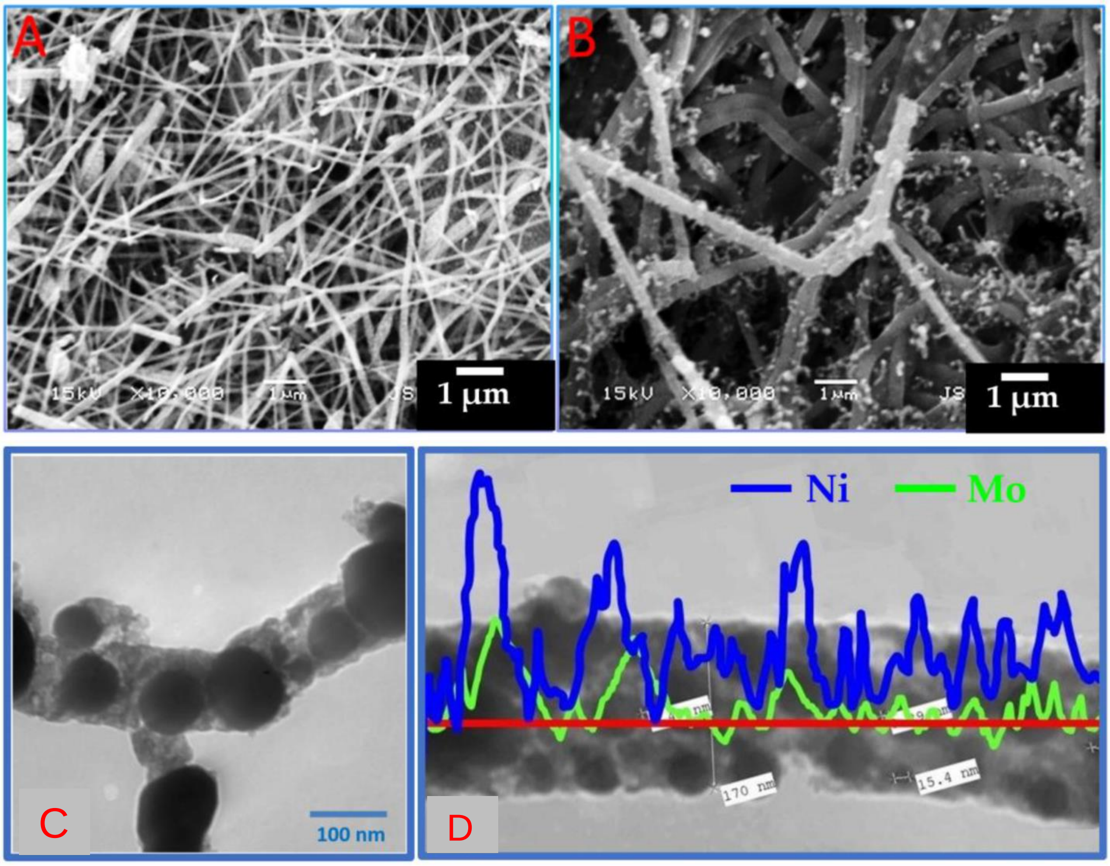


Fig. 2. SEM images of the produced Mo_2C–Ni–C composite nanofibers calcined at 850 °C and obtained from electrospun nanofibers containing 10 (A) and 35 (B) wt.% $MoCl_2$ compared to $Ni(AC)_2$. TEM image of Mo_2C/Ni/graphite composite nanofibers generated from 10% Mo/electrospun solution calcined at 850 °C (C) and linear elemental mapping for Ni and Mo along randomly selected (D). Reproduced with permission from Marwa M. Abdel-A, Polymer; published by MDPI, 2023 [47].

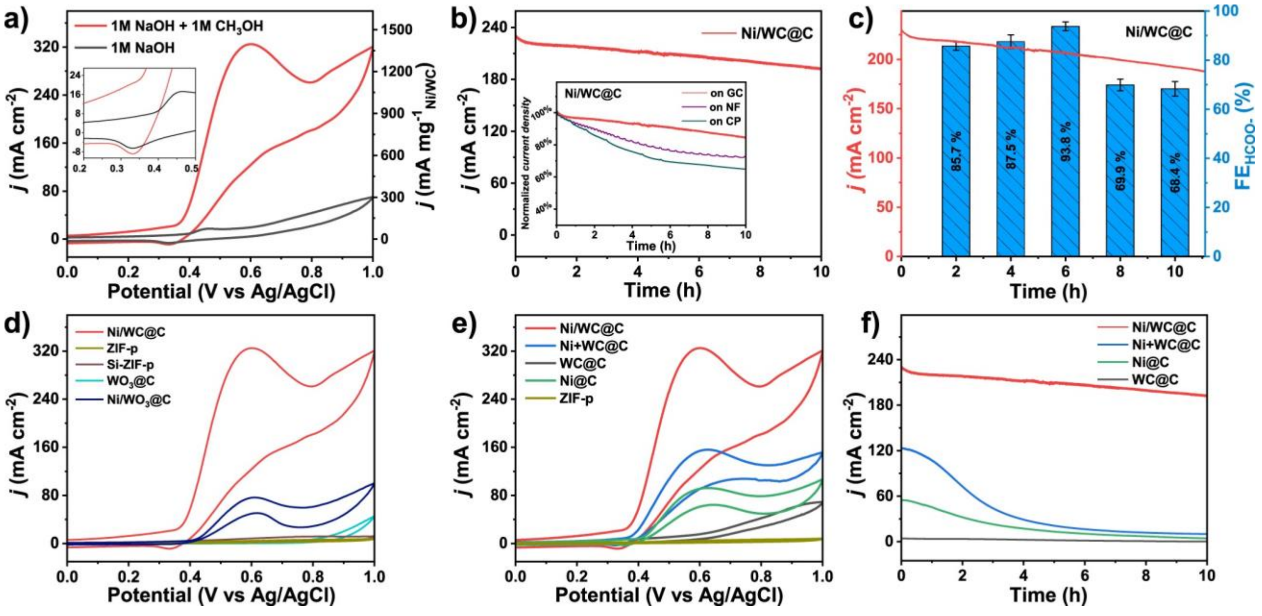


Fig. 3. (a) CV curves of Ni/WC@C in 1 M NaOH with and without 1 M methanol. (b) Chronoamperograms of Ni/WC@C in 1 M NaOH +1 M CH_3OH at 0.5 V versus Ag/AgCl/3.5 M KCl with a salt bridge. [Inset: chronoamperograms of Ni/WC@C when using GC (red), NF (purple),and CP (green) as substrate]. (c) Chronoamperograms (red line) and FE_{HCOO^-} (blue columns) of Ni/WC@C at 0.5 V versus Ag/AgCl/3.5 M KCl with a salt bridge. (d) CV curves of different samples for MOR in 1 M NaOH + 1 M CH_3OH. (e) CV curves of different catalysts for MOR in1 M NaOH + 1 M CH_3OH. (f) Chronoamperograms of different catalysts in 1 M NaOH + 1 M CH_3OH at 0.5 V versus Ag/AgCl/3.5 M KCl witha salt bridge. Reprinted with permission from [45]. Copyright (2022) American Chemical Society

Notably, the integration of Mo has demonstrated exceptional efficacy in electrocatalytic applications. For instance, Abdel-Aty and her team [47] developed an electrocatalyst, Mo_2C/Ni-CNFs (5%) for MOR, where the CNFs provide one-dimensional support for well dispersion of Mo_2C/Ni as shown in Fig. 2. The catalyst, necessitating a 1.0V overpotential vs Ag/AgCl to yield a current density of 107 mA/cm^2 in a 3.0 M CH_3OH and 1.0 M KOH electrolyte as shown in Fig. 4. This catalyst was synthesized through electrospinning a blend of poly(vinyl alcohol), nickel acetate, and molybdenum chloride, followed by vacuum calcination. This procedure resulted in the formation of zero-valent nickel and molybdenum carbide nanoparticles within amorphous graphite nanofibers due to the breakdown of metal constituents and polymer graphitization. The optimization of molybdenum content significantly contributed to achieving consistent and efficient electrocatalytic performance in methanol electrooxidation. For attaining the maximum methanol electrooxidation rate alongside electrode regeneration, employing a 5 wt.% molybdenum precursor relative to nickel acetate in the initial electrospun solution was identified as ideal. The calcination temperature played a pivotal role, notably enhancing methanol electrooxidation activity at 850°C. Employing Taguchi's robust design approach facilitated the identification of optimal conditions, resulting in the highest achievable current density. The parameters derived from this approach were as follows: 5 wt.% molybdenum content, 2.65 M methanol concentration, and a reaction temperature of 50°C. Interestingly, the reaction rate exhibited an inverse relationship with the medium temperature. The peak rate of methanol electrooxidation was attained at 45°C, while Taguchi's analysis pinpointed the optimum at 50°C. Given its remarkable performance, the proposed nanofibrous composite of Mo_2C/Ni-incorporated carbon emerges as a strongly recommended electrocatalyst for methanol oxidation, warranting further exploration of its potential with other organic substrates. The exceptional material response stems from the synergistic effects of multimetal interactions, particularly the bonding of Mo with carbon, leading to significant alterations in electronic configuration and the generation of a substantial electronic cloud at the junction. This electronic cloud was further augmented by the inclusion of Ni. Furthermore, the well-dispersion of active materials with minimum agglomeration and maximum active spots for reaction enhanced its application. The presence of carbon nanofibers, with their conductivity and one-dimensional structure, enhances electron transport and catalytic application of the final material. The catalytic application response can be further improved through morphological engineering and by providing a conductive support to enhance electron transport and achieve excellent MOR performance. In this context, Xie et al. [26] developed CNT-Ni/SiC, an electrocatalyst for MOR application. The system yielded an outstanding current density of 210 mA/cm^2 at an overpotential of 0.8 V vs Ag/AgCl in an electrolyte of 3.0 M CH_3OH and 1.0 M KOH. The catalyst exhibited exceptional durability for 4000 seconds continuously. The remarkable electrochemical performance of the composite stems from the uniform dispersion and secure anchoring of Ni nanoparticles, combined with the favorable electrical conductivity of the network-style framework established by CNTs and SiC. This three-dimensional structure offers a substantial surface area, optimizing reactive sites and minimizing diffusion paths. The synergistic effects of Ni and SiC amplify the electronic cloud at the junction, resulting in configuration changes that further enhance the response. Furthermore, the conductive surface and one-dimensional architecture accelerate electron transfer, leading to an enhanced response. Anticipations suggest that this cost-effective and practical synthesis method could be extended to create varied carbon-based and metallic hierarchical nanostructures with a wide range of applications.

Metal carbides open up another intriguing avenue that could enhance energy applications. Particularly, Ni-based metal carbides show promise in converting methanol into formate, exhibiting impressive performance and yielding high current densities. Moreover, this formate could be subjected to further oxidation to harness more energy or could find applications across diverse industries. In line with this, Li et al. [46] introduced Ni_3C as an electrocatalyst for methanol oxidation to formate, achieving a noteworthy current density of 127 mA/cm^2 at an overpotential of 0.6V vs Ag/AgCl. The catalyst also demonstrated stability over 5 hours in an electrolyte containing 1.0 M CH_3OH and 1.0 M KOH. This excellent performance arises from the strong nickel-carbon bonding, which enhances electron flow at their junction by modifying their configuration to facilitate the reaction. Furthermore, the morphology also plays a vital role: the material exhibits a nanostructure with nanoneedles that amplify surface area, diminish diffusion kinetics, and maximize active sites for reactions. This research is immensely valuable and merits further attention due to its exceptional energy response while emitting zero carbon.

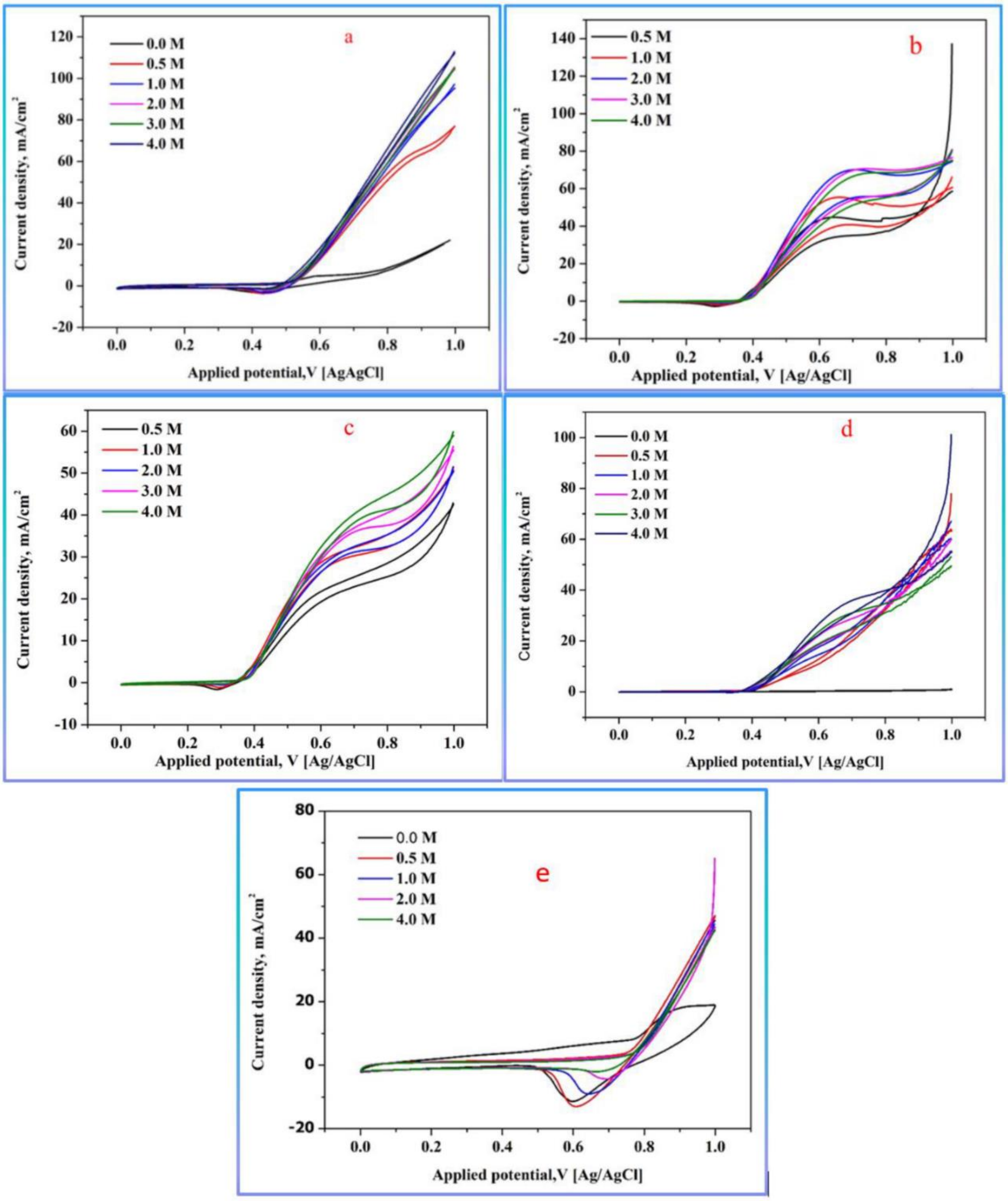


Fig. 4. Influence of molybdenum carbide content on the electrocatalytic activity of Mo_2C–NiCNFs prepared at 850 °C calcination temperature from electrospun solutions having different molybdenum chloride content: 5; (a), 10; (b), 15; (c), 25; (d) and 35 wt.%; (e), at different methanol concentration and scan rate of 50 mV/s. Reproduced with permission from Marwa M. Abdel-A, Polymer; published by MDPI, 2023 [47].

In contrast, other fuel cells that undergo complete methanol oxidation release carbon dioxide (albeit at low levels). This field requires additional exploration to enhance performance, whether through the introduction of multimetal catalysts, surface engineering, conductive support surfaces, and more. In this regard, Zhang et al. [45] employed the concept of multimetal synergy to achieve a high electronic cloud for exceptional MOR application. They prepared an electrocatalyst, Ni/WC, which required an overpotential of 0.6 V vs Ag/AgCl to achieve a current density of 325 mA/cm^2 in an electrolyte of 1 M CH_3OH and 1 M NaOH aqueous solution as shown in Fig. 3. The catalyst exhibited outstanding stability over a duration of 10 hours, confirming its robustness and practicality for MOR application in fuel cells.

The hybrid Ni/WC nanoparticles synthesized in this study display remarkable electrooxidation capabilities when employed for the oxidation of methanol, ethanol, iso-propanol, ethylene glycol, and propylene glycol in an alkaline solution. Particularly noteworthy in the context of methanol oxidation, the Ni/WC nanoparticles exhibit heightened reaction activity (with a mass activity of 1363 mA/mg) alongside exceptional stability (with only approximately a 6.8% drop in catalytic current after 4 hours). During the initial 6-hour electrolysis period, methanol efficiently transforms into formate with an approximate Faraday efficiency of 93.8%. Through the utilization of in situ IR spectra and control catalyst experiments, it has been established that both tungsten carbide (WC) and nickel oxyhydroxide (NiOOH, derived from Ni) species are capable of activating distinct functional groups within methanol. Importantly, their synergistic hybrid structure (Ni/WC) leads to an enhanced catalytic performance in converting methanol into formate. The catalyst's exceptional performance can be attributed to its nanosized particles, which provide an excellent large surface area for electrochemical reactions.

Table 1. Comparison of Ni based metal carbide MOR performance

S.No	Catalyst	Potential	Current density	Electrolyte	Ref
1	CNT–Ni/SiC	0.8 V vs Ag/AgCl	210 mA/cm^2	1.0 M CH_3OH 1.0 M KOH	[26]
2	PtNiPb/WC	0.85 V vs RHE	2.67 mA/cm^2	0.5 M CH_3OH 0.5 M H_2SO_4	[43]
3	Pt/Ni-WC	0.4 V vs Ag/AgCl	0.51 mA/cm^2	1.0 M CH_3OH 0.5 M H_2SO_4	[44]
4	Ni/WC	0.6 V vs Ag/AgCl	325 mA/cm^2	1.0 M CH_3OH 1.0 M NaOH	[45]
5	Ni_3C	0.6 V vs Ag/AgCl	127 mA/cm^2	1.0 M CH_3OH 1.0 M KOH	[46]
6	Mo_2C/Ni-CNFs (5%)	1.0 V vs Ag/AgCl	107 mA/cm^2	3.0 M CH_3OH 1.0 M KOH	[47]
7	10Pt/Ni-MoC*x*/C	0.9 V vs RHE	260.5 mA/mg	1.0 M CH_3OH 0.5 M H_2SO_4	[48]
8	Ni-WC	0.8 V vs SCE	105.7 mA/cm^2	0.5 M CH_3OH 1.0 M KOH	[49]
9	Ni/TaC	0.4 V vs SHE	1.1 mA/cm^2	--- 1.5 M H_2SO_4	[50]

It is highly interesting and needs more attention that Burstein et al. [50] conducted a study on metal carbides; the Ni/TaC catalyst displayed an excellent response to heated methanol when introduced to a chamber for catalytic applications. The system exhibited a current density of 1.1 mA/cm^2 at an overpotential of 0.4 V vs SHE in an electrolyte of 1.5 M H_2SO_4. This study demonstrates the superiority of methanol-based fuel cells over hydrogen oxidation reactions. The described electrocatalyst, composed of tantalum, nickel, and carbon, demonstrates higher catalytic activity in the anodic oxidation of methanol compared to hydrogen. This differentiation is attributed to the functionalization of surface carbon atoms through anodic oxidation, enabling them to adsorb and react with methanol. The proposed surface intermediate adopts a ring structure. This innovative mechanism for the anodic oxidation of methanol is exclusive to carbon-based surfaces and doesn't apply to metal electrocatalysts. Furthermore, it is specific to the anodic oxidation of carbon-based fuels and isn't relevant to hydrogen oxidation. The presence of the nickel and/or tantalum component is thought to enhance this observed behavior.

CONCLUSION AND FUTURE PERSPECTIVE

The growing concern over energy crises and environmental issues has prompted significant research endeavors toward the development of renewable energy sources as potential solutions. Among these, fuel cells emerge as a promising technology to address these challenges. Extensive research has been dedicated to exploring diverse electrocatalysts capable of efficiently oxidizing methanol to generate energy. Within this landscape, nickel-based metal carbide materials have garnered notable attention, attributed to their cost-effectiveness, efficiency, and suitability for electrochemical methanol oxidation reactions (MOR). Hence, the focus of this study is directed toward nickel-based metal carbides.

The heightened catalytic efficacy of metal carbides can be traced to the formation of metal-carbon bonds arising from the hybridization of carbon's *s*- and *p*-orbitals with the metal's *d*-orbitals, corroborated by DFT calculations. This hybridization leads to the expansion of the metal d band, rivaling that of Pt. Empirical evidence affirms that electrochemical MOR applications are positively correlated with diminishing catalyst size. Similarly, enhanced morphology facilitates optimal utilization of the expansive surface area and maximal incorporation of metal carbide atoms. Moreover, the catalytic impact can be further enhanced when metal carbides are amalgamated with other active materials. Incorporating doped and multi-metal elements in electrocatalysts has demonstrated improved sensing activity.

To markedly enhance catalytic performance and achieve practically efficient electrocatalysts for MOR, it is recommended to reduce and control the catalyst size down to the nano or sub-nano scale. Counteracting nanoparticle agglomeration is pivotal to preserving a heightened active surface area and attaining elevated activity levels. In this context, various supporting materials, such as 3D graphene, boron nitride, graphitic carbon nitride, and carbon nanotubes, can be employed to mitigate nanoparticle agglomeration. These materials, in addition to curbing agglomeration, offer high conductive surfaces that expedite electron transport, further facilitating catalytic applications.

Morphology also exerts a substantial influence on catalytic activity. Transforming metal carbides into diverse morphologies, such as nanoflowers, nanoneedles, urchins, nanotubes, nanofibers, porous structures, and ultrathin layers, can amplify their activity. These unique morphologies confer extensive surface areas, enabling optimal utilization of active materials for targeted reactions while minimizing wastage of materials embedded deep within the catalyst's bulk structure. Additionally, the strategic integration of multiple metals within a single catalyst can augment activity by introducing a greater pool of active materials for catalytic processes. The observed synergistic effects in multi-metal-based electrocatalysts contribute to their heightened activity levels as well.

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МЕТАЛНИ КАРБИДИ ШТО СОДРЖАТ НИКЕЛ КАКО КАТАЛИЗАТОРИ ЗА РЕАКЦИЈАТА НА ОКСИДАЦИЈА НА МЕТАНОЛОТ

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Катализаторите играат важна улога за подобрување на ефикасноста на процесот на оксидација на метанолот. Голем број катализатори се предмет на тековни истражувања, при што од неодамна постои значителен интерес за катализатори што содржат никел. Нивната соодветност произлегува од постоењето на метал-јаглеродна врска, како и од фактот дека тие се евтини и значително ефикасни. Метал-јаглеродната врска се формира меѓу *s*- и *p*-хибридните орбитали на јаглеродот и *d*-орбиталите на никелот, слично како кај платинските катализатори, според заклучоците на теоретските студии. Каталитичкиот ефект може да биде зголемен и преку комбинирање на металкарбидите со други активни метали. Од друга страна, морфологијата и големината на каталитичките честички имаат значајна улога. Притоа, особено е важно оптимизирањето на морфологијата на честичките во насока на поголема достапноста на супстратот до металкарбидната врска на катализаторот. Покрај тоа, особен интерес побудува комбинацијата на металкарбидите со честичките на различни метали зашто овозможува значително подобрување на каталитичките особини. Оваа целокупна област на истражување овозможува дизајнирање на ефикасни и евтини методи за развој на горивни ќелии што користат метанол.

Клучни зборови: никел, метал карбиди, горивни ќелии, енергија, нула-јаглеродна емисија