

Molybdenum carbide/Ni nanoparticles-incorporated carbon nanofibers as effective non-precious catalyst for urea electrooxidation reaction

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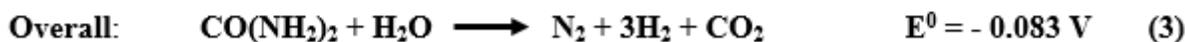
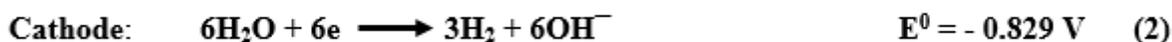
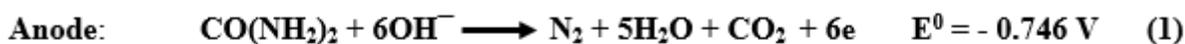
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Abstract

In this study, molybdenum carbide and carbon were investigated as co-catalysts to enhance the nickel electro-activity toward urea oxidation. The proposed electrocatalyst has been formulated in the form of nanofibrous morphology to exploit the advantage of the large axial ratio. Typically, calcination of electrospun polymeric nanofibers composed of poly(vinyl alcohol), molybdenum chloride and nickel acetate under vacuum resulted in producing good morphology molybdenum carbide/Ni NPs–incorporated carbon nanofibers. Investigation the composition and morphology of the proposed catalyst was achieved by XRD, SEM and TEM analyses which concluded formation of molybdenum carbide and nickel nanoparticles embedded in a carbon nanofiber matrix. As an electrocatalyst for urea oxidation, the electrochemical measurements indicated that the proposed composite has a distinct activity when the molybdenum content is optimized. Typically, the nanofibers prepared from electrospun nanofibers containing 25 wt% molybdenum precursor with respect to nickel acetate revealed the best performance. Numerically, using 0.33 M urea in 1.0 M KOH, the obtained current densities were 15.5, 44.9, 46.5, 38.2, 87.9 and 12.6 mA/cm² for nanofibers prepared at 850 °C from electrospun mats containing 0, 5, 10, 15, 25 and 35 molybdenum chloride, respectively. Study the synthesis temperature of the proposed composite indicated that 1000 °C is the optimum calcination temperature. Kinetic studies indicated that electrooxidation reaction of urea does not follow Arrhenius’s law. To investigate the advantage of the nanofibrous morphology, the proposed catalyst has been synthesized in nanoparticulate morphology, the later showed trivial activity compared to the nanofibers catalyst.

1. Introduction

Scientists have discovered that urea pollution can cause ocean algae to develop a fatal poison known as domoic acid¹. Paradoxically, urea can be manipulated as a non-toxic, non-flammable hydrogen-carrying molecule with an energy density of 16.9 MJ.L⁻¹ (approximately 10 times more than hydrogen). Moreover, compared to water, electrolysis of urea consumes lower electrical power². Theoretically, hydrogen extraction from urea is a straight forward process as it depends on an exothermic reaction according to the following equations²⁻⁶:



However, due to the high overpotentials over the reported electrodes, there is no any known anode material could achieve the task without power addition. Beside the low required energy (ca. 0.37 V) compared to water (1.23 V), there are other advantages for hydrogen extraction from urea electrolysis: 1)

producing non-self-ignited gas mixture due to absence of oxygen, 2) converting the nitrogen pollution in the wastewater to an environmentally safe product; N_2 and 3) arousing the researchers to develop new electrode materials having low overpotentials⁷.

Nickel attracts the attention of the researchers as an anode material in the urea electrolysis cell from the biological degradation of urea by urease. This enzyme consists of two Ni^{+2} attached two water molecules and bridging hydroxide group^{8,9}. A vast number of studies have demonstrated that, in an alkaline media, nickel and nickel-based compounds are oxidised to nickel's active state ($NiOOH$) and subsequently operates as a urea oxidation reaction (UOR) catalyst^{10,11}. However, the electrocatalytic activity of the unmodified nickel does not meet the minimum requirements to be an applicable anode which could be translated as poor formation of the required active sites. Enhancing the electrocatalytic activity of nickel toward urea electrooxidation has been conducted in two main strategies; shape development and invoking co-catalyst(s). In the first route, the transition metal has been formulated either in its pristine or metal hydroxide ($Ni(OH)_2$). In this regard, several nanostructural formulations have been investigated including nanowire arrays¹², nanomeshes¹³, nanoribbons¹⁴, nanoflakes¹⁵ and nanosheets¹⁶.

As a co-catalyst, several metallic and non-metallic species have been investigated including cobalt^{17,18}, iron¹⁹, manganese^{20,21}, tin², tungsten²², nitrogen²³, phosphorous^{24,25}, graphene^{5,26}, CNTs^{27,28}, and carbon nanofibers²⁹. The main function of the co-catalyst is either decreasing the onset-potential and/or enhancing the generated current density of the urea electro-oxidation reaction. For these two objectives, molybdenum draws the attention of the researchers as a promised element for enhancing the activity of the nickel-based materials³⁰. For instance, Yang et al.³¹ introduced nickel-molybdenum oxide ($NiMoO_4$) nanorods for urea oxidation using simple hydrothermal and low-temperature heat treatment. When the precursors' Ni/Mo ratio is 2, the resulting catalyst has fast kinetics, low electron transfer resistance, and a low Tafel slope for urea oxidation. Yu et al.³² describe a porous rod-like $NiMoO_4$ with high metal element oxidation states that enables very effective UOR electrocatalysis and can be easily made by annealing solid $NiMoO_4 \cdot xH_2O$ as a starting precursor in Ar. When the shielding gas is changed from Ar to H_2/Ar , the resulting Ni/ NiO / MoO_x nanocomposite exhibits platinum-like activity for the hydrogen evolution process (HER) in alkaline electrolytes. Shi et al.³³ used a simple reduction technique to synthesize Ni-Mo/graphene and then studied the efficacy of urea electrooxidation. Ni_2Mo/Gr demonstrated exceptional performance, including high current density and long-term stability, due to structural activity and electron effect. Beside the oxide and zero-valent forms, MoS_2/Ni_3S_2 catalyst has been reported as a new 3D-heteropore dual-function catalyst which exhibits low urea electrolysis cell voltage³⁴. Overall, molybdenum doping has shown effective delay polarisation and increase the range of electric oxidation potential. However, the content as well as the molybdenum chemical state have to be optimized as it strongly affects the site distribution of the surface Ni^{3+} electroactive centre³⁵.

In this study, influence of both of the morphology as well as the chemical composition has been investigated by synthesizing molybdenum carbide/nickel NPs–incorporated carbon nanofibers (Mo_2C/Ni -

incoportaed CNFs). Compared to other nanostructures, the large axial ratio of the nanofibrous morphology distinctly enhances the electron transfer rate which positively impacts the electrocatalytic activity³⁶. The proposed catalyst has been synthesized by calcination of electrospun nanofibers composed of nickel acetate, molybdenum chloride and poly(vinyl alcohol) under vacuum atmosphere. The utilized physiochemical characterizations confirm decomposition of the metal precursors to zero-valent nickel and molybdenum carbide, and graphitization of the used polymer to produce carbon nanofibers embedding the crystalline metallic nanoparticles. Electrochemical measurements emphasize the high activity of the new composite and the advantage of the nanofibrous morphology over the nanoparticulate form.

2. Experimental

2.1 Materials

The used chemicals have been utilized as-received without any further treatment. The used polymer to prepare the electrospun solution (PVA, poly(vinyl alcohol), MW = 65.000 g/mol) was purchased from DC Chemical Co., South Korea. Nickel acetate tetrahydrates (NiAc, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.99 purity) and molybdenum chloride (MoCl_2 , purity 99.99%) were obtained from Sigma Aldrich, USA. Deionized water was utilized as solvent.

2.1 Preparation of the nanofibers and nanoparticles.

NiAc/PVA aqueous stock was prepared by mixing 10 wt% PVA and 20 wt% NiAc aqueous solutions in a 3:1 weight ratio. The mixture was stirred for 5 h at 50 °C to get full poly(condensation) of the acetate ion. Later on, specific amounts of molybdenum chloride were dissolved in the minimum amount of de-ionized water and mixed with certain amounts of the prepared NiAc/PVA solution to prepare different solutions having 0, 5, 10, 15, 25 and 35 wt% of MoCl_2 compared to NiAc. The electrospinning procedure was carried out at a voltage of 20 kV in a room setting with a distance of 15 cm between the syringe and the revolving drum collector. After vacuum drying of the electrospun mats, a 5-hour calcination procedure was performed under vacuum at various temperatures (700, 850, and 1000 °C). The nanoparticles were made by drying the aforementioned sol-gels under vacuum for 24 hours at 80 degrees Celsius. The solids were then thoroughly crushed and ground into tiny particles before being subjected to the calcination process.

2.3 Characterization

Scanning electron microscopy was used to validate the nanofibrous morphology (SEM and FESEM, Hitachi S-7400, Japan). X-ray diffraction was used to investigate the chemical composition of the produced nanostructures (XRD, Rigaku, Japan). Potentiostats were used to conduct the electrochemical tests (VersaStat 4, USA). A three-electrode cell configuration was used, with a working electrode of glass carbon electrode (GCE), a reference electrode of Ag/AgCl, and a counter electrode (CE) of Pt wire. The working electrode was made by smearing 15 μl of catalyst ink onto the GCE's active surface. The catalyst

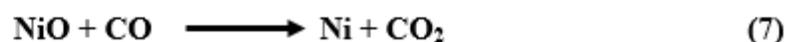
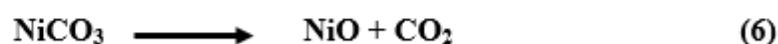
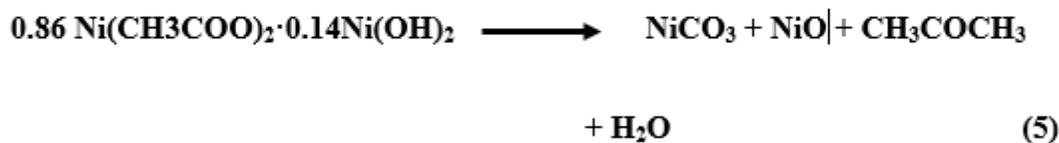
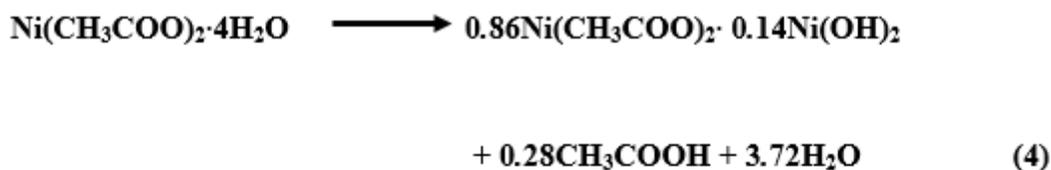
ink was made by dispersing 2 mg of the functional ingredient in a solution of 20 μl Nafion and 400 μl isopropanol. After deposition, the electrodes were dried at 80 $^{\circ}\text{C}$ for 30 min³⁷.

3. Results And Discussion

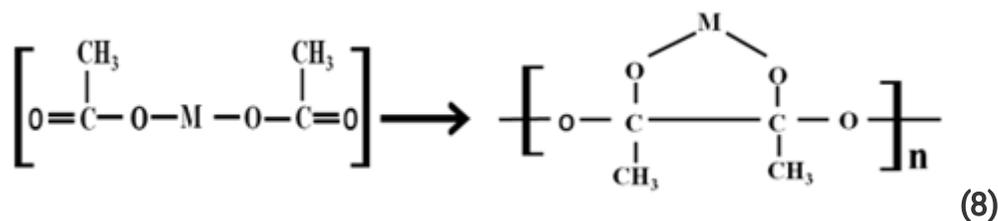
3.1. Crystalline structure, surface morphology, and composition of the prepared materials

PVA has significant high carbon content when compared to other vinyl polymers. However, because PVA melts and decomposes into volatile low molecular weight molecules at low temperatures, using it to make carbon nanofibers is uncommon due to the difficulties of attaining acceptable shape and/or a high carbon yield³⁸. To solve this problem, two primary tactics have been used: 1) pretreatment before the carbonization process, and 2) the use of certain catalysts during the heat treatment process to improve graphitization. Both procedures rely on cyclizing the PVA straight chain, which results in high melting point compounds that increase the graphitization process significantly. Figure 1 shows a conceptual representation of the best destructive disintegration of PVA to get the highest yield^{39,40}. Dehydration and dehydrogenation methods may be used to extract aromatic carbon from the PVA straight chain, as demonstrated.

Utilizing nickel acetate as precursor has a dual function. First, under the inert atmosphere, this precursor fully decomposed to zero-valent nickel instead the expected nickel oxides. As it was proved by many researchers, heating this salt in an inert atmosphere leads to abnormal decomposition of the acetate anion to generate reducing gases (namely, carbon mono oxide and hydrogen) which results in producing of pure metal^{41,42}. Formation of pure nickel was described by the following equations:



Second, nickel acetate has a polycondensation tendency which distinctly maintains the nanofibrous morphology during the calcination process. The polycondensation reaction can be explained as follow ⁴³



Where M is the nickel atom. Therefore, the utilized precursors initially formed a good gel with the used polymer which facilitates the electrospinning process and consequently produces good morphology nanofibers.

X-ray diffraction analysis is a powerful and trustable tool to check the chemical composition of the crystalline materials. Figure 2 displays the XRD patterns for selected samples after the calcination process. The results supported the aforementioned discussion about the decomposition track of nickel acetate. As shown, the representative peaks of the zero-valent nickel clearly appeared with all formulations. Typically, the observed strong peaks at 2θ values of 44.30° , 51.55° , 76.05° and 92.55° corresponding to (111), (200), (220) and (311) crystal planes, respectively confirm the formation of pure nickel (JCDPS# 04-0850). Moreover, the successful graphitization of the used polymer was also proved by the broad peak at 2θ of 26.3° corresponds to an experimental d spacing of 3.37 \AA indicating presence of graphite-like carbon (graphite-2H, $d(002)$, JCPDS#; 41-1487). Therefore, it can be claimed that the formed nickel catalyzes graphitization of PVA. On the other hand, molybdenum has combined with the formed carbon to form a thermally stable compound; molybdenum carbide (Mo_2C). However, due to evolution of the reduced gases, the molybdenum has been formed in its lowest oxidation number (2) ⁴⁴. The Mo_2C indexed peaks in the graph match the standard peaks of molybdenum carbide in International Centre for Diffraction Data Sample (JCPDS); # 35-0787. The representative peaks get strong with increasing the molybdenum precursor in the samples as shown in the figure.

Figure 3 displays SEM images of randomly selected samples after performing the heat treatment process; 10 and 35 wt% MoCl_2 samples prepared at 850°C . As can be concluded, subjecting the prepared electrospun nanofibers at high temperatures did not annihilate the nanofibrous morphology. It is worth mentioning that all formulations reveal almost similar results regardless the utilized calcination temperature and Mo content (data are not shown). Maintaining the nanofibrous morphology can be attributed to the polycondensation feature of nickel acetate (Eq. 8) as well as the smart graphitization of the used polymer.

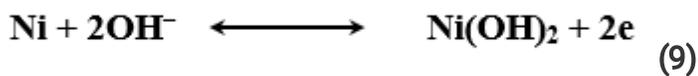
Transmission electron microscopy (TEM) is an authorized analytical technique to detect the internal structure of the nanostructures. Figure 4 demonstrates normal TEM image of the produced nanofibers after calcination of 10 wt% sample at 850°C . The images can build a solid conclusion about the internal structure of the produced nanofibers. In TEM analysis, the dark areas represent crystalline materials due

to the high reflection of the used electron beams. Therefore, it can be alleged that the dark appeared dots represent the inorganic materials counterpart in the prepared nanofibers while the gray matrix is the detected graphite in the XRD analysis. Accordingly, the utilized physicochemical characterizations deduced that the proposed preparation methodology leads to prepare Mo₂C/Ni NPs–incorporated carbon nanofibers as a final product.

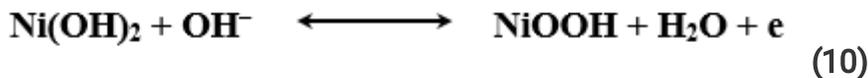
3.2. Electrochemical performance

3.2.1 Electroactive service area

Surface activation of the nickel-based is a mandatory to be applicable electrocatalyst for urea oxidation. The activation process is carried out by generation of Ni(OOH) species on the surface through sweeping in a strong alkaline solution or simultaneously with the electrooxidation reactions⁴⁵. The activation process is performed in two main steps which appear as two regions in the voltammograms; the first which is observed at a negative potential region (at ~ -650 mV) is attributed to the formation of nickel hydroxide⁴⁶:



It is noteworthy mentioning that the corresponding peak of this reaction is usually very small in the first cycle and vanishes in the subsequent ones^{46–48}. At the positive side, the second transformation is done which is associated with appearance of a strong peak due to the oxidation of Ni(OH)₂ to NiOOH^{48–50}:



Increasing the number of sweeping cycles leads to a progressive increase of the current density values of the cathodic peak due to the entry of OH⁻ into the Ni(OH)₂ surface layer, which results in a progressive formation of a thicker NiOOH layer⁴⁶. The entrance of OH⁻ into the Ni(OH)₂ surface layer causes a gradual increase in the current density values of the cathodic peak as the number of sweeping cycles increases, resulting in the creation of a thicker NiOOH layer⁴⁶.

The activity of the nickel-based electrocatalysts directly proportions with the amount of the formed active species; the electroactive surface area (ESA). The ESA can be calculated from the cyclic voltammetry of the activation process using the following Eq. 1^{4,51,52}

$$ESA = \frac{Q}{mq} \quad (11)$$

where Q (mC) is the charge required to reduce NiOOH to Ni(OH)₂, m (mg) is the nickel amount in the functional catalyst and q is the charge associated with the formation of a monolayer from Ni(OH)₂.

Because only one electron is required for the $\text{NiOOH} \rightarrow \text{Ni(OH)}_2$ transition, q can be set to $257. \mu\text{C}/\text{cm}^2$ ^{53,54}. Q can be determined from the area of the cathodic peak after redrawing the curve as current (mA) versus time (s). The cyclic voltammograms for nanofibers with varied molybdenum contents and calcined at 850°C are shown in Fig. 5A. The $\text{Ni(OH)}_2/\text{NiOOH}$ transition peaks are clearly visible in all formulations, as illustrated.

The effect of molybdenum concentration on the ESA of produced nanofibers is seen in Fig. 5B. Based on the findings, it can be inferred that by optimizing Mo content, the ESA may be significantly improved. The ESA of nanofibers generated from a solution containing 25 wt percent molybdenum precursor rose to be 45 times greater than that of Mo-free nanofibers, as indicated; the estimated ESAs for the two formulations were 28.27 and $0.64 \text{ cm}^2/\text{mg}$, respectively. The results also indicated that the slight addition of the proposed co-catalyst does not have a distinguished improvement on the formation of the Ni(OOH) active layer. Numerically, almost similar ESA values were determined from the 0 and 5 wt% samples as shown in the figure. More increase in the MoCl_2 content in the initial electrospun solution results on a relatively good enhancement in the ESA. Numerically, ESAs generated on the surface of nanofibers obtaining from solutions having 10 and 15 wt percent Mo precursor are 4.52 and $2.38 \text{ cm}^2/\text{mg}$, respectively, which are 7 and 3.7 times greater than those created on the surface of Ni/C nanofibers, respectively. However, the relationship between the ESA and the Mo content is not linear as shown. The relationship can be interpreted by a polynomial function as further increase in the co-catalyst precursor more than the optimum content leads to have decreasing in the ESA value. For the 35% sample, the detected ESA value was $6.37 \text{ cm}^2/\text{mg}$.

3.2.2 Urea electrooxidation

The performance of the suggested materials in the electrooxidation of urea was tested to scientifically show the impact of the ESA on the electrocatalytic activity of the proposed composites. Figure 6 shows the electroactivity of nanofibers synthesized at 850°C for urea oxidation (1.0 M urea in 1.0 KOH, scan rate $50 \text{ mV}/\text{s}$) at varied Mo concentrations. The nanofibers with the highest ESA (25 wt. % Mo), as shown, have the highest activity.

In contrast to alcohols, urea oxidation reactions are complicated so no a confident mechanism could be assured. Many researchers tried to explain the urea oxidation mechanism. Among these trials, the density functional theory (DFT) reported by Botte et al. is the most reliable⁵⁵. In that report, the authors have suggested three possible paths for urea dissociation. The most important finding, they concluded that carbon dioxide desorption is the common rate-controlling step. Therefore, it can be claimed that ESA is not the unique parameter governing the electrocatalytic activity. Consequently, as shown in Fig. 6, the obtained catalytic activity does not match the ESA behavior (Fig. 5B). In details, although 5 wt% sample is not the second order in term of ESA, these nanofibers reveal the second best electrocatalytic activity toward urea oxidation. Moreover, this sample shows the minimum difference between the cathodic and anodic peak potentials which reflects maximum reversibility among all other formulations except the Mo-

free electrode. In the completely reversible redox reactions, the redox peaks potentials difference ($\Delta E_p = E_{pa} - E_{pc}$) is independent on the sweep speed and possesses a very small value verifying this Eq. 5⁶.

$$\Delta E_p = \frac{0.0565}{n} \quad (12)$$

Where n is the number of electrons sharing in the reactions; equals 6 for urea oxidation reaction. However, satisfying this equation is an ideal hope and cannot be achieved in the practical situation. Another important finding which can be extracted from the obtained results in Fig. 6 is the location of the redox peaks potentials for the samples revealing the highest current densities. As shown, the cathodic peaks corresponding to the nanofibers prepared from initial solutions having 10 and 25 wt% molybdenum chloride are close to the Ni(OH)₂/Ni(OOH) one (Fig. 5A). This finding is interesting as it indicates a self-regeneration of the used electrodes as it was aforementioned that the increase in the current density values of the cathodic peak indicates the creation of a thicker NiOOH layer⁴⁶. Our previous detailed study concluded that activation of the active Ni-based electrocatalysts can be performed simultaneously with the oxidation reaction⁴⁵. Considering that the Ni(OOH) is a reactant, this characteristic is important as it suggests sustainable electrode. For other formulations, the cathodic peaks are close to urea oxidation assigned in many reports^{7,57}. Although urea oxidation is mainly anodic reaction, the cathodic peaks, which have usually lower current densities compared to the anodic peaks, represent oxidation of some intermediates⁵⁵. However, for the 10 and 25 wt% samples, the cathodic peaks are broad and can be attributed to both of Ni(OH)₂/Ni(OOH) transformation and urea oxidation.

3.2.3 Effect of concentration

Like any non-zero order chemical reaction, the concentration of the main reactant (urea) strongly affects the reaction rate. However, this impact depends on the catalytic activity of the used catalyst. Figure 7 displays the cyclic voltammograms for different prepared catalysts at various urea concentrations. For most of the investigated formulations, it clearly appears that addition of urea resulted in a sharp increase in the current density which confirms the good electrocatalytic activity of these electrodes toward urea oxidation process. Mass transfer operation distinctly affects the kinetics of the heterogeneous catalytic reactions. In this regard, increasing the reactants concentration does not only enhance the reaction rate but also improve the mass transfer process. However, the rate-limiting step for the whole process can be mass transfer of the reactant(s) or the reaction(s) rate(s) or the mass transfer rate of the product(s). Therefore, increasing the reactant(s) concentration can show an influence when it represents the rate-limiting step for the whole process, after that a negligible or even negative impact might be observed. These hypotheses are proved in Fig. 7. In details, as shown in Fig. 7A, for the nanofibers obtained from sol-gel having 5 wt% MoCl₂, increasing urea concentration from 0.33 to 1.0 M led to have a high jump in the anodic peak current density. More increase in urea concentration did not show a noticeable change in the peaks current density, but, a considerable increase in the current can be observed at higher applied potential with increasing the concentration. Therefore, for these nanofibers, it can be claimed that urea

concentration is the rate-limiting process at high range of concentration which reflects high electrocatalytic activity of this electrode. There is a slight change in the situation in case of 10 wt.% electrode as shown in Fig. 7B. As shown, there is a realizable increase in the current density upon increase the concentration of urea from 0.33 to 1.0 M. However, 1.0 M concentration stilled the predominant within the used potential window; 2.0 and 3.0 M urea concentrations demonstrated equal and lower (compared to 1.0 M) current densities.

Although, the electrode prepared from the solution having 25 wt% molybdenum precursor revealed the maximum current density, the increase of urea concentration from 0.33 to 1.0 M did not result in an observable increase in the current density as shown in Fig. 7C. Moreover, more increase in the reactant concentration led to have a negative influence in the detected current density. As a high current density was obtained, it is believed that the rate-limiting step in case of utilizing this electrode is the mass transfer of the products. In other words, low desorption rate of CO_2 gave rise to decrease the reaction rate which was translated into getting relatively small current density at high urea concentrations. For the last sample (35 wt% MoCl_2 ; Fig. 7D), the results confirm the low activity of the proposed nanofibers at this composition.

3.2.4 Effect of synthesis temperature

It is known that the catalytic activity of the solid materials depends mainly on the surface electronic structure which is usually a follower to the material crystallinity. Consequently, effect of the synthesis temperature of the catalyst on the electroactivity has been investigated in Fig. 8. The results display the obtained voltammograms in case of utilizing 10 wt% electrode prepared at different temperatures using two concentrations of urea solutions; 1.0 M (Fig. 8A) and 2.0 M (Fig. 8B). As it can be plainly concluded, preparing the proposed nanofibers at high temperature (1000 °C) mightily enhances the electrocatalytic activity of the proposed functional material in two terms; obtaining high current density and clear appearance of the urea oxidation peak. This finding can be attributed to the high crystallinity of the inorganic material prepared at this elevated temperature. On the other hand, increasing the treatment temperature from 700 to 850 °C did not reveal a high difference in the electrocatalytic activity.

3.2.5 Electrode stability

Stability is an important parameter for the practical electrodes. Figure 9 depicts the chronoamperometry analysis for a randomly selected formulation from the proposed electrodes; 10 wt% prepared at 1000 °C. The results confidently support the stability of the used electrode. Briefly, as the analysis was conducted in a stagnant solution, the sharp decrease in the current density is attributed to the exhaustion of the urea in the zone nearby the electrode active surface area, and the inability of the mass transfer process to compensate the decrease in the reactant concentration. Later on, after reaching to the equilibrium between the mass transfer rate and urea oxidation rate, a stable current density was observed. As shown in Fig. 9, after around 1500 s, the current density behaves as a straight horizontal line. Accordingly, this measurements arises the stability of the proposed electrocatalyst.

3.2.6 Reaction kinetics

In the homogeneous chemical reactions, Arrhenius equation is applicable because rising the temperature leads to increase the kinetic energies of the reactants molecules which results in increasing the collisions between the reactants. Consequently, the reaction rate improves with increasing the medium temperature. However, in the case of the heterogeneous catalytic reactions, enhancement the reactants molecules acceleration can give negative effect as it can lead to running the reactants away from the catalyst surface⁵⁸; analogy to the adsorption process. Figure 10 explains the effect of reaction temperature on the dissociation of urea. As shown, increase the temperature from 25 to 45 °C reveals positive influence as the dissociation rate increases. However, more increase in temperature to 55 °C led to a sharp decrease in the reaction rate. Moreover, at 65 °C, urea oxidation process was almost annihilated. Therefore, it can be claimed that urea oxidation reaction using the proposed electrocatalyst does not follow Arrhenius equation. Kinetic calculations have been done to estimate the reaction constant at each temperature. Table 1 summarizes the obtained data. As shown, at 45 °C (318 K), the reaction constant is close to unity while it diminishes to be very small (0.019 s^{-1}) at the highest applied temperature; 65 °C.

Table 1
Urea electrooxidation reaction constants at different reaction temperatures

Temperature (K)	298	318	328	338
Reaction constant (s^{-1})	0.457	0.985	0.046	0.019

3.2.7 Influence of the scan rate

Figure 11A presents the influence of scanning rates evaluated using CV in presence of 0.33 M urea (in 1.0 M KOH) using the nanofibers obtained from 25 wt% MoCl_2 solution. As it was previously explained, the cathodic peak represents the $\text{Ni}(\text{OH})_2/\text{Ni}(\text{OOH})$ transformation⁵⁹. The reduction peak current density (j_{ca}) decreased continuously with the scanning rates. j_{ca} value presented an excellent linear relationship against $v^{0.5}$ in the range from 10 to 100 mV/s ($R^2 = 0.9978$) in Fig. 11B, indicating that the electrochemical characteristic of the diffusion process of OH^- from the solution to the used electrode was a typical diffusion-controlled process⁶⁰. In addition, by the increasing of scanning rates, the peak potential (E_{pc}) moved in the direction of the negative potential. Figure 11C shows that E_{pc} depended linearly on $\ln(v)$ (10 to 100 mV/s) with the equation of $E_{pc} \text{ (V)} = 0.36838 - 0.0494 \ln(v) \text{ (V/s)}$ ($R^2 = 0.9925$) which shows very good matching to Laviron theory for thin-layer quasi-reversible electrochemical process⁶¹.

3.2.8 Effect of nanostructural morphology

The electrocatalyst performance is heavily influenced by electron transfer resistance. As a result, the shape of the catalyst might have a significant influence. Aside from the electrocatalyst's ohm resistance, the electron must overcome another type of resistance to pass through the catalyst layer; interfacial

resistance. As a result, the axial ratio is a crucial property. In other words, a low interfacial resistance can be obtained with the long axial ratio nano-morphology. In particular, there are several contact sites with relatively tiny contact surfaces in the case of spherical nanoparticles, resulting in a high interfacial resistance. The long axial ratio of the nanofibrous morphology, on the other hand, leads to the formation of direct channels to the current collector, lowering the interfacial resistance significantly. The electron passes through the nanoparticles and nanofibers are shown schematically in the right panel in Fig. 12. The electron must pass through numerous contact sites in a zigzag pass in the case of nanoparticles, as depicted, resulting in significant interfacial resistances. The long axial ratio, on the other hand, aids in the creation of straight routes for electrons to reach the current collector⁶². The notion was scientifically proven by synthesizing nanoparticles from the same sol-gel used in the electrospinning process and calcining them at the same temperature (5 wt% MoCl₂ at 850 °C). As shown, there is an incredible difference between the electrocatalytic activities of the two formulations which strongly emphasizes utilization of prepared catalyst in the nanofibrous morphology.

4. Conclusion

Calcination of electrospun mates composed of poly(vinyl alcohol), nickel acetate and molybdenum chloride under vacuum atmosphere leads to decomposition of the metallic ingredients to zero-valent nickel and molybdenum carbide nanoparticles incorporated in amorphous graphite nanofibers. The proposed composite nanofibers can be exploited as efficient and stable electrocatalyst for urea oxidation process when the Mo content is optimized. To get maximum urea dissociation rate with in-vivo electrode regeneration, the molybdenum precursor in the initial electrospun solution has to be kept at 25 wt% with respect to the nickel acetate. Synthesis temperature is a critical factor as preparing the proposed electrocatalyst composite at 1000 °C strongly enhances the catalytic activity toward urea. Unlike the conventional chemical reactions, increasing the reaction media temperature does not generally enhance the reaction rate; the highest urea dissociation rate can be achieved if the temperature is maintained at 45 °C. Finally, it is highly recommended to use the suggested Mo₂C/Ni-incorporated carbon composite in nanofibrous morphology to get high performance.

Declarations

Availability of Data and Materials

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

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Figures

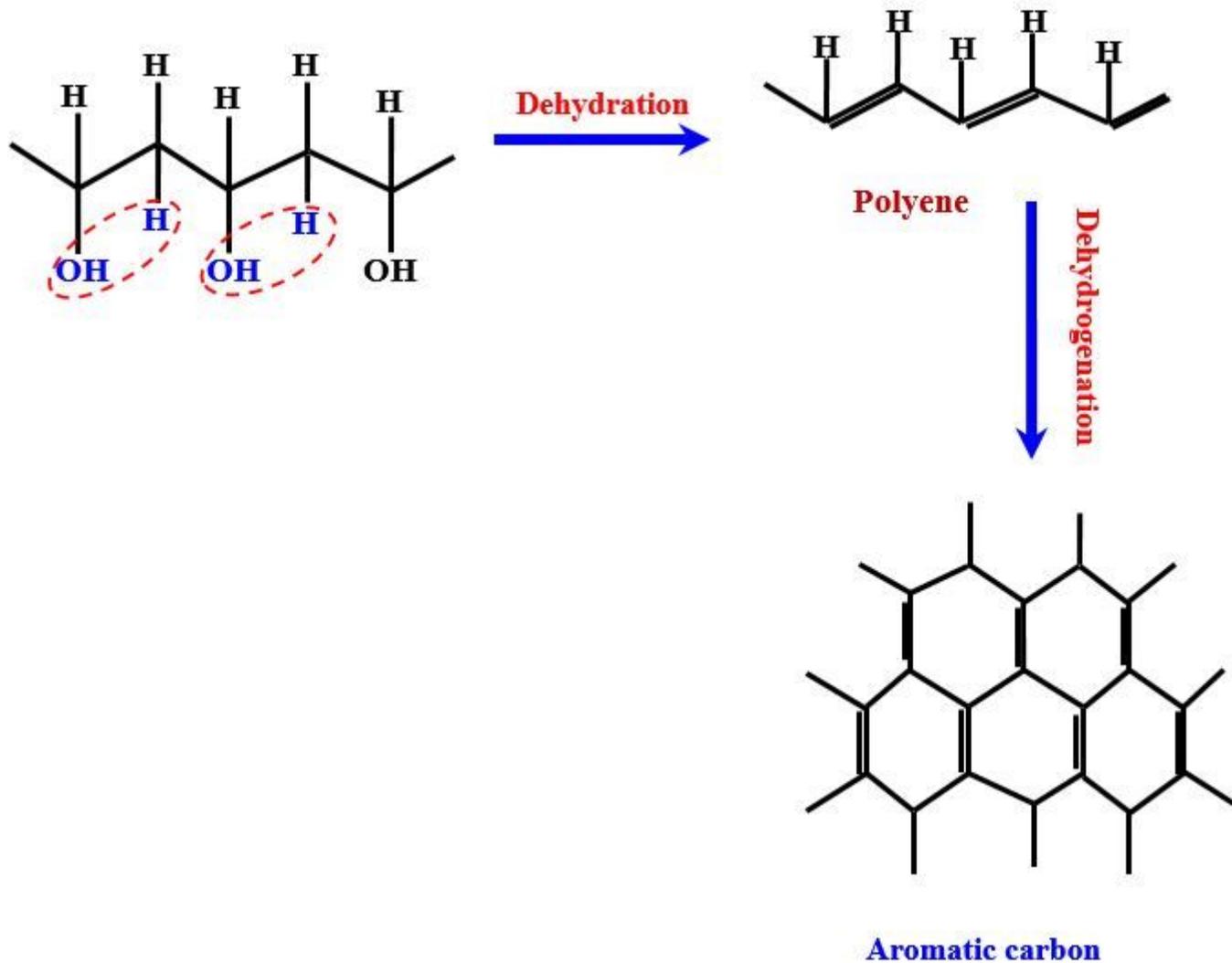


Figure 1

Schematic diagram for the expected optimum destructive of the PVA⁴⁰

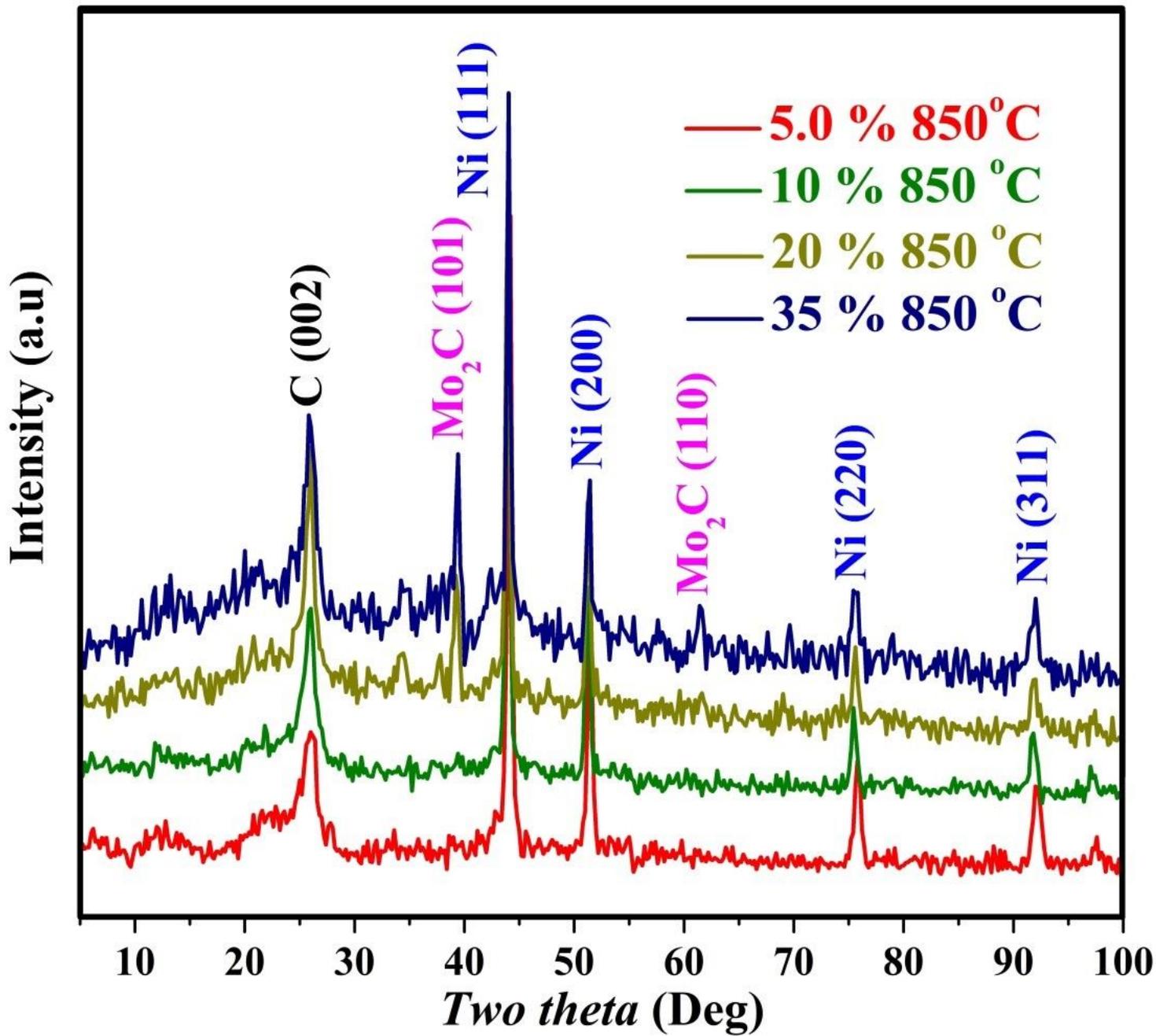


Figure 2

XRD results for the obtained powder after calcination at 850 °C of electrospun nanofiber mats prepared from sol-gel containing different amount of molybdenum precursor contents.

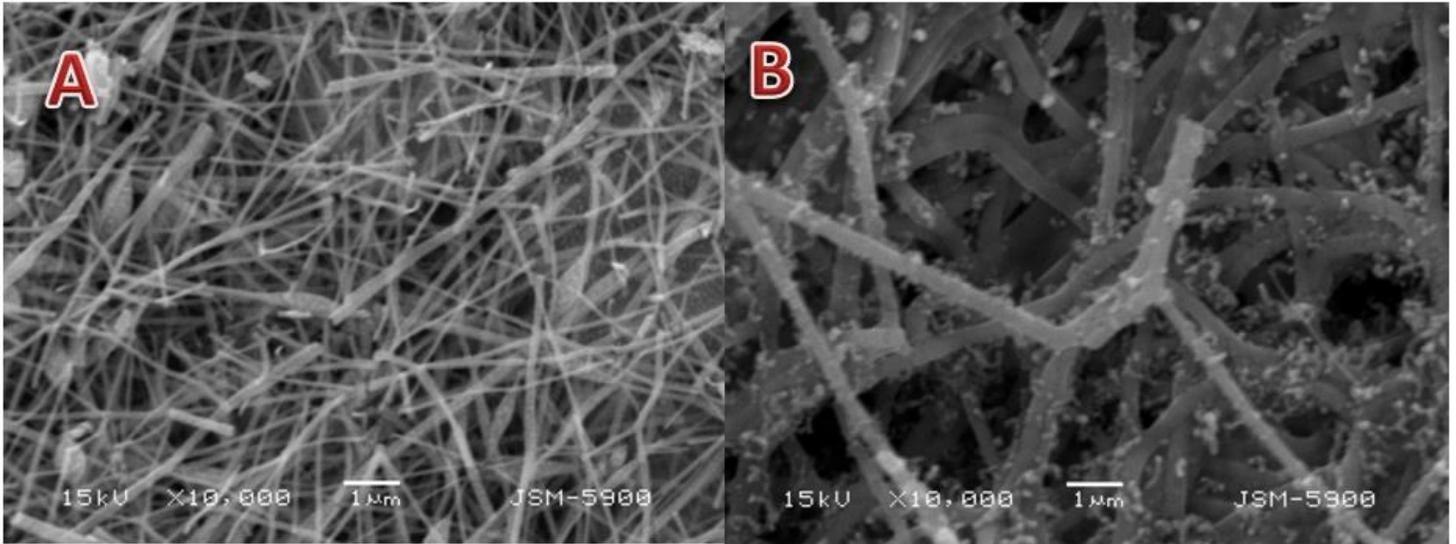


Figure 3

SEM images for the produced $\text{Mo}_2\text{C-Ni-C}$ composite nanofibers prepared at $850\text{ }^\circ\text{C}$ calcination temperature and from original solution having 10; (A) and 35; (B) molybdenum chloride

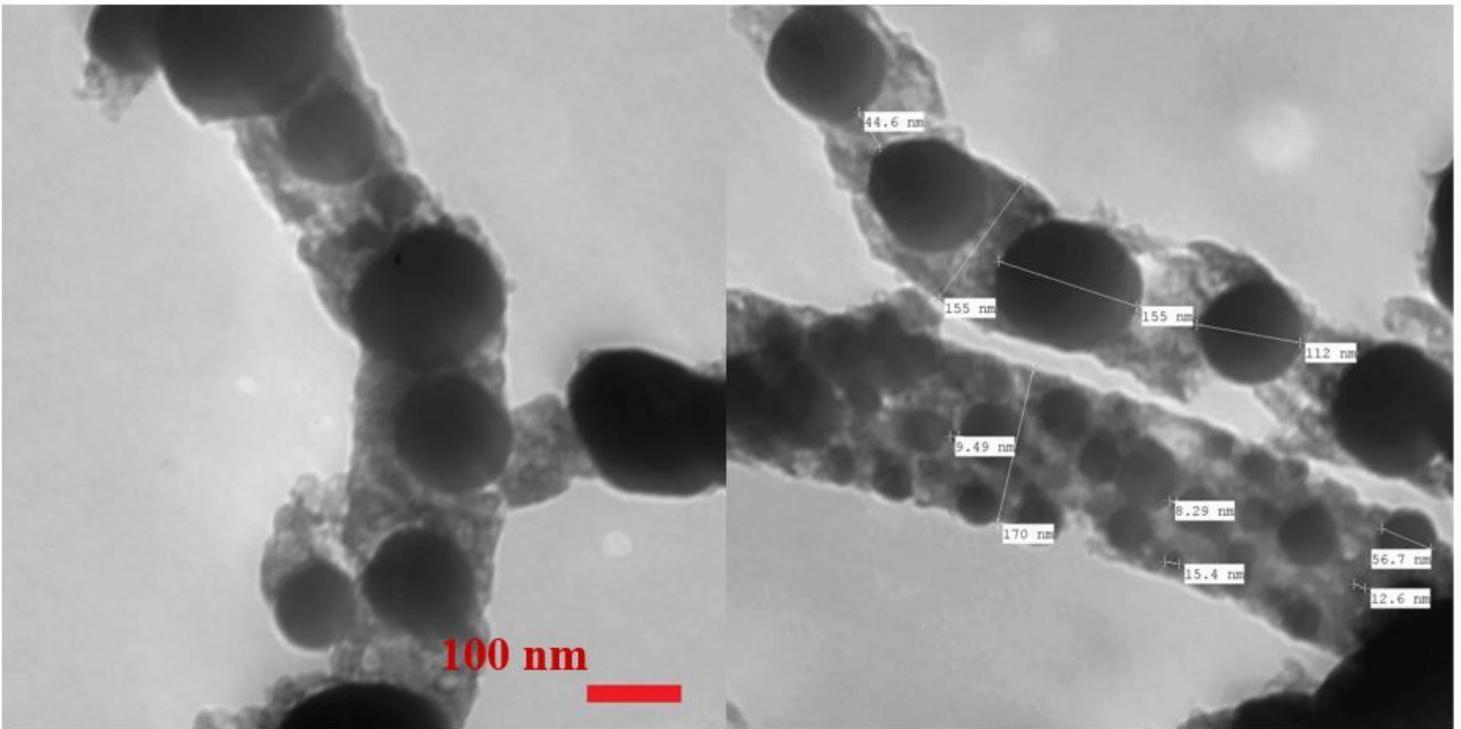


Figure 4

TEM image of $\text{Mo}_2\text{C/Ni/graphite}$ composite nanofibers prepared from an electrospun solution containing 10 % molybdenum precursor at $850\text{ }^\circ\text{C}$.

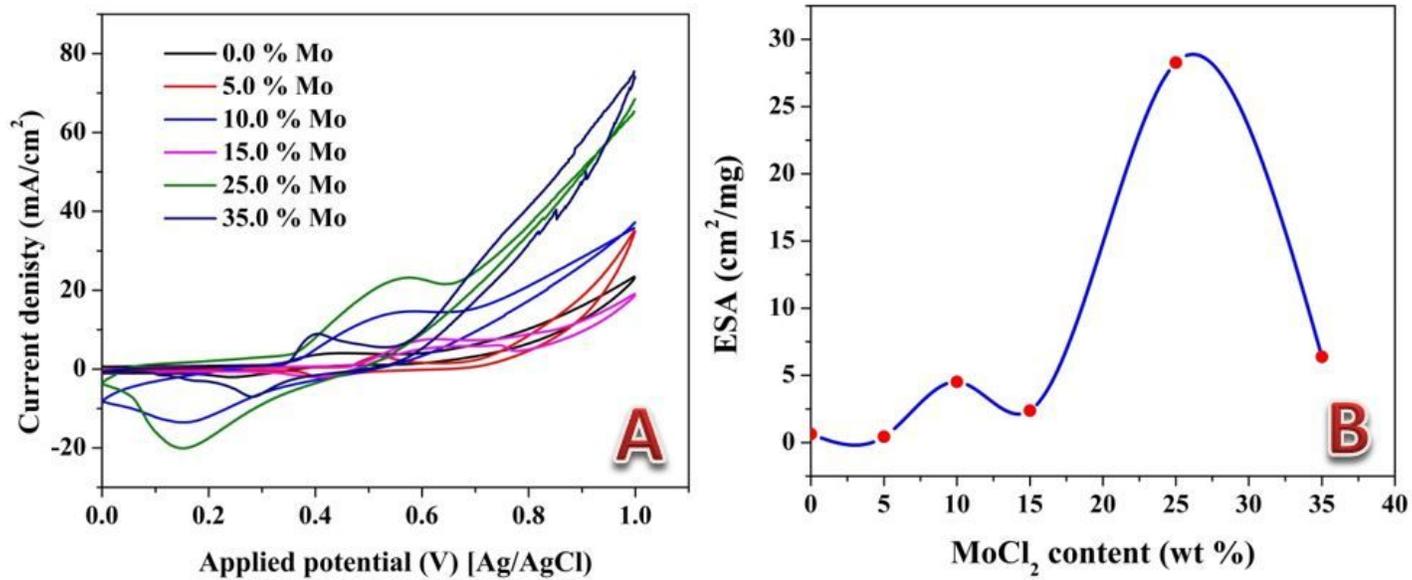


Figure 5

Activation of Mo₂C/Ni-incorporated carbon nanofibers with different Mo content and prepared at 850 °C; (A), and influence of the Mo content on the electrochemical surface area; (B).

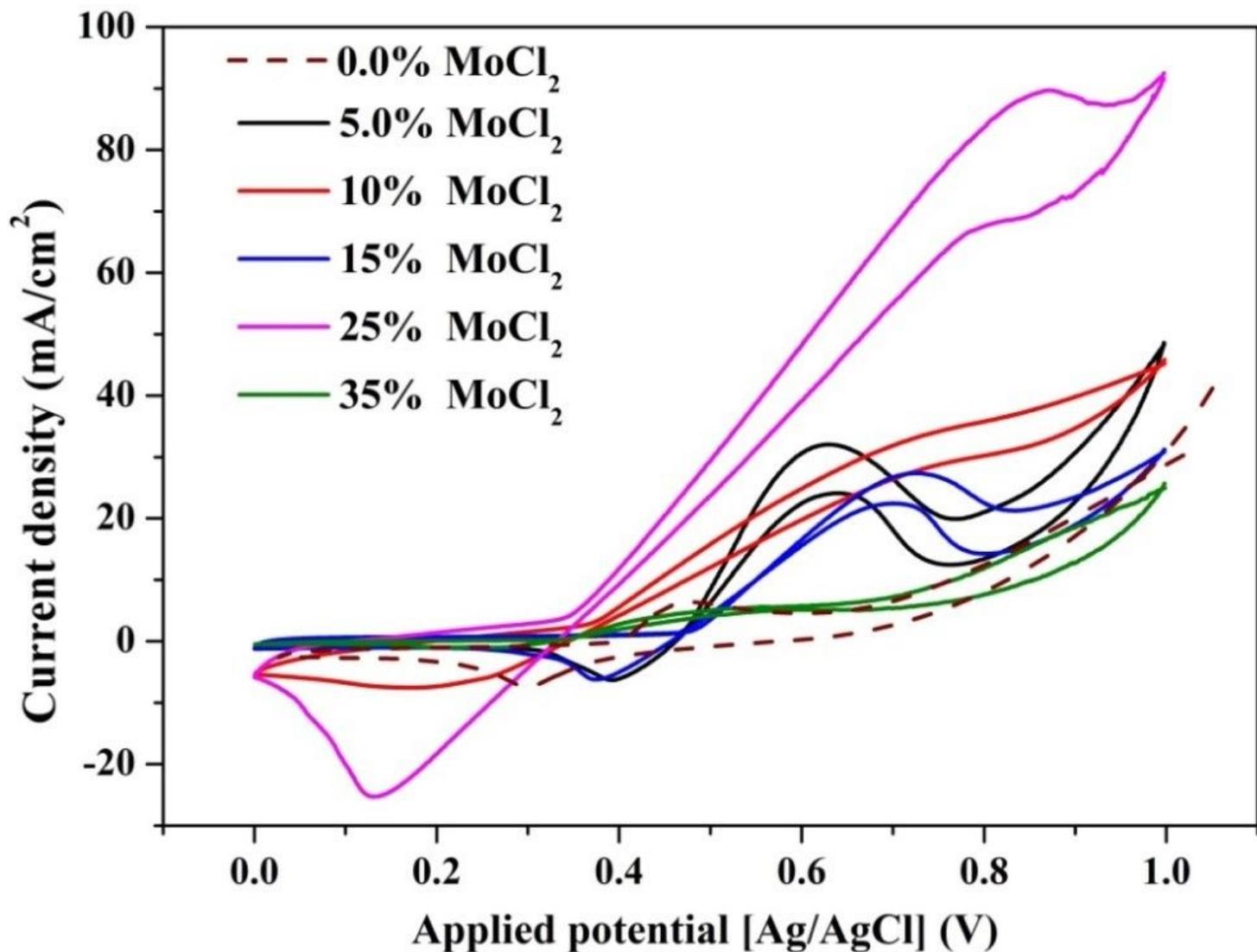


Figure 6

Influence of molybdenum precursor content in the initial electropolymerization solution on the electrocatalytic activity of the produced nanofibers toward urea oxidation (0.33 M urea in 1.0 M KOH) at scan rate of 50 mV/s and 25 °C.

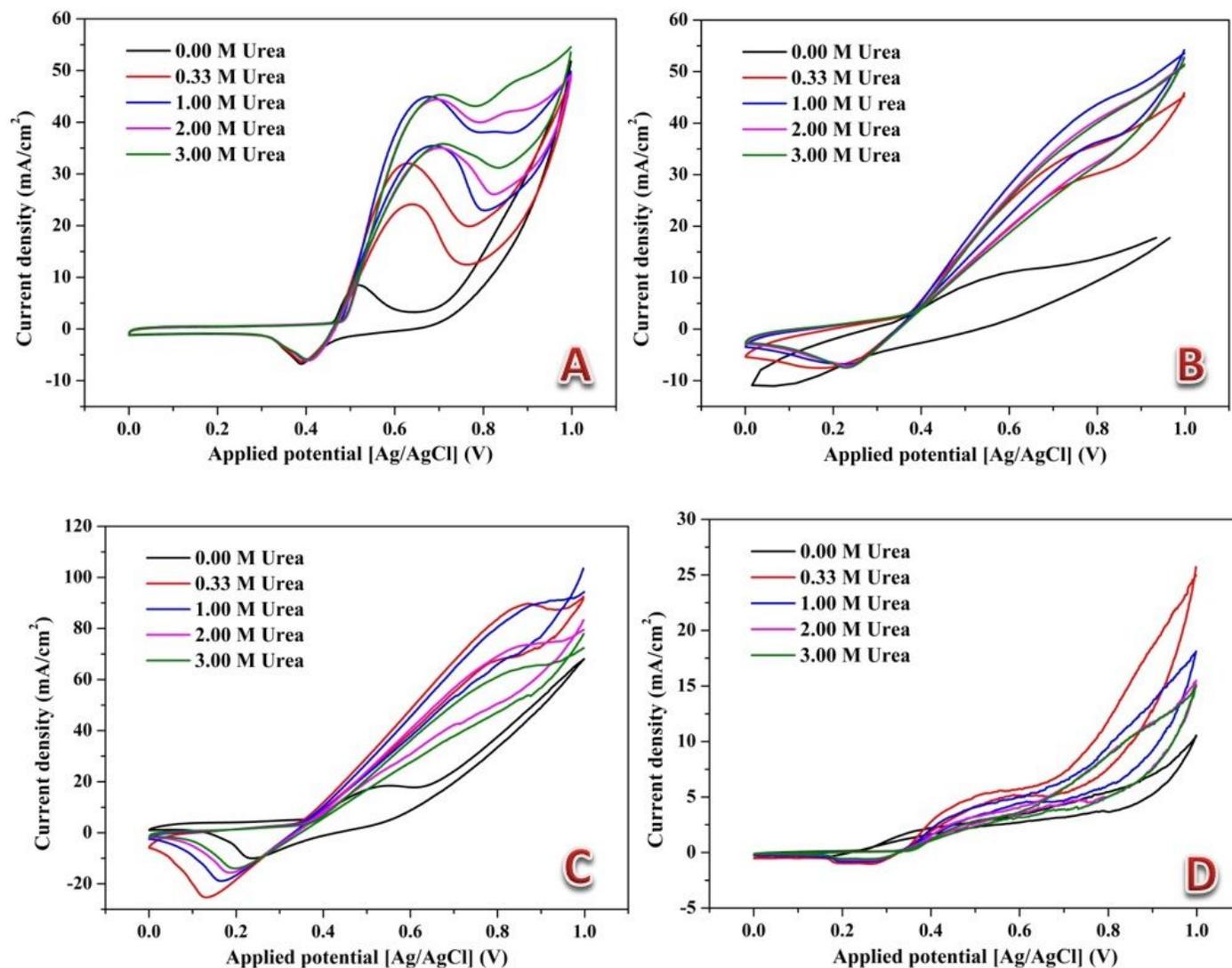


Figure 7

Electrocatalytic activity of the proposed NiMo-incorporated carbon nanofibers toward urea oxidation at different Mo precursor contents; 5; (A), 10; (B), 25; (C); and 35; (D), at 850 °C and 50 mV/s scan rate and 25 °C.

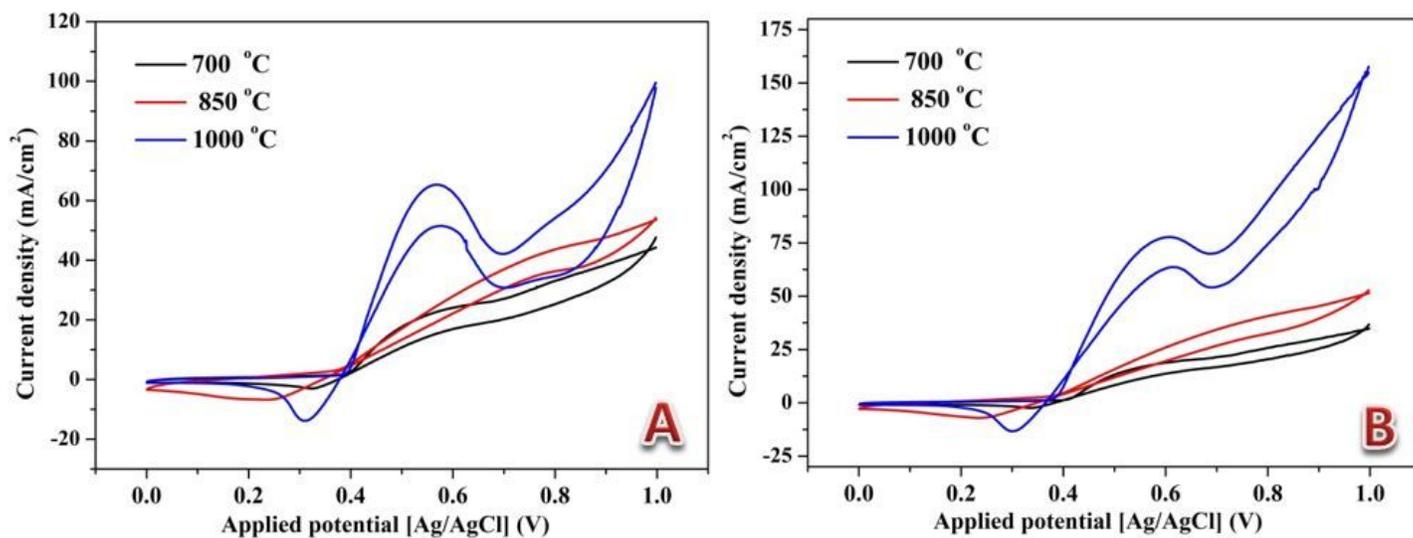


Figure 8

Influence of the calcination temperature on the electrocatalytic activity of the proposed NiMo-incorporated carbon nanofibers (10% Mo precursor) toward urea oxidation at different urea solution concentration, 1 M; (A) and 2 M; (B) at 50 mV/s scan rate and 25 °C.

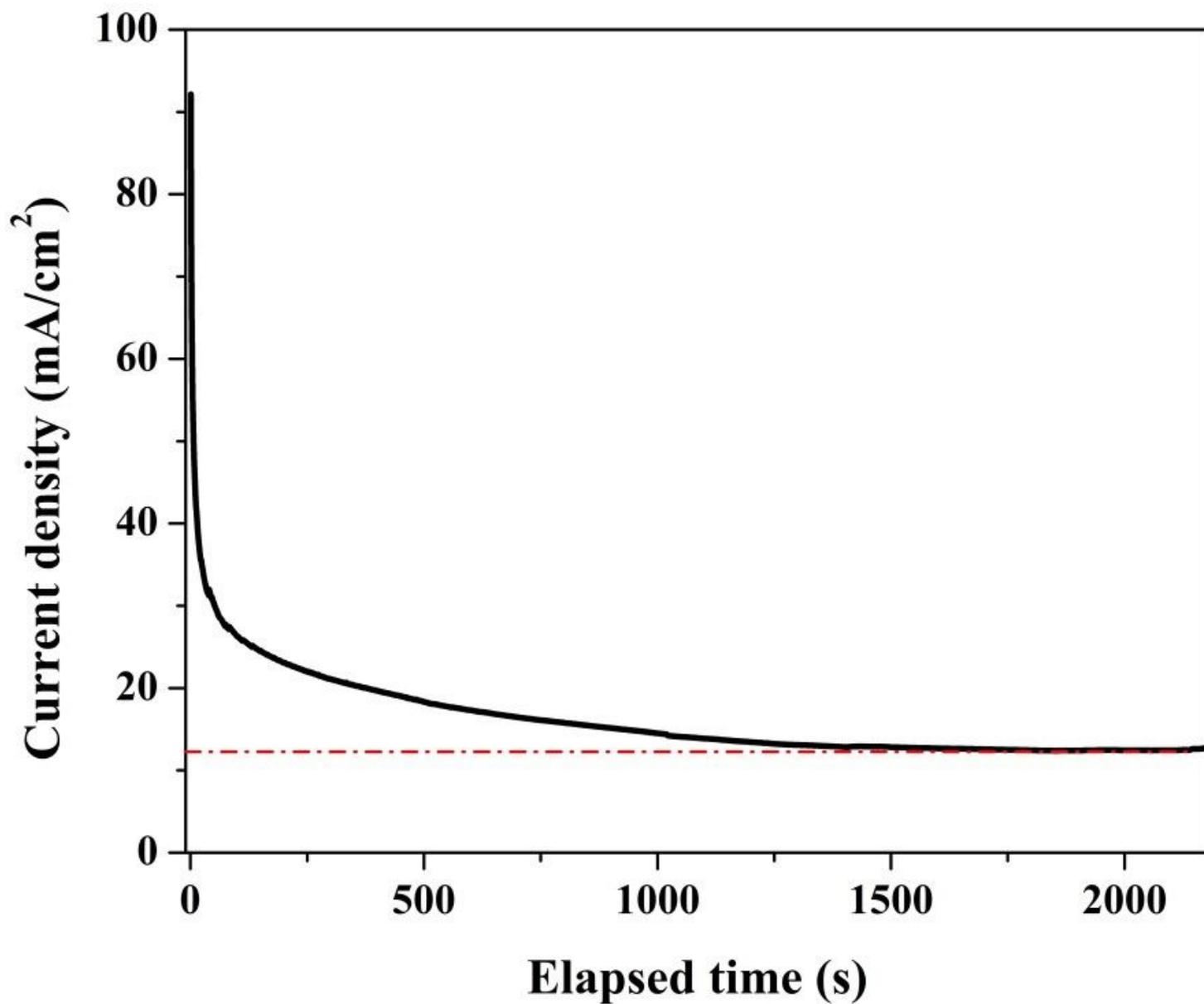


Figure 9

Chronoamperometry analysis at a potential of 0.6 V for the nanofibers obtained from sol-gel having 10 wt% MoCl₂ and thermally treated at 1000 °C in presence of 1.0 M urea (in 1.0 M KOH) at room temperature.

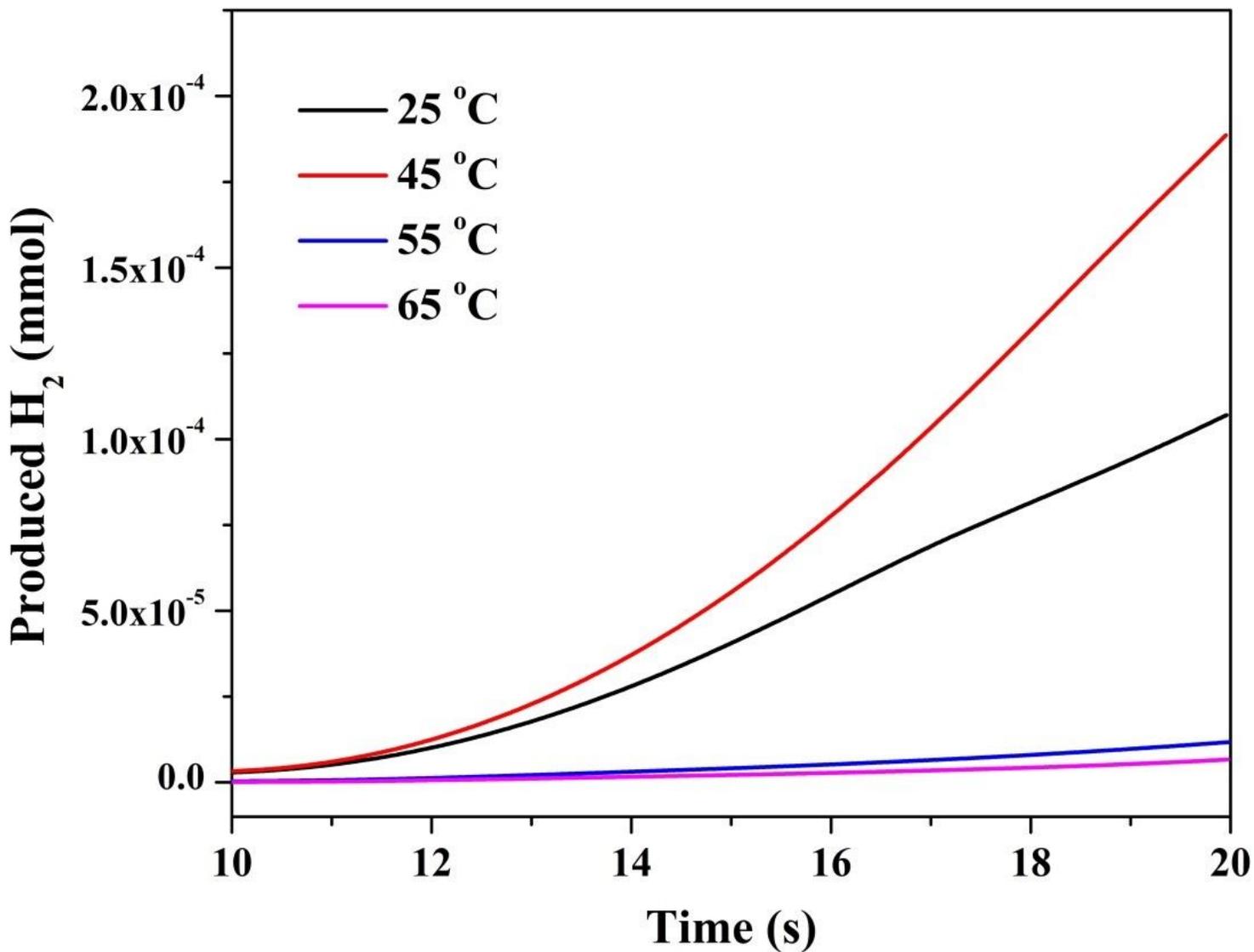


Figure 10

Influence of the reaction temperature on the hydrogen production rate using the proposed composite (15 % Mo precursor) calcined at 850 °C at 0.05 V/s scan rate.

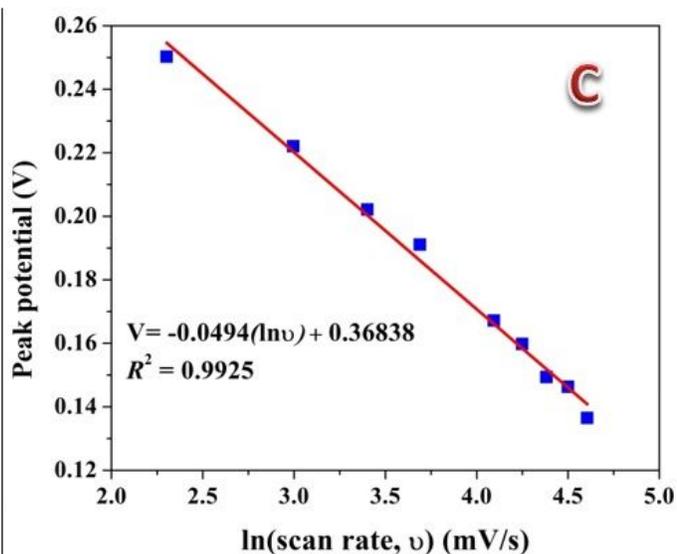
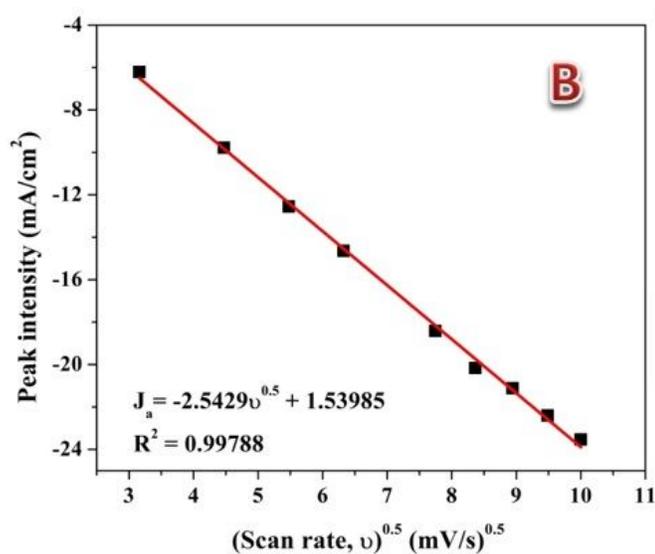
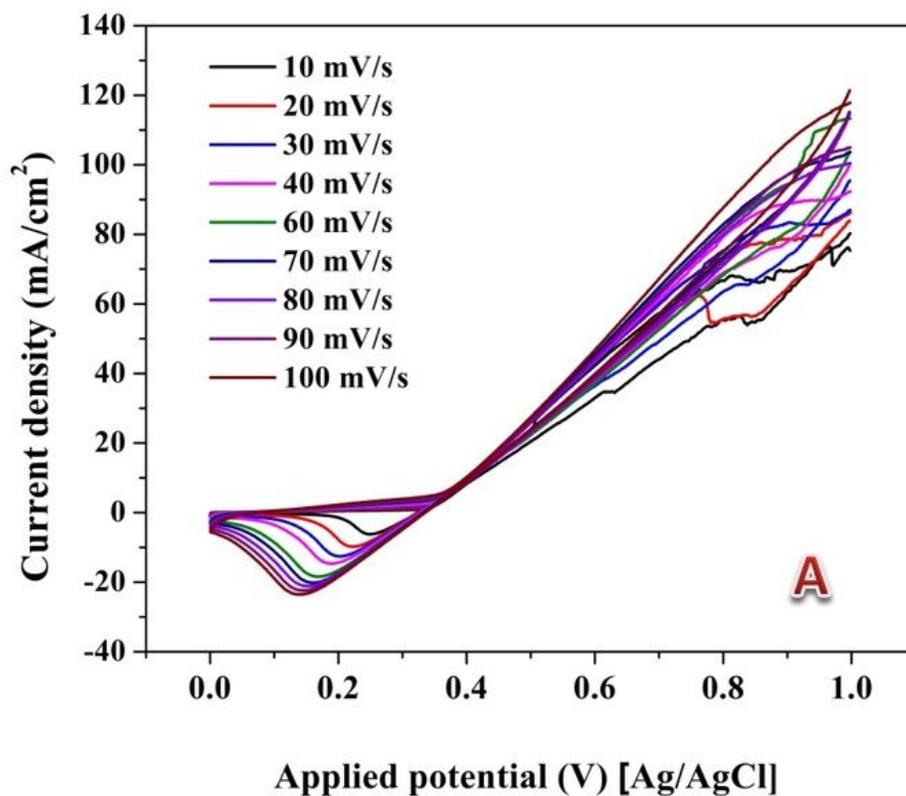


Figure 11

(A) Cyclic voltammograms of Mo₂C/Ni-incorporated carbon nanofibers (25 wt%) at different scanning rates in 0.33 M urea (in 1.0 M KOH); (B) plots of J_{pa} vs. scanning rates from (A); (C) Laviron's plots of cathodic peak potential vs. $\ln v$ from (A).

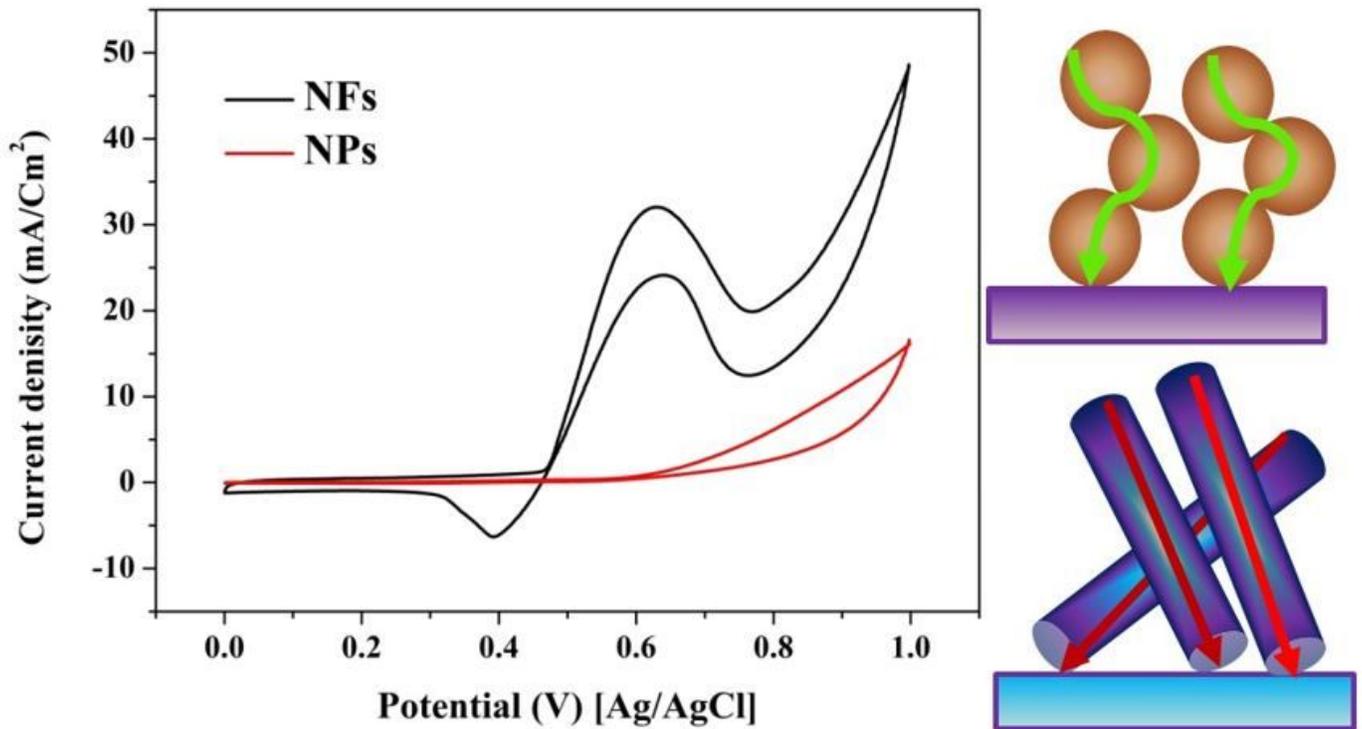


Figure 12

Impact of the nanofibrous morphology on the electro catalytic activity of the introduced MoC_2/Ni -incorporated carbon nanofibers toward urea oxidation (5% sample in 0.33 M urea (in 1.0 M KOH), scan rate 50 mV/s at room temperature).