Electrocatalytic oxidation of glucose using metal oxide nanoparticle-based electrodes

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ABSTRACT
The research on finding new and efficient catalysts for important electrochemical reactions such as glucose oxidation has never ceased since it is of core interest in the development of important devices such as fuel cells and biosensors. Electrocatalytic oxidation of glucose is an important topic both from the academic and technological points of view. While many researchers have treated the issue from the analytical chemistry point of view, others have studied this reaction (oxidation of glucose) as a half-cell reaction in biofuel cells. Precious metals such as platinum, gold and palladium are in many cases unavoidable candidates for glucose oxidation. However, these noble metals, in addition to their high cost, suffer from high susceptibility to poisoning by oxidation products. Thus scientists have been offering solutions to replace such costly noble metals with low-cost metals and metal oxides such as NiO, CuO and MnO2. In recent years metal oxide nanoparticle-based electrodes have been used for glucose oxidation in alkaline solutions. On one hand, they meet the necessities of the development of biofuel cells and on the other, they aid the development of biosensors directed towards glucose sensing in blood and in food industry. In this context, this review is intended to shed some light on the electrocatalytic oxidation of glucose using metal oxide (both single and binary) nanoparticle-based electrodes. Special attention is given to the methods of synthesis of such nanoparticles, surface techniques for their characterization and applications to glucose oxidation in alkaline solutions.

KEYWORDS: binary, nanoparticles, glucose, oxide, electrocatalyst

1. Introduction
Glucose electrooxidation is of prime importance for the diagnosis of diabetes mellitus, for food preparation processes and for the development of biofuel cells [1-5]. Glucose electrosensing is achieved either through enzyme-based or enzymeless methods. When using enzyme-based methods, it can be carried out in the presence of either a free enzyme or an immobilized one. Enzyme-based electrosensing is characterized by its high selectivity and it is the widely accepted approach since 1967 [6]. Most of enzymatic sensors are operated in the presence of either mediators or catalysts which are used to carry out the effective electrical contact of the enzyme active center with electrodes [7, 8]. The enzyme is utilized in the conversion of the analyte into electroactive species. This method of analysis is constrained by some restrictions such as the prerequisite of a biocompatible matrix as support, limited stability and oxygen deficit under low oxygen pressure, in addition to the difficult immobilization of the enzyme [9, 10].
Since their invention by Clark and Lyons in 1962, enzyme-based electrodes have been further developed and modified during the last few decades to meet the requirements of use as glucose enzymatic biosensors [11]. In general, glucose oxidase (GOD)-based method has been the most widely used. Analysis of glucose is based on reaction 1 (see below) where GOD can convert glucose to gluconic acid, liberating hydrogen peroxide ($H_2O_2$). Thus the glucose was sensed either by measuring the consumption of oxygen or the liberated $H_2O_2$ [12].

\[
\text{GOD} \\
\text{glucose} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{gluconic acid} + \text{H}_2\text{O}_2
\]

(1)

Enzyme-based electrodes have been fabricated either by physical entrapment of enzyme molecules within conducting polymer films or by covalent bonding of the enzyme with the functional group of an underlying matrix. In the former modification, the enzyme is entrapped deeply into the conducting matrix and hence it contributes little to the sensing ability [13-23]. Immobilized enzymes have many operational advantages over free enzymes such as the possibility of continuous operation, modulation of catalytic properties, lower cost of operation, reusability, good stability and wider working concentration range of analytes [24-26]. However, the lifetime of the enzyme-based sensors is limited [27, 28]. Therefore, several other procedures have been developed to overcome the above problem. They include immobilization of the enzymes onto metallic substrates through a thin film of self-assembled monolayer and conducting polymers [29-33]. Recently, nanostructured materials have been used as substrates or platforms for immobilizing enzymes because of their favorable intriguing properties such as large surface-to-volume ratio and high catalytic and surface reaction activity. However, most of these nanomaterials require cross-linking reagents or Nafion films to prevent enzyme leaching from electrode surface [34]. Hence, this calls for new methods that can overcome the above-mentioned obstacles.

Enzymeless glucose sensors have found their use as a promising alternative for enzyme-based analysis [35]. Considerable efforts have been focused in this direction in the last decade. Electrocatalysts designed for sensing or electrocatalysis of glucose oxidation usually use a single or bimetallic catalyst fabricated from metal and/or metal oxide nanoparticle-based electrodes.

Noble metals, as an important category of transition metals, have been extensively used for the purpose of enzymeless electroanalysis of glucose owing to their unique electrocatalytic properties, biocompatibility, fascinating surface structure, good electrical and mechanical properties, good electrocatalytic activity, strong stability and limited aggregation, and high performance [36, 37].

Gold is an important candidate for electrocatalysis of glucose oxidation as it presents high selectivity as well as sensitivity. The high selectivity is attributed to the electro-oxidation of glucose at Au electrodes at relatively high negative potential both in neutral and alkaline media [38]. However, the electro-oxidation of glucose at Au electrodes has been faced with two main problems. First is the interference from ascorbic acid (AA), and the other one is the deactivation of the electrode activity by $Cl^-$ ions [39, 40]. Chlorides, getting adsorbed at gold active sites inhibit the glucose oxidative-adsorption, which is the first and key step of the failure of the oxidation mechanism [41]. Toghill and Compton reported this problem earlier in 2010 [35]. After that, a number of approaches have been reported including that of gold-modified electrodes [42-46]. Au electrode surfaces with porous structures have been successfully used to eliminate interference from AA [47-52].

Several strategies have been explored for the preparation of nanostructured Au-modified electrodes in recent years. Nanoporous gold electrodes have been prepared mainly by de-alloying [53, 54] and anodization [55-59]. Pd coated nanoporous gold films [60] have been shown to improve the catalytic activity and enhance the stability for glucose oxidation [61, 62]. Pd nanoparticles have been dispersed on a variety of substrates such as indium tin oxide, carbon nanotubes [63, 64], epoxy-silver [65], graphene nanohybrids [66], boron-doped diamond [67], and polymers [68-70]. Cu-modified electrodes, characterized by their low cost and ease of fabrication, have received
considerable attention due to their electrocatalytic activity for glucose oxidation [71]. The effect of the underlying substrate on the electrocatalytic properties of copper-modified electrodes has also been reported [72, 73]. Recently, combining copper based materials with carbon nanotubes for glucose detection has been widely investigated. This has been achieved by sputtering cupric oxide on multi-walled carbon nanotubes (MWCNTs) [74, 75], electrodepositing copper nanocubes onto vertically-well-aligned MWCNTs [76], electrochemical deposition of copper oxide nanoparticles on horizontally-aligned single-walled carbon nanotubes (SWCNTs) [77], seed-mediated growth synthesis of copper nanoparticles on carbon nanotubes (CNTs) [78], copper oxide nanoleaves decorated CNTs [79] and nanospindle-like cuprous oxide/straight CNT nanohybrids [80].

Ni-based nanomaterials have exhibited remarkable catalytic oxidation for glucose originating from the redox couple of Ni(II)/Ni(III) formed on the electrode surface in alkaline medium [81, 82]. Most of the Ni-based glucose sensors were fabricated by modifying traditional electrodes with Ni-based nanomaterials such as dispersing Ni nanoparticles in disordered graphite-like carbon [83], doping carbon paste electrode with nano-NiO powder [84] and mixing powdered nanoscale nickel hydroxide with graphite powder in ionic liquid [85].

Platinum was the first discovered material that demonstrated electrocatalytic activity for glucose oxidation [86]. However, glucose sensors using Pt electrode suffer from poisoning by adsorbed intermediates and interfering species in addition to the oxidation of glucose at relatively higher potentials. This results in low sensitivity and poor selectivity [87-91]. This problem had been partially resolved by using another metal (e.g., Ni and Co) as a co-catalyst. Beside reducing Pt loading, the metal offers better tolerance to the poisoning of Pt by acting as a sacrificial active site on which the oxidation products are preferentially adsorbed [92, 93].

Pt-based electrocatalysts, PtM (M = Ru, Pd, Au, Ni, Ag, Bi, Pb) are currently drawing much attention because of their unique catalytic behavior compared to that offered by single-metal catalysts. They provide rapid response, good stability, and high catalytic efficiency [94-113]. Also, Au-based bimetallic catalysts, AuM (M = Pt, Pd, Ag) have been reported [105, 106]. Other bimetallic catalysts have been reported albeit not extensively as those of the combination of either Pt or Au with other metals [107].

Recently, large numbers of transition metal oxides, including both bulk and nanostructures-based ones, such as NiO, FeOOH, CuO, MnO₂, RuO₂, CuO, ZnO and Co₃O₄ have been reported for use as non-enzymatic electrocatalysts for glucose oxidation as an alternative for costly noble metals [114-124]. Among these oxides, NiO and CuO received substantial attention because of their low cost and environmental safety [125-140].

Copper oxides (CuO, Cu₂O), as an important class of p-type semiconductor metal oxides, have attracted considerable attention for use in enzyme-free glucose sensors due to their high electrocatalytic activity resulting from the multi-electron oxidation mediated by surface metal oxide layers [141-148]. Since the catalytic activities of the nanoscale materials are closely related to their shapes, many efforts have been made on amperometric determination of glucose using nanostructured copper oxides with various morphologies including platelets [142], fibers [144], spindles [144], particles [144], wires [144, 147], rods [145], flowers [145, 146], urchins [147], cubes [118] and spheres [148].

Among many possible electrocatalytic materials, those with the nickel redox couple Ni(II)/Ni(III) are of particular interest and have been the subject of much investigation. A survey of the literature shows that various studies have been devoted to investigations of the electrochemistry of a nickel hydroxide/oxyhydroxide couple [149-152]. Nickel oxyhydroxide strongly adsorbs some of the organic substances and has high electrocatalytic efficiency for the oxidation of organic molecules via cyclic mediation electron-transfer processes in alkaline solutions.

2. Glucose oxidation on NiOₓ and MnO₂/NiOₓ

In this part, our recently published work on electrocatalytic glucose oxidation at single and binary catalyst-modified glassy carbon electrodes is reviewed [153-157]. In single catalyst-modified electrodes, NiOₓ-nanoparticles were electrodeposited
on either bare or anodically-oxidized glassy carbon electrodes. In binary catalysts, NiO\textsubscript{x} and MnO\textsubscript{y} modified glassy carbon electrodes were used for the electrocatalytic oxidation of glucose in alkaline solutions. Although binary catalysts composed of nickel with either manganese oxides or copper oxides have been documented [152], both metals were deposited simultaneously from a mixture of their ions. In our work, the bicatalyst (NiO\textsubscript{x} and MnO\textsubscript{y}) was electrodeposited in a well-ordered sequence. The order was found to have significant impacts on the electrocatalytic properties of the binary catalysts on glucose oxidation.

2.1. Binary catalysts

This section presents the electrocatalytic activity of a new catalyst composed of nickel and manganese binary oxides, prepared by sequential electrodeposition, for glucose electrooxidation in an alkaline solution.

2.1.1. Electrode modification

Glassy carbon electrode (GCE) modification with NiO\textsubscript{x} and MnO\textsubscript{y} were achieved in two sequential steps. First was the potentiostatic deposition of metallic nickel on the GCE from an aqueous solution of 0.1 M acetate buffer solution (pH = 4.0) containing 1 mM Ni(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O by applying a constant-potential electrolysis at -1 V (Ag/AgCl/KCl) for different time durations. Next, the deposited Ni was passivated in 0.1 M phosphate buffer solution (PBS, pH = 7) by cycling the potential between -0.5 and 1 V for 10 cycles at a scan rate of 200 mV/s [154]. Then the modification with MnO\textsubscript{y} was achieved by cycling the potential from 0 to 0.4 in 0.1 M Na\textsubscript{2}SO\textsubscript{4} containing 0.1 M Mn(CH\textsubscript{3}COO)\textsubscript{2}.5H\textsubscript{2}O for 60 cycles, then activation by potential cycling for 5 cycles in 0.5 M NaOH solution in the potential range -0.2 to 0.6 V [154]. The sequence of the deposition of the two catalysts, i.e., NiO\textsubscript{x} deposited first and then MnO\textsubscript{y} or vice versa, was achieved by keeping the number of MnO\textsubscript{y} cycles constant at 60 cycles and changing the deposition time of NiO\textsubscript{x}.

2.1.2. Morphological and electrochemical characterizations

Fig. 1 shows scanning electron microscopy (SEM) images taken for bare glassy carbon electrode (GCE) (A), MnO\textsubscript{y}/GC (B), NiO\textsubscript{x}/GC (C), MnO\textsubscript{y}/NiO\textsubscript{x}/GC (D), and NiO\textsubscript{x}/MnO\textsubscript{y}/GC (E) electrodes. In image (A), the GC substrate is featureless whereas MnO\textsubscript{y} is deposited exhibiting a porous nanorod-texture (image B) [155]. The NiO\textsubscript{x} nanoparticles are uniformly deposited on the GC substrate with an average particle size of about 90-100 nm (image C). In image (D) (MnO\textsubscript{y}/NiO\textsubscript{x}/GC sample, NiO\textsubscript{x} is deposited first), the microstructure is significantly different compared with the image of direct deposition of MnO\textsubscript{y} on bare GC (image B), and it appears as a combined feature of images (B) and (C), where particles of NiO\textsubscript{x} are partially covered with MnO\textsubscript{y}. In image (E) (NiO\textsubscript{x}/MnO\textsubscript{y}/GC sample, MnO\textsubscript{y} deposited first), NiO\textsubscript{x} is extensively deposited compared with image (C). It seems also that NiO\textsubscript{x} partially covers the previously deposited MnO\textsubscript{y}. This means that the previously deposited MnO\textsubscript{y} improves the interface properties in a way that enhances the deposition of NiO\textsubscript{x}. Finally, it is clear that the order of deposition significantly affects the morphology of the deposited oxides.

It is well known from literatures that nickel oxide and not metallic nickel is the appropriate electrocatalyst for alcohol oxidation in alkaline medium [154, 155]. Hence the deposited nickel was passivated by the process described in Sec. 2.1.1 in order to convert Ni to NiO\textsubscript{x}.

Fig. 2 compares cyclic voltammograms (CVs) of the (a) bare and the (b-e) modified GCE in 0.5 M NaOH solutions. The CV of the bare GCE (curve a) is featureless, as expected. At the MnO\textsubscript{y}/GC electrode (curve b), a significant increase in the charging current is shown as a characteristic feature of MnO\textsubscript{y}-modified electrodes; this featureless CV corresponds to the continuous change in the valences of Mn following the anodic and cathodic potential scanning [157]. At the NiO\textsubscript{x}/GC electrode (curve c), the well-defined redox waves of the surface-confined Ni(II)/Ni(III) transformation is observed [158]. It has been reported that there are four possible phases produced over the anodic and cathodic scans for the nickel hydroxide electrode substrate, namely, β-Ni(OH)\textsubscript{2}, α-Ni(OH)\textsubscript{2}, β-NiOOH and γ-NiOOH [153]. The transformations among the four phases can be identified well using the Bode diagram [159, 160]. The formation of γ-NiOOH phase is associated with the swelling or volume expansion of nickel film electrodes.
Fig. 1. FE-SEM images of GCE (A), MnO$_x$/GC (B), NiO$_x$/GC (C), MnO$_x$/NiO$_x$/GC (D), and NiO$_x$/MnO$_x$/GC (E) electrodes.
with subsequent microcracks and disintegration. Lower inter-electrode spacing results in lower internal resistance and therefore better efficiency of the electrode for electrooxidation processes in alkaline medium [161, 162]. Therefore, the $\beta$-NiOOH phase is expected to be a better electroactive material for high electrochemical performance in alkaline solutions [161]. The Ni(II)/Ni(III) conversions occur via two pathways, by a proton diffusion mechanism in which $\beta$-NiOOH is likely formed (Eq. 2), and by a solvent mechanism in which $\gamma$-NiOOH is formed through the diffusion of OH$^-$ (Eq. 3) [153].

\[
\begin{align*}
\text{Ni(OH)}_2 & \leftrightarrow \text{NiOOH} + H^+ + e^- \quad (2) \\
\text{Ni(OH)}_2 + \text{OH}^- & \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (3)
\end{align*}
\]

Interestingly, in the case of the MnO$_y$/NiO$_x$/GC electrode (curve d), where NiO$_x$ is deposited first, the current of the Ni(II)/Ni(III) couple significantly decreases in comparison with NiO$_x$/GC electrode; this is probably due to the partial deposition of MnO$_y$ on the previously deposited NiO$_x$ which is consistent with the SEM images shown in Fig. 1D.

For the NiO$_x$/MnO$_y$/GC electrode (curve e), where MnO$_y$ is deposited first, we may conclude the following; the current of the Ni(II)/Ni(III) redox couple is markedly enhanced, the peak current is almost doubled as compared with NiO$_x$/GC (curve c).

The amount of the deposited Ni (estimated from I-t deposition curves), in the case of the NiO$_x$/GC and NiO$_x$/MnO$_y$/GC equal to 14.4 and 16.7 $\mu$g, respectively. It is likely that the enhancement in the current of the Ni(II)/Ni(III) couple may be attributed to the increase of the Ni$^{3+}$ content by doping the NiO$_x$ with MnO$_y$. According to Das et al. [163], Mn(IV) can be converted during the anodic scan to a powerful and unstable oxidant, Mn(V), which can convert some of the Ni$^{2+}$ to Ni$^{3+}$ resulting in an increase in the conductivity of the former according to the following reaction.

\[
\text{Mn(V)} + \text{Ni}^{2+} \rightarrow \text{Ni}^{3+} + \text{Mn(IV)} \quad (4)
\]

### 2.1.3. Electrocatalytic oxidation of glucose at the modified electrodes

The glucose oxidation reaction at the GC and MnO$_y$/GC electrodes has been studied in our laboratory (data are not published). It was found that bare GCE is ineffective for the oxidation of glucose. While at the MnO$_y$/GC electrode, at the same conditions, the CV is characterized by large charging currents which is a characteristic feature of MnO$_y$-modified electrodes [155, 158]. However, on addition of glucose, the oxidation current is enhanced. It has been reported that glucose oxidation is electrocatalyzed at MnO$_y$-modified electrodes [161]. That is to say Mn(IV) is oxidized to Mn(V), then, in a subsequent chemical step, glucose is
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oxidized according to Eq. 5, i.e., electrocatalytic (EC)
mechanism.

\[
\text{Mn(V)} + \text{glucose} \rightarrow \text{Mn(IV)} + \text{products} \quad (5)
\]

Fig. 3 shows linear scan voltammetry (LSV) responses obtained at the NiO\textsubscript{x}/GC; (a), MnO\textsubscript{y}/NiO\textsubscript{x}/GC (b) and NiO\textsubscript{x}/MnO\textsubscript{y}/GC (c) electrodes in 0.5 M NaOH solutions containing 20 mM glucose (inset shows the blank responses). At the NiO\textsubscript{x}/GC electrode (curve a) glucose oxidation is markedly enhanced; glucose molecules adsorbed on the surface are oxidized at higher potentials coinciding with the oxidation of Ni(II) oxide. The oxidation of Ni(II) has the consequence of decreasing the number of sites for glucose adsorption, along with the poisoning effect of the products or intermediates formed during the reaction. This tends to decrease the overall rate of glucose oxidation. Thus, the anodic current passes through a maximum as the potential is anodically swept.

A number of mechanisms have been reported for the electrooxidation of alcohols on Ni in alkaline solutions. Those mechanisms can be summed up into two ways; while Fleischmann \textit{et al.} \cite{150, 164} assumed catalytic/intermediate role for NiOOH, others \cite{165-167} reported that methanol oxidation takes place after the complete conversion of Ni(OH)\textsubscript{2} to NiOOH in the course of an anodic potential sweep. Hence we assume that a part of the anodic current is due to glucose oxidation by NiOOH and the other part of the current is due to glucose oxidation on the surface of the oxide layer by direct electrooxidation.

The first step in the whole process is the redox transition of nickel species from Ni(II) to Ni(III), followed by the second step which is the glucose oxidation on the modified surface via the following reactions:

\[
\text{Ni(III)} + \text{glucose} \rightarrow \text{intermediate} + \text{Ni(II)} \quad (6)
\]

\[
\text{Ni(III)} + \text{intermediate} \rightarrow \text{products} + \text{Ni(II)} \quad (7)
\]

The Ni(III) sites are regenerated by the anodic potential afforded by the power source. Glucose oxidation can also take place on the NiOOH surface by direct electrooxidation \cite{166, 167}:

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\[
\text{Mn(V)} + \text{glucose} \rightarrow \text{Mn(IV)} + \text{products} \quad (5)
\]
Ni(III) – glucose → Ni(III) – intermediate \( (8) \)
Ni(III) – intermediate → Ni(III) – products \( (9) \)

Equations (6) and (7) are according to the Fleischmann mechanism [149, 165], and in Eqs. (8) and (9), Ni\(^{3+}\) is used as an active surface for glucose oxidation. Gluconolactone [167, 168] as well as methanoates and oxalates [169, 170] have been reported as the oxidation products of glucose electrooxidation.

Recalling Fig. 3 in which the glucose oxidation at MnO\(_y\)/NiO\(_x\)/GC and NiO\(_x\)/MnO\(_y\)/GC electrodes in 0.5 M NaOH is shown as curves b and c, respectively, it is obvious that the order of the deposition of the nano-MnO\(_y\) and NiO\(_x\) dramatically affects the performance of the binary catalyst. For instance, the peak current for glucose oxidation is much higher in the case of NiO\(_x\)/MnO\(_y\)/GC and the onset potential of glucose oxidation shifted to less positive values in the case of NiO\(_x\)/MnO\(_y\)/GC (c) compared to MnO\(_y\)/NiO\(_x\)/GC (b). When the MnO\(_y\)/NiO\(_x\)/GC is used (NiO\(_x\) is deposited first) (curve b) the electroactivity significantly decreases. However, the highest response is obtained on the NiO\(_x\)/MnO\(_y\)/GC electrode, i.e., when MnO\(_y\) is deposited first, followed by the electrodeposition of NiO\(_x\). The larger response at the binary catalyst NiO\(_x\)/MnO\(_y\)/GC in comparison with NiO\(_x\)/GC electrode may be the result of two factors; first, glucose is expected to be adsorbed quite easily on MnO\(_y\) due to the possibility of hydrogen bond formation using the multiple hydroxyl groups present in the molecule [169, 171]. Thus the accessibility of glucose at the electrode surface increases. Second, MnO\(_y\) plays a significant role; Ni\(^{2+}\) can be oxidized to Ni\(^{3+}\) by the strong oxidant Mn(V), which increases the concentration of Ni\(^{3+}\) in the matrix. As a result of this, the conductivity of the matrix increases and this leads to enhancement of the glucose oxidation [170, 171].

2.1.4. Effect of the loading level of NiO\(_x\)

Fig. 4 compares linear scan voltammograms of NiO\(_x\)/GC (A), and NiO\(_x\)/MnO\(_y\)/GC (B) electrodes, at different loading levels of deposited NiO\(_x\) in 0.5 M NaOH solution containing 20 mM glucose. MnO\(_y\) loading is kept constant at 60 cycles for all experiments. NiO\(_x\) and MnO\(_y\) were electrodeposited as described in Sec. 2.1.1. As mentioned above, NiO\(_x\) is responsible for the electrocatalytic oxidation of glucose due to the presence of the Ni(II)/Ni(III) redox couple; smaller loadings of the NiO\(_x\) at the GCE results in a significant enhancement in the electrocatalytic activity of the GCE for glucose oxidation. At both electrodes, as the loading level of NiO\(_x\) increases, the peak current of glucose oxidation increases and the onset potential shifts to lower positive values.

The effect of scan rate on the electrooxidation of glucose at the optimum loading level was studied in our laboratory (data not published), and it was found that, at scan rates larger than 100 mVs\(^{-1}\), the \( I_p / \nu^{1/2} \) function does not change significantly with the scan rate. The above observation is a characteristic feature of catalytic reactions [171, 172]. It becomes clear that the deposition of NiO\(_x\) onto the MnO\(_y\)/GC-modified electrode significantly enhances the glucose electrooxidation due to two considerations; first, MnO\(_y\) enhances the adsorption of glucose and the second is the mediation by the second oxide (NiO\(_x\)) in an EC mechanism as represented by Eqs. 5 and 6 and confirmed by the \( I_p / \nu^{1/2} – \nu \) relation.

In order to get further insight, Tafel plot of \( E \) vs. \( \log I \) was plotted using the rising part of the current-voltage data, i.e., in the potential range 0.35-0.45 V (Fig. 3), at a scan rate of 5 mVs\(^{-1}\) for a 0.5 M NaOH containing 20 mM glucose (Fig. 5). Tafel slopes for NiO\(_x\)/GC (a), MnO\(_y\)/NiO\(_x\)/GC (b), and NiO\(_x\)/MnO\(_y\)/GC (c) were found to be equal to 108.44, 115.25 and 113.54 mV decade\(^{-1}\), respectively. The similarity of the Tafel slopes (average value ca. 112 mV decade\(^{-1}\)) for the different electrodes indicates that the glucose oxidation proceeds via a common rate-determining step in all the cases, which is the one-electron transfer step (Eq. 6).

2.1.5. Long-term stability of the prepared electrocatalysts

One of the main objectives of using the binary oxide of NiO\(_x\) and MnO\(_y\) is to enhance the stability of the NiO\(_x\) (the active oxide)-modified GCE. Hence, to investigate the stability of the proposed catalysts, current-time curves were recorded for glucose oxidation at the proposed electrodes at a constant potential of 0.5 V and 0.62 V for NiO\(_x\)/GC (a), and NiO\(_x\)/MnO\(_y\)/GC (b).
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2.1.6. Tolerance of glucose electrocatalytic oxidation

Generally, using non-enzymatic sensors for the analysis of glucose often suffers from drawbacks among the coexisting oxides. Fig. 4. LSV response obtained at (A) NiO$_x$/GC and (B) NiO$_x$/MnO$_y$/GC electrodes with different loading levels of NiO$_x$ in 0.5 M NaOH solutions containing 20 mM glucose at a scan rate of 100 mV/s. In panel (B) the MnO$_y$ loading is fixed at 60 cycles of MnO$_y$ deposition.

electrodes, respectively and the data are shown in Fig. 6. The figure depicts that the NiO$_x$/MnO$_y$/GC electrode supports higher oxidation currents than that obtained at the NiO$_x$/GC electrode. This level of enhancement could still be observed after three hours of continuous measurement. This indicates a better mechanical stability and good adhesion among the coexisting oxides.

2.1.6. Tolerance of glucose electrocatalytic oxidation

Generally, using non-enzymatic sensors for the analysis of glucose often suffers from drawbacks...
of low sensitivity and interference of other oxidizable components such as ascorbic acid and uric acid [173]. The adsorption of chlorides, which decreases significantly the operational stability is another challenge. It has been reported that CuO_x-modified electrodes are good non-enzymatic catalysts for glucose oxidation in alkaline medium, and thus the poisoning by chloride at this modified electrode has been extensively studied [173]. High tolerance of NiO_x/MnO_y/GC binary catalysts towards poisoning products resulting from glucose oxidation and also towards poisoning by halide ions has been

Fig. 5. Tafel plots for (a) NiO_x/GC, (b) MnO_y/NiO_x/GC and (c) NiO_x/MnO_y/GC electrodes in 0.5 M NaOH solution containing 20 mM glucose at a scan rate 5 mV/s.

Fig. 6. Current-time relation obtained during glucose oxidation at (a) NiO_x/GC and (b) NiO_x/MnO_y/GC electrodes in 0.5 M NaOH containing 20 mM glucose at (a) 0.5 V and (b) 0.52 V, respectively.
Consecutive LSV responses for the forward and backward scans were obtained at NiOx/MnOy/GC electrode in 0.5 M NaOH containing 20 mM glucose with either 0.1 M Cl\(^-\) or 0.1 M Br\(^-\) [154]. To quantitatively compare the poisoning effect of Cl\(^-\) and Br\(^-\) ions, the oxidation peak currents for the forward scan in the halide-free glucose and after adding Cl\(^-\) and Br\(^-\) are plotted as a function of the number of potential cycles as shown in Fig. 7. The following inferences can be obtained from Fig. 7:

(i) In the presence of Cl\(^-\) or Br\(^-\) ions, the oxidation peak currents for the first cycle are similar to that in the absence of both species. During potential cycling the peak current decreases in the presence of any of the above halide ions, albeit to different extent.

(ii) The decreasing rate of the oxidation peak current follows the sequence: Br\(^-\) > Cl\(^-\) > halide-free (glucose only). This behavior is due to the differences in the electronegativity of Cl\(^-\) and Br\(^-\) ions, ionic radii and solvation ability [174].

(iii) The peak current changes with the number of potential scan cycles. However, the recovery of the electrode activity in the presence of Cl\(^-\) is faster than in the presence of Br\(^-\). Note that in the presence of Cl\(^-\), the initial peak current is completely recovered, while in the case of Br\(^-\) it is not.

Fig. 7. The relationship between peak current at each run and number of runs.
(iv) The largest decrease in the peak current is about 22 µA for the Cl\(^-\) ions and 26 µA for the Br\(^-\) ions, i.e., 4.0% and 4.7% from the original current, respectively.

The above results reveal the tolerance of NiO\(_x\)/MnO\(_y\)/GC electrode to poisoning by chloride and bromide ions at NiO\(_x\)/MnO\(_y\)/GC electrodes during glucose oxidation. This may be attributed to the low adsorbability and high solvation of the Cl\(^-\) and Br\(^-\) ions. It could also be attributed to the high reversible oxidation potentials of Cl\(_2\)/Cl\(^-\) and Br\(_2\)/Br\(^-\) reactions (1.36 and 1.06 V, respectively vs. standard hydrogen electrode (SHE)) [175].

2.1.8. Effect of iodide ion

Fig. 8 shows the consecutive LSV responses for the forward scans (I) and backward scans (II) obtained at the NiO\(_x\)/MnO\(_y\)/GC electrode in 0.5 M NaOH containing 20 mM glucose and different iodide ion concentrations ranging from 10\(^{-5}\) to 10\(^{-2}\) M. Note that, the concentration range used for the effect of iodide is much lower than that used above for Cl\(^-\) and Br\(^-\). This is because I\(^-\) has significant adsorbability and so, at high concentrations it blocks the electrode surface active sites.

In the case of the iodide-free glucose solution (curve a), the forward scan current corresponds to the combination of two reactions, that is, oxidation of Ni\(^{2+}\) to Ni\(^{3+}\) and glucose electrooxidation by interaction with Ni\(^{3+}\). The backward scan corresponds to the combination of Ni\(^{3+}\) reduction to Ni\(^{2+}\) and the glucose electrooxidation with the already present Ni\(^{3+}\) [154, 155, 176].

It has been reported that iodide ion is oxidatively adsorbed at Pt and Au electrodes as a zero-valent atomic iodine at potentials between -0.4 V and +0.4 V (Ag/AgCl reference) [177]. The amount of the adsorbed iodine increases upon scanning the potential to more positive values than -0.4 V until the surface is saturated with a monolayer of close-packed iodine atoms of coverage limited by Van der Waals interactions. Additional iodine atoms forced into the already space-limited interfacial layer leads to the formation of molecular iodine, which evolves into the solution as aqueous I\(_2\) (2 I\(^-\) \(\rightarrow\) I\(_2\) + 2e). At the surface of Pt and Au anode, at considerably higher positive potentials and before oxygen evolution, the zero-valent adsorbed iodine is oxidized to aqueous iodate

---

**Fig. 8.** Consecutive LSV responses for the forward scan (I) and backward scan (II) obtained at NiO\(_x\)/MnO\(_y\)/GC electrode in 0.5 M NaOH containing 20 mM glucose at different iodide ion concentrations. (a) 0.0, (b) 10\(^{-5}\), (c) 10\(^{-4}\), (d) 10\(^{-3}\) and (e) 10\(^{-2}\) M. Scan rate: 100 mVs\(^{-1}\).
(I₂ ↔ IO₃⁻) along with the oxide formation on the electrode surface. Finally, it is quite probable that the iodates formed at the electrode diffuses back into the solution and react with the iodide, forming iodine again [178, 179].

In Fig. 8, upon the addition of the iodide ions, a significant effect appears in the forward and backward scans at each concentration (curves b-d). In the presence of 10⁻³ M I⁻ (curve b), the LSV for the forward and backward scans are similar to that of iodide-free glucose solution (curve a), and there is no significant change in both the forward and backward scan. In curve c (10⁻⁴ M I⁻), again the forward scan is similar to the case of iodide-free glucose solution, while the backward current is lower than the iodide-free glucose solution (curve a). The forward scan current does not decrease as is expected from the poisoning effect by iodide. This can be explained as follows: the anodic current is a combination of two processes; the oxidation of glucose and the oxidation of the adsorbed I₂ to IO₃⁻. The decrease in the current corresponding to glucose oxidation due to poisoning is compensated by the oxidation of the adsorbed I₂ to IO₃⁻. Hence the current in the forward scan is kept almost unchanged. On the other hand, the decrease in the backward current in the presence of iodide ions might be attributed to the adsorption of iodine or iodates formed in the forward scan that blocks some of the active sites. Another factor is the presence of another reduction reaction for iodide derivatives in parallel with the Ni³⁺ reduction, and the combination of these two processes can decrease the overall back-oxidation current of glucose in the backward scan, and hence glucose oxidation current in the backward scan decreases in comparison with the case of iodide-free glucose solution.

In the case of 10⁻³ M I⁻ (curve d), the forward scan current is higher than the iodide-free glucose solution case and the backward scan current is lower than iodide-free glucose case (curve a). The increase of current in the forward scan may be attributed to the oxidation of the adsorbed zero-valent iodine to aqueous iodine atoms and/or iodates as they are available in the present potential range as revealed in Fig. 9 (curve d), in which the CV responses obtained at the NiOₓ/MnOᵧ/GC in 0.5 M NaOH at different I⁻ concentrations is shown. The current increases in the potential range between 0.4 to 0.6 V at NiOₓ/MnOᵧ/GC during the forward scan in the presence of 10⁻³ M I⁻. The decrease in the backward scan current (Fig. 8, curve d) is attributed to the same reasons as in the case of

![Graph](image-url)

**Fig. 9.** CV responses obtained at NiOₓ/MnOᵧ/GC electrode in 0.5 M NaOH at different I⁻ concentrations. (a) 0.0, (b) 10⁻⁵, (c) 10⁻⁴, (d) 10⁻³ and (e) 10⁻² M. Scan rate: 100 mVs⁻¹.
10^{-4} \text{ M I}$. However the decrease in the backward scan current in the present case is more significant as the adsorbed species in the forward scan is higher in the present case compared with the case of $10^{-4} \text{ M I}$. In the case of $10^{-2} \text{ M I}$ (curve e), where the concentration of iodide ions becomes close to glucose concentration, the transformation from adsorbed iodine to aqueous iodine and/or iodates become more considerable. Thus, the current of the forward scan becomes higher than that of the iodide-free glucose solution case and lower than the case of $10^{-3} \text{ M I}$. The increase in the current in curve e in Fig. 9 covers a wide potential range from the onset potential of the peak to 0.65 V, in accordance with that found in Fig. 8 where no glucose was added. The increase in the current in the forward scan in the presence of $10^{-2} \text{ M I}$ is not much higher than in the case of $10^{-3} \text{ M I}$, which could be attributed to the fact that glucose oxidation is more inhibited in the forward scan than in the case of $10^{-3} \text{ M I}$, and hence the current difference between the case of $10^{-3} \text{ M}$ and $10^{-2} \text{ M I}$ in the presence of glucose is negligible. In the backward scan (Fig. 8 (curve e)), the peak current becomes much lower than in the case of $10^{-3} \text{ M I}$, as the poisoning in this case is much higher than cases of $10^{-3}$ and $10^{-4} \text{ M I}$.

Figs. 10(A), 10(B) and 10(C) show consecutive LSV responses for the forward scan (I) and backward scan (II) obtained at NiOx/MnOy/GC electrode in 0.5 M NaOH containing 20 mM glucose and $10^{-4}$ (A), $10^{-3}$ (B), and $10^{-2}$ (C) M I, respectively. We can see that with increase in the number of potential scan cycles, both the forward and backward currents decrease, and this decrease depends on the iodide concentration. In addition, in cases (B) and (C), with the increase in the concentration of the I, a small peak appears in the backward scan (II) with the increase in the number of potential scan cycles especially in the latter case. That peak may be attributed to the reduction of the remaining NiOOH, as the surface poisoning by iodates and iodine hinder glucose from interacting with Ni^{3+}. Fig. 11 shows the relationship between the peak current for the forward scan ($I_p$) with the number of potential scan cycles (data were taken from Fig. 10). This figure demonstrates an interesting drop in the oxidation peak current with increase in the potential sweep number and with increase in the I concentration. It is worth mentioning that
the peak current for the first run in cases (c) and (d) (Fig. 11) is higher than the blank (0.5 NaOH) itself (curve a). This behavior was attributed to the adsorbed iodine as it is available in the present potential range. In the subsequent potential scan cycles, the peak current decreases with the increase in the potential scan number to values lower than that of the blank. The fact that the peak
radii and the electronegativity of the halide ions have a profound influence on their adsorption process. Electronegativity increases from I\(^{-}\) to Cl\(^{-}\) (I\(^{-}\) = 2.5, Br\(^{-}\) = 2.8, Cl\(^{-}\) = 3.0) while atomic radius decreases from I\(^{-}\) to Cl\(^{-}\) (I\(^{-}\) = 135 pm, Br\(^{-}\) = 114 pm, Cl\(^{-}\) = 90 pm). Hence, the iodide ion is more predisposed to adsorption than the bromide and chloride ions, and this is a reason behind the difference in their poisoning effect [174]. In addition to these, from the thermodynamic point of view, potentials for the reversible Cl\(_2\)/Cl\(^{-}\), Br\(_2\)/Br\(^{-}\) and I\(_2\)/I\(^{-}\) reactions are, respectively, 1.36, 1.06 and 0.54 V vs. SHE. This also explains why chloride and bromide ions do not affect glucose oxidation reaction even at these high concentrations. While for the iodide ion, the state is very different as the iodide can be oxidized easily to iodine or iodates that are also possible in the present experimental conditions [175, 178, 179].

2.2. Single catalyst at electrochemically activated GC substrate

Many articles have been published in the area of using single catalysts such as NiO\(_x\)-modified GC electrode in the electrocatalytic oxidation of glucose [156, 180-184]. NiO\(_x\) is usually deposited on...
unmodified GC electrodes. In this part, we examine [156], the effect of anodic oxidation of glassy carbon (GC) electrode on the deposition of nickel oxide (NiOx) nanoparticles and the electrocatalytic oxidation of glucose on the thus prepared modified electrode. In our work [156], the GC was pretreated by anodic oxidation in 0.1 M H2SO4 solution at different anodic potentials for different time periods. Different shapes and sizes of NiOx nanoparticles were obtained when NiOx was deposited on anodically-oxidized GC electrode. The purpose of the anodic oxidation was to manipulate the GC surface such that it gave higher surface concentration of C-O functional groups and higher surface area, which leads to an extraordinary increase in the activity of NiOx for glucose electrooxidation [156].

Usually, preparation of NiOx for electrochemical applications using different techniques is performed on ordinary untreated glassy carbon (GC) electrodes. Such techniques include sol-gel preparation of powder NiO, followed by casting [180], electrodeposition [181] and other techniques [96, 182].

Functional groups have been shown to be responsible for the electrochemical activity of carbonaceous surfaces by providing electrochemically-active surface sites on them. For increasing the reactivity of carbon electrodes, “activation” has been used frequently to avoid adsorption of impurities; increase of surface area entails the formation of particular active sites on the carbon surface. Several activation methods have been used for the GC surface. These methods include electrochemical pretreatment (ECP) [183-186], laser irradiation [185-187], vacuum heat treatment (VHT) [188] and ultraclean polishing [189]. The mechanisms of GC activation procedures are related with surface cleaning, oxide film formation, formation of graphite edge planes, and changes in the microscopic surface involved [185, 190, 191]. Oxidation of GC is known to enhance its electrocatalytic properties in many applications such as electrochemical oxidation of many organic molecules [192-195]. For instance, Jovanović et al., [193-195] published a series of articles on the oxidation of small organic molecules on an oxidized GC-modified electrode with Pt nanoparticles. They attributed the enhancement of the electrooxidation of such molecules to the increase in the surface area and creation of C-O functional groups on the GC substrate. While the effects of GC pretreatment by anodic oxidation on the electrooxidation of some of the smaller organic molecules have been studied [193-195], none has studied such effects on the glucose electrocatalytic oxidation albeit of equal importance.

In this part, we discuss the effects of surface modification of glassy carbon substrate via its anodic pretreatment, on the electrodeposition of NiOx nanoparticles and electrocatalytic properties of GCox/NiOx for oxidation of glucose in alkaline solution. In our work [157], GC was oxidized in 0.1 M of H2SO4 at 1.0, 1.5 and 2.0 V for different time periods (60, 120 and 300 s, respectively). The oxidized GC (GCox) was modified with NiOx as discussed above.

2.2.1. Morphological characterizations
GC/NiOx and GCox/NiOx electrodes were characterized [157] by microscopic and electrochemical techniques i.e., by SEM, energy-dispersive X-ray spectroscopy (EDX) and cyclic voltammetry (CV). The SEM images (Fig. 12A, and B) demonstrate the morphology of glassy carbon surface before oxidation, (A) GC, and after oxidation, (B) GCox, of the GC in 0.1 M of H2SO4 at 2 V for 300 s. Image (B) clearly shows rough surface of the GCox compared to image (A) (GC). This is evidence on the increase in the GC surface area due to surface oxidation.

EDX chart for GC before and after anodic oxidation (at 2 V for 300 s) were taken at the same conditions as cited in captions of Fig. 12A, and B. The percent of carbon and oxygen at the surface of glassy carbon electrode before and after activation of the surface is shown in Table 1. Formation and growth of oxide layer at the GCox surface compared with GC surface (without activation) is evident from Fig. 12 and Table 1. The increase in the percentage of oxygen (O%) in the case of GCox with respect to GC is due to the formation of C-O functional groups with the oxidation of the GC. The above increase in the C/O ratio is in accordance with an X-rays photon spectroscopy (XPS) spectrum measured for an anodically-oxidized GC under similar conditions [196].

Fig. 13 presents SEM images of GC/NiOx (A) and GCox/NiOx (B). The images show the morphology and particle size distribution of the NiOx on the surface of GC before activation (A)
Table 1. The percent of oxygen and carbon obtained from EDX charts of GC and GC$_{ox}$. The GC$_{ox}$ was prepared by oxidation of GC at 2 V in 0.1 M H$_2$SO$_4$ for 300 s. The peak of carbon and oxygen appears at the same energy peak for both GC and GC$_{ox}$ but with different percentages.

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>GC</th>
<th>GC$_{ox}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%C</td>
<td>97</td>
<td>90</td>
</tr>
<tr>
<td>%O</td>
<td>3</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 12. FE-SEM images of GC (A) and GC$_{ox}$ (B). The GC$_{ox}$ was prepared by oxidation of GC at 2 V in 0.1 M H$_2$SO$_4$ for 300 s.

Fig. 13. FE-SEM images of GC/NiO$_x$ (A) and GC$_{ox}$/NiO$_x$(B).
and after activation (B) of the surface in 0.1 M of H₂SO₄. An interesting feature that can be seen in Fig. 13B is that the NiOₓ is bearing a bird-like structure with nanoparticles of uniform size, and ordered shape and direction, with much smaller particle size. Analysis of the SEM images in Fig. 13 obtained from different parts of the samples shows that the predominant particle size of NiOₓ is 130 ± 20 nm and that after oxidative treatment of GC is (70 x 650 nm) ± 10 nm.

### 2.2.2. Electrochemical characterizations

Table 2 shows the time required for deposition of a fixed amount of Ni on pretreated GC. The latter was pretreated by anodic oxidation at different anodic potentials \( E_{\text{anodic}} \) for different time periods. The fixed amount of Ni corresponds to a fixed amount of electrodeposition charge \( Q \), equal to 15 mC in the present case. This amount of charge, assuming 100% Columbic efficiency, corresponds to a loading of Ni equal to ~0.065 mg cm⁻². The time required for deposition of the same loading of Ni, i.e., the same amount of \( Q \) decreases with the oxidation potential and time periods used in the GC oxidation. The modification of GC with nanoparticles of NiOₓ was performed as discussed earlier in this review. Two GC electrodes were used; glassy carbon without activation (GC) and GC after anodic oxidation at a specific anodic potential for different time periods (GCox). Since the rate of electrochemical reaction increases with the increase in the electrode surface area, the time for electrodeposition decreases with the increase in the GC surface area (due to anodic oxidation, see Fig. 12B). This is clearly evident from Table 2. For instance, while 240 s is required to pass 15 mC at the untreated GC electrode, it requires only 95 s to pass the same amount of charge (same amount of the deposited Ni) at the oxidized GC. This was attributed to the larger surface area and higher reactivity of the GCox compared to GC. Note that a 15 mC of charge was chosen in this study since it is enough to obtain a high concentration of NiOₓ and it is not too high with respect to the practical limit since it is reported that higher loadings of NiOₓ than the above value do not increase the activity of NiOₓ [197, 198].

### 2.2.3. Glucose oxidation

Fig. 14 shows CV responses for glucose oxidation on GCox/NiOₓ using 20 mM glucose in 0.5 M NaOH. Prior to the electrodeposition of Ni, the GC was oxidized at 1 (D), 1.5 (E) and 2 V (F). The same amount of charge \( Q \) was used to deposit Ni on GC and GCox electrodes. Curves A and B in Fig. 14 show CV responses for glucose oxidation on GC and GCox, respectively. The peak current for glucose oxidation increases dramatically on the GCox/NiOₓ (D-F) compared to GC after activation (B) of the surface in 0.1 M of H₂SO₄. An interesting feature that can be seen in Fig. 13B is that the NiOₓ is bearing a bird-like structure with nanoparticles of uniform size, and ordered shape and direction, with much smaller particle size. Analysis of the SEM images in Fig. 13 obtained from different parts of the samples shows that the predominant particle size of NiOₓ is 130 ± 20 nm and that after oxidative treatment of GC is (70 x 650 nm) ± 10 nm.

<table>
<thead>
<tr>
<th>Time period for anodic oxidation of GC/s</th>
<th>( E_{\text{anodic}}/\text{V} )</th>
<th>( t_{\text{dep}}/\text{s} )</th>
<th>( I_p/\mu\text{A} )</th>
<th>RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 Untreated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>130</td>
<td>411</td>
<td>3.04</td>
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<tr>
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<td>1.5</td>
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<td></td>
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<td>653</td>
<td>3.32</td>
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<tr>
<td></td>
<td>2</td>
<td>45</td>
<td>735</td>
<td>2.86</td>
</tr>
</tbody>
</table>
that on the GC/NiO\textsubscript{x} (C). As the potential used for GC oxidation increases, the peak current for glucose oxidation increases (from curve D to F). The same results were obtained for different time periods of anodic oxidation of GC. As seen from curves A and B in Fig. 14, the GC or GC\textsubscript{ox} do not have any significant electrocatalytic activity for glucose oxidation and hence NiO\textsubscript{x} nanoparticles are essential for higher rates of the glucose oxidation.

Note that 15 mC was passed during Ni electrodeposition on both GC and GC\textsubscript{ox} at all conditions (see Table 2). That is to say, the enhancement in the peak current of glucose oxidation is not attributed to different loadings of NiO\textsubscript{x} but rather to the modification of the GC surface by anodic oxidation. The reproducibility of the peak current of glucose oxidation $I_p$ was evaluated by estimating the relative standard deviation (RSD) with ($n = 3$, i.e., three replicate measurements) and the values of RSD are given in Table 2. The RSD values ranging from 2.5 to 3.5% are obtained which points to good reproducibility.

It can be concluded that the enhancement is attributable to the increase in the substrate (GC) surface area which gives rise to a better exposure of the NiO\textsubscript{x} nanoparticles to glucose oxidation. As evident from the SEM images in Fig. 13, the size of NiO\textsubscript{x} nanoparticles deposited on GC\textsubscript{ox} is much lower than that deposited on the untreated GC. The decrease in the size of NiO\textsubscript{x} nanoparticles is accompanied by an increase in its surface area and hence an increase in the peak current of glucose oxidation. Also, a possible synergism between NiO\textsubscript{x} and the newly generated C-O functional groups exists. Further possibility is that the preferable deposited phase may be the active $\beta$-NiOOH rather than less active $\gamma$-NiOOH.

It is well documented in literature that anodic oxidation of GC in H\textsubscript{2}SO\textsubscript{4} results in an increase of the percentage surface composition of C-O functional groups bearing the OH group. For instance, see XPS work performed in [198], and other important work by Jovanovic \textit{et al.}, [195, 196]. The electrocatalytic oxidation of glucose [197, 198] and other small organic molecules such as methanol [197] is enhanced by the presence of the OH group adsorbed on the GC surface (i.e., OH\textsubscript{ads}).

The authors in Ref. [194] showed that the predominant C-O functional groups on glassy carbon (either polished or treated) are phenolic, carboxyl...
and carboxyl. XPS examinations of GC oxidized in H₂SO₄ showed the enhancement in the fraction of all C-O functional groups; highest increase was in the phenolic and carboxyl groups and lowest increase was in the carboxyl group. Accordingly, the higher percentage of acidic groups on the oxidized GC should promote the higher fraction of oxygen containing species in the GC₉ox/NiO₉ catalyst than in the GC/NiO₉. Consequently, the GC₉ox/NiO₉ is more active in glucose oxidation compared to GC/NiO₉.

Another potential role of GC substrate in the higher activity of GC₉ox/NiO₉ electrodes is that OH-like functional groups on glassy carbon (phenolic, carboxyl) participate in the oxidation of the adsorbed intermediate species formed during glucose dissociation [197, 198]. Increased activity of GC₉ox/NiO₉ electrode can be attributed to the higher percentage of acidic, i.e., OH-containing groups at oxidized GC surface compared to the polished one. Besides, NiO₉ of smaller particle size (see Fig. 13), uniformly distributed at oxidized GC have higher number of active sites closely located to OH-like groups on GC₉ox. Thus, the effect of OH-like groups participating in the oxidation of the adsorbed intermediates must be much higher and therefore the activity of GC₉ox/NiO₉ electrode must be remarkably increased for glucose oxidation in comparison with GC/NiO₉.

Further investigation of the enhancement and increase of the sensitivity of GC₉ox/NiO₉ for glucose oxidation was demonstrated by performing LSV at different glucose concentrations at both GC/NiO₉ and GC₉ox/NiO₉ at the same conditions. These are shown in Fig. 15. Two LSVs corresponding to two concentrations of glucose are only shown for simplicity. The inset shows the relationship between the peak current of glucose oxidation and the glucose concentration at the range of 2-40 mM. The onset potential of glucose oxidation shifts to more negative values at GC₉ox/NiO₉ and also at higher concentrations of glucose. As the concentration increases, the peak current increases linearly up to [glucose] < 20 mM. The fact that the rate of glucose oxidation increases with the [glucose] indicates that glucose oxidation on both electrodes is a

**Fig. 15.** LSV responses for glucose oxidation in 0.5 NaOH containing different glucose concentrations at a scan rate of 100 mV s⁻¹ at GC/NiO₉ (A) and GC₉ox/NiO₉ (B) electrodes where GC was pre-treated by oxidation at 2 V in 0.1 M of H₂SO₄ for 300 s. The digits 1 and 2 refer to [glucose] = 2 and 40 mM, respectively. The inset shows the relationship between the peak current Iₚ and [glucose] at GC/NiO₉ (A) and at GC₉ox/NiO₉ (B) electrodes.
typical electrocatalytic response. It can be suggested that the above relation between \( I_p \) and [glucose] is due to a diffusion-controlled process. Thus, diffusion plays an important role at the concentration range < 20 mM.

### 3. Conclusion

In this article, we reviewed the different aspects of electrocatalytic oxidation of glucose. One main purpose was to focus on the general outline of the electrocatalytic oxidation of glucose and its potential use as a half-reaction in direct glucose fuel cell or biochemical fuel cells. On the other hand, a potential use of such reaction is in biosensor and determination of glucose concentration in blood and in food industry. Our previous work was also reviewed here.

A novel binary catalyst of nickel and manganese oxide, with considerable stability, was electrochemically fabricated on the GCE in a specific order. It was found that electrochemical activity for glucose oxidation depends critically on the loading level and order of electrodeposition of the two catalysts. Under the present conditions, it has been found that the optimum loading level is 60 cycles of MnO\(_y\) followed by 10 min. of nickel deposition. At this loading level, the relationship between the \( I_p/v^{1/2} \) function and scan rate confirm the fact that glucose reaction is a catalytic process. The rate-determining step was found to be the one electron transfer process, which demonstrates the catalytic role of nickel hydroxide.

Halide ions have significant poisoning effect on the electrocatalytic activity of NiO\(_x\)/MnO\(_y\)/GC electrode for glucose oxidation in alkaline medium. The poisoning degree of halide ions depends largely on their chemical structure and concentration in solution. Our fabricated electrode has high tolerance towards chloride and bromide ions even at high concentrations up to 0.3 M. While for iodide ion, it was found that, it has a significant effect on glucose oxidation in our operating conditions at concentrations much lower in comparison with that of the other two halide ions. The NiO\(_x\)/MnO\(_y\)/GC can be considered as a good catalyst for glucose oxidation even in the presence of a large concentration of Cl\(^-\).

The anodic oxidation of GC in 0.1 M H\(_2\)SO\(_4\) has significant effects on the electrodeposition of Ni on GC and subsequently on the catalytic oxidation of glucose from alkaline solutions. The effects of the potential and time period used in the anodic oxidation of GC on the glucose oxidation were studied. The shape and size of NiO\(_x\) nanoparticles electrodeposited on GC\(_{ox}\) is different than those electrodeposited on GC. The pretreatment of GC by anodic oxidation has its impact on the redox couple of NiO\(_x\), i.e., on the Ni(OH)\(_2\) ↔ NiOOH. This was attributed to the increase in the GC surface area and to the concentration of C-O functional groups. The peak current of glucose oxidation is increased at GC\(_{ox}\)/NiO\(_x\) compared to GC/NiO\(_x\) which is an indication of the enhanced glucose oxidation at the former electrode.

### CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interest.

### REFERENCES

Metal oxide nanoparticle-based glucose electro-oxidation