Glucose sensing characterization of non-enzymatic nickel film and nickel foam electrodes in sodium hydroxide solution

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Abstract. Recently, a non-enzymatic glucose sensor has gained a lot attention, because it is reusable, fast and simple, as opposed to traditional enzymatic glucose sensor. In this work, two types of electrodes, including electroplated Ni film and Ni foam, were used as sensing electrodes for a non-enzymatic glucose sensor. The studied sensing properties of the Ni film and Ni foam included glucose-detecting sensitivity, selectivity, and detection limit. For the sensitivity and selectivity analysis, the sensing electrodes, with geometrical working area of 1 and 2 cm² for Ni foam and Ni film respectively, were submerged in a 1M NaOH solution, connected as a working electrode with Ag/AgCl and Pt as a reference and counter electrodes, respectively. Amperometric scanning measurement was used for the sensitivity and selectivity analysis. Sensitivity measurement was tested by dropping glucose solutions into 1M NaOH solution and recording the amperometric response of these sensors under varying sugar contents. The glucose-detection sensitivities are 1.1048 and 6.4228 mA mM⁻¹ cm⁻² for Ni plate and Ni foam, respectively. Limit of detection (LOD) of Ni film and Ni foam are 0.0072 and 0.0144 mM, respectively. The selectivity of electrodes were tested by dropping 3 types of disturbing agents: Quinine, Acetic acid and NaCl. The disturbing agents showed no effect on the current density signal during the amperometric measurement for both of the Ni plate and Ni foam electrodes.

1. Introduction
Electrochemical analysis methods have become one of the industrial standards for glucose sensing due to high sensitivity, low detection limit, simple operation, and low cost [1]. For early generations, the electrochemical glucose sensors are based on enzyme-based electrodes using glucose oxidase (GOx) as a catalyst for the oxidation of glucose to gluconic acid [2, 3]. However, the performance of the enzyme-based sensors is prone to degrade due to narrow ranges of enzyme’s operating conditions, enzyme’s instability over long time. Non-enzymatic electrochemical sensors have been widely developed to overcome the limitations of the enzyme-based ones [1]. The mechanism of the non-enzymatic electrocatalytic activity begins with the adsorption of the glucose molecule and hydroxyl radical (OH⁻) to the electrode surface via d-orbital bonding. The OH_ads or hydroxide compounds then oxidizes the...
glucose molecule [3]. Transition metals, Cu and Ni, have been alternatively developed as non-enzymatic electrodes, exploiting the redox couples, i.e. Cu^{2+}/Cu^{3+} or Ni^{2+}/Ni^{3+}, as intermediate catalytic species. Under an alkaline environment, the metal oxide or hydroxides (e.g. Cu(II)O, Ni(II)O, Ni(II)(OH)₂) from the transitional metal surface, which, under a certain potential, can be oxidized to form oxyhydroxide compounds (Cu(II)OOH, Ni(III)OOH) [4, 5]. Subsequently, the oxyhydroxide compounds oxidize glucose to form gluconolactone [2]. Most of Cu-based and Ni-based non-enzymatic glucose sensors are prepared with nanostructures for high surface area per volume ratio (S/V) to increase the catalytic activity and sensing sensitivity. However, nanostructures are fragile and prone to mechanically breakdown. Metallic foams are good candidates for sensing electrode due to their high specific surface area as well as good mechanical strength and toughness [4 – 6].

In this work, two types of electrodes, including electroplated Ni film and Ni foam, were used as sensing electrodes for a non-enzymatic glucose sensor. The Ni film and Ni foam sensing electrodes were investigated for their quantitative and qualitative sensing properties for glucose. The studied sensing properties of the Ni film and Ni foam included sensing sensitivity, selectivity, and detection limit.

2. Materials and Methods

2.1. Sensing Electrodes: Ni film and Ni foam
A Ni film sensing electrode was prepared by the electrodeposition method using Potentiostatic Galvanostat (Metrohm AutoLab Potentiostatic Machine: PGSTAT302N). The Ni film was deposited on a 2 cm² copper plate from Ni Watt’s bath solution (NiSO₄·H₂O 300 g/L, NiCl₂ 54 g/L, H₃BO₃ 45 g/L), with a platinum mesh as a counter electrode and Ag/AgCl as a reference electrode. The deposition current density and time were 50 mA/cm² and 30 minutes, respectively, at ambient temperature. A Ni foam sensing electrode was a commercial Ni foam (Porosity ≥ 95%, MTI Corporation). The effective geometrical area of the Ni foam was 1 cm² with 1.6 mm thickness.

2.2. Activation of the Sensing Electrodes
Before analysis, the Cyclic Voltammetry (CV) technique was used to activate the surfaces of the sensing electrodes and to determine oxidation peaks and respective potential values where the oxidation peaks were located. The surfaces of both Ni film and Ni foam sensing electrodes were undergone CV scans at a scanning rate of 20 mA/cm², a potential range of 0 – 0.8 V in a 1 M NaOH solution for 50 cycles [5]. The CV curves for both Ni film and Ni foam are shown in figure 1.

The oxidation peaks and their respective potential values were stable after the activation process. The oxidation peaks were founded at 0.45 and 0.5 V for Ni film and Ni foam, respectively, as shown in figure 1. The oxidation potentials are consistent with prior reported values, at which the oxidation of Ni to oxyhydroxide compounds (NiOOH) took place under alkaline environment [5].

2.3. Sensitivity and Limit of Detection Analysis
Electrocatalytic activities of the Ni film and Ni foam electrodes were measured by Amperometric mode in a 1 M NaOH solution by setting a voltage at 0.45 and 0.5 V for Ni film and Ni foam, respectively. The glucose concentration was added in the 1 M NaOH solution incrementally and the resultant increase in the current density response was measured for the sensitivity analysis. Limit of detection (LOD) was calculated by the equation LOD = 3S/a/b, where S is standard deviation of current density when glucose concentration equal to 0; b is sensitivity of electrodes.

2.4. Selectivity Analysis
The selectivity test was done by dropping, into a 1 M NaOH solution, a composition of 100mM per drop glucose, alternating with drops of disturbing agents including Quinine, Acetic acid, NaCl, which are the compound sources for bitter, sour, salty tastes, respectively [6]. The amperometric response was recorded over time during the dropping process.
3. Results and Discussion

3.1. Sensitivity Analysis

The current density response under varying glucose concentration for the Ni film and Ni foam electrodes are shown in figure 2. The sensitivity results were summarized in table 1. The Ni foam electrode exhibited better sensitivity for glucose detection than the Ni film. Higher surface area to volume ratio ($S_a/V$) of the Ni foam than provides higher surface areas for electrocatalytic activity and, hence, better detecting sensitivity. However, the Ni foam electrode showed a higher level of the limit of detection (LOD) than that of Ni film, because the amperometric measurement with the Ni foam electrode showed more background noise ($S_n$) than that of the Ni film electrode. The electrolyte concentration may not be distributed homogeneously throughout the complex porous channels of the Ni foam electrode during the measurement. As a result, local electron transfers due to the redox reactions of Ni$^{2+}$/Ni$^{3+}$ fluctuated along the Ni foam surfaces, resulting high noise feedback and poor LOD.

Over similar range of glucose concentrations (0.1 mM to 5 mM), the average sensitivity of the Ni foam (6.4228 mA mM$^{-1}$ cm$^{-2}$, this work) is higher than that of the Cu foam, 3.39748 mA mM$^{-1}$ cm$^{-2}$, as reported in [6]. The LOD of the Ni foams (0.0144 mM from this work) and the Cu foams (0.013 mM from [6]) are comparable.

3.2. Selectivity Analysis

The selectivity results are shown in figure 3. Both Ni film and Ni foam electrodes exhibit good selectivity characteristics. Both electrodes did not respond to the disturbing agents, while showed high current density response with a drop of glucose solution. It should be noted that high background noise...
could be observed for the Ni foam electrode (figure 3(b)), as opposed to that of the Ni film (figure 3(a)), which is consistent with the LOD results discussed in section 3.1.

Table 1. Glucose detection sensitivity (mA mM⁻¹ cm⁻²) and the limit of detection (LOD, mM).

| Sensing Electrodes | Detection sensitivity (mA mM⁻¹ cm⁻²) over different glucose concentration | Avg. sensitivity (mA mM⁻¹ cm⁻²) | LOD (mM) |
|--------------------|-------------------------------------------------|---------------------------------|---------|
|                    | 0.005 – 0.05 mM | 0.1 – 0.55 mM | 1.05 – 5.05 mM |                      |
| Ni Film            | 1.3366           | 1.4049           | 1.0469           | 1.1048 | 0.0072 |
| Ni Foam            | 7.4697           | 9.0241           | 5.773            | 6.4228 | 0.0144 |

Figure 3. Selectivity analyses of (a) Ni film (b) Ni foam electrodes.

4. Conclusion
The non-enzymatic glucose sensing properties of the Ni film and Ni foam sensing electrodes were studied using the electroplated Ni film and a commercial Ni foam. The glucose detecting sensitivity of the Ni film and foam were measured to be 6.4228 and 1.1048 mA mM⁻¹ cm⁻², respectively. The LOD of the Ni film and Ni foam were 0.0072 and 0.0144 mM, respectively. Compared to the electroplated film, the Ni foam exhibited better sensitivity, but higher LOD level due to high amperometric noise. Both Ni film and Ni foam show good selectivity characteristics by showing no response to disturbing agents including Quinine, Acetic acid, NaCl, which are the compound sources for bitter, sour, salty tastes, respectively.

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