Naural phosphate modified iron electrodes for the anode of the glucose fuel cell

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\textbf{ABSTRACT}

This work aims to investigate the electrolytic oxidation of glucose on Ni-natural phosphate modified electrode investigating the cyclic voltammetry. The electrodes were obtained by depositing the Ni-natural phosphate onto substrates. The Ni-natural phosphate modified iron electrode display high electrolytic activity for the glucose oxidation.

\textbf{KEYWORDS}

Modified electrode; Glucose oxidation; Natural phosphate; Cyclic voltammetry.

\textbf{INTRODUCTION}

The modification of an electrodes by inorganiques films has been broadly studied due to their potentials applications. Various inorganic such as clays\textsuperscript{11}, zeolites\textsuperscript{12}, metal oxides\textsuperscript{13}, metal phthalocyanines\textsuperscript{14}, metal porphyrines\textsuperscript{15}, transition metals\textsuperscript{16}, polyoxometallates\textsuperscript{17}, and polynuclear transition metal cyanides\textsuperscript{18-10}, have been used to prepare inorganic film modified electrodes.

Natural phosphates\textsuperscript{111} are appealing host materials owing to the ability of their open crystallites to selectively exchange and incorporate both charged and neutral species and incorporate within the void spaces and interconnecting channels. Modification of electrodes with phosphate has evoked considerable interest in the past decade\textsuperscript{12}.

Since the pioneering work of Neff and Itaye\textsuperscript{144} on Prussian blue modified electrode, the preparation and electrochemical investigation of various modified electrodes have been reported based on different transition metal hexacyanoferriate such as chrome\textsuperscript{15}, nickel\textsuperscript{16}, cobalt\textsuperscript{18}, copper\textsuperscript{19}, palladium\textsuperscript{20}, molybdenum\textsuperscript{21}, cadmium\textsuperscript{24}, and zinc\textsuperscript{25}.

In order to extend the fuel cells based on the electrocatalytic oxidation in the modified electrode, some research activities have been oriented on the electrochemical synthesis of new materials, such mixed transition metal natural phosphates\textsuperscript{26}.

The electrocatalytic oxidation of glucose has only been the subject of a few investigations. The chemical oxidation of sucrose was firstly mentioned in\textsuperscript{27-29} analysed the oxidation products of fructose, glucose, glucono-\textgreek{deltao}-lactone and sucrose in 0.5 M NaHCO\textsubscript{3}. The author concluded that the main reaction products were
CO₂ and H₂O. Bockris et al. investigated the electrochemical oxidation of different carbohydrates at platinum electrodes for their possible use in fuel cells. They noticed that the electroactivity was better in alkaline medium than in acidic medium, and that the reactivity of the molecule decrease with increasing molecular weights. Court used cyclic voltammetry for comparing the activity of different catalytic metals towards the electrooxidation of sucrose. However, in spite of some attempts, the analytical techniques available at that time did not allow the identification of the reaction products. Other studies, although they were also carried out by cyclic voltammetry on noble metal electrodes (Pt and Au) and on nickel electrodes, aimed to improve the amperometric detection of carbohydrates and were thus not directly related to our purpose.

Shabd and al. compared the hydrodynamic properties and the electroosmotic permeability of D-fructose, sucrose and urea through Pyrex sinters. They found a relation between the phenomenological coefficients and the structure of the molecule.

The carboxylic acids derived from sucrose may find some use in pharmaceutical and agricultural chemistry. The uronic and 2-keto-aldonic acids obtained by hydrolysis of these compounds represent a great industrial interest for the production of detergents, foods, emulsifiers and pharmaceuticals. Edye and al. stated that with a catalyst consisting of platinum deposited on carbon, the chemical oxidation by oxygen, at 100°C and at a constant neutral pH, was highly specific for the production of carboxylic acids at the 6-and 6'-positions of sucrose.

The reaction kinetics of the glucose oxidation in known to be sensitive to electrode materials and crystalline orientations of electrode surface. Gold displays interesting reactivity towards electrocatalytic oxidation of glucose in alkaline solution. Gold electrodes modified by submonolayer silver underpotential deposition display higher electrocatalytic activity than bare gold electrodes for the glucose oxidation, resulting in about 0.1 V negative shift in oxidation potential. On the other hand, platinum electrodes show serious self-poisoning in the glucose oxidation. Surface modification was carried out by depositing a second metal on the platinum electrodes to decease sensitivity of the electrodes towards the poisoning, and bismuth modification was reported effective, but the glucose oxidation on the electrodes showed peaks at much higher potentials.

In this regard we reported the preparation of nickel natural phosphate film modified electrode prepared by electrodeposition of modifier (nickel, natural phosphate) in iron substrate. The stability of this modified electrode in also increased.

The electrocatalytic oxidation of glucose was studied by voltammetric measurements. The advantage of voltammetric measurements about the redox transformation of an analyte including thermodynamic, kinetic, and mechanistic information. An additional advantage of voltammetric measurements is that many analytes are extremely sensitive to the chemical environment at the electrode surface. For example, analyte/surface interaction (adsorption and electrostatic interactions) can result in changes in the thermodynamic and kinetic behavior.

**EXPERIMENTAL PART**

**Reagents**

A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco). Prior to use this material was treated by techniques involving attrition, sifting, calcination (900°C), washing, and recalcination.

**Preparation of the natural phosphate modified iron electrode (NPI-electrode) and Ni-Natural phosphate modified iron electrode (Ni-NPI-electrode)**

The modified electrodes were obtained by electrodepositing of NP and Ni-NP into iron plate (1 cm²). Prior to use, the iron plate was polished by smooth paper. Electrical contact was established by a wire of cooper. The resulting electrode is hereby denoted as Ni-NPI-electrode.

**Instrument**

Cyclic voltammetry, Square wave voltammetry, chronoamperometry and colometry were carried out with a volalab potentiostat (model PGSTAT 100, Eco Chemie B. V., Utrecht, the Netherlands) driven by the general purpose electrochemical systems data process-
ing software (Voltalab master 4). The electrochemical cell was configured to work with three electrodes; using NPI-electrode or Ni-NPI-electrode as the working, platinum plate (1 cm²) for counter and saturated calomel (SCE) as reference electrodes. The pH-meter (Radiometer Copenhagen, pH-M210, Tacussel, French) was used for adjusting pH values.

**Procedure**

The glucose oxidation on the prepared electrode was performed in sodium chloride containing glucose by using platinum counter electrode and calomel reference electrode at a scan rate of 10 mV/s. The scan was started at -1.5V in the positive direction and retraced at 1.2V. All potentials were referred to calomel electrode.

**RESULTS**

**Natural phosphate characteristics**

The surface structure of natural phosphate was observed using scanning electron microscopy (Figure 1). The treatment of NP describes above lead to a fraction between 100 μm and 400 μm that is rich in phosphate and as can be seen that compact natural phosphate appearance was evident. The treated NP has following chemical composition: CaO (54.12%), P₂O₅ (34.24%), F (3.37%), SiO₂ (2.42%), SO₃ (2.21%), CO₂ (1.13%), Na₂O (0.92%), MgO (0.68%), Fe₂O₃ (0.36%), K₂O (0.04%) and several metals in the range of ppm.

Figure 2 shows IR spectra of NP and Ni-NP. We observe the presence of the very broad bands. These bands phosphates are characteristic of amorphous calcium phosphates. According to X-rays diffraction and the IR spectra we note that the network of phosphate is very tolerate to various substitutions.

In the spectrum IR corresponding to the Ni-NP composite, we note a light displacement of the bands 963, 1029 and 1092 cm⁻¹. This phenomenon can be allot to substitution of Ca²⁺ by Ni²⁺.

![Figure 1: Scanning electron micrograph of natural phosphate modified iron electrode](image1)

![Figure 2: Infrared reflection absorbance for NP and Ni-NP composites](image2)

**Behavior of Ni-NPI electrode in HClO₄ media**

Figure 3 shows a cyclic voltammogram in the potential range -1V to 1.5V recorded, respectively, for iron (IE), Natural Phosphate modified iron electrode (NPIE) and Nickel-Natural phosphate modified electrode (Ni-NPIE) in 0.1 M HClO₄ at 50 mV/s.

The voltammograms take different forms. no peak
Full Paper

Figure 3: Cyclic voltammograms recorded for IE, NPIE and Ni-NPIE, in 0.1M HClO₄ at 50 mV/s.

Cyclic voltammogram of a Ni-NPIE electrode in 0.1M HClO₄, during repetitive scans at 50 mV/s.

is observed in the case of Ni-NPIE electrode, however, a light resemblance is observed in the case of IE and NPIE electrodes. The voltammograms recorded for Ni-NPIE electrode remains stable after several cycles, the current densities decrease, probably, because of the reduction of various ions present in the matrix (Figure 4).

Cathodic and anodic polarization curves for the three composites (IE, NPIE and Ni-NPIE), recorded in 0.1M HClO₄, are shown in Figure 5. We note that the three curves are almost confused, which lets suggest that the studied composites present the same electrochemical behavior in medium HClO₄. The corrosion kinetic parameters derived from these curves are shown in TABLE 1. The corrosion current densities have comparable values for the three composites.

Figure 4: Cyclic voltammogram of a Ni-NPIE electrode in 0.1M HClO₄, during repetitive scans at 50 mV/s.

Figure 5: Curves of global polarization of IE, NPIE and Ni-NPIE electrodes, enregisrted in 0.1M HclO₄.

| Electrochemical parameters obtained from Tafel curves of three composites. |
|-----------------------------|----------------|-----------------|------------------|----------------|
| Ecorr/mV                    | Rp:Ω·cm²       | Icorr/mA·cm²    | ba/mV            | bc/mV          |
| IE                          | -529           | 3.78            | 11.9713          | 326.9          | -260.5         |
| NPIE                        | -137.3         | 2.70            | 14.2918          | 409.1          | -195.1         |
| Ni-NPIE                     | -510           | 2.31            | 18.7602          | 268.3          | -271.9         |

Impedance measurements were made under open circuit conditions for various electrodes considered. The Nyquist plots obtained showed a widely open arc at high frequencies for IE, but in the other electrodes (NPIE and Ni-NPIE) the Nyquist plots changed from capacitive semi circle to a inductive semi circle allots to a diffusion phenomenon.

Electrocatalytic oxidation of glucose

Glucose oxidation on the iron electrode

The glucose oxidation on iron electrode is shown in Figure 7. The voltammograms recorded for the iron electrode, in HClO₄ medium containing or not glucose, are almost confused what lets suggest that the iron does not have any activity towards the oxidation of glucose.

Glucose oxidation on the NPIE electrode

On the contrary the NPIE electrode present a considerable activity for glucose oxidation. The voltammogramme recorded in the presence of glucose in electrolytic medium keeps the same pace as that recorded in absence of glucose but the current densities
are more important. (Figure 8).

The square wave voltammograms obtained for various concentrations of glucose present only one redox peak. From Figure 9 and TABLE 2, it was obsereved that peak current versus glucose added into electrolytic solution increased linearly. are given by Figure 9 and TABLE 2.

The glucose oxidation on the NPIE electrode
TABLE 2: Evolution of the oxidation peak with glucose concentration.

<table>
<thead>
<tr>
<th>NPIE elect</th>
<th>E (V)</th>
<th>di (°A.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0M glucose</td>
<td>-0.637</td>
<td>5.809</td>
</tr>
<tr>
<td>2. 10⁻²M</td>
<td>-0.4235</td>
<td>15.2</td>
</tr>
<tr>
<td>3. 10⁻²M</td>
<td>-0.3985</td>
<td>19.34</td>
</tr>
<tr>
<td>3.8. 10⁻²M</td>
<td>-0.3609</td>
<td>20</td>
</tr>
<tr>
<td>4.4. 10⁻²M</td>
<td>-0.5062</td>
<td>15.38</td>
</tr>
<tr>
<td>5. 10⁻²M</td>
<td>-0.4135</td>
<td>12.26</td>
</tr>
<tr>
<td>5.5. 10⁻²M</td>
<td>-0.3859</td>
<td>12.74</td>
</tr>
</tbody>
</table>

showed a rapid current increase for the weak concentration. At high glucose concentrations we note a decrease of current, which is attributed to the further oxidation of gluconolactone that was produced in the first oxidation[46] and remained being adsorbed on the electrode surface.

**Glucose oxidation on the Ni-NPIE electrode**

Surface modification of an electrode by another composite is an effective method to improve electrocatalytic activity of an electrode. For the application to the glucose oxidation, the amount of nickel introduced into phosphate matrix should be controlled to get higher catalytic activity. Figure 10 shown cyclic voltammograms recorder for Ni-NPIE electrode in 0.1M HClO₄ solution in presence of the glucose. The modified electrode exhibited a high reactivity towards the glucose oxidation.

![Figure 10](image)

**Figure 10 :** Cyclic voltammograms of the Ni-NPIE electrode in 0.1M HClO₄ (a) without glucose, (b) in presence of glucose.

**Figure 11 :** Square wave voltamograms at Ni-NPIE electrode, recorded in 0.1M HClO₄ in the presence of various concentrations of glucose (from 2.10⁻²M to 9.10⁻²M).

**CONCLUSIONS**

The Ni-NPIE electrode display high electrocatalytic activity for the glucose oxidation. This electrode can electrocatalyse the oxidation of glucose. The proposed modified electrode was very attractive for the electrocatalytic oxidation of glucose. Compared with the other studied electrodes (IE and NPIE), the Ni-NPIE electrode do not show any effect of surface surface. These results revealed that Ni-NPIE modified elecrode is quite promising for the anode of the glucose fuel cell.

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