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N I N P N I A N D E S W I T H V A R Y I N G N I N P R A T I O P R E P A R E D B Y E L E C T R O D E P O S I T I O N F O R T H E D I R E C T M E T H A N O L F U E L C E L L

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# Ni-NP/Ni Anodes with Varying Ni: NP Ratio Prepared by Electrodeposition for the Direct Methanol Fuel Cell

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## I. INTRODUCTION

Direct methanol fuel cell (DMFC) is a new generation alternative energy harnessing device [1-3]. The electrochemical processes that yield energy are essentially pollution free. Water formed during the operation of the device is beneficial in space travel and submarines. Applications of fuel cells are diverse ranging from stationary (individual homes or district schemes) or mobile (transformation as cars, buses, etc.), mobile phones and lap top computers [4, 5].

The liquid feed direct methanol fuel cell (DMFC) is considered as a potential power source for stationary and transportation application because of characteristics such as simple construction, easy operation, liquid fuel and high efficiency [5, 6]. However, obstacles still prevent their widespread commercial applications [7, 8], e.g. low activity of methanol electrooxidation catalysis, methanol crossover from the anode to the cathode, carbon dioxide gas management and water management [9].

Hydrogen is currently the only practical fuel for use in the present generation of fuel cells. The main reason for this is its high electrochemical reactivity compared with that of the more common fuels from which it is derived, such as hydrocarbons, alcohols, or coal.

Also, its reaction mechanisms are now rather well understood [10, 11] and are characterized by the relative simplicity of its reaction steps, which lead to no side products.

Pure hydrogen is attractive as a fuel, because of its high theoretical energy density, its innocuous combustion product (water), and its unlimited availability so long as a suitable source of energy is available to decompose water. One of the disadvantages of pure hydrogen is that it is a low density gas under normal conditions, so that storage is difficult and requires considerable excess weight compared with liquid fuels.

Methanol has been considered for fuel cell power generation for a number of years because it can be processed into a hydrogen-rich fuel gas fairly, easily and efficiently, by steam or auto thermal reforming. Methanol, as a liquid fuel is easily transported and stored in comparison to hydrogen gas. The methanol fuel has a superior specific energy density (6000 Wh/kg) in comparison with the best rechargeable battery, lithium polymer and lithium ion polymer (600 Wh/kg) systems. This means longer conservation times using mobile phones, longer times for use of laptop computers and more power available on these devices to support consumer demand. Another significant advantage of the direct methanol fuel cells over the rechargeable battery is their potential for instantaneous refueling [12-13]. The methanol fuel cells in alkaline solutions have many advantages such as increasing their efficiency, a wider selection of possible electrode materials, a better efficiency of oxygen cathode, and the oxidation reactions of organic fuels exhibit almost no sensitivity to the surface structure [14, 15].

Moreover, the use of the methanol fuel cells is limited by the poor anode performance and counteract the poisoning effects at the cathode due to the methanol cross-over [16, 17]. In the electro oxidation of methanol, the electrode material is clearly an important parameter where a high efficient electro catalyst is needed.

The use of Pt alone is limited by the adsorption of several incompletely oxidized intermediates [18, 19] which provoke deactivation of platinum surface. For this reason, there are several studies investigating modified Pt, for methanol electro oxidation, such, Pt-Ru [20], Pt-Pb [21], Pt-Ni and Pt-Ru-Ni [22].

Several studies of the alcohols electro oxidation on Ni have been investigated [23-26] due to its surface oxidation properties.

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In this work, Ni-NP/Ni anodes with varying Ni: NP ratio are prepared by electrodeposition NiNP catalyst layer onto Ni plate and tested for methanol oxidation.

## II. EXPERIMENTAL DETAILS

### a) Electrode Preparation

Electrochemical measurements were performed on nickel plate electrode of apparent surface area of 1 cm x cm. Catalyst coating on the nickel plate was prepared using electrodeposition. The nickel electrode was mechanically polished using smooth paper, and then it was subsequently degreased with acetone and rinsed with distilled water. Before each experiment, the electrode surface was activated via the cyclic voltammetry at scan rate of 500 mV/s for 20 cycles. The working electrode (Ni and NP-Ni) were sealed in Teflon jacket. The apparent surface area was calculated from geometrical area and the current density was referred to it.

### b) Reagents

A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco) [27]. Prior to use, this material was treated by techniques involving attrition, sifting, calcinations (900 °C), washing, and recalcination [28]. Measurements were carried out in aerated 1M KOH at room temperature ( $20 \pm 0.2$  °C).

### c) Instrument

Cyclic voltammetry, chronoamperometry, chronopotentiometry, impedance spectroscopy (EIS), polarization curves and square wave voltammetry were carried out with a Voltalab potentiostat (Model PGSTAT 100, Echochemie B.V., Utrecht, the Netherlands) driven by the general purpose electrochemical systems data processing software (Voltalab Master 4 software). The electrochemical cell was configured to work with three electrodes using prepared electrode as the working electrode, platinum plate (1cm x cm) for counter electrode and Ag-AgCl as reference electrode.

## III. RESULTS AND DISCUSSION

### a) Natural Phosphate Characteristics

The surface structure of natural phosphate (NP) was observed using scanning electron microscopy (Fig. 1). The treatment of NP describes above lead to a fraction between 100  $\mu\text{m}$  and 400  $\mu\text{m}$  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%),  $\text{P}_2\text{O}_5$  (34.24%), F<sup>-</sup> (3.37%),  $\text{SiO}_2$  (2.42%),  $\text{SO}_3$  (2.21%),  $\text{CO}_2$  (1.13%),  $\text{Na}_2\text{O}$  (0.92%),  $\text{MgO}$  (0.68%),  $\text{Fe}_2\text{O}_3$  (0.36%),  $\text{K}_2\text{O}$  (0.04%) and several metals in the range of ppm.

It is seen that the morphology of NP catalyst surface is porous.

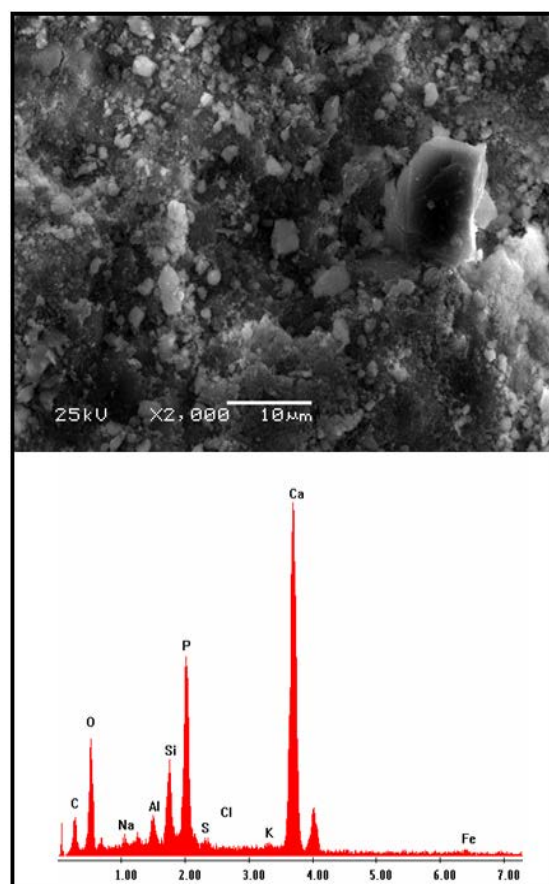


Figure 1 : Scanning Electron Micrograph of Natural Phosphate

The crystal-structure of matter is similar to that of fluorapatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ), as shown by X-ray diffraction (Fig. 2) and infrared emission spectroscopy (Fig. 3). The network of fluorapatite is very tolerant of substitutions in vacant sites, such as Ca can be replaced by Sr, Pb, Co and Na,  $\text{PO}_4$  by  $\text{AsO}_4$ ,  $\text{VO}_4$  and  $\text{SO}_4$  and F<sup>-</sup> can be replaced by OH<sup>-</sup> and Cl<sup>-</sup>. The phosphate has a low specific surface area of about 1m<sup>2</sup> g<sup>-1</sup>.

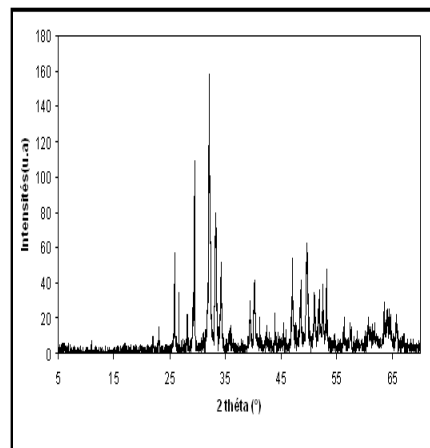


Figure 2 : XRD Pattern of the Natural Phosphate

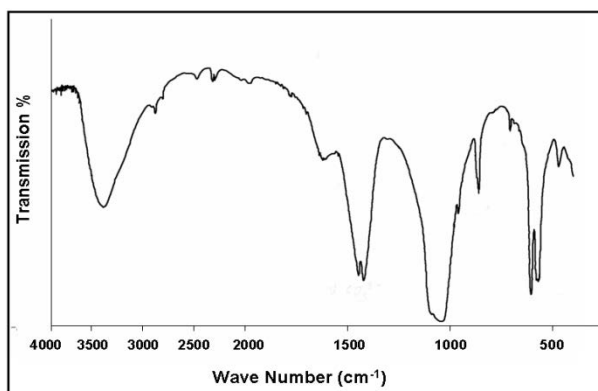


Figure 3 : IR Spectra of the Natural Phosphate

b) Electrochemical Characterization of Prepared Electrode

The cyclic voltammograms (CVs) of the Ni plate, NP/Ni plate and NP-Ni/Ni electrodes were recorded in the supporting electrolyte (1M KOH solution). The change of the CVs shapes (Figs. 4, 5 and 6), before and after modification, is a major sign that Ni electrode was, effectively, modified with NP and NP-Ni layers.

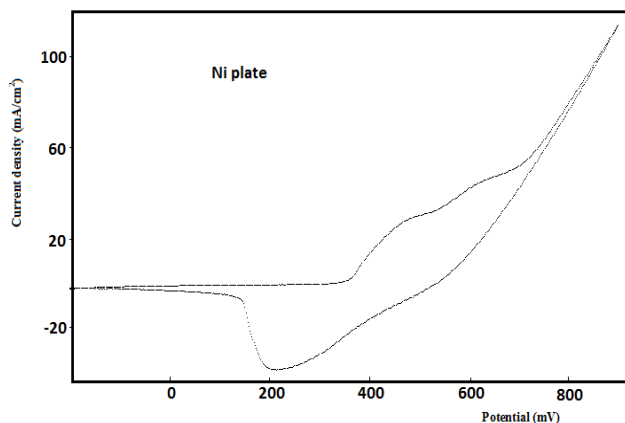


Figure 4 : Cyclic Voltammogram Obtained by Ni Electrode, at 100 Mv/S, In 1M KOH Solution

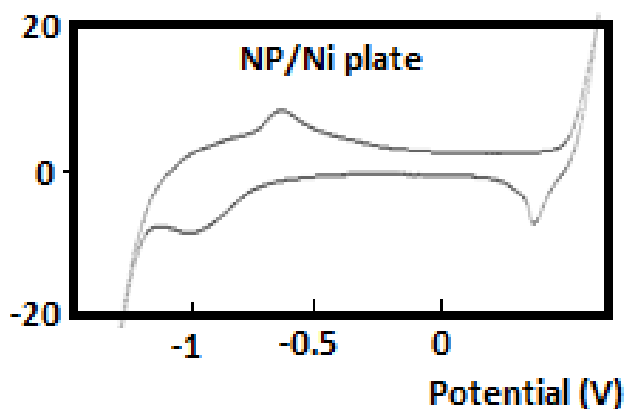


Figure 5 : Cyclic Voltammogram Obtained by NP/Ni Electrode, at 100 Mv/S, In 1M KOH Solution

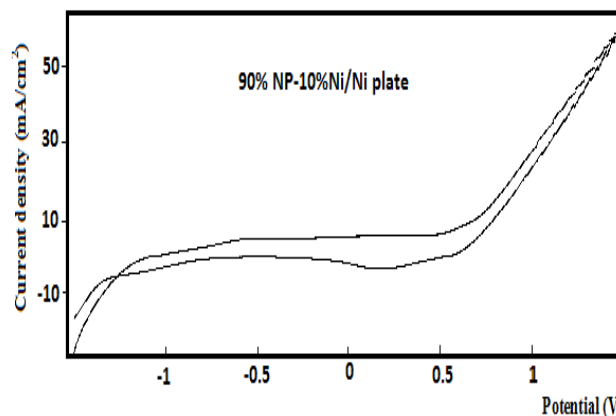


Figure 6 : Cyclic Voltammogram Obtained by NP-Ni/Ni Electrode, at 100 Mv/S, In 1M KOH Solution

The collected parameters deduced from the polarization curves, recorded respectively, for the prepared electrodes, such as the corrosion potential ( $E_{corr}$ ), corrosion current density ( $J_{corr}$ ), cathodic and anodic Tafel slopes ( $\beta_c$  and  $\beta_a$ ), are shown in Table 1.

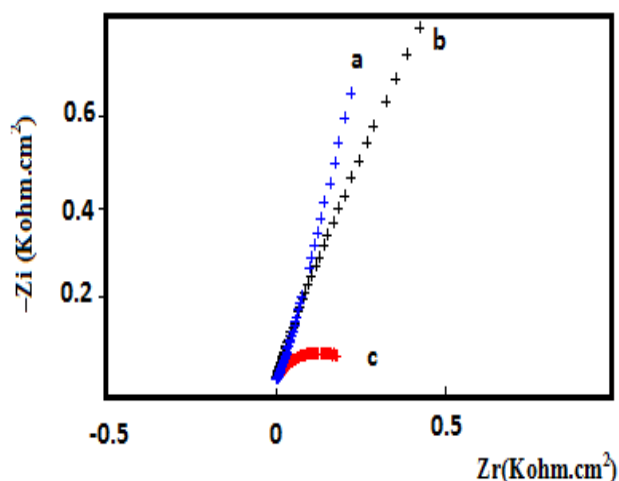
We find that the Ni electrode is more resistant to corrosion than Np/Ni electrode modified. However the addition of a small amount of Ni to NP matrix results in improved surface.

Table 1 : Electrochemical Parameters

| Electrodes        | $E(i=0)$<br>(mV) | $R_p$<br>(ohm/cm²) | $I_{corr}$<br>(mA/cm²) | $B_a$<br>(mV) | $B_c$<br>(mV) |
|-------------------|------------------|--------------------|------------------------|---------------|---------------|
| Ni                | 232.6            | 279.01             | 0.0669                 | 88.4          | -250.7        |
| NP/Ni             | -1098.7          | 58.21              | 1.026                  | 560.1         | -216.8        |
| NP90%-Ni 10% / Ni | -970.6           | 124.66             | 0.4852                 | 440.1         | -247.7        |

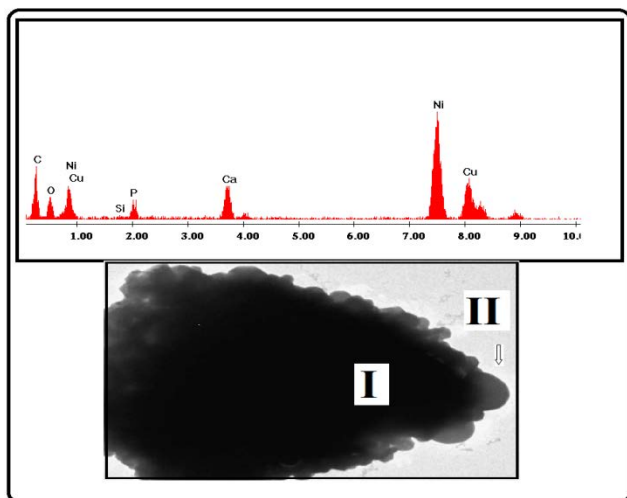
The results of the potentiodynamic polarization experiments were confirmed by impedance spectroscopy measurements. The Nyquist plots for the tested electrodes (Ni, NP/Ni and Ni-NP/Ni) in alkaline solution are presented in Fig. 7.

The locus of Nyquist plots is regarded as one part semi circle in NP/Ni electrode (curve c), but in Ni and Ni-NP/Ni electrodes (curves a and b), the plot was not perfect semi circle. This feature had been attributed to frequency dispersion of interfacial impedance.



**Figure 7 :** Electrochemical Impedance Spectroscopy Recorded for Ni, NP/Ni and NP-Ni/Ni Electrodes, in 1M KOH Solution

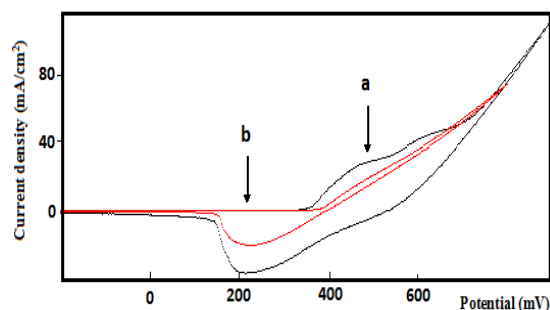
A typical EDX spectrum is shown in Fig. 8 the atomic ratio of Ni (electrodeposited onto NP/Ni) in Ni NP/Ni electrode is about (40%). The characteristic peak of Ni can not be found in Fig. 8. It indicates that Ni plate is almost fully covered by the Ni-NP catalyst layer.



**Figure 8 :** EDX Spectra Analysis of the Ni-NP/Ni (40 At % Ni) Scanning Electron Micrographs of the Cross-Section of Ni-NP/Ni Anode: I: Ni And II: Ni-NP Catalyst

#### c) Methanol Oxidation

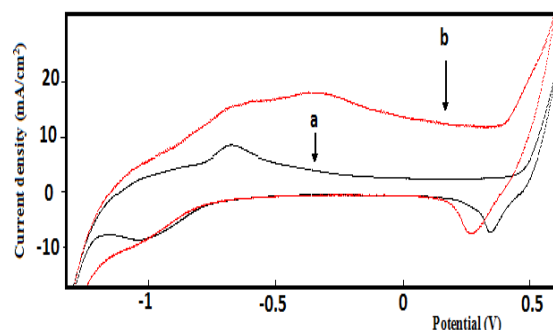
Fig.9 compares the CVs of the Ni plate electrode recorded in alkaline solution containing methanol (curve b) and without methanol (curve a). It is clearly seen that nickel has little activity of methanol oxidation.



**Figure 9 :** Cvs Recorder for Ni Plate Electrode, in N<sub>2</sub>-Saturated 1M KOH A- in Absence of Methanol, B- in Presence of 0.1M Methanol

The cyclic voltammetry (Cv) for the NP/Ni electrode in KOH is shown in fig. 10. The CV was carried out to analyze the activity of the synthesized catalyst towards methanol electro-oxidation in alkaline media. It should be recorded here that the using of natural phosphate (NP), electrodeposited onto Ni plate, to catalyze the methanol oxidation has proved better performance than using pure nickel.

It could be noticed from fig. 10 that the onset potential for methanol electro-oxidation of in alkaline medium using the catalyst NP/Ni was about -1000 mV. But the current densities are very low.



**Figure 10 :** Cvs Recorder for NP/Ni Plate Electrode, in N<sub>2</sub>-Saturated 1M KOH A- in Absence of Methanol, B- in Presence of 0.1M Methanol

Using Ni-NP/Ni (atomic ratio Ni: NP=1:9) catalyst the onset potential for electro-oxidation of methanol in alkaline medium was 400 mV, with higher current densities (fig. 11). The change of onset potentials could be associated to the structure change after Ni was alloyed with NP. The current density values have been increased in case of Ni-NP/Ni, more than NP/Ni and Ni plate, due to the increase in active electrochemical surface area.



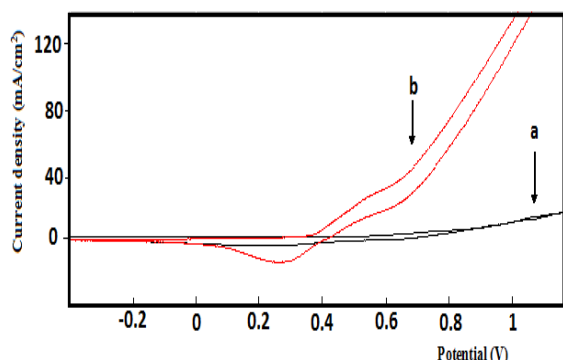


Figure 11 : Cvs Recorder for Ni-NP/Ni Plate Electrode, in  $N_2$ -Saturated 1M KOH A- In Absence of Methanol, B- In Presence of 0.1M Methanol

It is found from figs. 12 and 13 that the current density and the power density increase with increasing methanol concentration. However, both the power density and the current density become stable at about 0.5 mol/L of methanol, probably due to saturation of the catalyst surface Ni-NP/Ni.

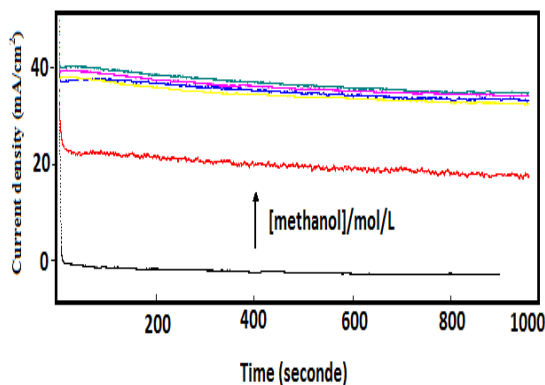


Figure 12 : Transient Current Density of Methanol Electro-Oxidation, at Ni-NP/Ni Electrode, at Room Temperature, in Alkaline Solution Containing Different Concentrations of Methanol

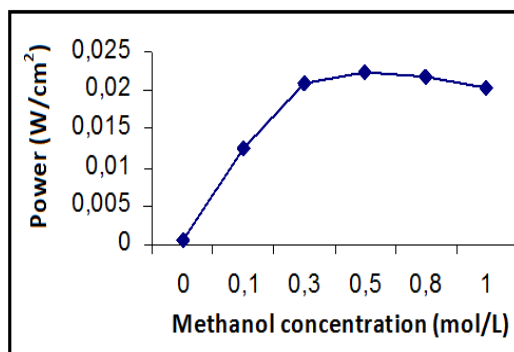


Figure 13 : Influence of Methanol Concentration on Power Density

## IV. CONCLUSION

A novel electrode was fabricated and tested for methanol electro-oxidation. The experimental results indicate that the Ni-NP/Ni catalyst has proved better activity, and the power density of the cell increases with methanol concentrations, and the maximum power density of 25 mW/cm<sup>2</sup> was achieved with 0.3 M methanol concentration.

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