Natural phosphate modified nickel anodes for the direct methanol fuel cell

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ABSTRACT

This article describes the fabrication and characterization of an anode based direct methanol fuel cell using natural phosphate (NP) electrodeposited into a perforated nickel plate. Ac impedance spectroscopy, cyclic voltammetry and square wave voltammetry were utilized alongside characterization to determine the influence of the presence of NP on the cell performance. It was found that NP shows a catalytic activity towards methanol oxidation better than massive Ni. The presented fuel cells also show a high peak power density.   © 2014 Trade Science Inc. - INDIA

KEYWORDS

Methanol fuel cell;
Electro-catalysis;
Modified electrodes;
Natural phosphate;
Square wave voltammetry.

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 pro-

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cessed 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[23,24] due to its surface oxidation properties.

In this work, NP modified Nickel (NP-Ni) anode was prepared by electrodeposition NP catalyst layer onto Ni plate. The morphology and structure of the catalyst layer were analyzed by SEM and XRD. The relative activities of the NP-Ni electrode was assessed in half-cell and single direct methanol fuel cell (DMFC) experiments and compared with a conventional Ni anode in a DMFC.

EXPERIMENTAL DETAILS

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.

Reagents

A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco)[25]. Prior to use, this material was treated by techniques involving attrition, sifting, calcinations (900 °C), washing, and recalcination[26]. Measurements were carried out in aerated 1M KOH at room temperature (20 ± 0.2 °C).

Instrument

Cyclic voltammetry, chronoamperommetry, chronopotentiommetry, 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) fot counter electrode and Ag-AgCl as reference electrode.

RESULTS AND DISCUSSION

Natural phosphate characteristics

The surface structure of natural phosphate (NP) 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%), P_2O_5 (34.24%), F⁻ (3.37%), SiO_2 (2.42%), SO_3 (2.21%), CO_2 (1.13%), Na_2O (0.92%), MgO (0.68%), Fe_2O_3 (0.36%), K_2O (0.04%) and
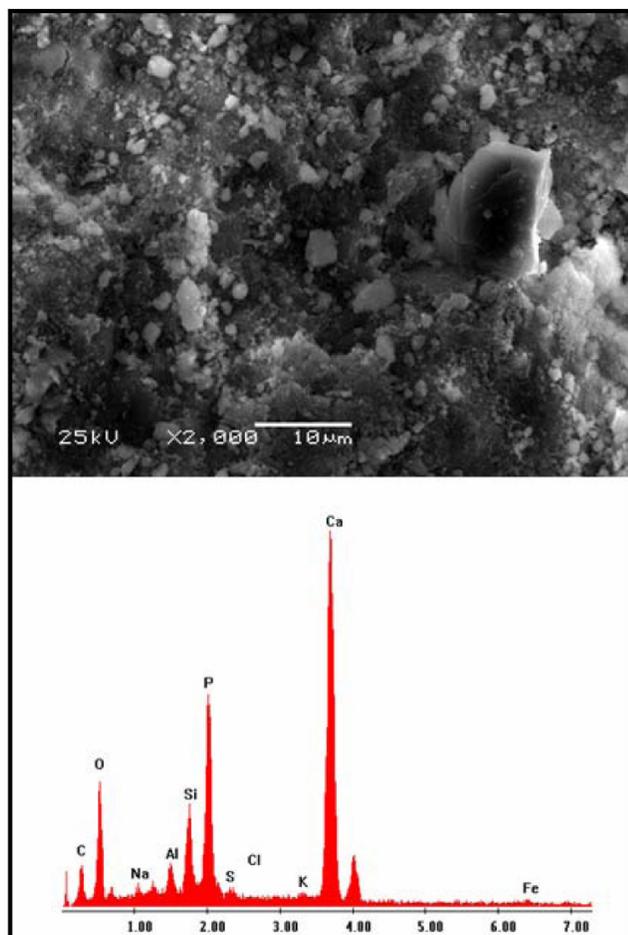
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Figure 1 : Scanning electron micrograph of natural phosphate

several metals in the range of ppm.

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

The crystal-structure of matter is similar to that of fluorapatite (Ca_{10} (PO_4) $6F_2$), as shown by X-ray diffraction (Figure 2) and infrared emission spectroscopy (Figure 3). The network of fluorapatite is very tolerant of substitutions is vacant sites, such as Ca can be replaced by Sr, Pb, Co and Na, PO_4 by AsO_4, VO_4 and SO_4 and F-can be replaced by OH^- and Cl^-. The phosphate has a low specific surface area of about $1 m^2 g^{-1}$.

Electrochemical characterization of prepared electrode

Figure 4 shows the polarization curves recorded for nickel and NP-Ni electrodes, respectively, in 1M KOH solution.

The cathodic current potential curves give rise to parallel Tafel lines, indicating that the hydrogen evolution reaction is activation controlled and the presence of the electrodeposition NP does not modify the mechanism of this reaction. In the anodic domain, the addition of NP catalyst increases the current densities in large domain of potential. The collected parameters deduced from the polarization curves, such as the corrosion potential ($E_{corr.}$), corrosion current density ($J_{corr.}$), cathodic and anodic Tafel
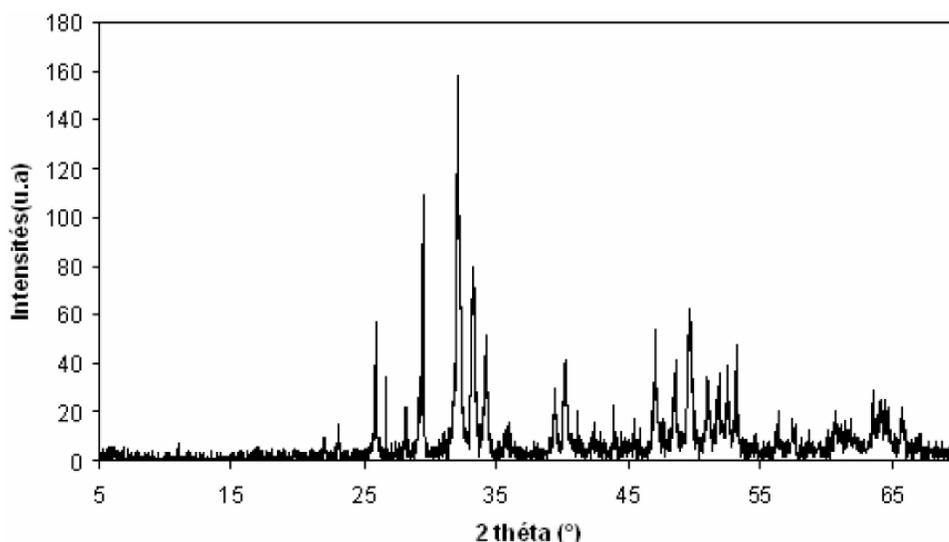

Figure 2 : XRD pattern of the natural phosphate

slopes (βc and β_a), are shown in TABLE 1.

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

Figure 5.

The locus of Nyquist plots is regarded as one part semi circle in NP-Ni electrode, but in Ni electrode the plot was not perfect semi circle. This feature had been attributed to frequency dispersion of interfacial imped-
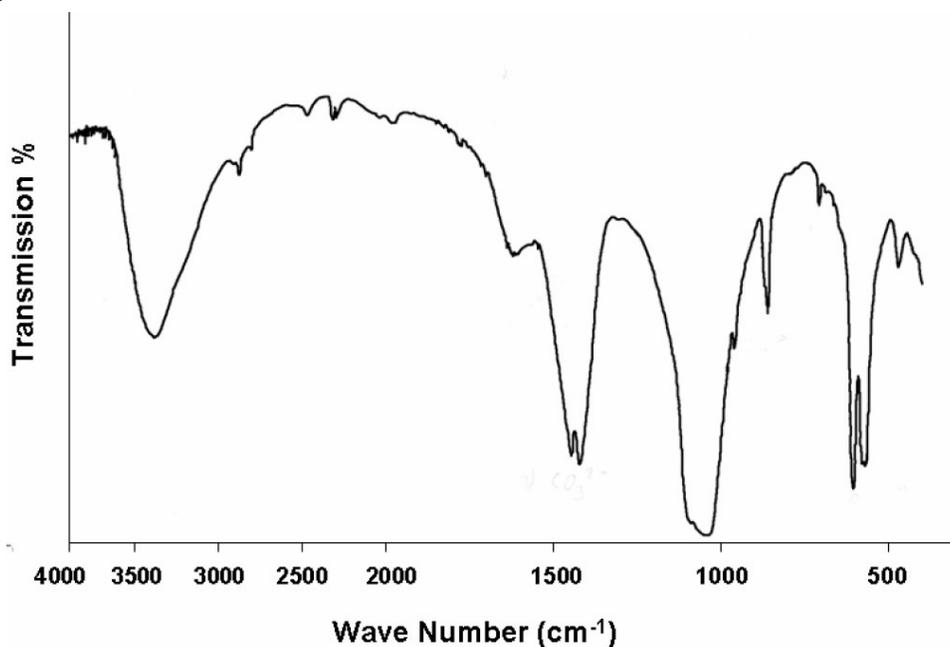
Figure 3 : IR spectra of the natural phosphate

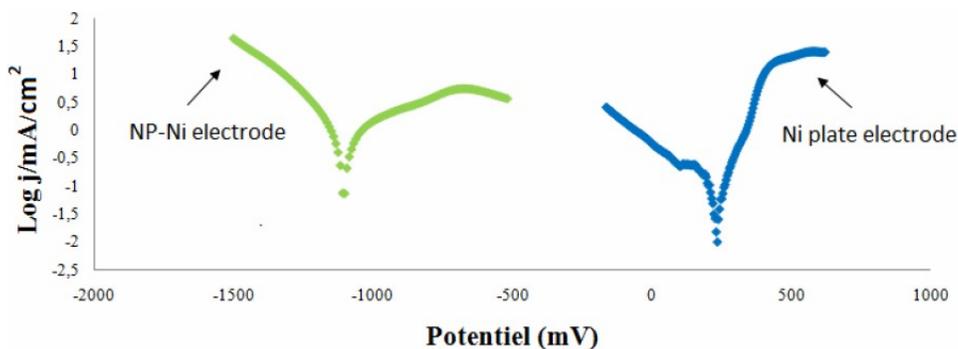**Figure 4 : Polarization curves for Nickel and NP-Ni electrodes in 1M KOH solution**

TABLE 1 : Electrochemical parameters

Samples	E(i=0) mV	Rp ohm/cm^2	J$_{corr.}$ (mA/cm^2)	βa (mV)	βc(mV)	corrosion
Ni	232.6 mv	279.01	0.0669	88.4	-250.7	782.4 μm/year
NP-Ni	-1098.7mv	58.21	1.026	560.1	-216.8	12.00 mm/year

ance.

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

Methanol oxidation

The cyclic voltammetry for the Ni and NP-Ni elec-

trodes, are shown in Figure 7. The CV was carried out to analyze the activity of the synthesized catalyst towards methanol electrooxidation in alkaline media and to analyze the effect of NP addition to Ni catalyst. The anodic oxidation behaviors on Ni and NP-Ni indicate that the Ni surface has changed after alloying with NP.

Considering that the cyclic voltammetry of 1 mol/L of NaOH + 0.3 mol/L of methanol, it could be noticed
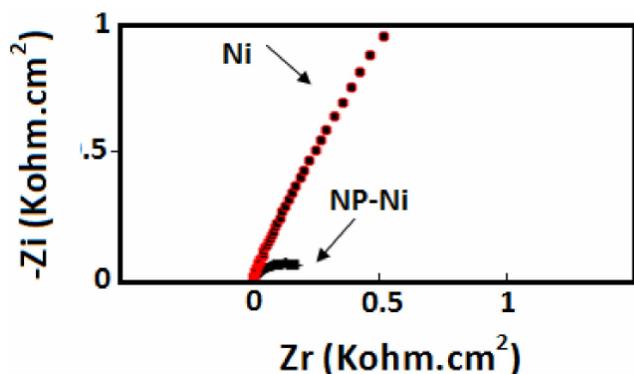
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Figure 5 : Electrochemical impedance spectroscopy recorded for Ni and NP-Ni electrodes, in 1M KOH solution

from Figure 7 that the onset potential for methanol electro-oxidation of in alkaline medium using the catalyst Ni was about 500 mV. On the other hand, using NP-Ni catalyst the onset potential for electro-oxidation of methanol in alkaline medium was 480 mV. Therefore the onset potential has decreased 20 mV after NP addition. The current density values have been increased in case of NP-Ni more Ni.

Addition of methanol to 1M KOH solution provokes change on the NP-Ni electrode voltammogram (Figure 8). This figure shows that the electro-oxidation of methanol causes a significant decrease of the onset
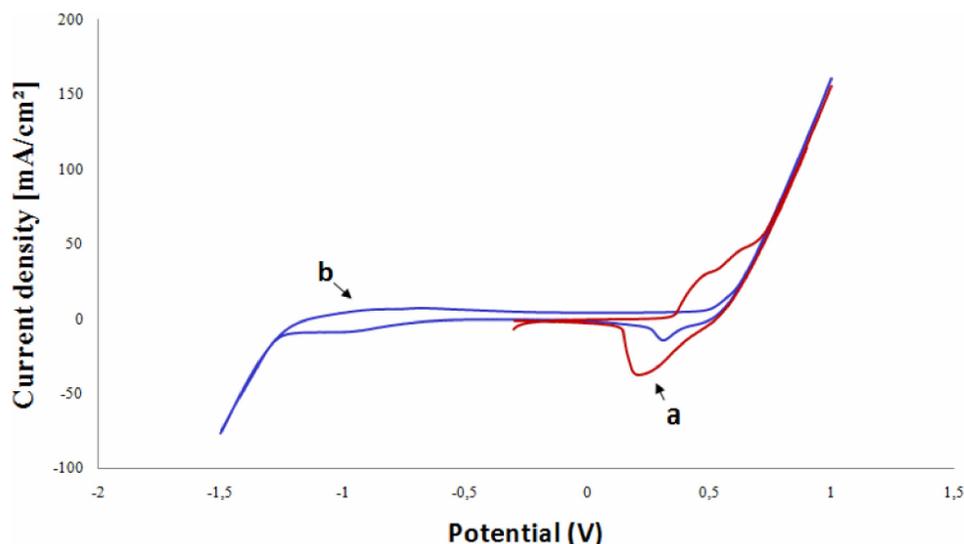

Figure 6 : Cyclic voltammograms obtained by a- Ni and b- NP-Ni electrodes at 100 mV/s in 1M KOH solution
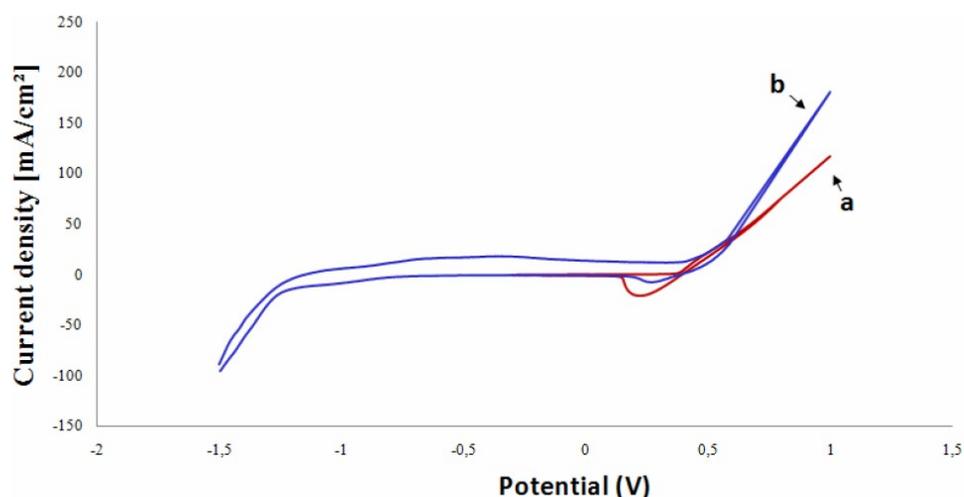

Figure 7: Cyclic voltammetry in N_2-saturated 1M KOH containing 0.3M methanol, a- Ni, b- NP-Ni

potential. The prepared NP-Ni electrode shows a good catalytic activity.

The methanol concentration effect was investigated. As we can observe, the oxidation current density of methanol, increases with the concentration of methanol (Figure 9). The effect of methanol concentration on fuel cell leads to an increase on the coverage of the electrocatalyst, increasing the methanol oxidation reac-
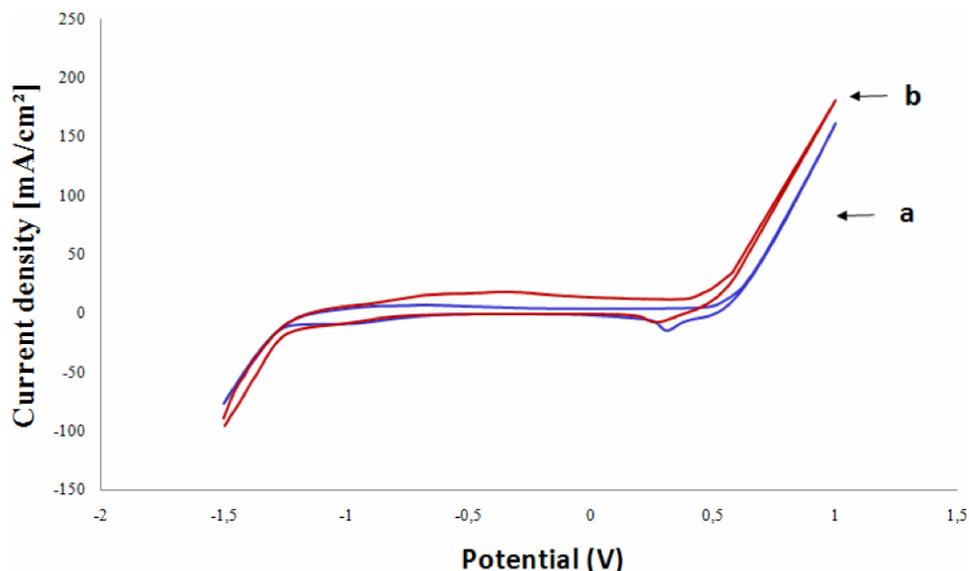
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Figure 8 : Cyclic voltammograms in N_2-saturated 1M KOH, a- without methanol, b- with methanol, recorded for Ni-NP electrode, scan rate 100 mV/s
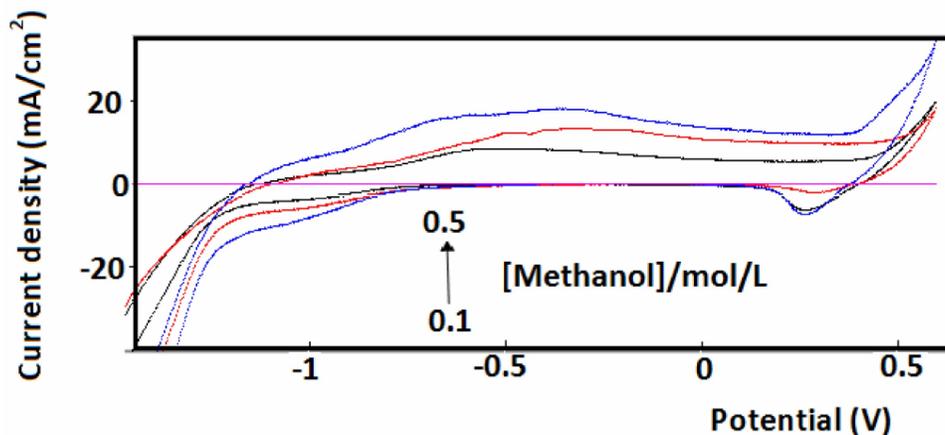

Figure 9 : Cyclic voltammograms in N_2-saturated 1M KOH, recorded at NP-Ni electrode in presence of various concentrations of methanol
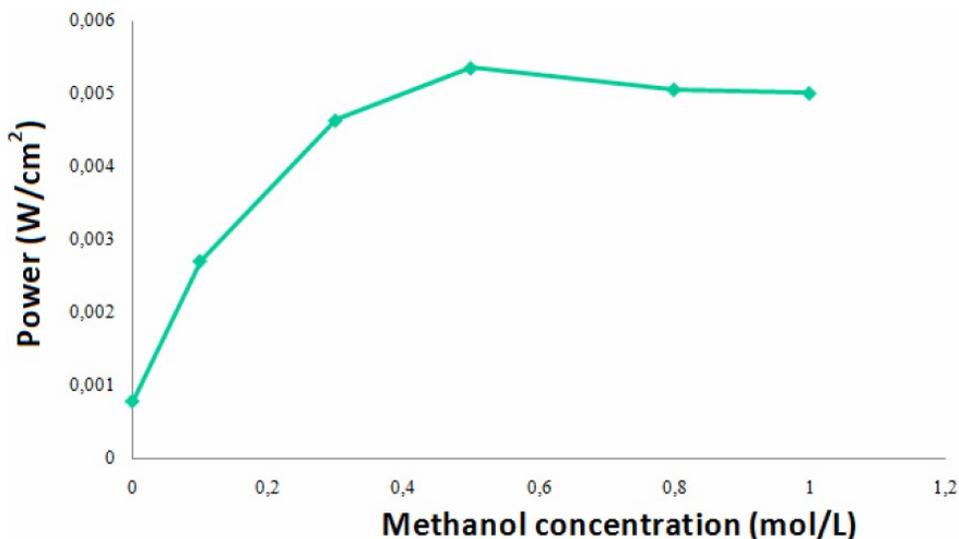

Figure 10 : Influence of methanol concentration on power density

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tion, and to an increase of the limiting current density.

In Figure 10 the power density curve for the NP-Ni electrode was presented. After 0.5 mol / L, the power density becomes stable. Probably, because of the saturation of the catalyst surface.

CONCLUSION

The current study introduces a novel anode for the electro-oxidation of methanol in alkaline medium. The NP-Ni anode was prepared by the potentiostatic deposition of natural phosphate onto nickel plate, appears to be a good catalyst for methanol oxidation. The power density of passive DMFC made of the modified electrode was better than Ni electrode.

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