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Ni-NP/Ni Anodes with Varying Ni: NP Ratio Prepared by Electrodeposition for the Direct Methanol Fuel Cell Abdelilah Chtaini¹ ¹ Universit Sultan Moulay Slimane *Received: 8 December 2013 Accepted: 1 January 2014 Published: 15 January 2014*

7 Abstract

14

⁸ Ni-NP/Ni anodes with varying Ni:NP ratio were prepared by electrodeposition of a thin

9 Ni-NP (Nickel-Natural Phosphate) catalyst layer onto Ni plate for a direct methanol fuel cell

10 (DMFC). The morphology and structure of the catalyst layers were analyzed by TEM and

11 EDX. The catalyst coating layer shows an alloy character. The results show that these

- ¹² electrodes are very active for the methanol oxidation and that the optimum Ni: NP surface
- ¹³ coverage was 50: 50 at

15 Index terms— anodes with varying, morphology and structure of the catalyst layers, operating at room 16 temperature.

17 **1** Introduction

irect methanol fuel cell (DMFC) is a new generation alternative energy harnessing device [1][2][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.

Author ? ? ?: Equipe d'Electrochimie Moléculaire et Matériaux Inorganiques, Université Sultan Moulay Slimane, Faculté des Sciences et Techniques de Béni Mellal, Maroc. e-mail: a.chtaini@usms.ma 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. 45 Another significant advantage of the direct methanol fuel cells over the rechargeable battery is their potential 46 for instantaneous refueling [12][13]. The methanol fuel cells in alkaline solutions have many advantages such as

47 increasing their efficiency, a wider selection of possible electrode materials, a better efficiency of oxygen cathode,

⁴⁸ and the oxidation reactions of organic fuels exhibit almost no sensitivity to the surface structure [14,15].

⁴⁹ Moreover, the use of the methanol fuel cells is limited by the poor anode performance and counteract the ⁵⁰ poisoning effects at the cathode due to the methanol cross-over [16,17]. In the electro oxidation of methanol, the ⁵¹ 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][25][26] due to its surface oxidation properties.

⁵⁷ 2 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.

⁶⁴ 3 b) Reagents

⁶⁵ A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco) [27]. Prior to ⁶⁶ use, this material was treated by techniques involving attrition, sifting, calcinations (900 °C), washing, and ⁶⁷ recalcination [28]. Measurements were carried out in aerated 1M KOH at room temperature (20 ± 0.2 °C).

⁶⁸ 4 c) Instrument

69 Cyclic voltammetry, chronoamperommetry, chronopotentiommetry, impedance spectroscopy (EIS), polarization 70 curves and square wave voltammetry were carried out with a Voltalab potentiostat (Model PGSTAT 100, 71 Echochemie B.V., Utrecht, the Netherlands) driven by the general purpose electrochemical systems data 72 processing software (Voltalab Master 4 software). The electrochemical cell was configured to work with three 73 electrodes using prepared electrode as the working electrode, platinum plate (1cm x cm) fot counter electrode 74 and Ag-AgCl as reference electrode.

75 **5 III.**

⁷⁶ 6 Results and Discussion

77 7 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 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 2 O 5 (34.24%), F-(3.37%), SiO 2 (2.42%), SO 3 (2.21%), CO 2 (1.13%), Na 2 O
(0.92%), MgO (0.68%), Fe 2 O 3 (0.36%), K 2 O (0.04%) and several metals in the range of ppm.

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

84 8 Phosphate

The crystal-structure of matter is similar to that of fluorapatite (Ca 10 (PO 4) 6F 2), as shown by X-ray diffraction (Fig. ??) and infrared emission spectroscopy (Fig. ??). 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 1m 2 g - 1. 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

91 (?c and ? a), are shown in Table ??.

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.

94 9 Conclusion

95 A novel electrode was fabricated and tested for methanol electro-oxidation. The experimental results indicate 96 that the Ni-NP/Ni catalyst has proved better activity, and the power density of the cell increases with methanol



Figure 1: D

 97 concentrations, and the maximum power density of 25 mW/cm 2 was achieved with 0.3 M methanol concentration. $^{1-2}$

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 $^{^2\}mathrm{Ni-NP/Ni}$ Anodes with Varying Ni: NP Ratio Prepared by Electrode position for the Direct Methanol Fuel Cell



Figure 2: Figure 1 :



Figure 3: Figure 2 : Figure 3 :



Figure 4: Figure 4 : Figure 5 :



Figure 5: Figure 6 :



Figure 6: Table 1 :



Figure 7: Figure 7 :

Electrodes	E(i=0) (mV)	Rp (ohm/cm²)	Icorr. (mA/cm ²)	Ba (mV)	Bc (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

Figure 8: Figure 8 :



Figure 9: Figure 9 :



Figure 10: Figure 10 :



Figure 11: Figure 11 :



Figure 12: Figure 12 : Figure 13 :

9 CONCLUSION

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- (*Morocco*), Casablanca. (It is readily available (raw or treated) from CERPHOS)