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Anode Development of Carbon Paste/NP by Cobalt Deposition for Direct Ethanol Application

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Abstract

This work aims to study the electrolytic oxidation of ethanol in alkaline solution by a carbon paste electrode modified with natural phosphate and cobalt (Co-NP/CPE). The electrodes were obtained by depositing the cobalt on carbon-NP substrates by electrodeposition, using potentiostatic and galvanostatic techniques. Morphological characterisation by optical microscopy techniques shows that the Co is well dispersed with the presence of NP particles on the surface of the electrode. The study of the electrode behaviour by voltammetric techniques exhibits a catalytic effect leading to a better result regarding the oxidation of ethanol. Compared to CPE-NP, the cobalt-modified CPE-NP electrode exhibits high electrolytic activity for ethanol oxidation.

Keywords

Electro-deposition, cobalt, cyclic voltammetry, oxidation of ethanol, natural phosphate

1 Introduction

In the general context of research aimed at both greater diversification and better efficiency of energy chains offering more favourable environmental balances, the fuel cell still appears as a technology with promising potential. Fuel cells are efficient conversion devices and environmentally acceptable. Electric current is generated in the fuel cell by the direct electrochemical oxidation of hydrogen (proton exchange membrane fuel cell, PEM) or methanol (Direct Methanol Fuel Cell, DMFC). The electrochemical processes that produce energy are essentially pollution-free. Water formed during operation of the appliance is beneficial for space travel and submarines. The applications of fuel cells are diverse: stationary or mobiles, mobile phones, and laptops.[1]

Direct methanol fuel cells and direct ethanol fuel cells have been projected as good candidates to complement with advanced batteries to power mobile and portable electronic devices due to their particularly high specific energy.[2] However, methanol is toxic to humans, it is easily volatile and flammable, as well as non-renewable.[3–5] Among the other alcohols available, ethanol appears to be an attractive and promising fuel because of non-toxicity, natural availability, renewability, and higher power density. On this basis, direct ethanol fuel cells (DEFC) appear to be more attractive technologies than methanol fuel cells (DMFC).[6–8] The performance of direct ethanol fuel cells (DEFC) is still limited by the available electrocatalysts for the oxidation of ethanol, which are mainly based on expensive noble metals such as platinum or its alloys.[9–12] Previous research on the development of DEFCs mainly concentrated on the PEMDEFC, which uses PEM as an electrolyte, a Pt-based catalyst on the anode and a pure Pt catalyst on the cathode.[13–14]

Several studies have had for objective the development of high-performance electrode materials.[15] Carbonaceous materials are widely used as anodes in PCMs, whether in the form of paper, fabric, felt, foam,[16–19] crosslinked vitreous carbon,[20] graphite sheets, rods, and granules or brush.[21–24]

The objective of this research was to synthesize new electrode materials which could constitute alternatives to platinum-based materials. As an anode, a carbon paste electrode (CPE) was mixed with natural phosphate (NP) paste on which the cobalt (Co) was electrochemically deposited. The choice of cobalt was justified by the fact that it has been very commonly used in recent years in HDL (Double Lamellar Hydroxides) phases in order to confer interesting electrochemical properties.

Indeed, it is possible to oxidise the Co^{2+} form present in the starting material to Co^{3+} by applying fairly low potentials of the order of 0.4 V/ECS (Saturated Calomel Electrode).[25] It should also be added that, in order to accelerate the reduction of oxygen, new catalysts based on ionic cobalt surrounded by nitrogen molecules have been developed.[26] Therefore, natural phosphate has been used as a carrier for modified electrodes in various studies.[27–28]

Co and NP were chosen to enhance these elements, which are among the recherché of our country, and the most electroactive metals used as a catalyst. The two together were used to modify the carbon paste electrode in our study to achieve good results.

The choice of fuel was focused on ethanol, as it is an attractive alternative to methanol.

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2 Experimental

2.1 Apparatus

Electrochemical experiments were performed using a voltalab potentiostat (model PGSTAT100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (*Voltalab Master 4 Software*).

All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The reference electrode was SCE and the counter electrode was platinum. All electrode potentials were referred to this reference electrode. The working electrode was a Co-NP/CPE electrode. To characterise the NP powder and the surfaces of the electrodes, SEM, EDX, and Optical Microscope were used.

2.2. Reagents and solutions

All chemicals were of the highest quality. Graphite powder (spectroscopic grade RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was obtained from Aldrich and used without further purification. Cobalt nitrate was obtained from Merck chemicals. Deionised water was used to prepare all the solutions. Electrolytic solution was 0.1 M NaOH, for manipulations in the presence of ethanol, the fuel was directly added to the support solution. The phosphate powder used in this work was taken from the province of Khouribga in Morocco. Before its use, the powder was treated by the following techniques: sieving, calcinations (900 °C) for one hour in order to get rid of any organic compound likely to interfere with the results.

2.3. Preparation of the modified electrode

The carbon electrode was prepared by mixing the carbon powder and liquid paraffin, which is a non-conductive binder. The resulting paste was shaped in a body. Mixture modified carbon electrode was prepared by mixing carbon powder and NP, and weighed to identical masses (50 % carbon and 50 % NP).[29] The Co was deposited on the surface of the CPE-NP electrode by electrochemical means. The anode was the modified CPE electrode of approximately 0.1 cm^2 in area, and 0.25 cm in cavity height. The direct current applied by a galvanostat was kept constant during handling. The metal was deposited at a constant potential of 0.1 V for 15 min.[30] Time and potential yielded a thin layer of metal over the entire surface of the electrode. The Co solution was 0.6 g/100 ml.

3 Results and discussion

Scanning electron microscopy (SEM) in Fig. 1 shows the surface structure of natural phosphate (NP). Treatment of NPs resulted in a fraction between 100 µm and 400 µm rich in phosphate. Compact natural phosphate appeared clearly. The treated NP had the chemical composition presented in Table 1.

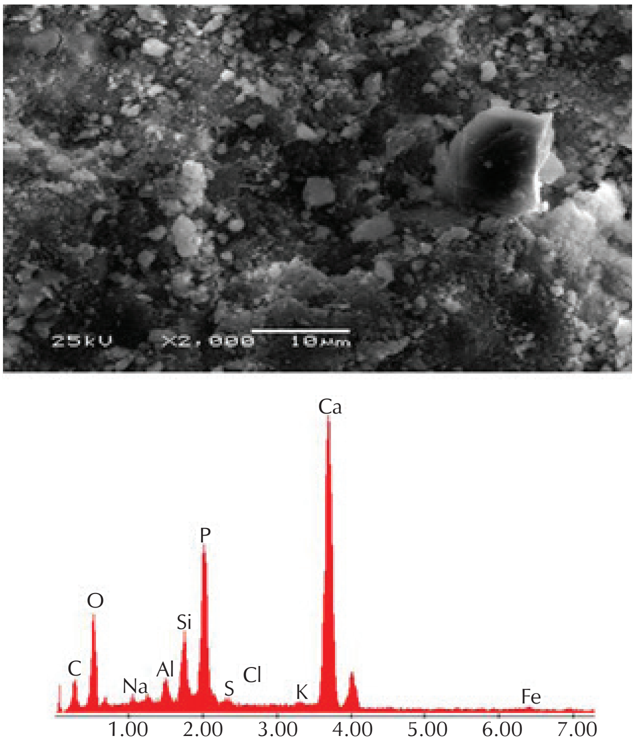


Fig. 1 – Scanning electron microscope (SEM) photomicrograph and EDX analyse of natural phosphate

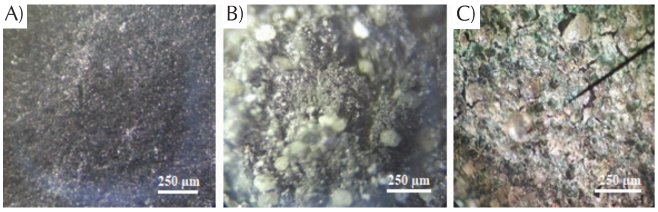


Fig. 2 – Optical microscopic image corresponding to: A) CPE, B) CPE-NP, and C) CPE-NP/Co

Fig. 2 shows the images taken by optical microscopy, recorded for (A) CPE electrode, (B) CPE-NP, and (C) CPE-NP/Co. Photos show agglomerates of mixed NP with carbon

Table 1 – Mineralogical composition of natural phosphate of the Khouribga Region

Substance	CaO	P_2O_5	F	CO_2	Na_2O	MgO	K_2O	Al_2O_3	Fe_2O_3	SiO_2
% mass	52.7	33.6	4.3	4	0.66	0.28	0.05	0.45	0.2	1.2

paste. The carbon paste film was continuous (CPE), and clusters of NP in the case of CPE-NP electrode could be seen. Optical microscopy for CPE-NP/Co (Fig. 2c) showed that the cobalt film, developed on the surface of the CPE-NP electrode, had a porous structure, the pore diameter was around 10 μm and the film was continuous.

Voltammograms had different shapes. In the case of the CPE-NP/Co electrode, two reduction peaks were observed, and an oxidation peak probably due to redox surface compounds. However, a slight resemblance was observed in the case of the CPE and CPE-NP electrodes, with a slight difference in the level of current density, CPE-NP had a slightly higher current density than CPE (Fig. 3).

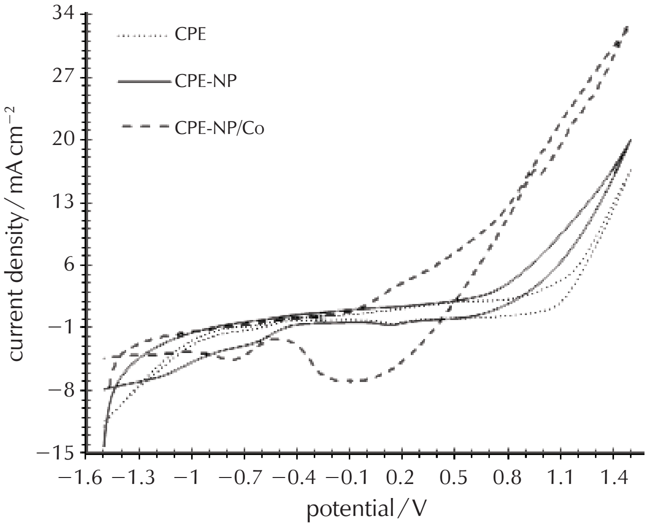


Fig. 3 – Cyclic voltammograms recorded in alkaline solution at CPE, CPE-NP, and CPE-NP/Co, scan rate: 100 mV s^{-1}, potential interval: from −1.5 to 1.5 V

The polarization curves of the three electrodes presented an identical shape in the anode part; however, the carbon paste electrode had a slightly different layout in the cathode part (Fig. 4). Table 2 shows the parameters collected from the polarization curves, such as corrosion potential (E_{corr}), corrosion current density (j_{corr}), slopes of cathodic and anodic Tafel (B_c and B_a).

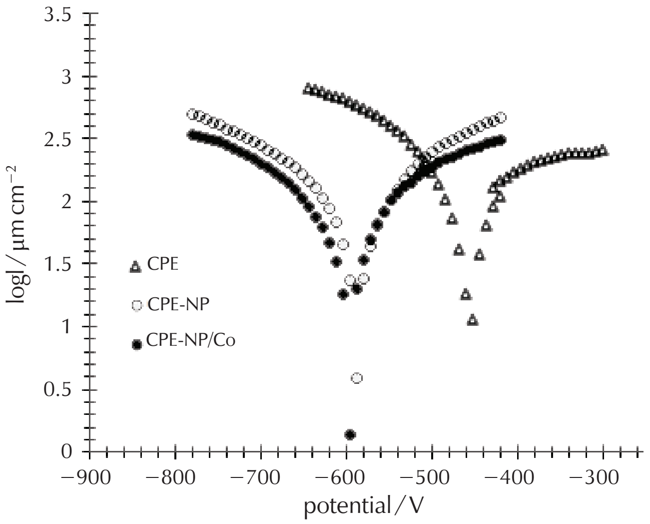


Fig. 4 – Curves of global polarization of CPE, CPE-NP, and CPE-NP/Co electrodes, registered in 0.1 M NaOH

The recorded impedance diagrams (EIS), respectively, for the CPE-NP electrode and the CPE-NP/Co electrode, are shown in Fig. 5. The shape of these curves demonstrates ohmic drop phenomena. The ohmic drop phenomena are indeed observed at high frequencies. In the absence of ethanol, the electrodes were characterized and this resulted in a high polarization resistance for CPE-NP/Co. In the presence of ethanol, the electrode showed good electroactivity, therefore reflecting the decrease in polarization resistance. The diagram obtained with CPE-NP/Co gave a smaller diameter than that of CPE-NP in the presence of ethanol. This reflected good electroactivity at the electrode surface, which could be explained by the presence of cobalt. In Nyquist diagram, low frequency range was well observed, unlike high frequency region.

The activity of the prepared electrodes was investigated by chronoamperometry (CA). Figs. 6 and 7 show the CPE-NP and CPE-NP/Co electrodes with and without ethanol. It may be seen from these figures that the two electrodes presented a remarkable activity towards the oxidation of ethanol. Fig. 8 presents a comparison between the CAs for the CPE-NP and CPE-NP/Co electrodes, against the oxidation of ethanol. It may be seen that the CPE-NP electrode exhibited low activity for fuel oxidation compared to the CPE-NP/Co electrode, which showed that cobalt brought added value to the carbon paste modified by natural phosphate.

Table 2 – Electrochemical parameters

Samples	E (j = 0) / mV	R_p / Ω cm^2	j_{corr} / mA cm^{-2}	B_a / mV	B_c / mV
CPE	−458.1	370.62	166.3	896	−236
NP/CPE	−589.7	381.45	153.3703	348.3	−379.7
Co-NP/CPE	−568.1	514.64	100.2901	344.4	−325.1

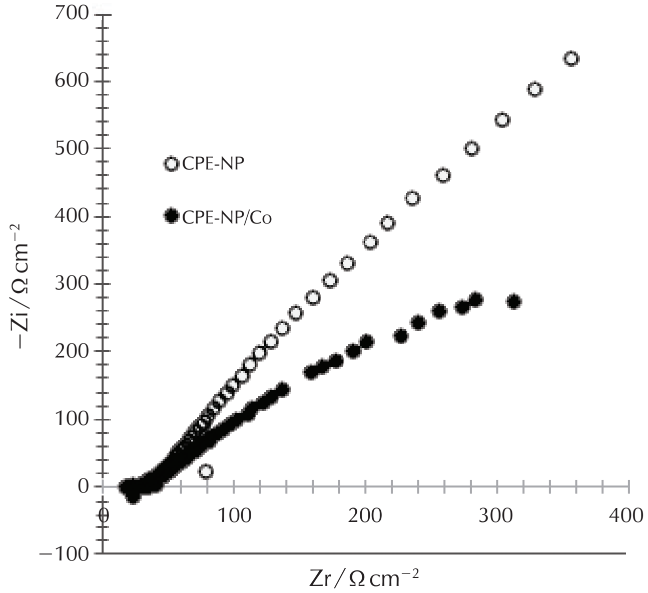


Fig. 5 – Electrochemical impedance spectroscopy recorded for CPE-NP electrode and CPE-NP/Co electrode for ethanol oxidation in 1 M NaOH solution, with 3.4 mM of ethanol, frequency interval: from 100 KHz to 100 mHz, AC sine wave amplitude: 10 mV, freq. *per* decade: 20

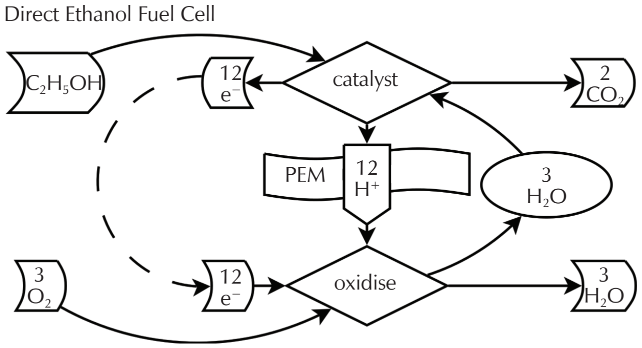
Mechanism of the oxidation reaction of ethanol in a basic medium:

$$C_2H_5OH + 12\ OH^- \rightarrow 2\ CO_2 + 9\ H_2O + 12\ e^- \quad \text{(anode)}$$

$$6\ H_2O_2 + 12\ e^- \rightarrow 12\ OH^- \quad \text{(cathode)}$$

$$C_2H_5OH + 6\ H_2O_2 \rightarrow 2\ CO_2 + 9\ H_2O \quad \text{(global reaction)}$$

H^+ ions are supplied to the electrolytic medium by the oxidation of ethanol Scheme 1.



Scheme 1 – Representative diagram of the reaction of a direct ethanol fuel cell

To evaluate the performance of the electrodes prepared, in Fig. 9 the evolutions of the electric power as a function of the concentration of ethanol is represented. It was found that the electric power of CPE-NP/Co was higher than CPE-NP in the concentration range below 30 mM of ethanol. This decrease may have been due to the decrease in the active sites, which were occupied by carbon molecules derived from ethanol, called the phenomenon of surface saturation of the CPE-NP/Co electrode. The difference between the two electrodes can be explained by the following proposition: the two electrodes had many active sites, except that the active sites of CPE-NP/Co were easy to access. This explains the rapid increase in current density, which had slightly decreased during the addition of fuel. In contrast, CPE-NP may have had active sites that were not easily accessible, which resulted in a slow increase in occupancy of active sites, but with continuity.

4 Conclusion

This study presents a new anode for the electrocatalytic oxidation of ethanol in alkaline medium. CPE-NP/Co anodes

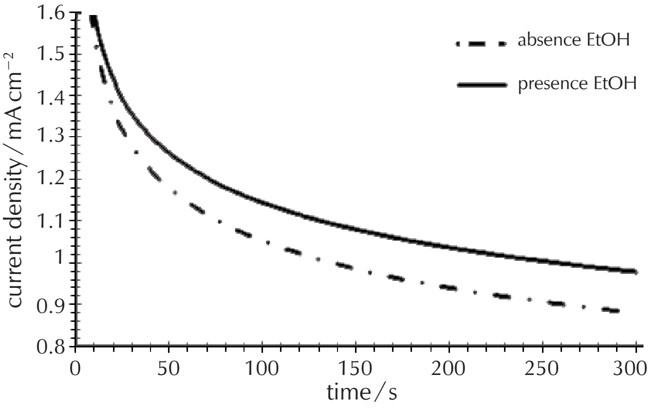


Fig. 6 – Chronoamperometry curves of CPE-NP in absence and presence of ethanol, in 0.1 M NaOH

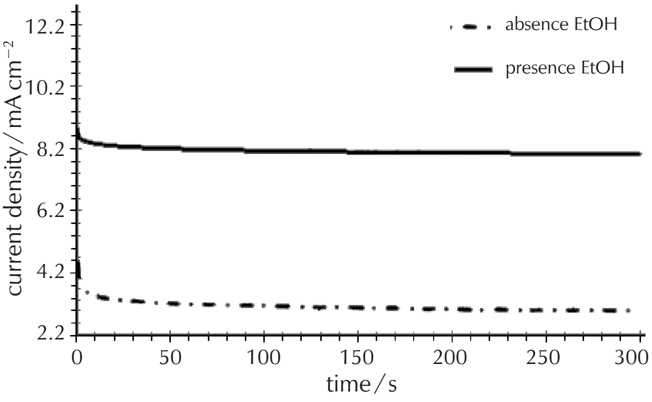


Fig. 7 – Chronoamperometry curves of CPE-NP/Co in absence and presence of ethanol, in 0.1 M NaOH

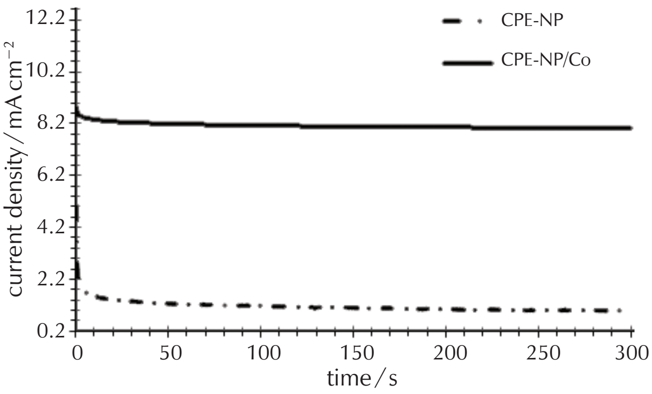


Fig. 8 – Chronoamperometry curves of CPE-NP and CPE-NP/Co for ethanol oxidation, in 0.1 M NaOH, with 3.4 mM of ethanol

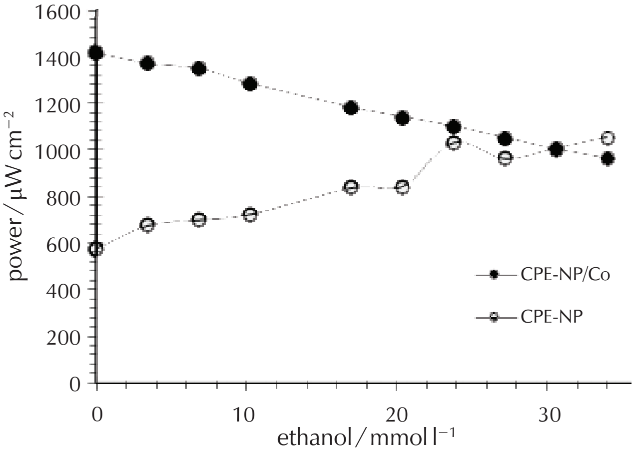


Fig. 9 – Influence of ethanol concentration on power density for electrodes CPE-NP and CPE-NP/Co

were prepared by potentiostatic deposition (Co on the surface of CPE-NP). The methods used were cyclic voltammetry and chronoamperometry. The oxidation current densities were significantly higher for the CPE-NP/Co electrode, suggesting that cobalt had better activity with respect to the oxidation of ethanol in the low concentration range. The performance of the developed anode of fuel cell was estimated by studying the evolution of electric power.

List of abbreviations
Popis kratica

SCE – saturated calomel reference electrode
CPE-NP/Co – carbon paste electrode modified by natural phosphate and cobalt
Co – cobalt
NP – natural phosphate
CPE – carbon paste electrode
XRD – powder X-ray diffraction
DMFC – direct methanol fuel cell
DEFC – direct ethanol fuel cell
PEMDEFC – proton-exchange membrane fuel cell
PEM – proton-exchange membrane
PCM – phase change material
EIS – electrochemical impedance spectroscopy
CA – chronoamperometry

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SAŽETAK

Razvoj kobaltom i prirodnim fosfatom modificirane anode od ugljikove paste namijenjene direktnoj elektrokatalitičkoj oksidaciji etanola

Sakina Touzara,[*] *Olivier François Aristide Bertrand Koffi* i *Abdelilah Chtaini*

Cilj ovog rada bio je ispitati elektrolitičku oksidaciju etanola u alkalnoj otopini pomoću elektrode od ugljikove paste modificirane prirodnim fosfatom i kobaltom (Co-NP/CPE). Elektrode su dobivene elektrodepozicijom kobalta na ugljik-NP supstrat, primjenom potenciostatskih i galvanostatskih tehnika. Morfološka karakterizacija modificiranih elektroda provedena je optičkom mikroskopijom koja je pokazala dobru raspršenost kobalta te prisutnost NP čestica na površini elektrode. Usporedbom dobivenih voltamograma vidljivo je da navedena elektroda pokazuje katalitički učinak što dovodi do bolje oksidacije etanola. U usporedbi s nemodificiranom CPE-NP elektrodom, elektroda modificirana kobaltom pokazuje visoku elektrolitičku aktivnost za oksidaciju etanola.

Ključne riječi

Elektrodepozicija, kobalt, ciklička voltametrija, oksidacija etanola, prirodni fosfat

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