

Development of Graphite-DNA Polymer Composites as Electrode for Methanol Fuel Cells

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Abstract

DNA aggregates were electro less deposited onto carbon paste electrode, firstly and electrode surface was coated by polymer film to protect the DNA film. Prepared electrode has shown great activity towards the oxidation of methanol, and no effect of empoisoning is observed. The effect of various parameters such as scan rate and methanol concentration, on the electro catalytical oxidation of methanol has also been investigated. The morphological study of electrode surface was investigated by Atomic Force Microscopy (AFM) and optical microscopy.

Keywords: Fuel cells; Methanol; Cyclic voltammetry; AFM

Introduction

Fuel cells are high energy density, energy conversion devices, which have application for portable power [1]. Electric current is generated in the fuel cell by the direct electrochemical oxidation of either hydrogen (proton exchange membrane fuel cell, PEM) or methanol (Direct Methanol Fuel Cell, DMFC). 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 (transportation as cars, buses, etc.), mobile phones and lap top computers [2,3]. 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 [4,5] 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 offers several advantages as a fuel. It is inexpensive but has a relatively high energy density and can be easily transported and stored. It can be supplied to the fuel cell unit from a liquid reservoir which can be kept topped up, or in cartridges which can be quickly changed out when spent.

To obtain high current densities, the used electrode must be a thin, porous and high surface area body activated by the presence of a suitable catalyst, which must make electronic contact with the remainder of the electronically conducting structure. The electrode must provide a large number of suitably active reaction sites where both the reactant and the electrolyte can come into contact. It must also maintain a stable interface between the electrolyte and the active species.

The carbon paste electrodes (CPEs) are cheaper and are suitable for preparing the electrode material with desired composition and pre-determined properties [6,7]. The electrochemical response of

CPE mainly depends on the properties of the modifying species. The modification of the carbon paste electrode can be done by different ways like grinding in an agate mortar [8,9] electro polymerization [10,11] and immobilization method [12]. The DMFC using superior membrane materials have been subject for extensive research [13-17].

In This study, the morphology of the Polyacrylic Acid membrane coating DNA deposit film onto CPE has been characterized via atomic force microscopy (AFM) and optical microscopy. The catalytic oxidation of methanol was studied at the prepared electrode, using cyclic voltammetry (CV) and square wave voltammetry (SWV). This study which uses graphite-DNA polymer composites as oxidation catalysts, indicating the DNA aggregates can be an anodic electro catalyst candidate for fuel cells.

Experimental

Apparatus

Electrochemical experiments were performed using a Volta lab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (Volta lab master 4 software). A conventional three-electrode systems consisting of the HAP-modified carbon paste working, platinum counter and SCE reference electrodes were used.

Reagents

All solutions used in this work, were prepared by dissolving the initial product, without further purification step. Carbon paste was supplied from (Carbone, Lorraine, ref 9900, French). All other reagents used were of analytical grade. Bid stilled deionized water (BDW) was

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used throughout the work. The DNA used in this work is taken from quail blood, according to the protocol below:

- 5 l of blood taken from the axillary vein is poured into an Eppendorf containing 500 μ l of danazol
- The solution is stirred for 5 min by vortexing and centrifuged at 6000 rpm/5 min
- The supernatant is removed and then 400 μ l of isopropanol is added to the residue remaining in the Eppendorf
- The mixture was vortexed and centrifuged at 6000 rpm/5 min
- The supernatant was removed and 500 μ l of pure water was added to suspend the DNA.

Preparation of the CPE

The carbon paste electrode (CPE) was prepared by thoroughly hand-mixing of graphite powder (CP). The obtained paste was dried at room temperature then a portion of the resulting paste was grounded and packed firmly into homemade PTFE cylindrical tube (geometric area 0.1256 cm^2) electrode. Electrical contact was established with a bar of carbon. DNA-CPE's were prepared by immobilizing the DNA system by soaking the preformed carbon paste electrode in a solution containing the DNA solution. And thereafter the surface of the prepared electrode is covered by the polymer, glued on the edges with Araldite.

Results and Discussion

Morphological study

Surface morphologies were characterized with AFM (Figure 1). The surface of the polymer shows a structure with reliefs, the size of the aggregates is not uniform over the entire surface. This structure shows the presence of pores of different sizes.

The electrochemical properties of carbon paste electrode coated or not by polymer in 0.1 M NaCl solution, were characterized with cyclic voltammetry. Figure 2 shows a typical cyclic voltammograms of the CPE and Polymer-CPE. We can see that the presence of the polymer on the surface of the CPE (Figure 2b), leads to a slight decrease in the current density, but the shape of CV is not reached.

Figure 3 shows the representative cyclic voltammograms recorded

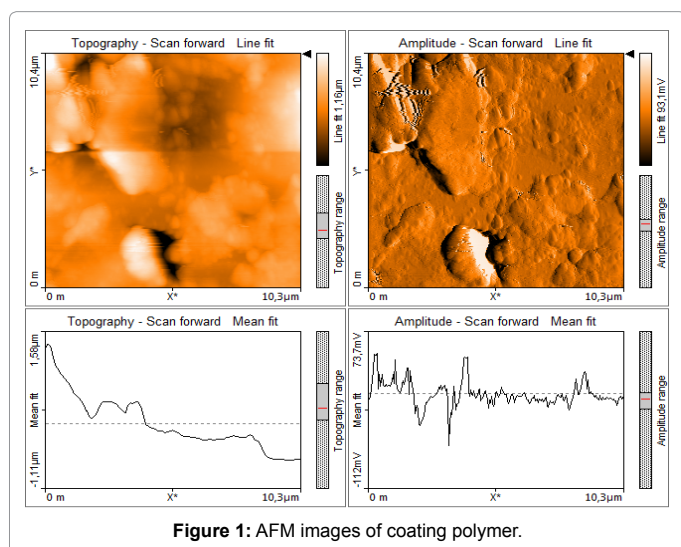


Figure 1: AFM images of coating polymer.

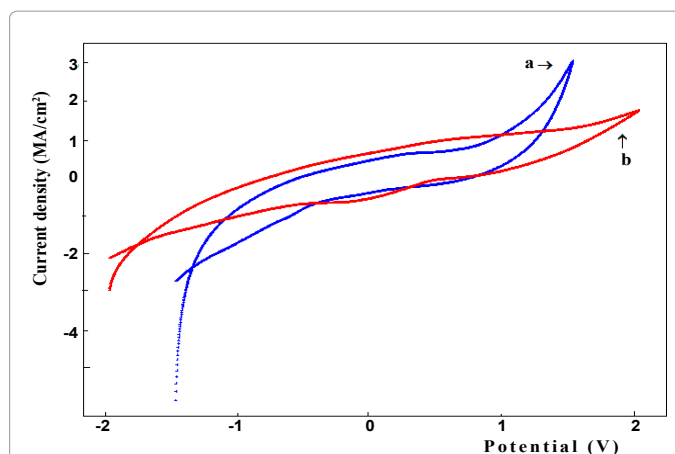


Figure 2: Cyclic voltammograms on CPE (curve a) and Polymer-CPE, recorded at a scan rate of 0.1 V/s. in a degassed solution of 0.1 M NaCl.

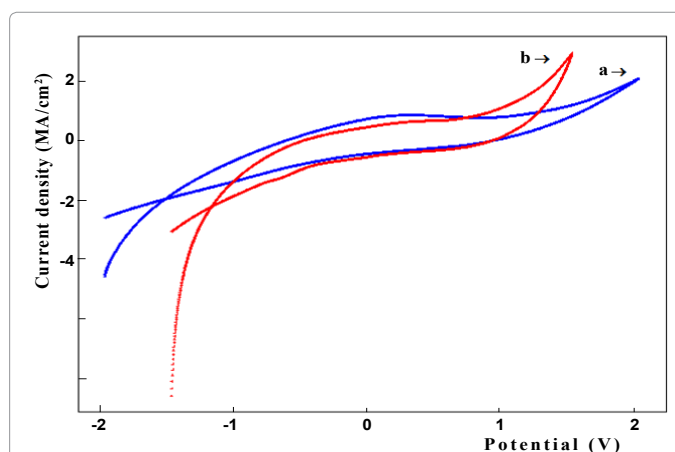


Figure 3: Cyclic voltammograms on CPE (curve a) and Polymer-CPE, recorded at a scan rate of 0.1 V/s in a degassed solution of 0.1 M NaCl containing 13.5 μ mol/L of methanol.

respectively, at CPE (curve a) and Polymer-CPE (curve b), in methanol fuel solution in 0.1 M NaCl. CPE is used control. The current densities are relatively high on the Polymer-CPE compared to the CPE. The methanol oxidation starts at 0.8 V, and characterized by a sudden rise in the current, which corresponds to the onset potential.

The electrochemical characterization of DNA-CPE and Polymer-DNA-CPE in a blank 0.1 M NaCl solution is given by Figure 4. The electroless deposition of DNA on the CPE surface is manifested by the appearance of two redox peaks on cyclic voltammograms, the first in the anodic scan direction at about 0.7 V and the second one on the of cathodic scan at -1.1 V.

By coating the surface of the DNA-CPE with the polymer, the VC retains its shape, whereas the current densities decrease, due to the non-conductive nature of the polymer (Figure 4b).

The electrochemical behavior of methanol was studied at the surface of different electrodes (DNA-CPE and Polymer-DNA-CPE) by CV experiments in 0.1 M NaCl. The results are shown in Figure 5. The addition of 13.6 μ mol/L methanol to the electrolytic solution causes an increase in the current density, in particular in the presence of the Polymer-DNA-CPE. The methanol oxidation starts at -1 V, this potential value corresponds to the onset point.

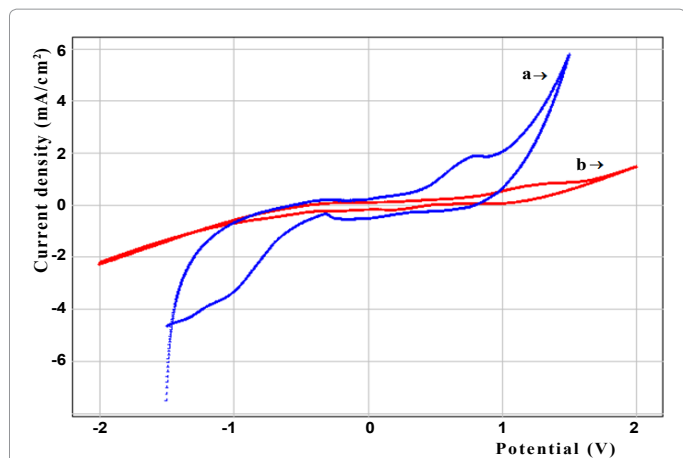


Figure 4: Cyclic voltammograms on DNA-CPE (curve a) and Polymer-DNA-CPE, recorded at a scan rate of 0.1 V/s in a degassed solution of 0.1 M NaCl.

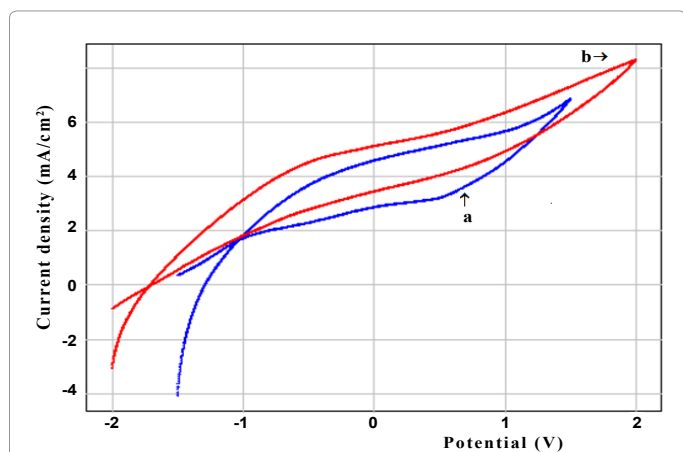


Figure 5: Cyclic voltammograms on DNA-CPE (curve a) and Polymer-DNA-CPE, recorded at a scan rate of 0.1 V/s in a degassed solution of 0.1 M NaCl containing 13.5 µmol/L of methanol.

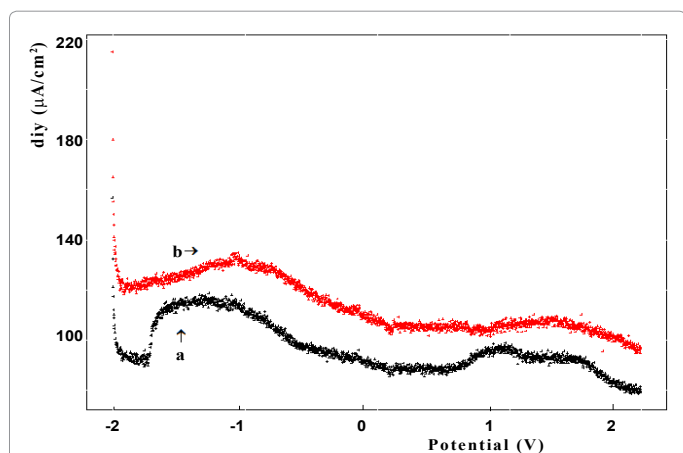


Figure 6: Square wave voltammograms on DNA-CPE (curve a) and Polymer-DNA-CPE, recorded in a degassed solution of 0.1 M NaCl containing 13.5 µmol/L of methanol.

The methanol oxidation is manifested in square wave voltammograms by the appearance of two peaks, the first towards

about -1 V and the second at 1 V. The current densities are remarkably higher in the case of the Polymer-DNA-CPE (Figure 6).

CVs for methanol electro oxidation on Polymer-NDA-CPE at different scan rates are illustrated in Figure 7. The methanol oxidation current density increase with increasing scan rate ranging from 10 mV/s to 100 mV/s in the presence of 13.6 µmol/L methanol. This linearity indicates that the methanol electrocatalytical oxidation is a diffusion controlled process.

The Figure 8 shows the cyclic voltammograms for different concentration of methanol from 3.4 µmol/L to 17 µmol/L in 0.1 M NaCl with a scan rate of 100 mV/s at Polymer-NDA-CPE. The methanol oxidation current density increase with increasing the concentration of methanol.

The optical microscopy images of the Polymer-DNA-CPE, Polymer-CPE, CPE, DNA-CPE and Polymer-CPE after methanol electro oxidation are presented in Figure 9. The images show adhesion of the polymer to the electrode surface, and protect the DNA film deposited on the carbon paste surface.

Conclusion

In this work, we have successfully prepared a novel electrode. The

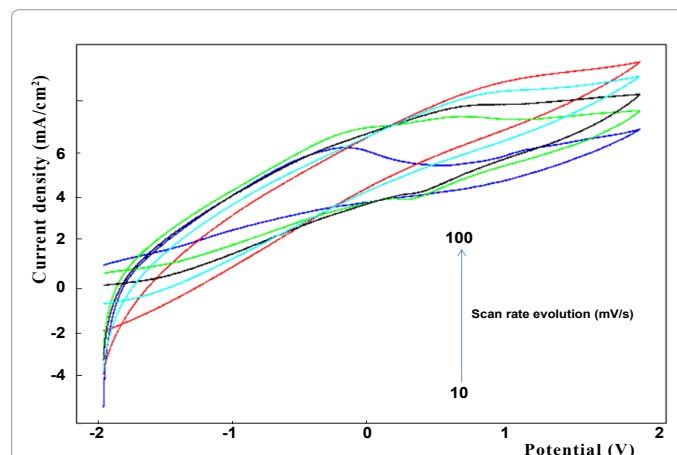


Figure 7: Cyclic voltammograms on Polymer-DNA-CPE, recorded at different scan rates in a degassed solution of 0.1 M NaCl containing 13.5 µmol/L of methanol.

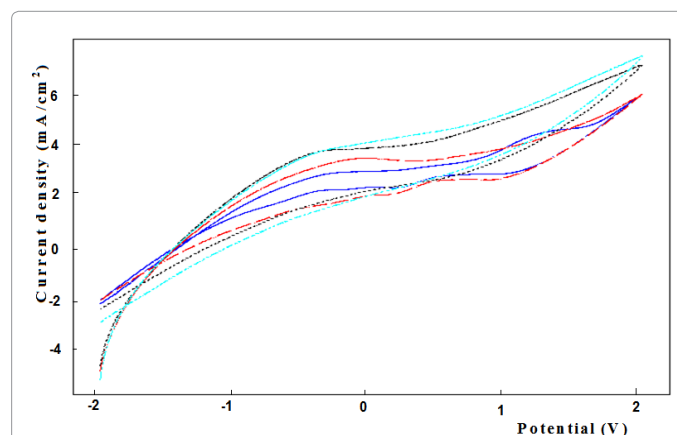
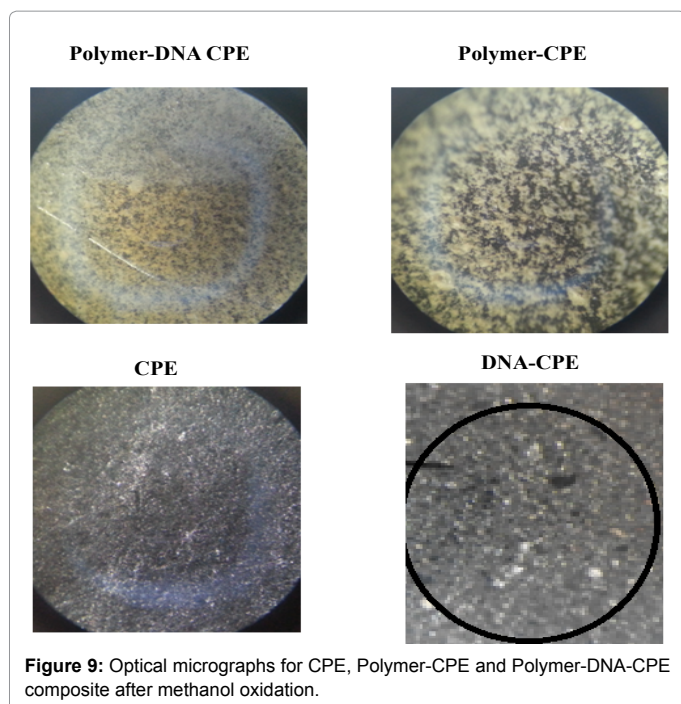


Figure 8: Cyclic voltammograms on Polymer-DNA-CPE, recorded at a scan rates of 0.1 mV/s in a degassed solution of 0.1 M NaCl containing different concentrations of methanol.



Polyacrylic Acid membrane coating DNA film electro less deposited at carbon paste electrode. We have shown that the new electrode has excellent activity in the presence of methanol. The polymer prevents deterioration of the DNA film, and therefore improves the life of the electrode. The prepared electrode (Polymer-DNA-CPE) is very simple and easy to prepare, and has the properties necessary for the methanol electro catalysis. No empoisoning effect is observed. The Volta metric techniques showed that Polymer-NDA-CPE increased the oxidation current of methanol with increasing methanol oxidation.

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