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ELECTROCHEMICAL BEHAVIOUR OF TRACK-ETCHED MEMBRANES WITH EMBEDDED COPPER NANOTUBES

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ABSTRACT

Track-etched membranes (TeMs) are thin polymer films with pores of various geometries made by irradiating on the DC-60 cyclotron and subsequent chemical etching. The objective of this work is to evaluate the electrochemical behavior of track-etched membranes with embedded copper nanotubes (TeMs/CuNT) using Cyclic Voltammetry. TeMs were prepared from 12.0 μm polyethylene terephthalate (PET) film by irradiation with $^{84}Kr^{+15}$ on the DC-60 heavy ion accelerator. The irradiated film was etched in a basic solution followed by H_2O_2/UV system. The characterization was performed by scanning electron microscopy (SEM). For the electroless plating consists of three successive stages: sensitization, activation and directly deposition. The electrochemical studies was performed in two different media KOH and Na_2SO_4 adding adding 100uL aliquots of nitrate solution using Pt as counter electrode, Ag/AgI as reference and the copper as work electrode. The results showed the potential of TeMs/CuNT as nitrate sensor in sodium sulfate medium.

1. INTRODUCTION

Track etched membranes (TeMs) are porous systems consisting of a thin polymer foil with channels , that have been used as templates for metals and semiconductors deposition to provide nanoscale devices, for instance, electrodes for fuel cells [1], solar cell panels [2], sensors, biosensors [3], for applications in different areas, such as Energy, Nanoelectronics, Environmental and Medical.

TeMs are produced by physico- chemical treatments to produce pores on thin films of polymers and mica irradiated by heavy ions. The track-etch procedure are made by bombarding a thin film of the polymer, usually polycarbonate and polyethylene terephthalate,

with high-energy particles, creating damage tracks [4,5]. The next stage of the process is to increase track etching rate, called sensitization stage, using UV to promote the photodecomposition of radiolysis products formed during heavy ion passage into low molecular weight species. A wide range of classes of materials can be deposited in the TeM pores using different methods e.g electrochemical deposition, electroless deposition, layer by layer self assembly, sol gel deposition, among others [6].

In this work it is described the potential track-etched membranes with embedded copper nanotubes to detect nitrate from water. The main concern about it that fertilizers are used with high nitrate content, which causes several environmental problems such as soil acidity, water eutrophication and, in some cases, the reduction of biodiversity [7]. Traditional procedures to detect nitrate depend on previous steps involving the stoichiometric conversion of nitrate to nitrite, on the other hand, electrochemical sensor is one step to measurement and detection of nitrate is based on potentiometric or voltammetry techniques.

2. MATERIAL AND METHODS

2.1. Polymer template preparation and treatment.

TeMs were prepared from 12.0 μm PET film by irradiation with $^{84}Kr^{+15}$ ions (energy = 1.75 MeV per nucleon, fluence =4.10^7 ions/cm^2) at the DC-60 heavy ion accelerator in Astana, Kazakhstan. Subsequently, the irradiated film was etched in 2.2 M NaOH solution at 85 ± 1°C. PET TeM samples were oxidized in H_2O_2/UV system [5].

2.2. Electroless plating

The PET template was exposed to activation and sensitization procedures according to procedure described in [8] for copper plating.

On the first step, a sample of PET TeM was immersed in a solution containing 50 g/l of $SnCl_2$ and 60 ml/l of 37% HCl for 6 minutes, then it was thoroughly rinsed under flowing warm water. At the next activation step, the sensitized membrane was immersed into solution of 0.1g/l of $PdCl_2$ and 10 ml/l of HCl to provide formation of the thin layer of Pd nuclei and finally dried in the air. Deposition was carried out in the temperature range of 2-25°C. The 10×15 cm activated polymer matrix was immersed in a thermostated deposition solution ($KNaC_4H_4O_6\times4H_2O$ - 18 g/l, $CuSO_4.5H_2O$ - 5 g/l, NaOH - 7 g/l) and carefully fixed to avoid the hydrogen gas.

The desired pH = 12.5 was adjusted by the addition of sulfuric acid. The copper deposition process started immediately after the addition of 0.13M formaldehyde, the deposition time did not exceed 40 min. the samples were washed in a 96% ethanol, deionized water and dried in an inert atmosphere.

2.3. Characterization

The thickness of the Cu NT walls was determined from the difference in the diameters of the pristine PET TeMs and the sample after deposition using the Hagen-Poiseuille equation.

Detailed structural and compositional studies were carried out using a scanning electron microscope (SEM) JEOL JFC-7500F and Hitachi TeM3030 instrument equipped with a Bruker XFlash MIN SVE microanalysis system. X-ray diffraction (XRD) measurements of the "as-prepared" composite membrane samples were obtained on a D8 Advance (Bruker, Germany). X-ray was generated at 40 mA and 40 kV and the scanning position ranged from 15-90˚ 2(θ). The crystal grain sizes were calculated using Scherrer equation.

2.4. Electrochemical Studies

Cyclic Voltammetry measurements were performed using a -Autolab Type III (Eco Chemie, the Netherlands) potentiostat connected to a microcomputer and controlled by Autolab Software GPES version 4.9.007. A conventional three-electrode cell, consisting of TeMs/CuNT, a platinum wire and a homemade Ag/AgCl/(sat KCl) electrode [15] was employed for all voltammetric measureme. CV studies were conducted at a scan rate of 100 mVs^{-1} in two different media: KOH medium(0.1 $mol.L^{-1}$) adding 100uL aliquots of 1 mmol L^{-1} NO_3^- solution, and 0.1 mol L^{-1} Na_2SO_4 and adding 100uL of 1 mmol L^{-1} NO_3^- solution in a scan rate of $100mV.s^{-1}$ and potentials range from -0,85 V until 0,20 V.

3. RESULTS AND DISCUSSION

TeMs functionalized with metallic nanotubes can be used as membranes for biomaterials biosensing. In this way, the goal of this work is to evaluate the electrochemical behavior of TeMs/CuNT using cyclic voltammetry (CV) in KOH solution.

TeMs was produced by irradiation as described by Korolkov et al.[5] Using the SRIM program (Table1), the total ranges of krypton ions, the specific energy losses due to the interaction with the electron shell and the nuclear [9].

Table 1-Energy loss and the total range of ^{84}Kr ions in PET film

MeV / MeV nucleon	dE/dx electr, keV/μm	dE/dx nucl, keV/μm	Full path, μm
147 / 1.75	7.567E+03	1.500E+01	26.55

For increasing of COOH- groups concentration, PET TeM samples were oxidized in H_2O_2/UV system.

SEM image of lateral chips of PET TeMs is shown in Fig. 1.

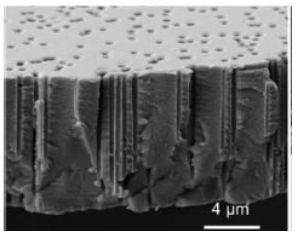

Figure. 1 – Cross sectional view of PET TeMs

Table 2 shows the structural data of the synthesized CuNTs.

Table 2: Structural data of the synthesized CuNTs

Pore density of PET template, (nm)	4.10^7
Pore diameter of PET template, (nm)	395±5
Inner diameter, (nm)	295.4
Wall thickness of tubes, (nm)	47.5±3.4
Deposition conditions (°C/min)	10/40

Electron micrographs of synthesized TeMs/CuNT nanocomposites is presented in Fig. 2.

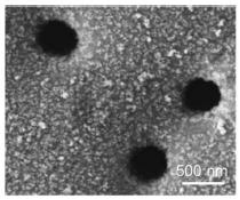

Figure 2: Electron micrographs of TeMs/CuNT surface

A TeMs/CuNT electrode was homemade for the electrochemical studies as shown in Fig.3.

Figure 3: TeMs/CuNT electrode

The cyclic voltammetry measurements were performed for direct nitrate sensing in water. Fig 4 shows the experiment performed in alkaline media.

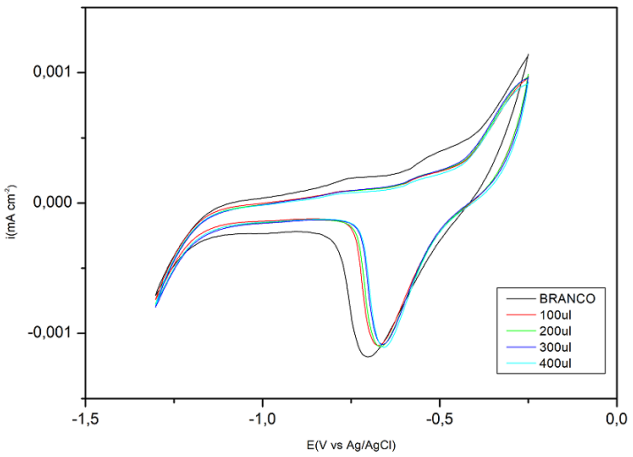

Figure 4: Cyclic voltammogram recorded in a 0.1M KOH adding 1 mmol L^{-1} NO_3^- solution.

It was observed that by adding 100 μL of nitrate solution the potential shift from -0,7V to 0,6V. Even though, the results showed the electrode potential to detect nitrate in water it could not be used as sensor, as in this condition the electrode did not measure the difference between the aliquots.

To evaluate the TeMs/CuNT electrode as sensor, the experiments were carried out in different media, using sulfate sodium as electrolyte. (Fig.5)

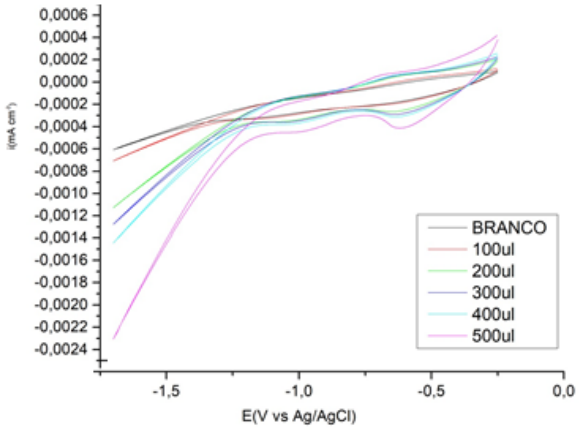

Figure 5: Cyclic voltammogram recorded in a 0.1M Na_2SO_4 adding 1 mmol L^{-1} NO_3^- solution.

In this condition the current intensity increases after 200 μL of nitrate solution (1 mmol L^{-1})

3. CONCLUSIONS

Track-etched membranes with embedded copper nanotubes (TeMs/CuNT) prepared by irradiation with $^{84}Kr^{+15}$ on the DC-60 heavy ion accelerator. The electrochemical studies showed (TeMs/CuNT) potential to be used as sensor to detect nitrate in water using 0.1M Na_2SO_4 as electrolyte.

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