NEW NANOHYBRIDE CATHALYTIC SYSTEMS FOR OXYGEN REDUCTION IN RENEWABLE FUEL CELLS

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Abstract - Electrocatalytic oxygen reduction (ORR) has become the focus of considerable attention due of its slow kinetics and the need for better electrocatalysts for fuel cell cathodes in the recent years.

In recent publications some results have been reported on the electrocatalytic activity of carbon supported polypyrrole (Ppy), polyaniline (Pani) and poly(3-methylthiophene) (P3MT), modified with cobalt or nickel salts. For these conductive polymer samples, the oxygen reduction occurred at high negative overpotential, since the polymer needs to be in reduced state before catalytic activity can be observed. In most of the cases the addition of cobalt or nickel in the composite, results in an improvement in electrocatalytic activity and a shift to electropositive values for the ORR potentials.

In this work the hybrid materials based on polypyrrole and cobalt-nickel oxide were studied as oxygen reduction catalysts. Polypyrrole was electropolimerized on carbon black and stainless steel supported materials and modified with nickel and nickel- cobalt oxide nanoparticles. TEM and SEM images show porous materials with a particle size 30 to 200 nm and EDAX test confirmed the presence of NiO and CoNiO nanoparticles into composite materials.

Key words: renewable fuel cells, Polypyrrole, ORR, nickel cobalt oxide, nanocomposite

1. INTRODUCTION

In recent years the development of fuel cells has taken fast advances. These systems use hydrogen and oxygen to produce electricity at high efficiency and with zero emission. Conventional fuel cells catalysts are based on carbon-supported platinum and some of its alloys. In the cathode, the catalyzed reaction is the Oxygen Reduction Reaction (ORR) [1-3]. This reaction is relatively slow, compared to the hydrogen oxidation reaction (HOR) in the anode and contributes up to 80% of the total loss in fuel cell performance [4]. The challenge is to substitute these precious metals for more abundant, cheaper and highly stable materials, diminishing the overpotential for the ORR [5,6].New polymeric electrocatalysts for the ORR have been reported based on conductive polymers [7], conducting polymers doped with heteropolyanions and metallic complex [8,9], and polymers modified with precious metals [10]. In recent publications have been reported on the electrocatalytic activity of carbon supported polypyrrole (Ppy), polyaniline (Pani) and poly (3-methylthiophene) (P3MT), modified with cobalt or nickel salts [11,12]. For these conductive polymer samples, the oxygen reduction occurred at high negative overpotential, since the polymer needs to be in reduced state before catalytic activity can be observed [7]. In most of the cases the addition of cobalt or nickel in the composite, results in an improvement in electrocatalytic activity and a shift for the ORR potentials.

The paper, presents the preliminary results concerning the structural and electrochemical behavior of carbon and stainless steel supported polypyrrole modified with nickel-cobalt and nickel oxide for ORR.

2. EXPERIMENTAL

Were used two types of materials as a support for electrochemical deposition of Ni and Ni-Co oxides in polypyrrole matrix: a 17%Cr ferritic stainless steel (SS) and carbon (C) sheets. Before electrodeposition, the sample's surfaces were mechanical prepared by polishing with emery paper, washed and ultrasonically cleaned with ethanol and distilled water for 10 minutes.

All used solutions were prepared with bidistilled water and analytical-reagent grade substances (Aldrich Fluka). As a disperse phase were use Aldrich-Fluka NiO and NiCoO nano powders.

The electrochemical experiments were performed with a PAR 273A potentiostat in a conventional three-electrode cell, by using a platinum auxiliary electrode (~ 3 cm^2) and an Ag/AgCl reference electrode, linked to the main compartment of the cell by means of a Vycor glass junction. The measurements were performed at room temperature (25°C) in normal aerated condition and under argon pressure.

Electrochemical deposition of polypyrrole was carried out on electrodes substrate from a 0.2 M oxalic acid aqueous solution containing 0.1 M pyrrole. The Pyrrole/oxide mixing ratio was 30% (weight percents) related to oxidic phase.

The polymeric hybrid materials were obtained using potentiostatic technique [13, 14] at 0.9V after cyclic voltammetry preliminary studies. The polypyrrole nickel material was electrodeposited on stainless steel surface oxide (SS/PpyNiO), and the polypyrrole Nickel cobalt oxide on carbon (C/Ppy NiCoO). Before electrolysis the solutions containing pyrrole and oxidic nano powders were stirred for homogenization for five hours at 1500 rpm.

The electrochemical behavior was carried out by cyclic voltametry technique in 0,5M Na_2SO_4 solution between +0.7V and -0.2V with 50 mV s^{-1} scanning rate.

The oxygen reduction reaction performance was evaluated in a 0.5 M KOH solution at room temperature, using cathodic polarization method between 0V and -0.7 V in an argon atmosphere and oxygen dissolved with 1mVsec^{-1} (quasi stationary state).

The morphological and compositional characterization was performed by using transition electron microscopy Jeol 200CX.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical characterization

Figure 1 show results obtained from electrochemical characterization using cyclic voltammetry technique in 0,5M Na_2SO_4 solution, for both electrode materials, C/PpyNiCoO and SS/PpyNiO. The cyclic voltammogrames show a very well stability of materials for about one volt width of potential range, between -0,2V and + 0,7V (figure 1). The curves have similar shape for both systems, however can be estimate that C/PpyNiCoO is more stable in oxidizing conditions comparing with SS/PPyNiO material.

In the other hand, in the case of C/PpyNiCoO, the entrapping of oxidic phase not lead to significant increasing of the active electrode surface. That can be seen in the very small increasing (less than 8%) of the voltammetric current do to solid particles (curve 2, fig. 2 a). Therefore it can be assumed that, unlike SS/Ppy/NiO, this increase is rather the result of active surface growth due to possible morphological changes of polymer layer and not of reversible transition involving different redox species of nickel or cobalt.
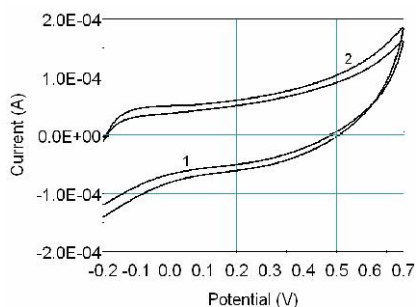

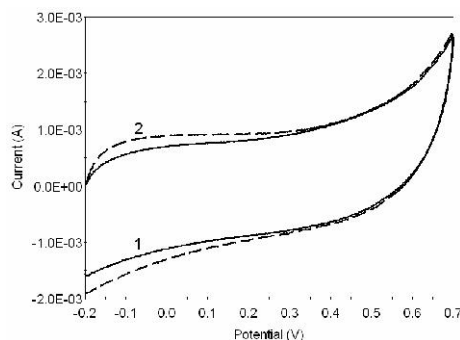**Fig. 1a - CV curves for: (a) graphite /polypyrrole (1), graphite /polypyrrole-NiCoO (2)**

Fig. 1b - CV curves for stainless steel /polypyrrole (1), stainless steel /polypyrrole-NiO (2). Test carried out in Na_2SO_4 0,5 M solution at 50 mV s^{-1}.

3.2. Structural characterization

As is shown in the figure 2, the polypyrrole NiCoO hybrid electropolimerized on carbon substrate has a relative homogeneous structure with micro and nano sized oxidic particles. The obtained film has an average thickness of 600-800 nm, figure 2c. These particles can be seen as an agglomerate one, with an average dimension between 100 nm and 300 nm (figure 2b).
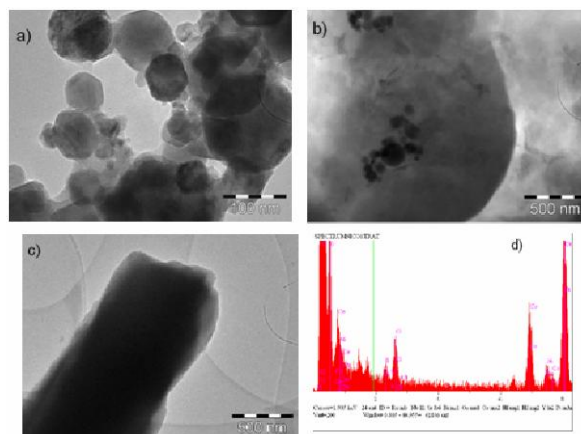

Fig. 2 TEM images of NiCoO powder (a), Ppy-NiCoO composite (b, c) and EDX spectrum of PPy+NiCoO composite.

3.3. Catalytic activity for ORR

To asses the electrocatalytic activity of NiCoO particles for oxygen reduction reaction, were carried out potentiostatic measurements under quasi stationary conditions (scan rate 1mVsec^{-1}) for C/PPy and C/PpyNiCoO systems. The figure 3 presents typical results obtained in aerated 0,5M KOH solution.

It is noted that the presence of NiCoO particles in polymeric matrix results an increasing of about 25% of reduction current of dissolved oxygen. Should be emphasized that this behavior can not be solely to the active surface increasing (which emerged as the cyclic voltametry measurements is only about 8%), proving that NiCoO have catalytic activity for oxygen reduction. The same conclusion is supported by the fact that in the presence of NiCoO particles the oxygen reduction process starts at lower electrode potential than in the electrocatalyst absence.
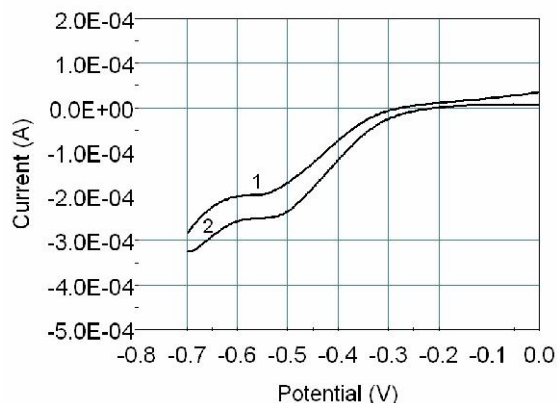
Fig. 3 - Polarization curves of oxygen reduction on graphite electrode modified with Ppy (1) and Ppy/NiCoO (2) in KOH 0,5 M solution and dissolved oxygen. Scan rate: 1 mV s⁻¹.

Figure 4 presents the polarization curves under quasi stationary condition for oxygen reductions reaction on SS/PpyNiO electrode.
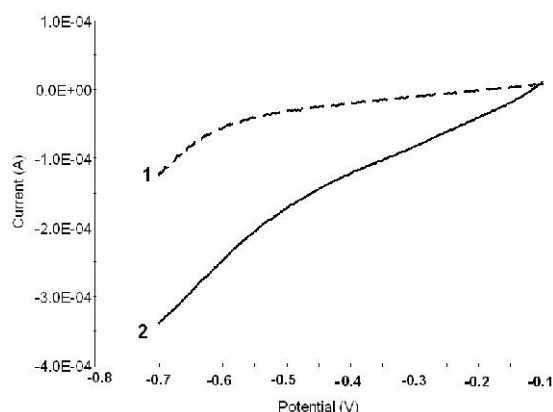

Fig. 4 - Polarization curves of oxygen reduction on stainless steel electrode modified with Ppy (1) and Ppy-NiO (2) in KOH 0,5 M solution and dissolved oxygen. Scan rate: 1 mV s⁻¹.

From this figure it can be assumed that the increasing of the cathodic current in the presence of NiO particles entrapped in polymeric matrix is due to either oxygen reduction reaction catalyzing (catalytic activity of Polypyrrole for this reaction is certainly negligible), either of the other reduction reaction on the surface which involve the nickel species.

To elucidate this point of view were the same type of measurements made with electrodes coated with PpyNiO in the absence and presence of the dissolved oxygen [15].

The figure 5 presents the reduction curves performed in 0,5M KOH solution after (curve 2) and before (curve 1) argon bubbling.

It is noted that presence of dissolved oxygen increases the cathodic current at lower potential value of -0,2V, suggesting that in this potential range occur catalytic effect of NiO on dissolved oxygen reduction reaction.
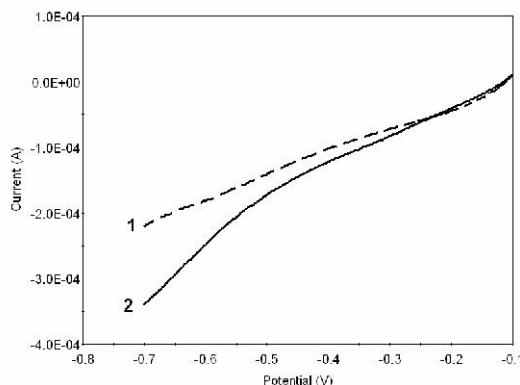

Fig. 5 - Polarization curves of oxygen reduction on stainless steel electrode modified with Ppy-NiO (1) under argon pressure and (2) in aerated 0,5 M KOH solution. Scan rate: 1 mV s⁻¹.

For an easier interpretation of these results, based on data from figure 5, was calculate the amount of oxygen reduction current values at the same potential for aeration (curve 2) and deaeration (curve 1) conditions. Thus in figure 6 is presented obtained current values as a potential function.
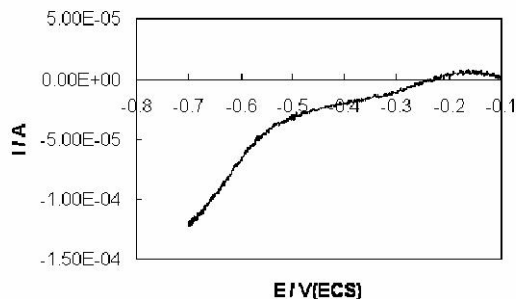

Fig. 6 - Variation of oxygen reduction current with potential of stainless steel electrode modified with Ppy/NiO.

From that it is obvious the electrocatalytic behavior of PpyNiO composite material, observing that the oxygen reduction begins at lower potential of about -0.25V. However, the curve from the figure 6 suggest that the oxygen reduction reaction occurs with significant rates only at electronegative potential than -0.5V

CONCLUSIONS

From these preliminary obtained results can be concluded the following:
The study of conducting polymer/oxide electrocatalysts represents a promising extension for oxygen reduction reaction in fuel cells.

Both studied materials have an electrocatalytic properties concerning oxygen electroevolution.

The C\PpyNiCoO hybrid material shows a better electrochemical behavior for largest potential range than SS/PpyNiO in neutral solution.

The SS/PpyNiO composite material seems to be better compared with C/PpyNiCoO for oxygen reduction reaction.

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