New Electrode Materials Composite (Carbon / Polymer-Metal) For Electrocatalysis

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Abstract

Recently, new electrode materials composite (carbon / polymer-metal) have been developed [1, 2]. The method of preparation of this type of electrode is based initially on the electrochemical deposition of a film of poly (pyrrole-malonic acid) having complexing properties to the surface of the electrode and in a second stage, the incorporation of particles of copper or nickel in the polymer film by complexation and electroreduction. [3].
The present study describes the electrosynthesis of Nickel-polymer composite electrode materials using the electrochemical reduction of nickel(II) complexes, incorporated by complexation into poly(pyrrole-benzoique) thin films coated by oxidative electropolymerization onto carbon electrodes. The electrocatalytic activity and the stability of the different composites have been then evaluated in the course of the electrocatalytic hydrogenation of ketones and enones in aqueous
electrolytes. Nickel-polymers composites electrode are characterized by a high catalytic activity and a good operational stability

Keywords: Functionalized polypyrrole; Electrodeposition; Polymer-metal nanocomposite; Nickel; Electrocatalytic hydrogenation

Introduction

The inclusion of small metal particles in organic matrix, particularly polymers, is attracting increasing research efforts. Studies on the incorporation by electrochemical reduction of metal particles with catalytic properties in polymer films have been mainly devoted to the incorporation of noble metals (Pt, Pd, Rh). However, only few examples are found in the literature concerning the inclusion in polymer films of particles of non-noble transition metals such as nickel, copper or cobalt. This led us to make our contribution to the development of other modified electrodes by immobilization on their surface chemical microstructures. The synthesis of metal particles-polymer composites were done by different approaches. One of them is the synthesis and characterization of the monomer pyrrole-succinic acid with complexing properties, with two carboxylic groups present in the monomer.
The electrochemical study showed the possibility on one hand that the preparation of stable films of controlled size and on the other hand, the inclusion of metallic particles of copper and nickel in the film of poly [pyrrole-succinic acid] by electroreduction and complexation of metal cations.
This study has demonstrated that this composite material can be applied as cathode electrocatalytic hydrogenation of both ketones and enones and showed a good electrocatalytic activity. The use of functional polymers as support for metal nanoparticles offer some exciting features via the generation of composites containing metal particles with controlled size and size distribution, thus providing a mean to influence the properties of the nanocomposite through the interaction of the metal surface with the functional groups of the

polymer. In this field, metal micro and nanoparticles dispersed inconducting polymer films are a class of promising electrode materials for catalytic applications [1].

Electrochemical procedures for the synthesis of metal nanoparticles, al though less common than chemical routes , have proven to be powerful and versatile means of preparing nanoparticles in a wide range of noble and transition metals [2]. Electrochemical methods have also proved to be effective in incorporating metal particles in either pre-deposited polymers or in growing films [3].

Preparation of the modified electrodes

The polymer films were grown from unstirred solutions of monomers [4] (4 × 10^{-3} mol L^{-1}) in CH_3 CN containing 0.1 mol L^{-1} TBAP as supporting electrolyte, by potentiostatic oxidative electropolymerization at 0,85-0,90 V vs Ag|Ag+ 0.01 mol L^{-1}[5]. Polymerization experiments were controlled through the anodic charge recorded during the electrolysis. The amount of pyrrole units in the films and thus, the apparent surface coverage in complexing units (GL, mol cm^{-2}) were determined after transfer of the modified electrodes into monomer-free CH_3 CN electrolyte from the integration of the polypyrrole oxidation wave recorded at low scan rate (10 mV s^{-1}).

For electrocatalytic hydrogenations, polymer films were grown on carbon felt (RVC 2000, 65 mg cm^{-3}, from Le Carbone Lorraine) electrodes (20 × 25 × 4mm). Procedures used for the incorporation of nickel metal into the different polymeric matrices will be described in the results and discussion section.

Electrocatalytic hydrogenation procedure

Electrocatalytic hydrogenations were carried out in a H-shaped three-compartment cell. The carbon felt electrodes modified with nickel-polymer composite films were placed in the cathodic compartment filled with 50 mL of a deaerated equivolumic water-methanol solution containing 0.1 mol L^{-1} NaCl + 0.1 mol L^{-1} H_3BO_3 (initial pH 5,3). The potential was maintained at –1.2 V for several min (hydrogen evolution). The current was then fixed at 20 mA and the substrate (1 mmol) was added. The working potential stabilized at around –1 V in these experimental conditions. The reaction progress was followed by periodic on GC comparison with authentic samples. Deposition of nickel in polypyrrole-succinic acid films It is well established that the dianions of succinic acid and its 2-substituted derivatives form various complexes with nickel(II) cations.

Deposition of Nickel in Polypyrrole-Succinic Acid Films

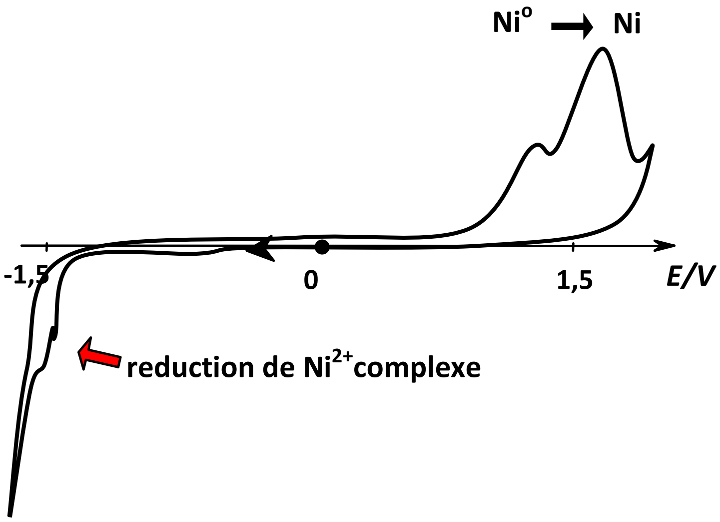

Figure 1. Cyclic voltammograms in 0.1 M Na_2SO_4 (pH 5.5) at a C|poly1 modified electrode (3mm in diameter), that has been immersed for 15 min in 0.1 M NiSO4, pH 5.5

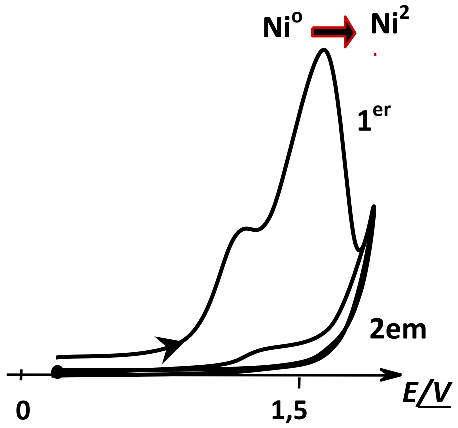

Figure 2. Anodic stripping wave in 0.1 M Na_2SO_4 + 0.1 M H_3BO_3 for nickel deposited in a poly1 film soaked for 15 min in 0.1 M NiSO4 (pH 5.5), then reduced at –1.4 V in clean 0.1 M Na_2SO_4 + 0.1 M H_3BO_3 (pH 5.3); curve 1st and 2nd scan

The electrochemical behavior of the pyrrole-succinic acid in CH_3 CN 0.1 M of TBAP. CV curves exhibit the regular irreversible oxidation peak (Epa ca. 1 V vs Ag|Ag+ 0.01 mol L^{-1}) systematically observed with N-substituted pyrroles, and an irreversible reduction peak (Ep c ca. –1.2 V on Pt) attributed to the reduction of the protons of the carboxylic acid groups. Poly films can be grown on platinum and carbon electrodes by cycling over the –0.4 V to 0.9 V potential range, or by controlled-potential oxidation at 0.85 V (Ag|Ag+ 0.01 mol L^{-1}). Films with apparent surface coverage (GL) around 10^{-7} mol cm^{-2} could be obtained with polymerization yields above 50%.

Electrocatalytic Hydrogenation at the Different Modified Electrodes

The poly(pyrrole-succinic acid)-nickel electrode material shows a catalytic activity, For example, the poly2-nickel electrode material appeared rather stable. As an example, results obtained in the course of the 5th ECH of a sample of 2-cyclohexenone at a C|poly-Ni(0) cathode show that the current yield remained high (Table 1). The results obtained in the course of the ECH of cyclohexanone (Table 2) at C|poly-Ni(0) complexation in 0.01 mol L^{-1} $NiSO_4$ (pH 7), followed by reduction at –1.5 V in clean 0.1 mol L^{-1} Na_2 SO_4 + 0.1 mol L^{-1} H_3 BO_3 (pH 5.5) in similar conditions (2 incorporations of nickel, using an accumulation solution in 0.01 mol L^{-1} $NiSO_4$). Cyclohexanol was produced.

Electrocatalytic Hydrogenation

Table 1: Electrocatalytic hydrogenation of cyclohexanone (cathodes C/poly-Ni(0))

Electrode	N°	1F	2F	3F	4F
C/Polysuccinique-Ni (1x10^{-5} moles of polymer)	01	18 %	36 %	56,6 %	73,3 %

C/Polysuccinique-Ni (1x10^{-5} moles of polymer)	03	21,6 %	44,7 %		
C/Polysuccinique-Ni (1,8x10^{-5} moles of polymer)	01	11 %	29,3 %	46,4 %	65 %
C/Polysuccinique-Ni (1,8x10^{-5} moles of polymer)	03	39%	68,8 %		

Table 2: Electrocatalytic hydrogenation of 2-cyclohexenone (cathodes C/poly-Ni(0))

Electrode	N°	product	1F	2F	3F	4F
C/Polysuccinique-Ni (1,8x10^{-5} moles of polymer)	02	Cyclohexanone	50	65	57	43
			112 %	111 %	91 %	78 %
		Cyclohexanol	5,4	22,7	39,7	57
C/Polysuccinique-Ni (1,8x10^{-5} moles of polymer)	04	Cyclohexanone	31,75	63	80,8	
			78,7%	79 %	71%	
		cyclohexanol	2,7	7,8	12,8	
C/Polysuccinique-Ni (1,8x10^{-5} moles of polymer)	05	Cyclohexanone	50,4	80,5	77,7	66,6
			106 %	97,6 %	80%	65%
		cyclohexanol	1,4	8,5	21	32

Conclusion

In this work, the methods providing an effective dispersion of nickel particles into electrogenerated functionalized polypyrrole were investigated, by electroreduction of nickel(II) cations complexed into poly(pyrrole-carboxylate) films. The electrocatalytic activity and the operational stability of various composite electrode materials have been evaluated in the course of the electrocatalytic hydrogenation of ketones and enones in aqueous media. The main result is that cathodes synthesized by the electroreduction of nickel(II) ions complexed into polycarboxylate films are characterized by a higher catalytic activity and a significant improvement of the operational stability, as compared to cathodes prepared by electroreduction of nickel(II) complexes incorporated by ion-exchange into functionalized polymer films. These features could be explained by the limited diffusion of metal species in the course of the electroreduction of metal complexes covalently bound to the polymer matrix, leading to a more uniform dispersion of metal throughout the polymer film and thus increasing the specific area of the catalyst. Moreover, the complexing polycarboxylate matrix may act as a stabilizer to prevent metal particles from aggregation, which can also be responsible of the better operational stability observed for these cathodes.

References

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