Electrochimica Acta 170 (2015) 311–320

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Elaboration of new electrodes with carbon paste containing polystyrene functionalized by pentadentate nickel(II)-Schiff base complex – Application to the electrooxidation reaction of methanol and its aliphatic analogs.

Ali Ourari [a,*], Hellal Nora [a], Charef Noureddine [b], Aggoun Djouhra [a]

[a] Laboratoire d'Electrochimie, d'Ingénierie Moléculaire et de Catalyse Redox (LEIMCR), Faculté de Technologie, Université Ferhat Abbas-Sétif -1, Route de Béjaia Sétif 19000, Algeria
[b] Laboratoire de Biochimie Appliquée, Faculté de Technologie, Université Ferhat Abbas-Sétif-1, Route de Béjaia Sétif 19000, Algeria

ARTICLE INFO

Article history:
Received 22 October 2014
Received in revised form 11 February 2015
Accepted 17 February 2015
Available online 2 May 2015

Key words:
Graphite paste electrode
Polystyrene-Ni(II)-Schiff base complex
Modified graphite paste electrode
Cyclic voltammetry
Oxidation of aliphatic alcohols

ABSTRACT

Polystyrene functionalized by a Schiff base ligand as N,N'-bis(salicylidenepropylene triamine)-N-para-aminomethylpolystyrene was synthesized from poly(4-chloromethylstyrene) and Schiff base ligand N, N'-bisalicylidenepropylenetriamine. Coordinated with nickel ion, this polystyrene Schiff base gives the expected nickel complex. The modified electrodes obtained from graphite paste and nickel complex covalently grafted onto the polystyrene were prepared in a ratio 70:30 wt%. Its voltammogram, recorded in alkaline solution, showed a well- defined redox process corresponding to Ni(II)/Ni(III) redox couple. This modified graphite paste electrode showed a good stability. The electrocatalytic activity of the oxidation reaction of some aliphatic alcohols has been studied by cyclic voltammetry with various concentrations and different scan rates. Thus, these electrodes revealed good electrocatalytic activity towards methanol, ethanol and isopropanol alcohols showing that the oxidation current peak increases linearly with alcohol concentration. However, the electrocatalytic current decreases with the increase of the length of the aliphatic chain as expressed by the following sequence: i_{cata} (methanol) > i_{cata} (ethanol) > i_{cata} (isopropanol).

1. Introduction

Chemical modification of electrode surfaces requires a special knowledge essentially on the building and manufacturing of immobilized molecular materials. The first pioneers of this chemical engineering are Lane, Hubbard, Murray and Miller [1–3]. Since more than three decades, an extensive research has been devoted to the design of diverse forms of electrode materials involving an important development in this area. So, the use of these electrodes chemically modified as tools for synthesis, analysis, electrocatalysis and detecting biomolecules was found to be attractive and very interesting [4]. The modified electrodes containing transition metals as catalytic sites, incorporated in phtalocyanine, porphyrins, Schiff bases etc, can be used as electrocatalytic membranes to evaluate the concentrations of several species. Their catalytic performances have improved advantages in the immobilization of an appropriate molecule for various applications [5–7]. Among these electrode materials currently used in electrochemistry, the carbon paste electrode was described in the literature since 1958 by Adams [8]. This research area was actively developed particularly in the manufacturing of new carbon paste modified electrodes by immobilization the desired compounds in order to improve their electrochemical performances in many applications such as in catalysis and electrochemical sensors [9–12]. The choice of this material of electrode can be justified by several advantages such as simple and easy fabrication, no easily poisoned, renewable surface, low price with an acceptable stability.

Transition metals Schiff base complexes are also intensively studied during the last decades owing to their diverse properties, catalytic efficiencies and their selectivity versu s most organic reactions. Therefore, this work studies the immobilization of pentadentate Schiff base nickel complex, covalently grafted on polystyrene backbone on carbon paste electrode to avoid any leaching of the electroactive molecules inducing a significant improvement of the electrochemical signal. In this case, it was

---

* Corresponding author. Tel.: +213 7.76.28.15.33; fax: +213 36.61.11.54.
E-mail address: alourari@yahoo.fr (A. Ourari).

http://dx.doi.org/10.1016/j.electacta.2015.02.154
0013-4686/© 2015 Published by Elsevier Ltd.

commonly known that the best linking in the design of modified electrodes is the covalent grafting of the complex molecule onto the solid phase either carbon paste or all other materials chemically inactive [13,14]. In one of our recent papers, the functionalized polystyrene by transition metals Schiff base complexes was reported for elimination and entrapment of heavy metals [15].

As continuation of this work, a new composite material is obtained from p-chlorinated polystyrene where the chlorine atom was substituted by N,N'-bisalicylidenepropylenetriamine (H_2L) leading to the formation of the material containing the Schiff base ligand (PS-H_2L). After metal coordination of this ligand, the expected compound (PS-Ni(II)L) was obtained. This polymeric material containing nickel(II) sites was mixed with graphite giving a new composite material used as modified electrode to oxidize methanol and its analogs as illustrated by the following Scheme 1.

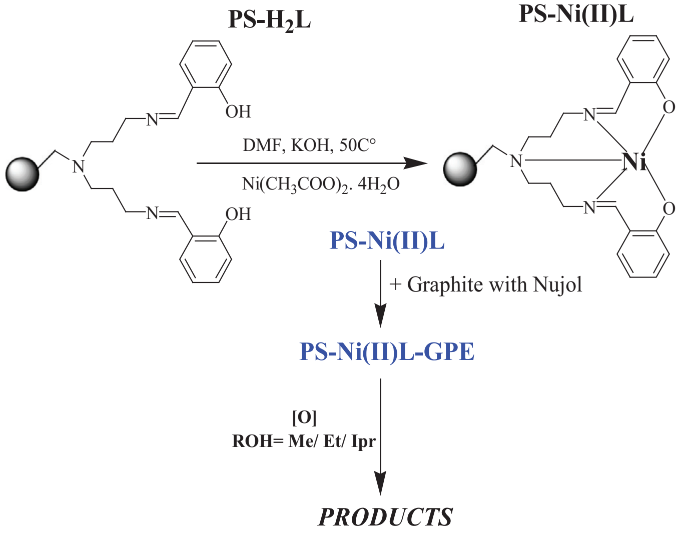
Thus, the Ni(II) catalytic sites are covalently grafted on the polystyrene backbone ensuring their non leaching to the solution and presenting a high stability for the obtained modified electrode. To our knowledge, this example was not previously reported in the literature. It is true that the electro-oxidation of methanol was extensively studied but, our contribution is to improve the electrocatalytic performances compared to those of the literature [16–25].

2. Experimental

2.1. 1Chemicals

All chemicals were obtained from commercial sources and were used as received without any further purification. The chloromethylpolystyrene (Merrifield polymer, Fluka) cross linked with 5,5% of DVB (porosity 16-50 mesh). All solvents DMF, dioxane, absolute ethanol and dichloromethane are obtained from Fluka while N, N'bis(3-aminopropyl) amine 99% and salicylaldehyde 99% are from Sigma Aldrich.

The functionalized polystyrene with Schiff base N,N'-bis (salicylidenepropylenetriamine)-N-para-aminomethylpolysterene PS-H_2L was prepared according to the literature [26]. For polymeric matrix complexation, nickel acetate tetrahydrated was purchased from Fluka. 0.1 M NaOH (Fluka) solution was used as electrolyte for all electrochemical experiments. Powdered graphite and nujol were used for carbon paste electrodes preparation. Different alcohols such as methanol, ethanol and isopropanol were obtained from Sigma Aldrich and were used in the electrocatalytic reactions.



Scheme 1. Polystyrene functionalized by Ni(II)-Schiff base complex (PS-Ni(II)L) mixed with graphite and nujol to give new modified electrode used in electro-oxidation of aliphatic alcohols.

2.2. Instrumentation

Electrochemical experiments were carried out using a 301/10 Potentiostat/Galvanostat type PGZ 301-Voltalab 10 Radiometer with PC work station and electrochemical interface IMT 301 with Volta Master 4 software. A standard three-electrode electrochemical cell of 10 ml was used. Potentials are referred to the (Hg/Hg_2Cl_2) saturated with KCl reference electrode. Platinum wire was used as auxiliary electrode. As for the SEM images, they were obtained using HITACHI TEM 300.

2.3. Preparation of Polymer-anchored by Ni(II) Schiff base complex

Polymer-anchored ligand PS-H_2(L) (0.445 g, 1 mmol) was allowed to swell in 15 ml of DMF and of KOH (0,168 g, 3mmol) for 24 h. A DMF solution (15 ml) of nickel acetate tetrahydrated (0.74 g, 3 mmol) was added to the above suspension and the reaction was heated in reflux with continuous stirring for 24 h. After cooling to room temperature, the reaction mixture was filtered off, washed with hot DMF followed by hot ethanol and dried in oven at 100 °C. So, the nickel(II) complex (Ni(II)L) is therefore covalently anchored on polystyrene backbone (PS-Ni(II) L) as above mentioned in the literature [26].

2.4. Elaboration of electrodes

2.4.1. Graphite paste electrode

Graphite paste electrodes were prepared by mixing graphite powder with mineral oil (Nujol) in the ratios 70 and 30% respectively. Both materials must be carefully mixed until to obtain a graphite paste sufficiently homogeneous (Agate mortar) for usual electrochemical uses. In our case, the composite material was compressed in a syringe body of polyethylene (3 ml) in the side of needle (depth 2.5 mm, diam. 2 mm) and the electric contact is ensured by introducing a copper wire from the piston side as shown in the following Scheme 2. A fresh electrode surface was generated rapidly by polishing the old one on a piece of white paper until obtaining a shiny appearance.

2.4.2. Modified graphite paste electrode

The modified graphite paste electrodes were prepared by the same manner than the previous electrode of graphite paste, but with adding the functionalized polystyrene by ligand (PS-H_2L) or by its nickel Schiff base complex **(**PS-Ni(II)L**)**. In these formulations, the experimental procedure was carried out using the following percentages of graphite paste as 0, 5, 10, 20, 30, 40, 50 and 60% (w/w). For this, it was revealed that the best percentage for the electrochemical study is 30% of PS-Ni(II)L as shown further in Fig. 1.

3. Results and discussion

3.1. Characterization of new composite material

The catalyst used in this study was characterized as described in the literature [26]. The ligand H_2L and its corresponding nickel(II) complex was covalently grafted on p-chlorinated polystyrene by substitution of the chlorine atom with pentadentate Schiff base ligand (H_2L). The resulting polymeric material was mixed with graphite and nujol to give a new composite material from which a modified graphite paste electrode (MGPE) was elaborated and applied for electro-oxidation of methanol and its analogs. The