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Electrooxidation of benzyl alcohol and benzaldehyde on a nickel oxy-hydroxide electrode in a filter-press type cell

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Abstract

The electrooxidation of benzyl alcohol and benzaldehyde in alkaline medium was carried out in a filter-press type cell on a nickel oxy-hydroxide electrode under different experimental conditions. An overpotential occurs in the presence of organic molecules in the solution shifting oxygen evolution towards higher potentials. The results obtained were conclusive that benzyl alcohol and benzaldehyde electrooxidation on NiOOH layers yielded benzoic acid as the main final reaction product. Chromatographic analysis of the bulk solution showed that the electrocatalytic oxidation of harmful molecules was carried out until the formation of acid compounds (benzoic acid) as an ultimate stage, suggesting that a Ni anode can be used successfully for waste remediation.

1. Introduction

In relation to environment protection, the complete oxidation of organic molecules contained in pollutants becomes a crucial problem. The degradation of such organic pollutants, aldehydes, phenols and alcohols, has attracted considerable attention due to their high toxicity. The treatment at reasonable costs of hazardous wastewaters containing such pollutants is a difficult challenge. Among various techniques proposed, electrochemical oxidation is a possible alternative for eliminating organic compounds contained in water [1]. It is a clean, attractive and one of the most environmentally friendly methods of treating industrial effluents [2–6]. However, due to the fact that organic pollutants are generally present in low concentrations in industrial effluents, their complete oxidation to carbon dioxide is difficult [7]. Among the molecules which need to be eliminated, aromatic compounds are the most difficult to oxidize due to their stability [7]. In this study we consider benzyl alcohol and benzaldehyde as model molecules. Such compounds are harmful to aquatic organisms [2, 8], and authorized emission levels are limited. Thus, it is crucial to reduce such emissions from industrial effluents.

Among possible electrode materials able to oxidize benzyl alcohol only NiOOH electrocatalysts will be considered in this work. Nickel oxides are, among others, one of the most used electrocatalysts for the oxidation of alcohols and aldehydes. It is well known that the mechanism of oxidation of alcohols on Ni/NiOOH depends on the position of the hydroxyl group in the molecule [3]. The oxidation of primary alcohols at a Ni/NiOOH electrode in alkaline medium leads to the formation of organic acids. In the oxidation of secondary alcohols ketones are formed while tertiary alcohols are not oxidized [9–13].

A general mechanism for the oxidation of primary alcohols was proposed by Fleischmann et al. [9, 10]:

$$\mathrm{Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-} \quad (1)$$

$$\mathrm{NiOOH + RCH_2OH \rightarrow Ni(OH)_2 + RC^{\cdot}HOH} \quad (2)$$

$$\mathrm{RC^{\cdot}HOH + 3OH^- \rightarrow RCOOH + 2H_2O + 3e^-} \quad (3)$$

where, step 1 corresponds to the oxidation of the surface of $Ni(OH)_2$ to NiOOH. Step 2 is the surface chemical reaction that involves the adsorption of alcohol on NiOOH and subsequent hydrogen removal from the alcohol by NiOOH. The $Ni(OH)_2$ layer formed in this same step is promptly re-oxidized to the oxy-hydroxide due to the high anodic potential, regenerating NiOOH (step 1) allowing again the oxidation process. Finally, step 3 illustrates the subsequent fast oxidation of the adsorbed intermediate forming the corresponding carboxylic acid. Step 2 was proposed as the rate-determining step in the oxidation of allyl and benzyl alcohols [9, 10, 14–17] where NiOOH participates as a reagent.

The oxidation of a variety of alcohols has been studied on Ni oxide electrodes and in all cases the selective formation of aldehydes and/or carboxylic acids is observed [18–21]. In an earlier paper [17] it was reported that at a nickel anode in aqueous hydroxide solution, benzyl alcohol was oxidized to benzoic acid and/or benzaldehyde depending on the solution pH. In 1 M hydroxide the main product is benzoic acid, but in 0.01 M the amount of aldehyde exceeds that of the acid by a factor of 26 and in neutral medium no benzoic acid was isolated.

Recently, the electrochemical reactivity of benzyl alcohol was studied on platinum and palladium electrodes [22–26]. Oxidation of the adsorbates formed from the alcohol adsorption led to CO_2 on both metals, but some reduction forming benzene was also observed at palladium. Benzyl alcohol and benzaldehyde were chosen as model molecules in order to follow their possible electrooxidation in a filter-press type cell in alkaline medium and at low concentrations of the organic species, typically in a concentration range corresponding to wastewater conditions ($<<100$ mM). The main purpose was to identify the main products formed and to investigate the effect of the variation of some parameters, such as duration and potential of electrolysis. For the type of reactions considered, it is important to investigate the influence of such parameters in relation to reaction mechanism. The nickel oxy-hydroxide electrode was chosen under potential conditions corresponding to oxygen evolution. The oxidation of the electrode surface was carried out under strictly controlled conditions prior to the experiment with organic molecules, so that it could be done in a more controlled way.

The products formed during the electrooxidation process were followed by HPLC. This technique enables direct chemical identification of the reaction products. This allows an assessment of the selectivity of the NiOOH electrocatalyst towards the formation of oxidation products from benzyl alcohol.

Nickel anodes have been used industrially in alkaline medium to produce hydrogen by water electrolysis. This material is very attractive for long-term use in alkaline medium. In addition, the possibility of electrodepositing a thin metallic nickel layer on a cheap substrate is of economic interest.

2. Experimental

All the electrolyses were carried out in a filter-press type cell, model AB (ElectroCell Systems), which contained two compartments separated by an ionic membrane (IONAC 3470) (Figure 1). The working electrode had a geometric surface area of 14 cm^2, while the counter electrode was a platinized titanium plate. In the filter-press type cell, the electrolyte was circulated through the two compartments using a peristaltic pump with a flow rate of 5 $cm^3\ s^{-1}$. The anolyte was a solution of benzyl alcohol or benzaldehyde (pro analysi grade – Merck) in 0.01 M NaOH (Merck Suprapur), and the catholyte was an aqueous solution of NaOH. Alkaline solutions were used to maintain the stability of the oxide electrode. All the solutions were prepared with ultrapure water provided by a Milli-Q Millipore system. In order to carry out the experiments potentiostatically, a reference $Hg/Hg_2SO_4/SO_4^{=}$ (MSE) electrode was used. This electrode was ionically connected through the IONAC membrane, part of which was immersed in a saturated solution of potassium sulphate. Some electrolyses were also conducted at a constant current using the same experimental set-up.

In order to observe the state of the electrode surface, a voltammogram was recorded before applying the electrolysis potential. Voltammetric experiments were carried out in a one-compartment conventional three-electrode Pyrex cell (V = 10 cm^3). The working electrode consisted of a disc of nickel with a geometric

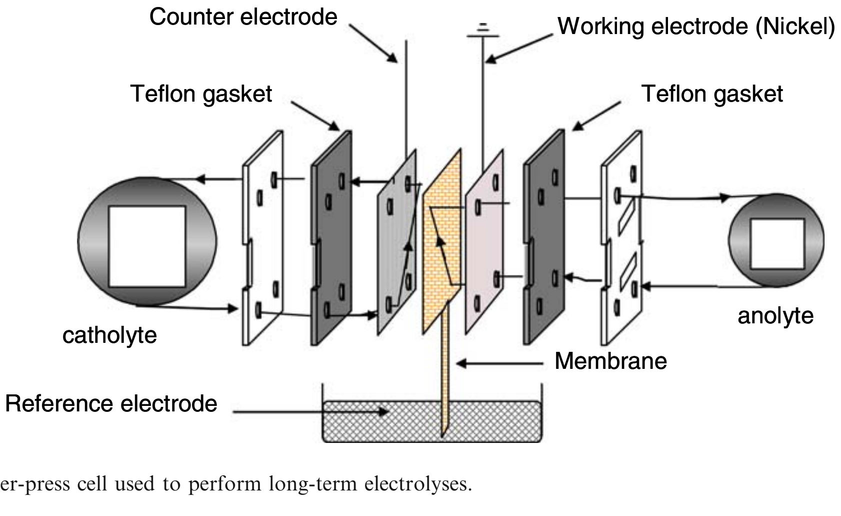


Fig. 1. Scheme of the filter-press cell used to perform long-term electrolyses.

surface area of 0.07 cm^2. The current densities are given based on the geometric surface area. A glassy carbon and a $Hg/Hg_2SO_4/K_2SO_4$sat. (MSE) ($E_{REF} = 0.65$ V vs. RHE at pH = 0) served as counter and reference electrodes, respectively. This electrode was separated from the solution by a Luggin–Haber capillary tip. All the electrochemical experiments were carried out at room temperature (21 ± 1 °C).

During electrolyses samples of the solution were taken at given times and analysed by High Performance Liquid Chromatography (HPLC). This equipment comprised a Spectra-Physic SP P100 pump, with a Spectra-Physic SP8490 UV Detector, set at 210 or 254 nm, and an integrator-calculator (Spectra-Physic Chromjet). The electrolysis products were separated using a RP18 Lichrospher 5 column, with an eluent composed of a 30/70 mixture of acetonitrile and water with 0.26% of sulphuric acid in order to keep the pH = 1. This composition of eluent, at a 1 cm^3 min^{-1} flow rate, gave the best results, mainly for the determination of the concentration of benzoic acid. The products formed during the bulk electrooxidation of benzaldehyde were determined by comparing their retention times to those of pure reference products under the same analysis conditions. The mass balance was calculated by determining the relative quantity of each reaction product as follows: $(\%) = \frac{C_i}{C_0 - C_t} \times 100$ where C_0 is the initial concentration of the substrate, C_t is its concentration at the end of electrolysis, and C_i is the concentration of the considered compound.

3. Results and discussion

Before each electrolysis the nickel electrode was maintained at a potential of 1.9 V vs. MSE for 30 min in the alkaline solution to renew the oxy-hydroxide layer. This procedure allowed reproducible results, as seen in the cyclic voltammogram of the Ni/NiOOH electrode taken before each experiment; however good control of the oxy-hydroxide layer thickness could be obtained by cyclic oxidation–reduction procedures [13].

Figure 2 shows the voltammogram of a Ni electrode in alkaline solution at a sweep rate (v) of 50 mV s^{-1}. The shape of the voltammogram in the supporting electrolyte (0.01 M NaOH) shows the expected behaviour for a $Ni/Ni(OH)_2/NiOOH$ electrode, with the surface oxidation peak at +0.21 V vs. MSE, during the positive sweep, and the reduction peak at −0.1 V vs. MSE, during the negative scan. The peak separation is 310 mV. This parameter depends on the electrolyte concentration and slightly on the scan rate, and it is described in the literature as having typical values ranging from 50 mV to 120 mV [17, 27–29]. Thus, an uncompensated IR drop of around 150 mV ($R \approx 3\ \Omega$) is influencing our data. This IR drop includes the electrolyte and the membrane resistivity, and the former component has the highest contribution. The charges under the oxidation and reduction peaks are approximately equal (≈3.5 mC cm^{-2} of geometric surface area) and indicate that, after the deep previous surface oxidation to form the oxy-hydroxide, the roughness factor is around 2.5, compared with the charge associated to a smooth surface prepared by polishing to a mirror-like finishing [24]. Several papers [27–37] have discussed the nature of the surface oxidation/reduction processes as described in Eq. (1). For the specific case of the electrode used in this work, where a nickel foil is covered by a layer of NiOOH, formed at high anodic potentials, in the lower potential region of the voltammogram (between −0.6 and −0.1 V vs. MSE), nickel hydroxide is expected to be formed as an overlayer on the Ni/NiOOH electrode, by surface reduction of the previously NiOOH anodically growth [24]. The $Ni(OH)_2$ layer is non-conducting so that the Faradaic current drops to zero. Further oxidation of Ni(II) to Ni(III) occurs in the anodic peak, regenerating the original NiOOH surface.

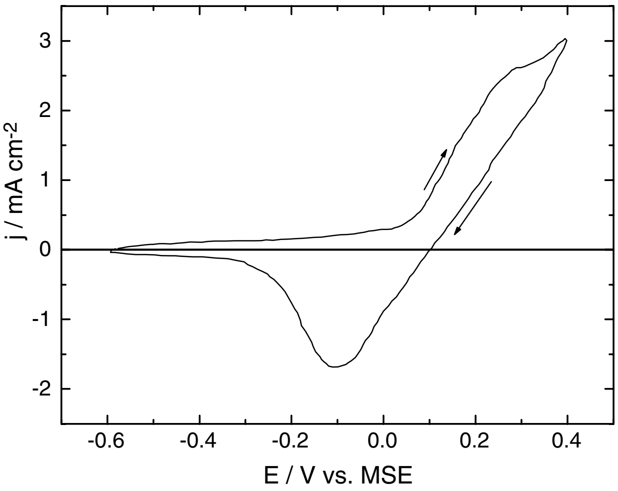


Fig. 2. Voltammogram of a nickel electrode (14 cm^2) in a 0.01 M NaOH alkaline medium recorded at 50 mV s^{-1} and at room temperature in the filter-press cell.

3.1. *Oxidation of benzyl alcohol in alkaline medium*

3.1.1. *Cyclic voltammetry*

The voltammograms of nickel were obtained with an electrode of a small geometric surface area (0.16 cm^2) in order to avoid the consumption of reagent during the study. In supporting electrolyte (Figure 3(a)), the voltammogram was recorded with a potential limit of 0.4 V vs. MSE just before oxygen evolution, i.e. after the formation of NiOOH which is the electroactive material.

Figure 3(b) presents the voltammogram in the presence of 17 mM benzyl alcohol in the same potential range as in the supporting electrolyte alone. The oxidation of the alcohol begins at 0.25 V vs. MSE i.e. at the NiOOH surface. The voltammogram of Figure 3(c) was recorded by setting the upper potential limit at 1.2 V in order to show the behaviour of the electroreactive species. It can be seen that oxidation of benzyl alcohol involves an

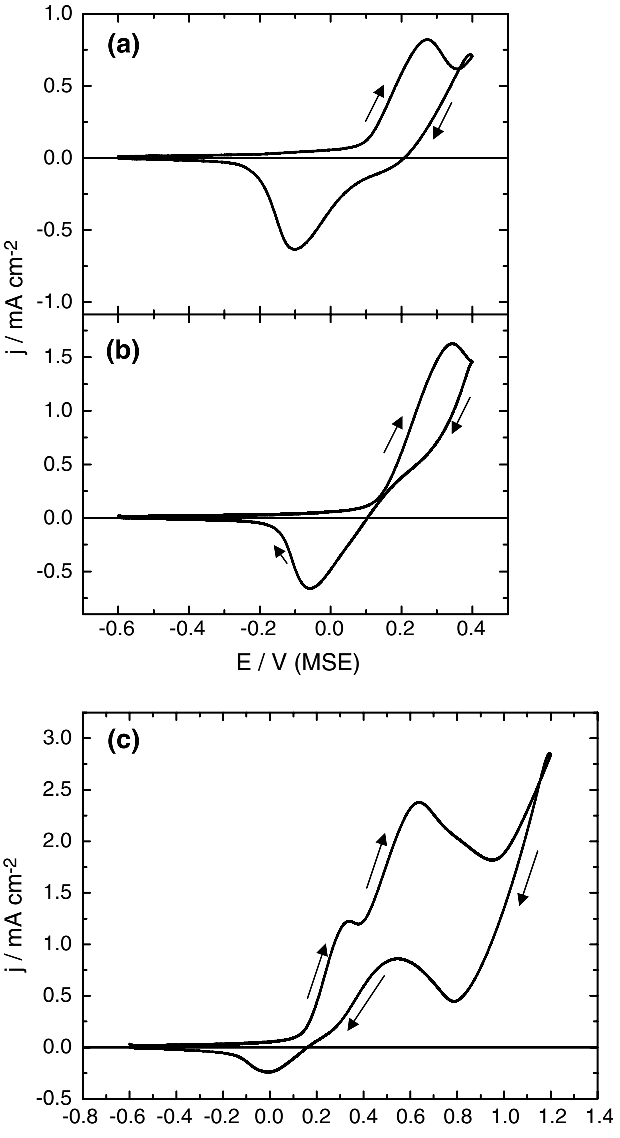


Fig. 3. Voltammograms of a nickel electrode in alkaline medium recorded at 50 mV s^{-1} (a) in the supporting electrolyte 0.01 M NaOH (b) in the presence of 17 mM benzyl alcohol (c) as in (b) with an upper potential limit of 1.2 V.

overpotential which shifts oxygen evolution to higher potentials. This is usual for the electrooxidation of alcohols at a nickel electrode [9–21].

3.1.2. *Electrolysis of benzyl alcohol*

A common problem during the oxidation of organics at anodic potentials close to the beginning of oxygen evolution is the significant decrease in anodic current as a consequence of surface poisoning by reaction intermediates which can be oxidized only at very high anodic potentials inside the oxygen evolution region. Then, the application of high anodic potentials into the oxygen evolution region, allows regeneration of the anode surface during oxidation of the organic compound. Thus, in this study the electrochemical oxidation of benzyl alcohol was carried out under conditions of simultaneous oxygen evolution.

Electrolyses of benzyl alcohol were carried out with a concentration of 0.017 M benzyl alcohol in 0.01 M NaOH. In order to investigate a possible effect of oxidation potential, different electrolyses were performed between the formation of NiOOH (0.25 V) and 0.5 V vs. MSE. This potential range is located inside that of oxygen evolution. A rapid decrease of current density was observed. Hundred μl samples were removed directly from the cell anolyte output and analysed by HPLC.

Two reaction products, benzaldehyde and benzoic acid, were detected and identified by chromatographic analysis. It clearly appears that there is some influence of the oxidation potential. When the oxidation potential increases, the formation of the aldehyde is favoured in comparison to that of benzoic acid, which decreases slowly. The mass balance, considering the three detected components, reaches at least 86% of the total mass, in the whole potential range studied.

During long-term electrolysis of a solution of benzyl alcohol carried out at 0.5 V vs. MSE, it was possible to follow the variation of the concentrations of the reactant and products. After chromatographic analysis, the concentrations of the remaining benzyl alcohol and of the two products formed, benzaldehyde and benzoic acid, were plotted as a function of the electrolysis time as shown in Figure 4.

The concentration of benzyl alcohol decreases regularly with time from 0.017 to 0.003 M in 330 min of electrolysis. Up to now, there is no experimental evidence for the formation of benzoic acid directly from benzyl alcohol. The kinetics of formation of the aldehyde and of the acid are different. The concentration of aldehyde increases much faster at the beginning of electrolysis, passes through a maximum after 150 min and then decreases slowly. Conversely, the concentration of benzoic acid increases slowly for times up to about 200 min and then increases faster for longer

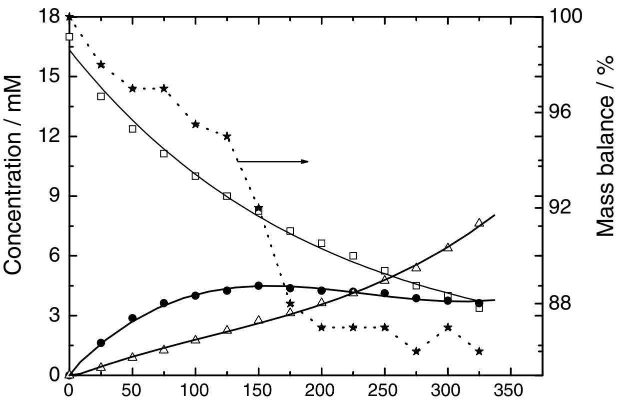


Fig. 4. Plots giving the distribution of reaction products vs. time, during the oxidation of 17 mM benzyl alcohol oxidation on a nickel electrode in 0.01 M NaOH; (□) benzyl alcohol, (•) benzaldehyde, (△) benzoic acid and (⋆) the variation of the mass balance.

electrolysis times. This behaviour can be explained by a partial competition of a direct conversion of benzyl alcohol to the final reaction product.

From the general shape of the curves in Figure 4, it is difficult to decide on a mechanism for the electrooxidation of benzyl alcohol. However, it clearly appears that benzaldehyde is the main primary product as it is formed immediately. But after some time, benzaldehyde is oxidized as can be seen in Figure 4. This decrease in the concentration of benzaldehyde corresponds to the faster increase in the rate of formation of benzoic acid after 200 min of electrolysis.

The total amount of reactant consumed and products formed decreases during electrolysis. After 330 min of electrolysis, a difference of about 14% between the total amount of both reactant and products, and the initial concentration of benzyl alcohol was observed. The main reason for this is that benzyl alcohol crosses over the membrane separating the anolyte and catholyte solutions. The consequence of this cross over is taken into account in the calculated mass balance. It was difficult to find a separator completely avoiding this phenomenon. At the end of electrolysis the main part of the missing amount of benzyl alcohol was detected in the catholyte. Also, it is possible that small amounts of gaseous products, or polymerized products remaining at the electrode surface were formed and not detected in the potential range where the oxygen evolution occurs. Benzaldehyde in the presence of an alcohol (benzyl alcohol in this case) can form a polymerized film at the electrode surface [3].

3.2. *Oxidation of benzaldehyde*

The voltammograms corresponding to the electrooxidation of benzaldehyde at a Ni oxy-hydroxide electrode are given in Figure 5. As described previously for benzyl alcohol, it can be seen that benzaldehyde starts being oxidized at the surface of NiOOH (0.25 V vs. MSE). These changes in the voltammogram suggest that the electrochemistry of the surface oxidation/reduction processes is affected by the organic species, by interaction with the NiOOH layer (Figure 5(a, b)). The voltammogram in Figure 5(c) was recorded with an upper potential limit set at 1.2 V vs. MSE to show that benzaldehyde behaves as many organic compounds on such electrodes by shifting the oxygen evolution to high potentials [38].

Electrolyses of benzaldehyde were carried out with a concentration of 0.014 M benzaldehyde in 0.01 M NaOH. Initially possible effects of the oxidation potential at values ranging from 0.4 to 1.1 V vs. MSE were investigated. Under these operating conditions the electrooxidation of benzaldehyde was carried out with simultaneous oxygen evolution at 1.1 V vs. MSE.

Figure 6 displays the results of a long-term electrolysis carried out at 0.9 V vs. MSE of a solution of 0.014 M benzaldehyde in 0.01 M NaOH. The chromatographic

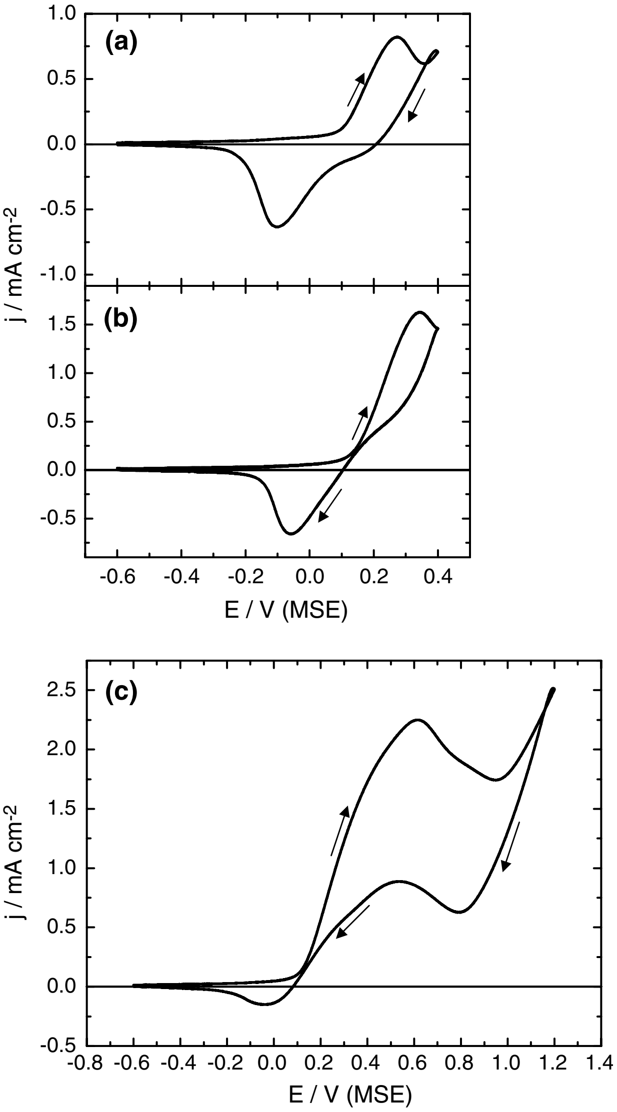


Fig. 5. Voltammograms of a nickel electrode in a 0.01 M NaOH alkaline medium recorded at 50 mV s^{-1} (a) in the supporting electrolyte 0.01 M NaOH (b) in the presence of 14 mM benzaldehyde. (c) as in (b) with an upper potential limit of 1.2 V.

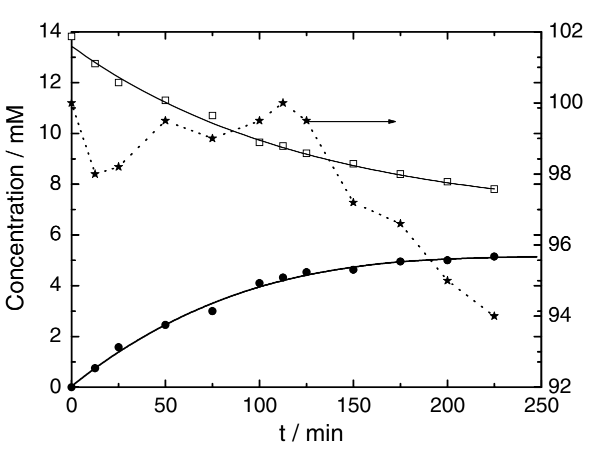
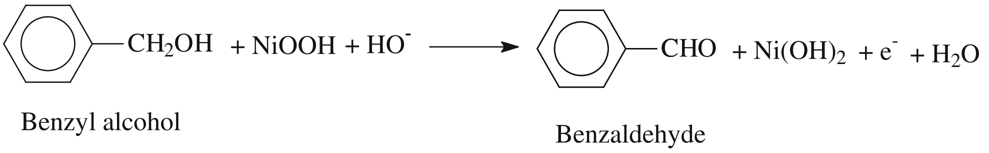


Fig. 6. Plots giving the concentration of reaction product vs. time during the benzaldehyde electrooxidation at 0.9 V vs. MSE on nickel in 0.01 M NaOH; (□) benzaldehyde, (•) benzoic acid and (★) the variation of the mass balance.

analysis of the bulk solution shows that benzoic acid is the main product of the anodic transformation of benzaldehyde at the NiOOH surface. Evaluation of the two detected components gives a total mass balance close to 94% and suggests the presence of small amounts another reaction product.

From the results of the electrolyses presented above, it is possible to infer the reaction mechanism of benzyl alcohol and benzaldehyde electrooxidation. Under the experimental conditions used with a nickel oxy-hydroxide electrode in alkaline medium, benzoic acid is the main final product of the oxidation of benzaldehyde. Provided that NiOOH is the oxidation state of the electrode surface when electrolysis is carried out at potentials higher than 0.25 V vs. MSE, it can be suggested that benzyl alcohol is oxidized as follows:



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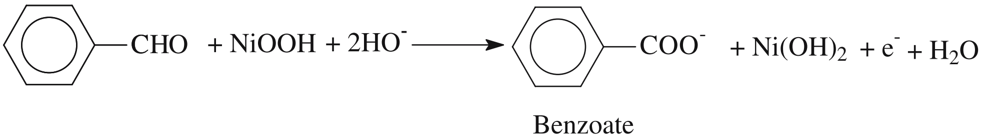
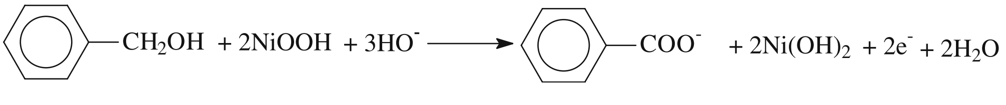


(5)

As HPLC was the main technique used to perform product analysis in the bulk solution, it can also be proposed that benzyl alcohol is transformed directly into benzoic acid at the NiOOH electrocatalyst:



(6)

No evidence of the cleavage of the C–C bond was observed. However, the conversion of benzyl alcohol and benzaldehyde to benzoic acid indicates that Ni anodes can be used successfully for wastewater remediation.

4. Conclusions

The electrooxidation of benzyl alcohol and its derivative was carried out on NiOOH layers in 0.01 M NaOH in order to minimize the Cannizzaro reaction that occurred in the presence of the aldehyde in a strong alkaline supporting electrolyte. As mentioned previously [17], a dilute supporting electrolyte induces successive reactions, which proceed by the oxidation of benzyl alcohol to benzoic acid via the corresponding aldehyde. Benzaldehyde and benzoic acid are mainly formed during the early stages of the reaction. However, in these experiments the initial rate of formation of benzaldehyde, 7.7×10^{-5} min^{-1}, is much higher than the rate of formation of benzoic acid, 1.9×10^{-5} min^{-1}. Additionally, the rate of formation of the aldehyde decreases regularly, while that of benzoic acid remains more or less constant up to 150 min and then increases twofold when the concentration of benzaldehyde starts diminishing. This confirms that Ni anodes can be used as electrocatalysts for waste remediation.

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