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Electrochemical oxidation of isobutanol to isobutyric acid at nickel oxide electrode: improvement of the anode stability

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Electrooxidation processes using nickel oxide anodes in alkaline electrolyte offer good alternatives to the chemical processes used for the oxidation of alcohols. However, they suffer from the low stability of the electrodeposited layer of nickel oxide, resulting in poor current efficiency. This requires periodic reactivation of the anode. In the present work, different parameters governing the stability of the nickel oxide layer have been identified and their influence on the current efficiency for oxidation has been investigated using oxidation of isobutanol (2-methyl-1-propanol) to isobutyric acid (2-methylpropionic acid) as a model system. Alternative anode activation procedures have been studied. The procedures employed resulted in a five fold increase in the anode stability over earlier reported procedures for anode activation and electrolysis.

1. Introduction

Alcohols can be converted to the corresponding acids in alkaline solutions at a nickel oxide anode and this method has been investigated for the manufacture of aromatic and aliphatic acids at laboratory/pilot plant scale. Recent applications include oxidation of isopropylideneglycerol to the corresponding carboxylic acid [1]. Its methyl ester is a versatile intermediate for the synthesis of chiral lipids. This process has also been extensively studied for the manufacture of diactone-2-ketogulonic acid which is an intermediate for vitamin C synthesis. It is superior to the conventional processes that employ chromium salts, hypochlorite, etc., particularly because of less pollution [2], but suffers from low stability of the active nickel oxide coated on the electrode surface. Loss of the active layer during electrolysis requires periodic reactivation of the electrode after electrolysis to maintain higher current efficiency. In a previous communication [3] we have reported on the oxidation of isobutanol to isobutyric acid at nickel oxide electrode. The present work is an extension of the previous work and deals with techniques to obtain a more stable nickel oxide coating resulting in higher electrode life and consequently stable high current efficiency for the oxidation process.

Various methods/procedures have been suggested to improve the stability of the nickel oxide anode. Briggs *et al.* [4] have studied different methods of preparation of nickel oxide electrode. These are (i) by chemical attack of NaOCl on nickel, (ii) electrodeposition of nickel oxide and (iii) anodic attack on nickel. Out of these three methods electrodeposition of nickel oxide was the most appropriate. Briggs *et al.* have characterized the nickel oxide layer formed at different activation current densities and the number of cycles of polarity reversal used during activation. In our previous investigation we used the electrodeposition method suggested by Briggs *et al.* However, this method yielded a low current efficiency of 60% and required reactivation of the anode before next use to maintain this current efficiency. Thus, the method of Briggs *et al.* was modified to give a current efficiency of 96% [3]. This modified method increased the anode life from 4 to 14 electrolysis hours for a drop in current efficiency upto 80%. Use of different electrolysis conditions solely with the objective of increased anode life is also possible. For example, addition of surfactants (substituted polyglycol ethers) to the electrolyte has been suggested for this purpose [5]. During electrosynthesis of diacetone-2-ketogulonic acid at iron oxide electrodes, solvents such as xylene or anisole have been used to suppress the rapid loss of electrode activity [6]. It is also reported that addition of small amounts of nickel salt during electrolysis maintains the activity of the anode over long periods [2]. In the present paper, various factors which govern the stability of the deposited nickel oxide layer are investigated and are optimized to give maximum current efficiency and anode life.

2. Experimental details

2.1. *Electrolyser*

The FM01-LC laboratory process package supplied by ICI Chemicals and Polymers (UK) was used in this work and details of the setup are given in our previous paper [3]. All experiments were carried out

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in an undivided cell with nickel oxide deposited on a nickel electrode ($0.0064\,m^2$) as anode and stainless steel electrode ($0.0064\,m^2$) as cathode. The interelectrode gap was maintained at 6 mm.

2.2. *Materials*

Analytical grade isobutanol, nickel sulfate, sodium acetate, lithium hydroxide and sodium hydroxide supplied by Loba Chemie, India, were used.

2.3. *Conditions of electrolysis*

Experiments were conducted galvanostatically. Isobutanol (30 g) was added to 500 ml of aqueous alkali as electrolyte in a three necked flask fitted with a condenser. The flask was placed in an electromantle which was used for temperature variation. The reaction mixture from the flask was pumped into the electrolyzer with a magnetically driven PTFE pump. Experiments were carried out at current density of $1094\,A\,m^{-2}$ ($I = 7\,A$). The flow rate was monitored using a rotameter.

2.4. *Activation of anode* [3]

Before each electrolysis, a thin layer of nickel oxide was deposited on the nickel anode from an aqueous solution containing 0.05 M nickel sulfate, 0.1 M sodium acetate and 0.005 M sodium hydroxide at a current density of $6.25\,A\,m^{-2}$[3]. By manual polarity switching the nickel electrode was alternatively used as anode and cathode for 1 min. This constitutes one cycle. Four such cycles were used followed by two cycles where polarity was changed after 2 min [4]. Keeping the nickel electrode as anode, activation was further continued for a total time of 1 h.

After 1 h of activation, the used electrolyte was replaced with a fresh electrolyte (aqueous solution containing 0.05 M nickel sulfate, 0.1 M sodium acetate and 0.005 M sodium hydroxide) and activation was continued without change in polarity of the electrodes (keeping nickel oxide electrode as anode) for the next 1 h. During activation the electrolyte temperature was maintained at 33 °C.

2.5. *Strategy of investigation*

For investigating the effect of a particular parameter on the anode stability, each parameter was studied in a series of batch experiments as described below:

(a) Activation of the anode was carried out using the procedure described in Section 2.4. Modifications made in the above procedure during investigation of a particular parameter are described in Section 3.

(b) Electrolysis was carried out till the charge required for 60% conversion of isobutanol was passed (26.01 A h) and current efficiency for the experiment was checked. This denotes one batch experiment.

(c) The second and subsequent batch experiments were carried out with the anode used in the first batch experiment (anode was not reactivated before electrolysis). Electrolysis was performed till 26.01 A h of charge was passed and the current efficiency was checked.

(d) Such batch experiments were carried out with the anode used in the previous batch experiment until there was a significant drop in the current efficiency.

The summary of experimental strategy is given in Table 1.

2.6. *Analysis*

Quantitative analysis was carried out using gas chromatography as described in our previous paper [3].

3. Results and discussion

3.1. *Effect of periodic addition of alkali on anode stability*

The layer of nickel oxide on the electrode surface mediates the oxidation of an organic substrate in alkaline conditions. The mechanism of the reaction is [1]:

$$Ni(OH)_2 + OH^- - e^- \rightarrow NiO(OH) + H_2O$$
$$NiO(OH) + RCH_2OH \rightarrow Ni(OH)_2 + RCH^{\bullet}OH$$
$$RCH^{\bullet}OH + 3OH^- \rightarrow RCOOH + 2H_2O$$

During the electrolysis, this black deposited layer of nickel oxide flakes off the electrode surface thus progressively lowering the current efficiency. Several workers have studied the loss of deposited oxide in alkaline medium. Sugita [7] found that, in alkaline batteries with nickel oxide electrodes, decrease in the discharge capacity was due to crystallization of the active nickel oxide by alkali, resulting in loss of active

Table 1. Summary of activation procedure

Parameter	*Anode activation*
Periodic addition of alkali	Procedure described in Section 2.4 [3]
High temperature activation	Procedure described in Section 2.4 [3] except temperature was maintained at 60 °C
Activation with LiOH	Procedure described in Section 2.4 [3] except in place of 0.005 M NaOH, 0.005 M LiOH was used
Electrolysis with LiOH/NaOH electrolyte	Procedure described in Section 2.4 [3]

surface. It was observed that addition of LiOH maintained the performance of the battery even after 5000 cycles and the amount of active material sedimented was lower whereas batteries without LiOH retained only 57% capacity after 3000 cycles. Addition of LiOH to the electrolyte prevents crystallization of active material, thus preventing loss of active material from the electrode surface. It appears that the alkali concentration in the bulk electrolyte has some influence on the stability and adherence properties of the nickel oxide layer and a highly alkaline condition is probably detrimental to the nickel oxide coating. Jones and Wynne-Jones [8] have also observed the influence of alkali concentration on the self-discharge of the nickel oxide layer resulting in loss of active layer. Therefore, it was decided to study the effect of the amount of alkali present in the bulk electrolyte during electrolysis. Activation of the anode was carried out using the procedure described in Section 2.4. Experiments were carried out with periodic addition of alkali to the electrolyte. Low alkali concentration in the bulk may increase the anode stability, but it decreases the process current efficiency [3, 9]. Thus to obtain an alkali concentration which is optimum for high current efficiency and maximum anode stability, experiments were carried out on the basis of the alcohol to alkali mole ratio. Moles of alcohol represents the amount of alcohol consumed equivalent to charge passed and moles of alkali represents alkali added to the electrolyte. Thus, at different mole ratios with the same conversion level (for the same amount of charge passed and different amount of alkali added to the bulk electrolyte) an optimum concentration of alkali with acceptable current efficiency and anode stability can be obtained. Thus, at a mole ratio of 0.485, 8.07 g of alkali was added to the reaction mixture (30 g of isobutanol and 500 ml water) at the start of the experiment and electrolysis was continued until 10.5 A h of charge was passed. After this 8.07 g of alkali was again added to the reaction mixture and electrolysis was continued to 10.5 A h. The experiment was recommenced after the addition of 3.86 g of alkali to the reaction mixture and was continued to 5.01 A h. Thus, 20 g of alkali was added to the reaction mixture for 26.01 A h of charge passed (8.07 g/10.5 A h + 8.07 g/10.5 A h + 3.86 g/5.01 A h). Similarly, for a mole ratio of 0.55 addition was (7.12 g/10.5 A h + 7.12 g/10.5 A h + 3.40 g/5.01 A h) and for mole ratio of 0.65 addition was (6.03 g/10.5 A h + 6.03 g/10.5 A h + 2.88 g/5.01 A h). Results of these experiments are shown in Fig. 1. Set (a) represents the experiment carried out at a mole ratio of 0.485 without periodic addition of alkali. Sets (b), (c) and (d) represent experiments carried out with periodic addition of alkali at mole ratios of 0.485, 0.55 and 0.65, respectively.

These results clearly show that for the same mole ratio of 0.485 for sets (a) and (b) there is an increase in the anode stability from 14 electrolysis hours to 35 electrolysis hours, respectively, for drop in current efficiency to 80%.

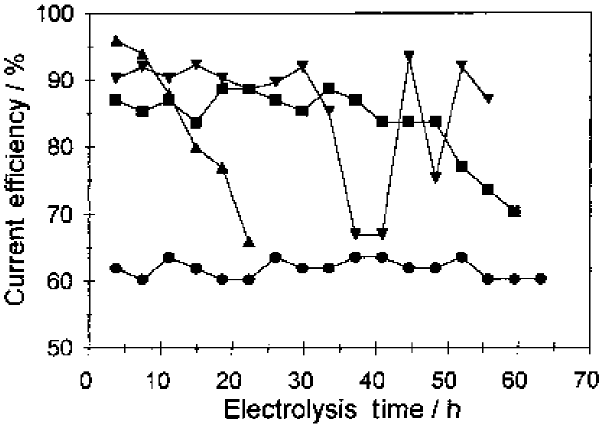

Fig. 1. Effect of periodic addition of alkali on anode stability. (▲) Set (a). Conditions: current density 1094 A m^{-2}, charge passed 26.01 A h, isobutanol 30 g, NaOH 20 g, temperature 33 °C. (▼) Sets (b), (■) (c) and (●) (d). Conditions: current density 1094 A m^{-2}, charge passed 26.01 A h, isobutanol 30 g, temperature 33 °C, periodic addition of alkali during electrolysis.

In set (c) at a mole ratio of 0.55, anode stability was increased to 50 electrolysis hours for drop in current efficiency to 80%. For a mole ratio of 0.65 (experimental set d), a very low current efficiency of 60% was obtained. During electrolysis with periodic addition of alkali, a continuous drop in the current efficiency from mole ratio of 0.485 to 0.65 was observed. The mole ratio of 0.55 was found to be ideal for consistently high current efficiency for a longer time.

Degner [2] has reported that small amounts of nickel salt added to the electrolyte during electrolysis maintains activity of the anode over a long period. Addition of nickel salt probably suppresses the loss of active layer from the electrode surface. Jones and Wynne-Jones [8] in their work on the electrochemical behaviour of the nickel oxide electrode in alkaline solution have observed dissolution of nickel oxide from the electrode surface under open circuit conditions. To suppress the loss due to dissolution, they used an electrolyte saturated with nickel hydroxide. However, this procedure produced a marginal effect. It is also possible that addition of nickel salt to the electrolyte during reaction may be causing electrodeposition of nickel oxide on the electrode surface thus maintaining the activity of the anode. To verify this, activation of the anode was carried out under alkaline conditions as follows. To the solution of 0.05 M nickel sulfate, a small amount of sodium hydroxide was added to make it sufficiently alkaline to precipitate nickel hydroxide and then the alkali concentration was increased to 1 M by addition of sodium hydroxide to the solution. This solution was used for anode activation using the activation procedure reported in Section 2.4 [3]. However, no deposition of nickel oxide on the electrode surface was observed. At a mole ratio of 0.485 in experimental set (b), after a drop in current efficiency to 66% when 2 g. of nickel sulfate was added to the reaction mixture, current efficiency was increased to 92%. However, it again dropped to 75% in the next experiment. When the same amount of nickel sulfate was added to the electrolyte in the next experiment, again the current efficiency increased to 92%, but dropped to 87% in the next experiment. These results suggest that addition of nickel sulfate to the electrolyte during electrolysis causes temporary deposition of the nickel oxide on the electrode surface which probably flakes off over a period.

3.2. *Effect of higher temperature activation of the anode on anode stability*

During activation, layers of nickel oxide are formed on the electrode surface when it is anodically polarized. However, they are rapidly built-up if the electrode is anodically/cathodically cycled. Thus when the electrode is made cathodic, nickel hydroxide deposits on the electrode surface which gets oxidized in the anodic cycle [4]. Electrolytic oxidation of $Ni(OH)_2$ depends on the removal of protons from the lattice by transport through the solid phase [8]. At ambient temperatures the transport of an ion through a solid phase is slow and likely to be the rate determining step [10]. At higher temperature, ion diffusion becomes faster compared to electron transfer and the adatom is likely to end up in a favoured position in the lattice [10]. At higher temperature, the lower IR drop is also likely to result in a more uniform rate of deposition over the electrode surface. Activation of the electrode was carried out using the activation procedure described in Section 2.4 except that the electrolyte temperature was maintained at 60 °C which is higher than the ambient but lower than the boiling point of the electrolyte. Electrolysis was carried out using a reaction mixture consisting of 30 g of isobutanol and 500 ml of 1 M sodium hydroxide at 33 °C. The results in Fig. 2. show a clear increase in the anode stability from 14 to 90 electrolysis hours for a drop in current efficiency to 80%, when the activation temperature was increased from 33 °C to 60 °C. It was also observed that the coating obtained with high temperature activation could not be easily rubbed off whereas the coating with low temperature activation was prone to rub off with the slightest physical contact/shear.

3.3. *Effect of anode activation using lithium hydroxide on anode stability*

A number of workers have worked on improving the performance of nickel oxide electrodes used in alkaline batteries. Kuchinskii and Ershler [11] detected a film of NiO at the metal surface that seriously limited the discharge capacity of the plate because the poorly conducting film isolated the active material electrically from the positive plate. Tichenor [12] suggested that, after addition of LiOH to KOH electrolyte, Li^+ion enters into the poorly conducting NiO film, thus imparting a high conductivity which increases the performance of the battery. According to Sugita [7], as described previously, in alkaline batteries with nickel oxide electrodes, a decrease in the discharge capacity is due to the crystallization of the active nickel oxide by alkali, resulting in loss in active surface. Addition of LiOH to the KOH electrolyte prevents the crystallization of the nickel oxide. In the present work the same principle was extended to increase the anode stability during electrochemical synthesis. Anode activation was carried out using the normal activation procedure [3] except that 0.005 M LiOH was used instead of 0.005 M NaOH. The anode thus obtained was used for oxidation experiments using a reaction mixture consisting of 30 g of isobutanol and 500 ml of 1 M sodium hydroxide at 33 °C. Results shown in Fig. 3 clearly indicate an

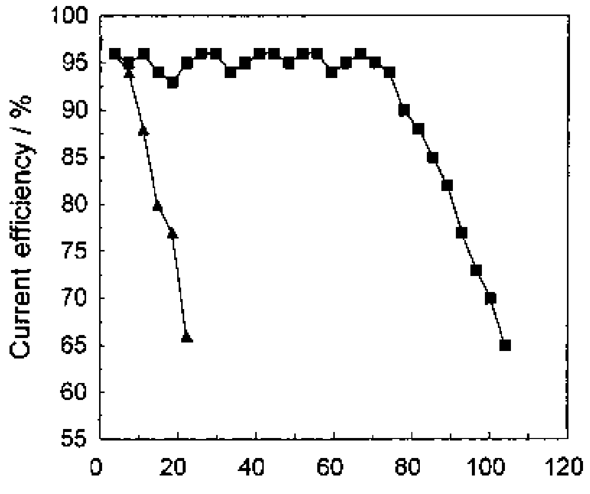

Fig. 2. Effect of higher temperature activation of the anode on anode stability. Temperatures: (■) 66 °C and (▲) 33 °C. Conditions: current density 1094 A m^{-2}, charge passed 26.01 A h, isobutanol 30 g, NaOH 20 g, temperature 33 °C.

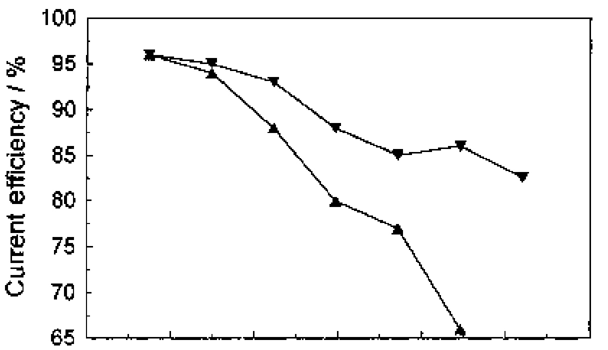

Fig. 3. Effect of the activation of the anode using lithium hydroxide on anode stability. (▲) Activation using NaOH and (▼) activation of anode using LiOH. Conditions: current density 1094 A m^{-2}, charge passed 26.01 A h, isobutanol 30 g, NaOH 20 g, temperature 33 °C.

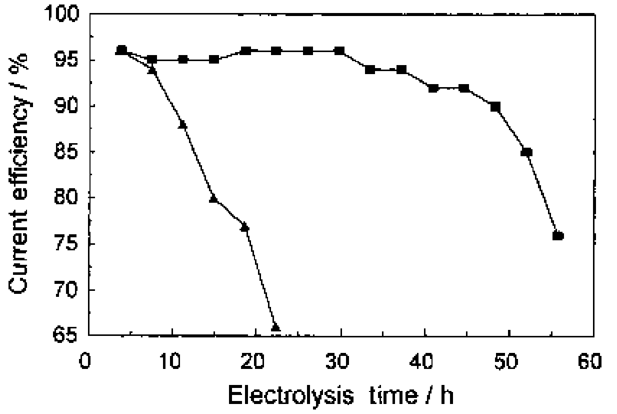

Fig. 4. Effect of addition of lithium hydroxide to the sodium hydroxide electrolyte on the anode stability. (▲) NaOH electrolyte. Conditions: current density 1094 A m^{-2}, charge passed 26.01 A h, isobutanol 30 g, NaOH 20 g, temperature 33 °C. (■) LiOH/NaOH electrolyte. Conditions: current density 1094 A m^{-2}, charge passed 26.01 A h, isobutanol 30 g, NaOH 18 g, LiOH 2 g, temperature 33 °C.

increase in nickel oxide stability due to the presence of LiOH. However, this increase in the anode life (from 14 to 26 electrolysis hours for drop in current efficiency upto 80%) is not very significant.

3.4. *Effect of addition of lithium hydroxide to the sodium hydroxide electrolyte on anode stability*

Since replacement of NaOH by LiOH during activation of anode resulted in some increase in the anode life, experiments were carried out by adding LiOH to the electrolyte used for actual electrolysis. Thus a LiOH/NaOH electrolyte (1:9 by weight) was used during electrolysis. Oxidation experiments were carried out using a reaction mixture of 30 g of isobutanol and 500 ml aqueous solution of LiOH/NaOH(2 g + 18 g) as electrolyte at 33 °C. The results shown in Fig. 4 clearly indicate increase in the anode stability from 14 to 55 electrolysis hours for drop in current efficiency to 80%.

4. Conclusions

Electrolytic processes for alkaline oxidation of alcohols at nickel oxide electrodes have the major disadvantage of poor anode stability. In the present work, an attempt has been made to improve anode stability using oxidation of isobutanol (2-methyl-1-propanol) to isobutyric acid (2-methylpropionic acid) as a model system. From the results obtained the following conclusions can be drawn:

(i) Periodic instead of single time initial addition of alkali favours anode stability.
(ii) Activation of the anode carried out at a higher temperature of 60 °C results in a firm deposit with increased anode stability.
(iii) Use of lithium hydroxide in the electrolyte during anode activation and during electrolysis increases anode stability.

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