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Short Communication

The use of hydrated nickel–cobalt mixed oxide electrodes for oxidation of aliphatic and aromatic alcohols

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Abstract

Voltammetric studies and galvanostatic oxidation results for the electrochemical oxidation of octyl. hexyl, butyl, isobutyl and benzyl alcohols on hydrated nickel-cobalt oxide electrode in alkaline media are reported. These compounds are oxidised to their corresponding acids with high efficiency. The electrodes are not contaminated and hence their repeated use for the oxidation of same or different compounds is possible. Oxidation of benzyl chloride leads to formation of benzyl alcohol, benzaldehyde along with benzoic acid.

1. Introduction

Electrodeposited nickel oxide ($NiOOH/Ni(OH)_2$) electrodes are commonly employed for the oxidation of alcohols to carboxylic acids. Pletcher and coworkers have employed the cathodic deposition of nickel followed by anodic polarisation in alkaline solutions [1–4]. Schäfer and coworkers have recommended a polarity reversal technique for the preparation of nickel oxide electrodes [5–7]. Additions of small quantities of nickel salts and even lithium hydroxide during electrochemical oxidation have also been recommended for improved results [8, 9]. In addition to oxidation of alcohols oxidation of benzyl chloride and related chloromethyl compounds have also been reported [10].

To improve the long-term electrode stability as well as catalytic activity during organic oxidation Trivedi and coworkers have employed alternate electrodeposition of nickel and cobalt layers from two different baths [11]. Pletcher and coworkers have recommended thermally coated spinel type nickel–cobaltite electrodes for this purpose [12, 13]. Further efforts towards improving the electrodeposition condition [14] and aging of the electrode [15] have been reported. Flow cells have also been employed [16]. Recently high surface area nickel foam itself has been recommended for this purpose [17].

Achieving anode stability and sustained catalytic activity during electrochemical oxidation of organic compounds still remain a challenge. Three dimensional porous $Ni(OH)_2$ electrodes with high surface area are commercially employed in the battery industry [18, 19]. Nickel–cobaltite hydrated electrodes are known for their stability and electrocatalytic activity in molten carbonate and solid oxide fuel cells [20]. The possibility of utilising these electrodes directly as anode materials for the oxidation of alcohols and benzyl chloride is evaluated in the present work. Some promising results are presented here.

2. Experimental details

Three types of nickel anodes were employed in the present work. High purity plain nickel (Johnson mathey specpure grade) and positive plate of nickel oxy hydroxide electrode used in Ni–Cd battery (AMCO Power Systems Ltd, Bangalore, India) were employed as such. The hydrated Ni–Co mixed oxide electrode was fabricated as described below.

About 15 g of nickel powder (particle size of about 100 μm) was dissolved in 50 ml of concentrated nitric acid and heated slowly to completely dissolve all the nickel powder in acid to get a saturated solution. The solution was diluted with 50 ml of double distilled water and added 10 g of urea and the solution was kept in a preheated furnace at 823 K. Within a short time combustion took place and a foamy mass of nickel oxide was obtained. The nickel oxide powder thus prepared was mixed with A.R grade cobalt oxide powder in the ratio of 1:1 in a high speed ball milling unit for about 4–5 days with addition of 15 ml of poly vinyl alcohol to get a slurry of mixed nickel oxide and cobalt oxide. Finally the slurry was tape cast or coated on titanium or stainless steel expanded mesh.

The mixed metal oxide powder coated electrodes were dried at 373 K in an oven and sintered in argon atmosphere for about 2–4 h at 773–973 K. The catalytic powder coating and heat treatment processes were repeated 3–4 times to achieve the required thickness. These electrodes were used for the oxidation of alcohols.

Cyclic voltammetric experiments were carried out in a two compartment glass cell. Hydrated nickel–cobalt mixed oxides coated on stainless steel substrate of surface area 0.8 cm^2 were used as the working electrode. A plain nickel electrode of surface area 0.2 cm^2 was also employed for comparison. Hg/HgO and a platinum foil served as reference and counter electrodes, respectively.

Galvanostatic experiments were carried out in an undivided glass cell of 250 ml capacity with a glass lid having provisions for introducing condenser, electrodes and thermometer. About 200 ml of 1 M NaOH was used as the electrolyte for oxidation of *n*-butanol, isobutanol, *n*-octanol, benzyl alcohol and benzyl chloride. 200 ml of 0.18 M KOH containing 50% tertiary butanol + 50% water was used as the electrolyte for oxidation of *n*-hexanol. Nickel–cobalt mixed oxide coated on titanium of area 24 cm^2 was used as the anode with stainless steel of the same size as cathode. The glass cell was placed in a water bath and the bath was maintained at specified temperatures within ± 2 °C.

L.R grade *n*-octyl alcohol, *n*-hexyl alcohol, *n*-butyl alcohol, isobutyl alcohol, benzyl alcohol and benzyl chloride etc were used as such for preparative and cyclic voltammetric studies. The theoretical amount (4 F/mol for alcohols and 5 F/mol for benzyl chloride) of current was passed. The well known procedure reported in the literature [3, 6] was employed for the product isolation and for separation of unreacted alcohol.

The products formed were analysed by GC using a HP6890 Gas chromatograph with FID detector and HPLC using a Shimadzu model LC10AT liquid chromatograph along with a Shimadzu SPD10A uv–vis detector for aliphatic and aromatic compounds, respectively. The material yield efficiency was calculated based on the purity of the product. The product formed was also confirmed by FTIR spectrophotometry. (Perkin-Elmer model Paragon 500).

3. Results and discussion

Cyclic voltammetric experiments were carried out to compare the electrochemical behaviour of the tape cast hydrated nickel–cobalt mixed oxide electrode with that of the plain nickel electrode. Typical cyclic voltammetric responses for plain nickel and hydrated nickel–cobalt mixed oxide electrode recorded in 1 M KOH at different sweep rates are shown in Figure 1(A, B) respectively. The Ni^{2+} and Ni^{3+} oxidation peak on hydrated nickel oxide electrode is shifted in the positive direction by around 100 mV when compared to the plain nickel electrode. At identical sweep rates the anodic peak current on nickel–cobalt mixed oxide electrode was found to be 3–4 times higher when compared to the plain nickel electrode (Compare Figure 1(A, B)). This is apparently due to the higher surface area of hydrated nickel–cobalt mixed oxide electrode. The cathodic peak due to the reduction of Ni^{3+} species is relatively sharp on the tape cast electrode (Figure 1(B)) when compared to plain nickel (Figure 1(A)). On plain nickel at least two overlapping cathodic peaks over a broad potential region are observed [15]. These cyclic voltammetric results suggest that there are some subtle differences between the plain nickel electrode and the hydrated mixed oxide electrode especially in terms of peak potential difference and higher peak current densities. This suggests that the utility of the hydrated electrode for oxidation of alcohols is due to a higher concentration of Ni^{3+} species available on the electrode surface.

Some cyclic voltammetric responses were also obtained for these two electrodes in 1 M KOH containing organic reactant *n*-hexanol. These results for plain nickel and mixed oxide coated electrodes are shown in Figure 2(A, B) respectively. The oxidation peak current as well as the reduction peak current for Ni^{3+} and Ni^{2+} species does not increase substantially with increasing alcohol concentration on both these electrodes. This once again suggests that the chemical oxidation rate (Equation 2) is much slower than the electrochemical generation rate of Ni^{3+} species (Equation 1). Similar influences of alcohols on the voltammetric behaviour of nickel electrodes have also been reported earlier [1–3].

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

$$\begin{aligned}&\mathrm{R - CH_2 - OH + 4NiO(OH) + H_2O}\\&\mathrm{\rightarrow RCOOH + 4Ni(OH)_2}\end{aligned} \qquad (2)$$

The hydrated Ni–CO mixed oxide electrode, however, is found to exhibit excellent stability and catalytic activity towards the oxidation of aliphatic as well as aromatic alcohols. Typical results obtained during galvanostatic oxidation studies are summarised in Table 1.

n-Octyl alcohol was found to be oxidised to *n*-octanoic acid on this electrode with yields greater than 70.0%. At an optimum current density of 40 mA cm^{-2} the material yield was found to be 88.6% (Experiments 1–3). The electrochemical oxidation was found to be efficient at 45 °C. The material yield was found to decrease at lower (Expt 4) as well as higher temperatures (Expt 5). The same electrode material, after repeated washing, could be used without any material loss under the same experimental conditions at least for 25 times. The average time required for each electrolysis was varied between 5 and 9 h. Hence the electrode could be easily used for over 200 h without any noticeable loss in activity.

The hydrated mixed oxide electrode also exhibits excellent stability and catalytic activity in 0.18 M KOH containing 50% tertiarybutyl alcohol + 50% water. This mixed solvent system is commonly employed for the oxidation of *n*-hexyl alcohol to *n*-hexanoic acid (Table 1, Experiments 6–10). A maximum material yield

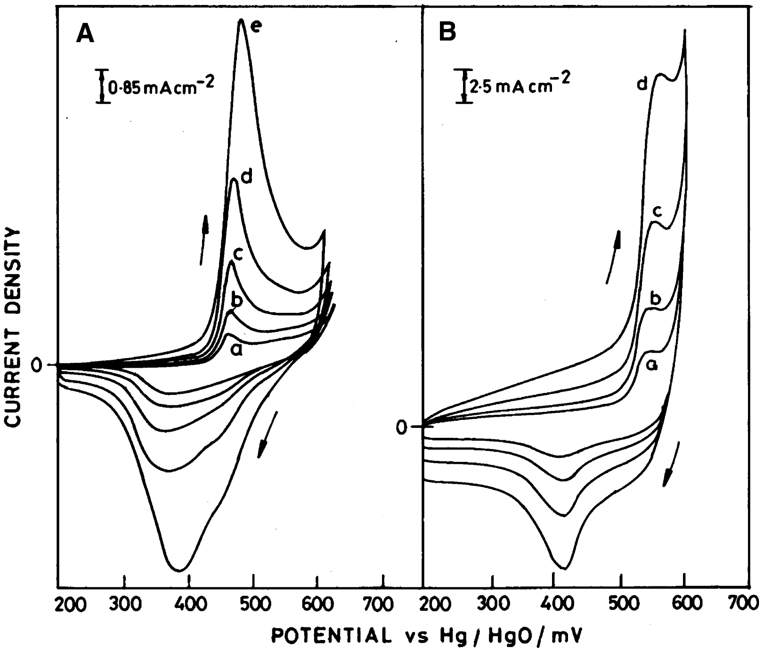

Fig. 1. Cyclic voltammetric behaviour of (A) nickel electrode and (B) nickel–cobalt mixed oxide hydrated electrode in 1 M KOH at sweep rates v = 10, 20, 40, 80 and 160 mV s^{-1} from *a* to *e* respectively.

of 85% was obtained at a current density of 30 mA cm^{-2} (Table 1, Expt 7). 45 °C once again appears to be the best temperature for the electrochemical process (Table 1, Experiments 7, 9 and10).

Electrochemical oxidation of *n*-butanol and isobutanol could also be carried out on this electrode in 1.0 M NaOH medium. Material yields for the oxidation of *n*-butanol (Table 1, Experiments 11–15) and isobutanol (Table 1, Experiments 16–20) were found to be generally above 70%. At a current density of 35 mA cm^{-2} and electrolysis temperature of 45 °C *n*-butanol gave a material yield of 96.5% (Expt 12). The optimum conditions for isobutanol oxidation was found to be 50 mA cm^{-2} current density and 35 °C electrolysis temperature. The material yield under these conditions was found to be 91.2%.

Fairly good yields were also obtained during the electrochemical oxidation of benzyl alcohol on this

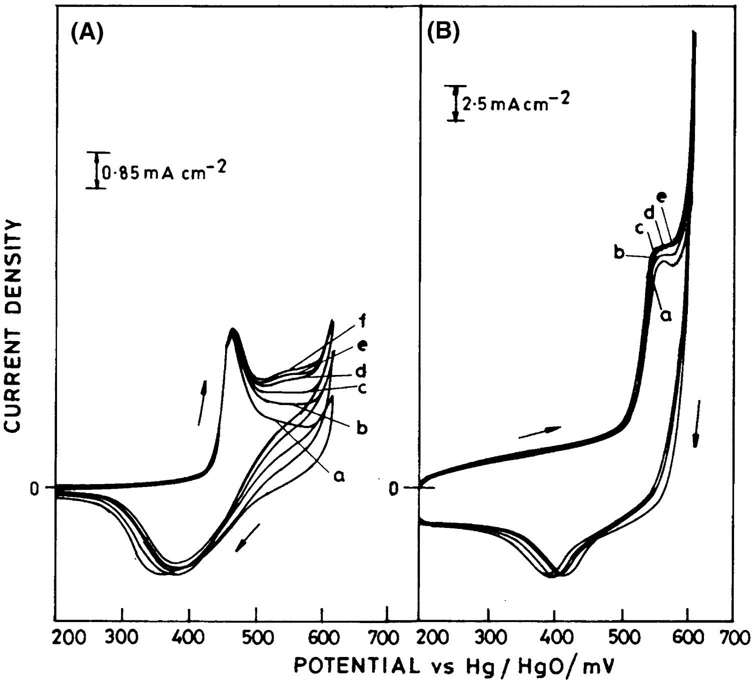

Fig. 2. Cyclic voltammograms showing the concentration effects of 0, 9.80, 19.23, 28.30, 37.0 and 45.4 mM of n-hexanol (*a*–*f* respectively) in 1 M KOH at 40 mV s^{-1} on (A) nickel electrode and (B) nickel–cobalt mixed oxide hydrated electrode.

Table 1. Galvanostatic oxidation of *n*-octyl, *n*-hexyl, *n*-butyl, isobutyl, benzyl alcohol and benzyl chloride to its corresponding carboxylic acids at hydrated nickel–cobalt mixed oxide electrode in 1 M NaOH

Sl. nos.	Compound name	Wt of reactant taken for oxidation (g)	Current density (mA cm^{-2})	Temp[b] (°C)	Wt of product formed (g)	Material yield (%)
1	*n*-Octyl alcohol	2.69	30	45	2.49	83.6
2		2.66	40	45	2.61	88.6
3		2.65	50	45	2.06	70.2
4		2.61	40	35	2.20	76.0
5		2.62	40	65	2.16	74.5
6	*n*-Hexyl alcohol	2.05	20	45	1.63	70.0
7		2.07	30	45	2.00	85.2
8		2.06	40	45	1.92	82.0
9		2.03	30	35	1.55	67.4
10		2.09	30	55	1.01	42.0
11	*n*-Butyl alcohol	2.19	15	45	1.75	67.3
12		2.23	35	45	2.56	96.5
13		2.30	50	45	2.35	86.0
14		2.29	35	35	2.30	84.5
15		2.29	35	55	2.23	82.0
16	Isobutyl alcohol	2.28	35	35	2.20	81.2
17		2.28	50	35	2.46	91.0
18		2.29	70	35	2.12	78.0
19		2.21	50	45	2.18	83.0
20		2.25	50	55	1.87	70.0
21	Benzyl alcohol	2.55	20	35	2.48	86.0
22		2.66	30	35	2.77	92.3
23	Benzyl chloride[a]	2.55	20	35	0.67	26.4
24		2.60	30	35	0.70	28.0

[a] In addition to benzoic acid, benzyl alcohol and benzaldehyde are also formed
[b] The bath temperature was controlled within ± 2 °C

electrode (Table 1, Experiments 21 and 22). A material yield of over 90% was achieved. Interestingly even the electrochemical oxidation of benzyl chloride is found to proceed on this electrode material (Table 1, Experiments 23 and 24). The material yield for the formation of benzoic acid was, however, found to be relatively poor when theoretical charge corresponding to 5F according to Equation (3) and (4) was passed.

$$\mathrm{R-CH_2-Cl+OH^- \rightarrow R-CH_2-OH+1/2Cl_2+1e^-} \tag{3}$$

$$\begin{aligned}&\mathrm{R-CH_2-OH+4NiOOH+H_2O}\\&\quad\mathrm{\rightarrow R-COOH+4Ni(OH)_2}\end{aligned} \tag{4}$$

The low yield of benzoic acid (28%) was accompanied by a significant yield of intermediates namely benzyl alcohol (15%) and benzaldehyde (29%) at a current density of 30 mA cm^{-2}. Passing excess overall charge may thus enhance the yields.

A few galvanostatic studies were also carried to compare the influence of plain nickel, nickel oxy hydroxide and nickel–cobalt mixed oxide anodes. *n*-Butyl alcohol and isobutyl alcohol were oxidised at two different current densities namely 20 mA cm^{-2} and 50 mA cm^{-2}. The results obtained under these conditions are compared in Table 2. As one would expect both nickel oxy hydroxide and hydrated nickel–cobalt mixed oxide electrode gave better results for both these compounds. This is especially true for both these anodes at a current density of 50 mA cm^{-2} (Table 2, Experiments 1–4). Highest yield for both these compounds are

Table 2. Comparative behaviour of different nickel oxide anodes for the oxidation of *n*-butyl alcohol and isobutyl alcohol in 1.0 M NaOH

Sl Nos	Compound name	Current density (mA Cm^{-2})	Temp[a] (°C)	Material yield (%)		
				Nickel	NiO(OH)	Ni–Co mixed oxide
1	*n*-Butylalcohol	20	45	24	39	68
2	*n*-Butylalcohol	50	45	26	75	86
3	Isobutylalcohol	20	45	20	54	69
4	Isobutylalcohol	50	45	29	60	83

Weight of reactant taken for oxidation = 2.2–2.3 g
[a] The bath temperature was controlled within ±2 °C

observed on hydrated nickel–cobalt mixed oxide electrode.

4. Conclusion

The major observation during these experiments is the excellent stability and reusability of hydrated nickel–cobalt oxide electrode during the oxidation of all the six reactants. The redoxcatalytic activity is similar to those reported in the literature. It appears that the hydrated electrode prevents a blocking type of organic adsorption including reactant, intermediates and products. The organic molecules do not contaminate the electrode surface ensuring continuous electrooxidation. While the practical application of this electrode in electro synthesis is obvious, the exact nature of the electrode/organic compound interactions deserves further investigation.

References

1. M. Fleischmann, K. Korinek and D. Pletcher, *J. Electroanal. Chem.* **31** (1971) 39.
2. M. Fleischmann, K. Korinek and D. Pletcher, *J. Chem. Soc Perkin* **II** (1972) 1396.
3. M. Amjad, D. Pletcher and C. Smith, *J. Electrochem. Soc.* **124** (1977) 203.
4. K. Manandhar and D. Pletcher, *J. Appl. Electrochem.* **9** (1979) 707.
5. J. Kaulen and H.J. Schäfer, *Synthesis* (1979) 513.
6. J. Kaulen and H.J. Schäfer, *Tetrahedron.* **38** (1982) 3299.
7. H.J. Schäfer, *Top. Curr. Chem.* **142** (1987) 101.
8. P.M. Robertson, P. Berg, H. Reimann, K. Schleich and P. Seiler, *J. Electrochem. Soc.* **130** (1983) 591.
9. A.S. Vaze, S.B. Sawant and V.G. Pangarkar, *J. Appl. Electrochem.* **27** (1997) 584.
10. G.P. Barsotti, M. Foa and N. Gatti, *Synthesis* (1990) 207.
11. D.C. Trivedi, K.S. Uduppa and H.V.K. Uduppa, *Proc. Indian Natl. Sci. Acad Part A* **48** (1982) 333.
12. P. Cox and D. Pletcher, *J. Appl. Electrochem.* **21** (1991) 11.
13. P. Cox and D. Pletcher, *J. Appl.Electrochem.* **20** (1990) 549.
14. S. Thangavelu, R.M. Krishnan, S. Sriveeraraghavan, C. Joseph Kennedy and A. Arunmozhi Selvan, Indian Patent No 185160 Mar (1993).
15. A.J. Rethinam and C.J. Kennedy, *J. Appl. Electrochem.* **34** (2004) 371.
16. A.S. Vaze, S.B. Sawant and V.G. Pangarkar, *J. Appl. Electrochem.* **25** (1995) 279.
17. C.J. Brown, D. Pletcher, F.C. Walsh, J.K. Hammond and D. Robinson, *J. Appl. Electrochem.* **24** (1994) 95.
18. V.A. Tracey, *Ind. Eng. Prod. Res. Dev.* **21** (1992) 626.
19. V. Falk and K.J. Salkind, ‘Alkaline Storage batteries’, (Wiley Interscience, New York, 1969) Chap 2, 111 pp.
20. S. Muzhumathi, I. Arul Raj, S. Dheenadayalan, R. Chandrasekaran and R. Pattabiraman, *Trans. SAEST* **27** (1992) 94.