

Evaluation of porous nickel hydroxide electrode for the oxidation of aliphatic and aromatic primary alcohols

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The positive plate of Ni-Cd battery was evaluated as Ni(OH)₂/NiOOH electrode for the oxidation of six aromatic and five aliphatic alcohols. In addition to galvanostatic preparative electrolysis, cyclic voltammetric experiments were also carried out. The anode material after electrolysis was evaluated using SEM and XRD. Except in the case of chlorine substituted aromatic alcohols the nickel hydroxide electrode showed excellent stability even after the reuse for nearly 10-15 times. In 0.1 M KOH containing 67% tertiary butanol + 33% water as electrolyte, aromatic alcohols gave predominantly aldehyde in good yield. In alkaline solutions without the co-solvent tertiary butanol aromatic alcohols were oxidized to their corresponding carboxylic acids. Short chain aliphatic alcohol (C5) gave reasonable yield of carboxylic acid. Long chain alcohols showed limited solubility in alkaline medium with and without co-solvent tertiary butanol and the yields of carboxylic acids were also poor.

Keywords: Alcohols, Catalytic activity, Porous nickel hydroxide electrode, Oxidation, Voltammetry

Electrochemical oxidation of aliphatic and aromatic primary alcohols on nickel oxy hydroxide [NiOOH/Ni(OH)₂] electrodes is extensively investigated for industrial applications¹⁻¹². The kinetics and mechanistic aspects of oxidation at oxide covered nickel anodes were also reported¹³⁻¹⁷. The electrochemical oxidation of low molecular weight alcohols like methanol and butanols were investigated using *in-situ* IR and electro analytical techniques¹⁸. Electrochemical oxidation of ethylene glycol and its homologs have also been achieved on nickel oxide electrode¹⁹. Apart from these electro synthetic works, surface bound Ni²⁺/Ni³⁺ redox couples have also been used for sensing of alcohols and sugars²⁰⁻²². Oxidative removal of trace quantities of benzyl alcohol and benzaldehyde was also reported²³.

Electrodeposited nickel oxide electrode could be employed only at very low current densities for organic oxidations. In addition, the electrode needs to be reactivated each time before electrolysis. The anode stability and sustained catalytic activity during electrochemical oxidation of organic compounds still remains a challenge. In a previous work, it was shown that a hydrated nickel-cobalt mixed oxide electrode employed in fuel cells could also be successfully used as a stable anode for oxidation of aliphatic alcohols

and benzyl alcohol²⁴. As a further simplification, the commercially available positive plates of Ni-Cd battery [High Energy Batteries (India) Ltd., Mathur, Tamil Nadu] are employed as anode for the present study. The importance of this nickel hydroxide positive plate over conventional nickel oxide electrodes is its excellent stability and sustained redox catalytic activity for the oxidation of organic compounds in alkaline medium. The electrode need not be reactivated each time before electrolysis and could be effectively used at high current densities without any loss in the electrode surface. The nickel hydroxide positive plate was evaluated as anode material for the oxidation of six aromatic and five aliphatic alcohols in alkaline medium with and without the use of co-solvent tertiary butanol. The electrodes were also evaluated for repeated use in batch processes using SEM and XRD and the results are reported herein.

Experimental Procedure

High purity plain nickel (Johnson mathey specpure grade) and positive plate of nickel hydroxide electrodes developed for Ni-Cd battery [High Energy batteries (India) Ltd., Mathur, Tamil Nadu] were employed as anodes. The commercially procured positive plate of Ni-Cd battery (nickel hydroxide

with the pore diameter of 10 μ) was fabricated by the electrochemical impregnation technique using nickel foam having 90% porosity as the substrate.

Cyclic voltammetric experiments were carried out in a two-compartment glass cell with high purity plain nickel (Johnson mathey specpure grade) electrode of surface area 0.196 cm² as working electrode. Hg/HgO and a platinum foil served as reference and counter electrode respectively.

Galvanostatic experiments were carried out in an undivided glass cell of 250 mL capacity with a glass lid having provisions for introducing electrodes and thermometer. The glass cell was placed in a REMI magnetic stirrer/hot plate containing water bath and the bath was maintained at specified temperatures within $\pm 2^\circ\text{C}$. The electrolyte was stirred throughout electrolysis using teflon magnetic stirrer. Plain nickel and positive plate of nickel hydroxide electrode developed for Ni-Cd batteries with geometric area of 26.0 cm² were employed as anode materials. Stainless steel of same size was used as cathode. A mixture of 33% of 0.1 M KOH and 67% tertiary butanol (referred as alcoholic medium) and 1 M NaOH without containing co-solvent tertiary butanol (referred as non alcoholic medium) each solution of 200 mL was used as electrolyte for oxidation of alcohols. The theoretical amount (2F/mole for the oxidation of alcohol to aldehyde and 4F/mole for the oxidation of alcohol to carboxylic acid) of current was passed at the current density ranges from 15 to 70 mA cm⁻². For product isolation and separation of unreacted alcohol the procedure described in the literature^{3,15} was adopted.

4-Methoxybenzyl alcohol, 4-methylbenzyl alcohol, 4-chlorobenzyl alcohol, cinnamyl alcohol, n-pentyl alcohol, isopentyl alcohol (Aldrich), benzyl alcohol, furfuryl alcohol, n-decyl alcohol, n-dodecyl alcohol (SRL) and n-nonyl alcohol (Across organic) were used as received for preparative electrolysis and cyclic voltammetric studies.

The products were analyzed by high-performance liquid chromatography (HPLC) using Shimadzu liquid chromatograph. Shimpack ODS-C18 column (120 \times 4.5 mm) was used as the stationary phase. The solvent consisted of methanol-water (70:30 & 80:20) at a flow rate of 1 mL/min. UV-Spectrophotometric detector at a wavelength of 254 nm was used for sample analysis. The HPLC of the crude product mixture obtained from alcoholic solution showed one major peak corresponding to aldehyde and a minor

peak corresponding to carboxylic acid. The product obtained from non-alcoholic solution showed one major peak corresponding to carboxylic acid. The aliphatic compounds were analyzed by GC using a HP 6890 gas chromatograph with FID detector. The GC of the product mixture showed one major peak corresponding to aliphatic carboxylic acid. The percentage purity of the product was determined by HPLC or GC and the material yield was calculated. The products were characterized by FTIR (Perkin-Elmer model paragon 500) and NMR spectroscopy (400 MHz Bruker NMR spectrometer).

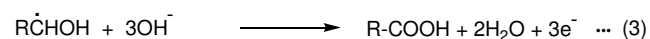
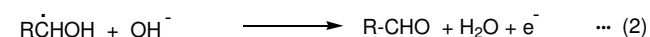
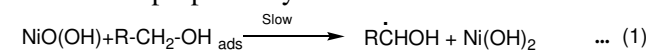
The electrode surface characterization studies were performed using JEOL JSM-35 CF Scanning electron microscope and XRD pattern of nickel hydroxide electrodes were recorded using X'pert Pro PANalytical (pw 3040/60 X' pert PRO) at 40 kV and 30 mA of Cu-K α radiation.

Results and Discussion

Electrochemical oxidation of aromatic primary alcohols

The commercially obtained positive plate of Ni-Cd battery was directly employed to obtain cyclic voltammetric responses in 1.0 M KOH medium. In the conventional potential range between 200 to 700 mV versus Hg/HgO substantially higher background current was noticed but no distinct anodic or cathodic peak corresponding to Ni(OH)₂/NiOOH redox processes could be obtained in this potential region. Hence the effect of alcohol addition on the voltammetric responses could not be assessed on these nickel oxy hydroxide electrodes. However, few cyclic voltammetric experiments were carried out on plain nickel electrode.

Typical cyclic voltammetric responses of nickel electrode in 1.0 M KOH containing up to 45 mM of 4-methoxybenzyl alcohol at a constant sweep rate of 40 mV s⁻¹ are presented in Fig. 1A. The anodic oxidation peaks were found to increase only slightly with increasing alcohol concentrations and the cathodic reduction peaks were found to decrease slightly with increasing alcohol concentrations. The cyclic voltammetric behaviour observed in the present study is similar to those reported earlier by Fleischmann *et al.*^{13,14} with the following general mechanism proposed by them.



The adsorbed 4-methoxybenzyl alcohol is chemically oxidized by nickel oxy hydroxide formed on the electrode surface. The chemical oxidation of adsorbed 4-methoxybenzyl alcohol by nickel oxy hydroxide is a slow reaction^{3,13}, which produces α -hydroxyl radical intermediate [Eq. (1)]. In presence of large excess of hydroxide ions the α -hydroxyl radical intermediate formed preferably undergoes further oxidation to give carbonyl products [Eqs (2) & (3)] rather than radical coupling.

Though the redox catalytic effect could not be ascertained in the voltammetric time scale, galvanostatic experiments indicate that the overall oxidation efficiency is much higher on nickel hydroxide electrode when compared to plain nickel electrode. This observation confirms the catalytic influence of nickel hydroxide electrode as indicated below in detail.

Galvanostatic electrolysis

The main objective in the oxidation of aromatic primary alcohols is to achieve maximum yield of aromatic aldehydes. Earlier experiments have suggested that 2:1 (v/v %) tertiary butanol: water mixture is a preferred medium for achieving higher selectivity of aromatic aldehydes. Typical

optimization studies for the oxidation of 4-methoxybenzyl alcohol done under different experimental conditions are summarized in Table 1. In tertiary butanol:water (alcoholic) medium good conversion yield of aromatic aldehyde was observed on nickel oxy hydroxide electrode after the passage of 2 F/mole of electricity. The preparative electrolysis experiments done at different current densities (Table 1, Expts 1-4) indicate a high aldehyde yield of 95.0% with 4% yield of *p*-methoxy benzoic acid at the current density of 30 mA cm⁻². Increasing the electricity charge to 4 F/mole at the same current density indicate a slight decrease in the yield of aldehyde and corresponding slight increase in the yield of 4-methoxybenzoic acid (Table 1, Expt 5). Similar galvanostatic experiments in 1.0 M NaOH medium without co-solvent tertiary butanol (non alcoholic) indicate very low yield of aldehyde and higher yield of carboxylic acid after passing 2 F/mole of electricity (Table 1, Expt 6). The yield of 4-methoxy benzoic acid was increased to 93% when 4 F/mole of electricity was passed under identical conditions. (Table 1, Expt 7). In alcoholic medium, plain nickel and platinum electrodes after passing 2 F/mole of electricity gave only 40.0 and 56.0% of 4-methoxybenzaldehyde respectively.

Table 1—Optimization studies for the galvanostatic oxidation of 4-methoxybenzyl alcohol

Sl No	Weight of 4-methoxy benzyl alcohol taken for oxidation (g)	Current density (mA cm ⁻²)	Weight of product formed		Material yield	
			4-Methoxy benzaldehyde (g)	4-Methoxy benzoic acid (g)	4-Methoxy benzaldehyde (%)	4-Methoxy benzoic acid (%)
1	1.04	15	0.92	0.04	90.0	3.5
2	1.04	30	0.93	0.04	95.0	4.0
3	1.04	50	0.87	0.03	85.0	3.0
4	1.03	70	0.80	0.03	79.0	3.0
5	1.02	30	0.89	0.10	89.0	9.0
6	1.01	30	0.35	0.70	35.0	63.0
7	1.01	30	0.06	1.03	6.0	93.0
8	1.01	30A	0.4	0.23	40.0	21.0
9	1.01	30B	0.56	0.06	56.0	5.0
10	1.01	30C	0.76	0.04	76.0	4.0
11	1.02	30D	0.70	0.16	70.0	14.0
Electrolyte	Alcoholic medium (0.1 M KOH in 67% tert-butanol + 33% H ₂ O for experiments 1-5 and 8-11. Non alcoholic medium (1.0 M NaOH) for experiments 6 and 7					
Cell temperature:	32 to 35°C					
Cell voltages:	7.0 to 15.0 V in alcoholic medium 1.5 to 2.0 V in non-alcoholic medium					
Electricity passed:	2 F/mole. For experiments 5 and 7 4 F/mole					
A Experiment carried out using nickel as anode						
B Experiment carried out using platinum as anode						
C Expt carried out with electrolyte bath temperature of 40-45°C						
D Expt carried out with electrolyte bath temperature of 50-55°C						

(Table 1, Expts 8 and 9). Some galvanostatic preparative experiments were also carried out at high temperatures. The aldehyde yields are found to decrease with increasing temperatures due to competitive gas evolution reaction. (Table 1, Expts 10 and 11). Since theoretically required current was passed, the current efficiency and material yield efficiency are equal in all the experiments.

In addition to 4-methoxybenzyl alcohol few other aromatic primary alcohols such as 4-methylbenzyl alcohol, 4-chlorobenzyl alcohol, cinnamyl alcohol and furfuryl alcohol were also subjected to electrochemical oxidations in alcoholic as well as non alcoholic media on the commercial nickel hydroxide electrodes. In alcoholic medium 2 F/mole of electricity was passed while in non-alcoholic medium 4 F/mole of electricity was passed with the primary objective of maximizing the yield of aldehyde in alcoholic solutions and the yield of carboxylic acids in non-alcoholic solution. The results are summarized in Table 2. In the case of benzyl alcohol and 4-methoxy benzyl alcohol aldehyde yields in alcoholic medium as well as carboxylic acid yield in non-alcoholic medium were found to be greater than 70%. Best yields of aldehyde as well as carboxylic acid were obtained during the oxidation of 4-methoxybenzyl alcohol. In the case of 4-methylbenzyl alcohol, conversion to aldehyde in alcoholic medium was greater than 87% and the conversion to carboxylic acid in non-alcoholic medium was only 45%. The trend

was found to be reverse in the case of cinnamyl alcohol with low yield of cinnamaldehyde and high yield of cinnamic acid.

In the case of 4-chlorobenzyl alcohol, the electrochemical conversion was found to be very low after the passage of 2 F/mole in alcoholic medium and 4 F/mole in non-alcoholic medium. Even after the passage of 6 F/mole, only up to 39% of aldehyde was obtained in alcoholic medium. It appears that 4-chlorobenzyl alcohol gets adsorbed on the catalytic electrode surface and blocks the catalytic activity towards alcohol oxidation. Thus probably enhancing oxygen evolution reaction leads to poor yield and selectivity. The conversion to acid in non-alcoholic solutions however was high at 80%. Furfuryl alcohol could also be efficiently oxidized on nickel hydroxide electrode (Table 2, Expt 6). In alcoholic medium aldehyde yield of 76% could be achieved.

Electrochemical oxidation of aliphatic primary alcohol

Cyclic voltammetric responses obtained for 45 mM of isopentyl alcohol on a plain nickel electrode in 1.0 M KOH presented in Fig. 1B are quite similar to those obtained for 4-methoxybenzyl alcohol (Fig. 1A). For these compound also, the oxidation peak current as well as reduction peak current does not increase substantially with increasing alcohol concentration. This once again suggests that the chemical oxidation rate is much slower than the electrochemical generation rate of Ni^{3+} species.

Table 2—Optimum conditions and yields for the oxidation of aromatic primary alcohols

Compound	Electrolyte	Yield (%)	
		Aldehyde	Acid
Benzyl alcohol	Alcoholic	85.0	10.2
	Non-alcoholic	17.0	72.0
4-Methoxybenzyl alcohol	Alcoholic	93.0	4.0
	Non-alcoholic	6.0	93.0
4-Methylbenzyl alcohol	Alcoholic	87.0	11.0
	Non-alcoholic	28.0	45.0
Cinnamyl alcohol	Alcoholic	49.0	25.0
	Non-alcoholic	10.0	80.0
4-Chlorobenzyl alcohol	Alcoholic	39.0	25.0
	Non-alcoholic	10.0	80.0
Furfuryl alcohol	Alcoholic	76.0	13.0
	Non-alcoholic	13.0	57.0
Electrolyte:	Alcoholic medium (0.1 M KOH in 67% tert-butanol + 33% H ₂ O) Non-alcoholic medium (1.0 M NaOH)		
Bath temp:	32 to 35°C		
Current density:	30 mA cm ⁻²		
Electricity passed:	2 F/mole in alcoholic medium 4 F/mole in non-alcoholic medium		

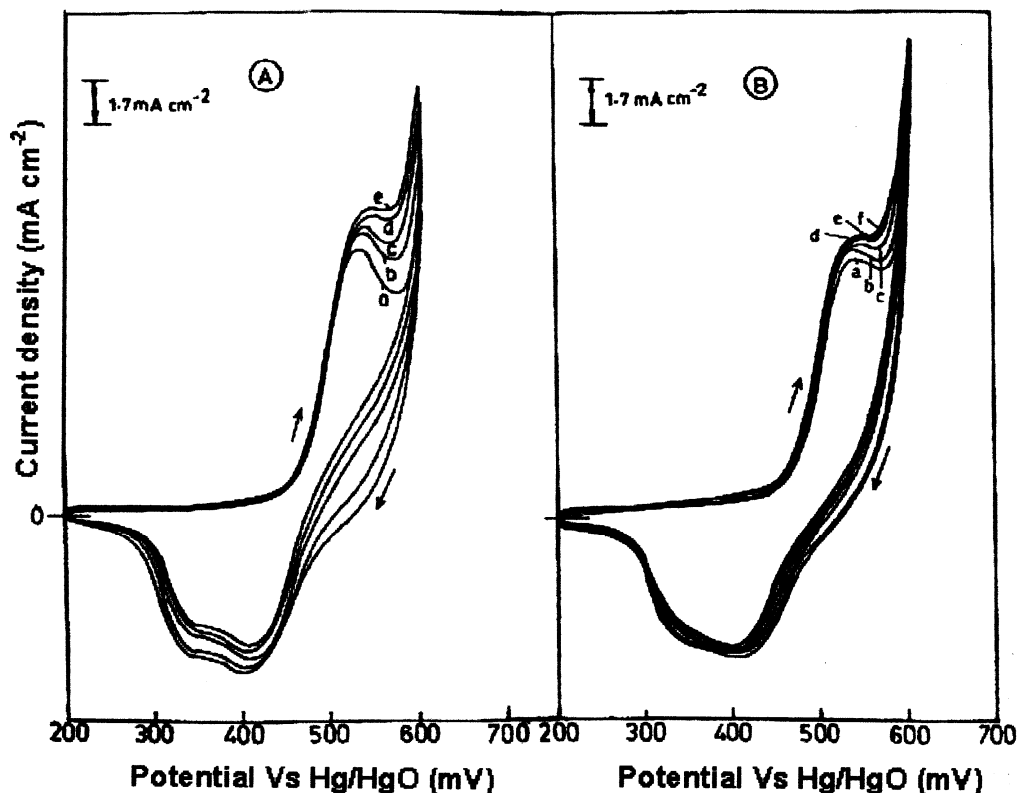


Fig. 1—Cyclic voltammograms showing the concentration effects of 0, 9.80, 19.23, 28.30, 37.0 and 45.4 mM of (A) 4-methoxybenzyl alcohol (B) Isopentyl alcohol (from a-e respectively) in 1 M KOH at 40 mV s^{-1} on nickel electrode

Galvanostatic electrolysis

Aliphatic alcohols under a 4 F reaction in non-alcoholic medium usually give their corresponding acids, which are quite valuable products. Hence galvanostatic experiments were generally carried out in non-alcoholic solution by passing 4 F of electricity. The influence of alcoholic medium and quantity of electric charge passed (2 F and 4 F) were also evaluated.

Galvanostatic experiments carried out with different anode current densities on a commercially available nickel hydroxide electrode indicate that maximum yield of 75% isopentanoic acid (3-Methyl butanoic acid) could be obtained at a current density of 50 mA cm^{-2} . Few experiments were also carried out in 2:1 (v/v %) tertiary butanol:water mixture. As one would expect only 22% yield of isopentanoic acid was obtained even after passing 4 F/mole of electricity. In such alcoholic medium, attempts to isolate and identify the generated aldehyde did not succeed. It appears that direct oxidation of alcohol to carboxylic acid and oxygen evolution are the main competitive processes in these media. The influence of electrolysis temperature on the overall process

efficiency was also evaluated in alkaline medium. At a current density of 50 mA cm^{-2} , the temperature range of $40\text{--}45^\circ\text{C}$ appears to be the suitable temperature for this electrochemical processes. A better yield of 79% isopentanoic acid was obtained at $40\text{--}45^\circ\text{C}$. Plain nickel electrode also served as a good anode material for this electrochemical oxidation; however the yield was significantly low at 65%. Platinum electrode gave very poor yield of isopentanoic acid under these experimental conditions.

Similar optimization studies were also carried out for aliphatic alcohols such as *n*-pentyl alcohol, *n*-nonyl alcohol, *n*-decyl alcohol and *n*-dodecyl alcohol. The optimum current density and temperature range for constant current electrolysis were also optimized for each compound. The results are summarized in Table 3. *n*-Pentyl alcohol gave maximum yield of 89% pentanoic acid with the current density of 30 mA cm^{-2} and temperature range of $30\text{--}35^\circ\text{C}$. Under optimum conditions isopentanol gave 79% yield of isopentanoic acid as reported above. Other long chain alcohols generally possess lower solubilities in alkaline medium and hence

the electrolysis was carried out at a slightly higher temperature range of 65-70°C. Even under these conditions these compounds gave only poor yield of their corresponding carboxylic acids. Even after the passage of 6 F/mole of electricity *n*-nonanol gave only 24% yield of nonanoic acid. It appears that with increasing chain length and decreasing solubilities of alcohols, their catalytic oxidation efficiency decreases. Once again this poorly soluble alcohol gets adsorbed on the electrode surface and reduces their catalytic efficiency.

Electrode surface characterization

Some studies were also carried out to characterize the electrode surface before and after electrolysis. The scanning electron micrographs of a fresh nickel hydroxide electrode with 500 and 1000 magnifications are presented in Figs 2A and 2B respectively. The surface layer is quite uniform, however some cracks are noticed. No corrosion or dissolution in the intergranular regions is noticed.

Figures 2C and 2D exhibit SEM pictures of nickel hydroxide electrode obtained after its use as an anode for oxidation of different alcohols in 11 batches.

The basic surface structure of the oxide layer remains intact however further cracks are seen on these surfaces. The overall sizes of the crack particles are generally smaller than 20 μm . The intergranular gaps between larger particles are also found to increase substantially (Fig. 2D).

Table 3—Optimum conditions and yields for the oxidation of aliphatic primary alcohols

Sl No	Aliphatic alcohol	Current density (mA cm ⁻²)	Temperature (°C)	Material yield of carboxylic acid (%)
1	<i>n</i> -Pentyl alcohol	30	30-35	89.0
2	Isopentyl alcohol	50	40-45	79.0
3	Nonyl alcohol	30	65-70	20.0*
4	<i>n</i> -Decyl alcohol	30	65-70	12.0
5	<i>n</i> -Dodecyl alcohol	30	65-70	20.0

Electrolyte: 1.0 M NaOH

Cell voltage: 1.5 – 2.0 V.

*Material yield of 24% was obtained even after the passage of 6 F/mole of electricity

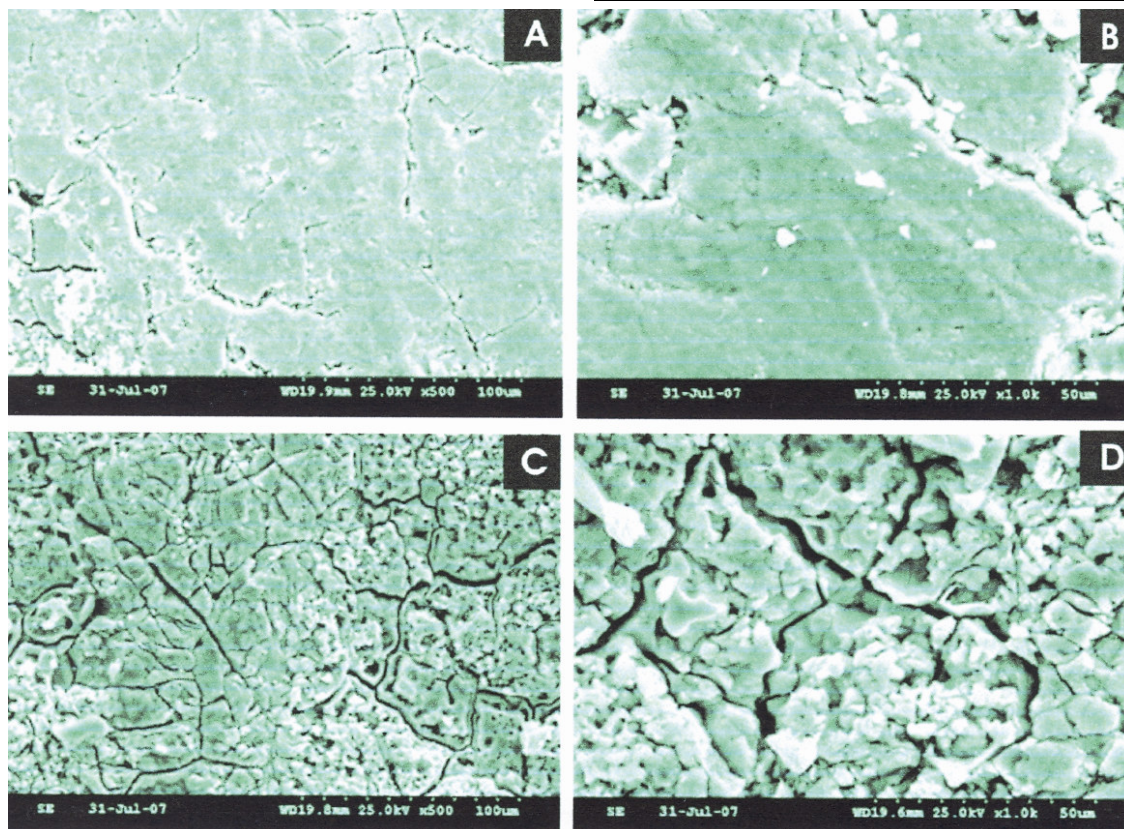


Fig. 2—Scanning electron micrographs of fresh Ni(OH)₂ electrode sample (A and B) and Ni(OH)₂ electrode after eleven trials of electrochemical experiments (C and D). Magnifications A and C X 500, B and D X 1000

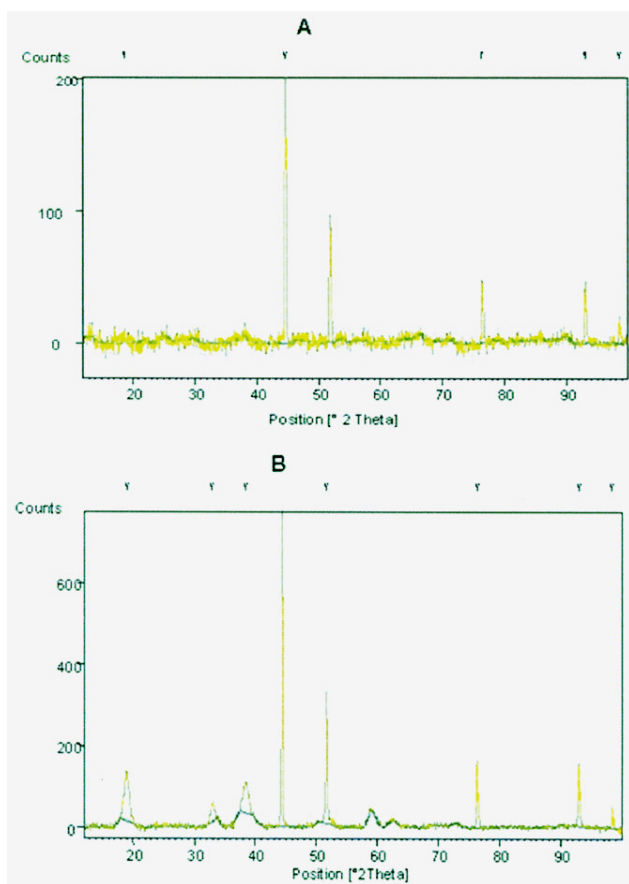


Fig. 3—XRD pattern of A. fresh $\text{Ni}(\text{OH})_2$ electrode. B. $\text{Ni}(\text{OH})_2$ electrode after fifteen times of reuse for the oxidation of 4-chlorobenzyl alcohol

Even after completion of 15 batches of electro oxidations of 4-methoxybenzyl alcohol, the surface structure remains more or less similar. However, when the same fresh electrode was employed for the oxidation of 4-chlorobenzyl alcohol, the electrode exhibited some visible pits on the surface. SEM micrographs also exhibited some non-uniform cracking and pit formation. These studies suggest that slight decrease in particle size of the oxide layer and slower intergranular attack occur on the nickel hydroxide electrode during electrochemical oxidation. However, the overall electrocatalytic activity of the electrode remains more or less intact during the course of the present sets of experiments.

The surface nature of the deposit was also evaluated through XRD measurements. The XRD response for the fresh anode surface and anode surface after using in more than 15 batch operations for the oxidation of 4-chlorobenzyl alcohol are presented in Fig. 3 A and B. The XRD peaks of maximum intensity are analyzed using data from

JCPDS. An intense peak at $2\theta = 44.5$ (d-spacing value of 2.03) with maximum relative intensity and two other peaks with $2\theta = 52.0$ and 76.3 (d-spacing values of 1.75 & 1.24) correspond to cubic crystalline nickel. Four other signals corresponding to hexagonal nickel hydroxide ($2\theta = 18.9, 33.0, 38.4$ & 51.7 with d-spacing values of 4.67, 2.71, 2.34 & 1.76) are noticed. The XRD pattern shows the crystalline deposit of nickel and nickel hydroxide. Some additional broader unidentified peaks are also noticed after electrolyses in 4-chlorobenzyl alcohol.

Conclusion

The positive plates employed in nickel cadmium battery exhibit good stability and electrochemical activity in alcoholic as well as non-alcoholic solutions in presence of both aromatic and aliphatic alcohols. These alcohols also undergo catalytic oxidation to carboxylic acids in non-alcoholic solutions. In alcoholic solution, aromatic alcohols gave their corresponding aldehydes in high yields and selectivity. Except for chlorine containing aromatic alcohol, other aromatic alcohols did not exhibit any fouling effect on the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ electrode. The present investigations thus show that the electrode widely employed in battery industry could be used successfully for electro organic synthesis.

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