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Electrosynthesis at oxide coated electrodes
Part 2. The oxidation of alcohols and amines at spinel anodes in aqueous base

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The oxidation of alcohols and primary amines at a $NiCo_2O_4$ anode in aqueous base has been investigated. It is shown that a range of compounds undergo oxidation at the same potential, that for the conversion of the oxide surface to a higher oxidation state, and that the limiting current densities approach those expected for mass transfer control. Using a flow cell, it is confirmed that the conversation of primary alcohols to carboxylic acids, secondary alcohols to ketones and primary amines to nitriles can all be achieved with high selectivity and reasonable current efficiency at high current densities. The oxide coating appears to be quite stable during repeated electrolyses.

1. Introduction

A recent review [1] highlighted the range of chemistry which can be achieved at a nickel anode in aqueous base. Although the reactions can be very selective, the current densities which may be used with smooth nickel are rather low and this restricts the applications. This has led to attempts to prepare stable, high area nickel oxide electrodes [2, 3] and, indeed, such electrodes have been used in a large pilot plant for the oxidation of a sugar derivative [4, 5]. A recent paper [6], however, reported a study of the oxidation of ethanol at spinel coated titanium electrodes and proposed a similar mechanism to that suggested at nickel [7, 8]; moreover, the limiting current density was markedly higher. Hence, in this paper, the kinetics of oxidation of several alcohols and amines at the spinel, $NiCo_2O_4$, have been studied. In addition, the results of some preparative scale electrolysis are reported.

2. Experimental details

The preparation of the spinel coating has been described previously [6] and with one exception the procedures for titanium and nickel were identical. The titanium substrate was etched in $8\,mol\,dm^{-3}$ hydrochloric acid at 333 K for 4 h while the nickel was etched for only 10 min at room temperature.

The cell and procedure for the kinetic experiments was also described [6]. The preparative electrolyses were carried out in a Microflow cell supplied by ElectroCell AB. It was used in the undivided mode with a steel cathode, the spinel coated nickel anode and turbulence promoters. The reservoir was a three-necked flask heated in an oil bath and the electrolyte was circulated at $0.5\,dm^3\,min^{-1}$ using a pump supplied by ElectroCell AB.

Samples of the electrolyte from one phase electrolyses were carefully neutralized with hydrochloric acid prior to analysis by gas/liquid chromatography (GLC) using either a Varian Model 3700 chromatograph with a OV 101 or Porapak Q column or a Perkin Elmar Model 8310 chromatograph with a BP/1 capillary column. After two phase electrolyses, the electrolyte was again neutralized with hydrochloric acid but the organic products were then extracted with ether; benzoic and octanoic acids were silylated prior to determination by GLC.

3. Results and discussion

3.1. *Kinetic experiments*

Current-potential curves were recorded for $0.1\,mol\,dm^{-3}$ solutions of several organic compounds in $2.5\,mol\,dm^{-3}$ potassium hydroxide at the $NiCo_2O_4$ electrode; the potential scan rate used was $1\,mV\,s^{-1}$. The primary aliphatic alcohols gave well-formed oxidation waves with half-wave potential close to 280 mV, see Fig. 1a, while the amines and benzyl alcohols gave similar curves except for a slight tendency to show a peak, see Fig. 1b. The responses for the secondary alcohols were more complex and two oxidation waves were observed although oxidation clearly occurs in the same potential range, see Fig. 1c. The limiting current densities after subtraction of the background current at +0.35 V are reported in Table 1.

The proximity of the oxidation potentials for such a diverse group of compounds supports the proposal [6] that the reaction mechanism, as at nickel anodes in aqueous base [7, 8], involves a chemical step between a higher oxidation state metal oxide and the organic molecule. The rates of oxidation at the spinel anode are, however, higher than at nickel [7] by a factor of 10–100. Moreover, when allowance is made for the difference in the number of electrons involved in the

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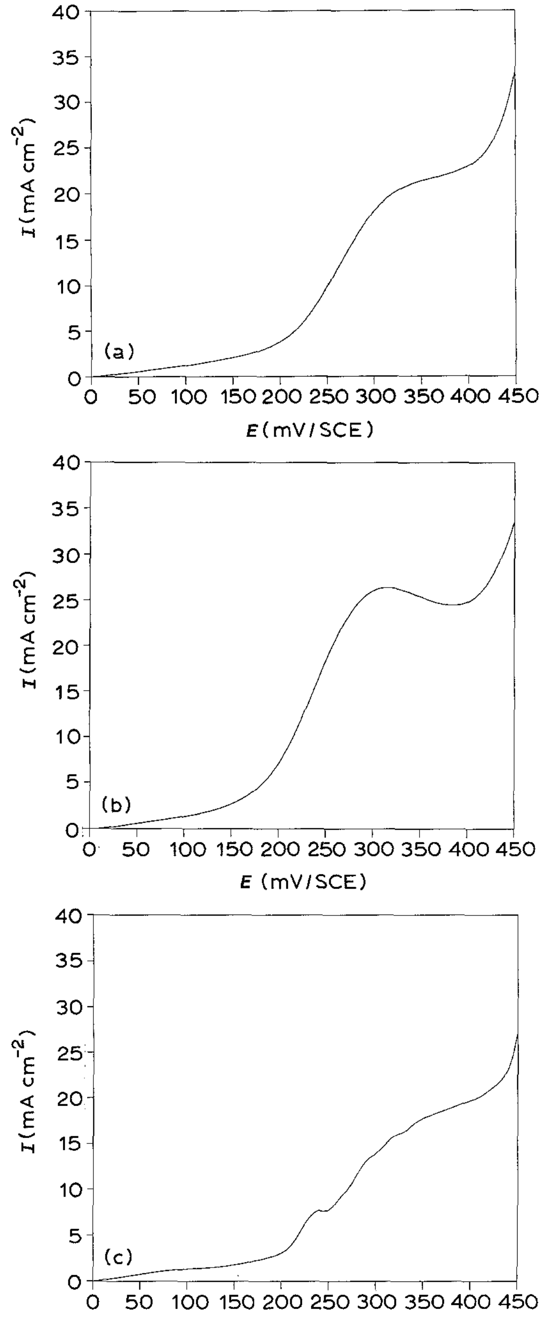

Fig. 1. I-E curves for the oxidation at a spinel ($NiCo_2O_4$) coated titanium anode of (a) butan-1-ol (b) 1-butylamine and (c) propan-2-ol, each 0.1 mol dm^{-3} in 2.5 mol dm^{-3} potassium hydroxide. Potential scan rate 1 mV s^{-1}. Temperature 293 K.

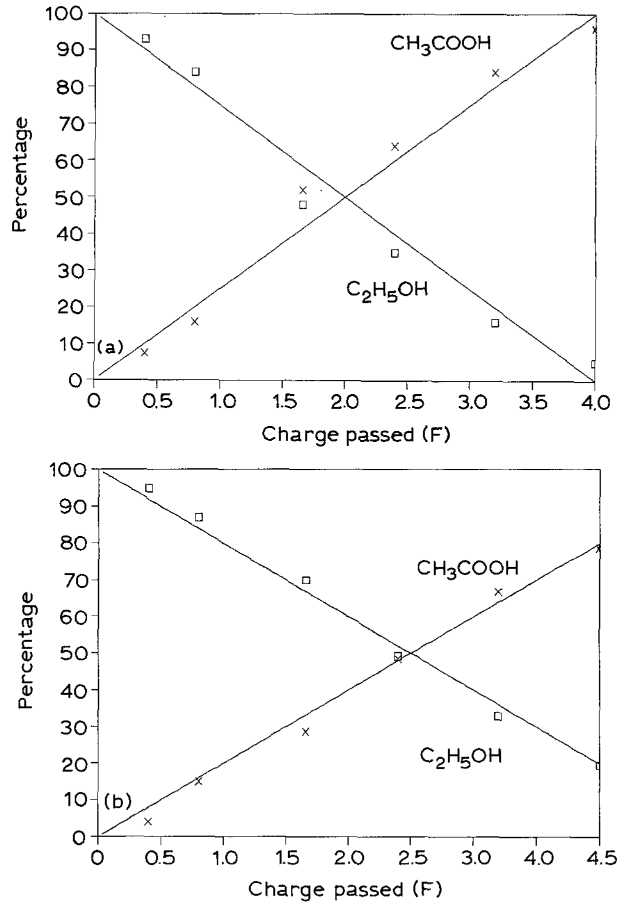

Fig. 2. Loss of ethanol and formation of acetic acid during anodic oxidation of 1 mol dm^{-3} ethanol in 2.5 mol dm^{-3} potassium hydroxide at a $NiCo_2O_4$ coated nickel anode. Current density (a) 0.12 and (b) 0.72 A cm^{-2}. Temperature 333 K.

oxidations, the rates of oxidation are quite similar for all compounds studied (at least, compared to the data at nickel anodes [7]). Such similarity is, however, to be expected if the rate of the chemical step is relatively fast so that the limiting currents are partially mass transport controlled as was found [6] for ethanol oxidation using several different methods of study. Certainly, for all compounds, the limiting currents are in the range 20–60% of that expected for a mass transport controlled reaction.

3.2. *Preparative electrolyses*

Ethanol solutions (1 mol dm^{-3}) in 2.5 mol dm^{-3} potassium hydroxide were electrolyzed in an undivided flow cell with a spinel coated nickel anode at 333 K. During electrolyses at both 0.12 and 0.72 A cm^{-2}, the electrolyte was periodically analysed for organic compounds and only ethanol and acetic acid were ever observed. The results are shown in Fig. 2 and it can be seen that the conversion occurs with excellect selectivity and good current efficiency up to high conversions. In fact, the current efficiencies are 100 and 78% after 4F at the two current densities; at the higher current density some oxygen evolution is also observed. Hence, it can be seen that the reaction occurs very well even at 0.72 A cm^{-2}.

In general, organic molecules are not as soluble as ethanol in water. In the case of benzyl alcohol, electrolyses were carried out with an emulsion of the substrate and the aqueous potassium hydroxide (0.01 mol of the alcohol in 100 cm^3 of aqueous solution). Three current densities (0.03, 0.12 and 0.24 A cm^{-2}) were employed; the selectivity for conversion to benzoic acid was always >97% but the current efficiency decreased with current density, dropping to 50% for the highest current density. A similar procedure was used for the oxidation of octanol. For other compounds, the electrolyses were carried out with an initial substrate concentration of 0.1 mol dm^{-3} and the results are reported in Table 2.

The primary alcohols are all oxidized to the corresponding carboxylic acid with a good selectivity

Table 1.

Substrate	I_L *(mA cm^{-2})*	I_L/n
Methanol	24.5	6.1
Ethanol	24.0	6.0
Butan-1-ol	17.8	4.5
Benzyl alcohol	20.1	5.0
Propan-1, 3-diol	42.0	5.3
Pentane-1, 3-diol	30.8	3.9
Propan-2-ol	13.9	6.9
Cyclohexanol	15.9	8.0
Ethylamine	24.8	6.2
1-butylamine	17.5	4.4
Benzylamine	27.0	6.7

Limiting current densities, I_L, and values of I_L/n for the oxidation of organic compounds (0.1 mol dm^{-3}) in 2.5 mol dm^{-3} potassium hydroxide at a stationary $NiCo_2O_4$ coated titanium disc anode. Room temperature 290 ± 2 K.

although the current efficiency appears to drop with increasing molecular weight. The current efficiencies also decrease with increasing current density as oxygen evolution becomes more important but good results are still obtained at 0.12 A cm^{-2}. The oxidation of crotyl alcohol clearly leads to some undetermined side products while the secondary alcohols must be oxidized at lower current density; the yield of acetone was adversely effected by evaporation and this may also be the case with the nitriles resulting from the oxidation of amines.

There appears to be every reason to believe that most of the interesting reactions reported at nickel anodes in base, may also be carried out with spinel anodes. The spinel, $NiCo_2O_4$, as a coating on nickel or titanium, appears, however, to allow the reactions to occur at much higher current densities (indeed, at current densities approaching mass transport control). This should make the reactions much more convenient in the laboratory as well as more attractive from an economic viewpoint and it should also be noted that the spinel coatings could be used for many electrolyses without apparent loss of activity or physical/chemical damage. It is, however, uncertain as to whether the higher activity compared to nickel oxide results from surface area or a specific chemical factor.

Table 2.

Substrate	*I (mA cm^{-2})*	*Product*	*Material yield (%)*	*Current efficiency (%)*
Ethanol	30	Acetic acid	94	91
	120		85	80
Butan-1-ol	30	Butanoic	83	75
	120	acid	80	60
Octan-1-ol*	30	Octanoic	81	48
	120	acid	90	43
Benzyl	30	Benzoic	99	97
alcohol*	120	acid	99	73
Crotyl	30	Crotonic	43	37
alcohol	120	acid	46	35
Propan-2-ol	15	Acetone	58	28
	30		58	21
Cyclohexanol	15	Cyclohexanone	70	40
	30		68	32
1-butylamine	30	Butyronitrile	73	64
	120		65	56
Benzylamine	30	Benzonitrile	70	48
	120		63	40

Results from the preparative scale electrolyses of 0.1 mol dm^{-3} solutions of organic compounds in 2.5 mol dm^{-3} aqueous KOH. The material yields and current efficiencies are quoted after the passage of stoichiometric charge. The electrolyses were carried out in the Microflow Cell. The electrolysis temperatures were 333 K for primary alcohols and 303 K for other compounds. Electrolyte flow rate 0.5 dm^3 min^{-1}.
* Emulsion.

Acknowledgement

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References

[1] H. J. Schafer, *Topics in Current Chemistry* **142** (1986) 101.
[2] G. W. Briggs, E. Jones and W. F. K. Wynne-Jones, *Trans. Faraday Soc.* **51** (1955) 1433.
[3] K. Manandhar and D. Pletcher, *J. Appl. Electrochem.* **9** (1979) 707.
[4] P. Seiler and P. M. Robertson, *Chimia* **36** (1982) 305.
[5] P. M. Robertson, P. Berg, H. Reimenn, K. Schleich and P. Seiler, *J. Electrochem. Soc.* **130** (1983) 591.
[6] P. Cox and D. Pletcher, *J. Appl. Electrochem.* (in press).
[7] M. Fleischmann, K. Korinek and D. Pletcher, *J. Electroanal. Chem.* **31** (1971) 39.
[8] P. M. Robertson, *ibid.* **111** (1980) 97.