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Electrosynthesis at oxide coated electrodes Part 1 the kinetics of ethanol oxidation at spinel electrodes in aqueous base

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The oxidation of ethanol at Ni/Co spinel coated electrodes in aqueous base has been investigated. It is shown that these electrodes are very stable and have a good catalytic activity for the conversion of ethanol to acetic acid (for example $24\,\mathrm{mA\,cm^{-2}}$ for the oxidation of $0.1\,\mathrm{mol\,dm^{-3}}$ ethanol), far superior to the nickel anodes previously used for the reaction in similar conditions. The *I–E* curve for the oxidation of ethanol at a spinel shows a well formed wave prior to oxygen evolution at a potential where the spinel surface itself undergoes oxidation. The limiting current is partially mass transport controlled. The influence of the electrolysis conditions, the composition of the spinel coated electrodes and of parameters in their preparation, on the rate of ethanol oxidation is described.

1. Introduction

The large, inorganic, electrolytic processes have benefitted enormously, both in terms of selectivity and energy efficiency, from the development of new electrode materials. For example, the chlor-alkali industry has, during the last twenty years, introduced both new metal anodes based on ruthenium dioxide and new cathodes based on high area nickel or precious metal catalysts [1–5]. Almost certainly, the prospects for smaller scale electrolytic processes for the manufacture of fine organic chemicals and specialist inorganic compounds would likewise be enhanced by the availability of electrode materials with properties tailored to the needs of each process [6, 7]. In practice, however, because the economic returns are insufficient, these smaller scale processes generally use very traditional electrodes such as lead, carbon, platinised titanium or lead oxide.

The success of lead dioxide used as a coating on lead, titanium or carbon, however, highlights the possibility of using anodes based on one of the more conducting metal oxides, provided that it has good stability in the electrolysis medium. Indeed, a considerable literature has developed describing the use of nickel (more correctly, nickel oxide) anodes in aqueous base for the oxidation of alcohols, amines and related compounds [8, 9], despite the fact that such syntheses are only possible at low current densities because the mechanism of these anode reactions involves slow chemical steps [10]. More recently, Beck and coworkers have attempted to develop chromium oxide anodes for electrosynthesis in acid solution [11, 12].

In this work we have examined the application of spinel oxides to the oxidation of organic compounds. While spinels are not stable in acid solutions, they show great stability in alkaline media. Hence in this and the following paper we report the study of the oxidation of alcohols in aqueous base at spinels prepared by the thermal decomposition of mixtures of aqueous cobalt and nickel nitrate solutions. Spinels are a group of oxides with the formula $M^{2+}(M^{3+})_2O_4$ and with a lattice structure related to the mineral, spinel ($MgAl_2O_4$) [13, 14]. The most widely used for electrochemistry have been Co_3O_4 and $NiCo_2O_4$, the latter being an example of an inverse spinel, Co(Co, Ni)O_4. Certainly, spinels are very stable in several aqueous environments and can have a conductivity above $10^{-2}\,\mathrm{ohm^{-1}\,cm^{-1}}$, very adequate for use as a coating on an inert metal support. The influence of preparation conditions on subsequent electrochemical parameters has been investigated [15–19] although there remains some uncertainty about details of their electrochemical behaviour; for example, the cyclic voltammetry of $NiCo_2O_4$ in aqueous KOH has been reported to have both two anodic peaks [15, 16] and one anodic peak [18, 19]. Even so, the application of spinel electrodes have been examined in some details and they have been demonstrated to have useful characteristics for oxygen reduction [20–22] and oxygen evolution [16, 23–26] in alkaline media and for chlorine evolution in weakly acidic chloride solutions [17, 27, 28].

2. Experimental details

All solutions were prepared with water purified with a Millipore system. The potassium hydroxide (M & B reagent grade), cobalt nitrate (Koch Light), nickel nitrate (BDH Analar grade) and ethanol (James Burrough) were all used without purification.

Electrochemical experiments were carried out in three electrode, three compartment cells. The working electrode was separated from a Pt gauze counter electrode by a fine glass frit and from the SCE reference electrode (Radiometer type K601) by a Luggin capillary. The Luggin capillary was mounted on a syringe barrel so that the position of its tip with respect to the working electrode could be adjusted. The instrumentation employed was a HiTek potentiostat, type DT 2101, and function generator, type PPR1, and curves were recorded on a Gould series 60 000 X–Y recorder. Steady state curves were generally recorded by applying a 1 mV s^{-1} potential scan from 0 V after the current at this value had fallen to a low value.

The disc electrodes were designed to be demountable from their PTFE surrounds so that the coatings could be formed thermally. They were machined from 5 mm lengths of 5 mm diameter Ti rod (Goodfellow Metals). These fitted snugly into the PTFE sheath and electrical contact was via a threaded brass rod within the sheath. The geometric areas of these discs were 0.2 cm^2 and this was used as the basis for the calculation of current densities. The spinel coatings were prepared by spraying the solution of nitrates with a Jet-Pak chromatography spray. The thermal decomposition of the nitrates was carried out in a Lenton Thermal Design Programmable Furnace.

Scanning electron micrograms and X-ray diffractograms were obtained on a Hitachi 570 electron microscope and a Phillips PW 1130 diffractometer respectively. For these experiments the spinels were deposited onto one side of an acid etched, 1 mm thick, Ti sheet.

3. Electrode preparation and characterization

The spinel layers were coated onto both titanium and nickel. In this study a titanium substrate was generally used for kinetic experiments and nickel for preparative electrolyses but it is believed that nickel and titanium could be used interchangeably, at least for short timescale experiments. Both metals were first degreased with acetone. The titanium was also acid etched to remove surface titanium dioxide; it was placed in 8 mol dm^{-3} hydrochloric acid at 360 K for four hours. The coatings were then prepared by repeating the following sequence five times: (i) an aqueous solution of cobalt and nickel nitrates, total concentration 1–1.5 mol dm^{-3}, was sprayed on the surface immediately after its removal from an oven at 573 K (or the chosen firing temperature); (ii) excess water was removed at 393 K and the nitrates decomposed by heating to a higher temperature (573 K unless otherwise stated) for ten minutes. At the end of the procedure the coating was annealed at the same, higher temperature for 90 minutes. Typically the weight of the coating was 8 mg cm^{-2}. With all compositions studied, the coatings were robust and could be used for many experiments.

Scanning electron microscopy, see Fig. 1, showed that the coatings had a uniform, high area surface while X-ray diffraction analysis confirmed that the layers had a spinel structure. The only other phase indentified was NiO and there was no CoO, Co_2O_3, Ni_2O_3 or $CoNiO_2$. Electrodes with compositions from $Ni_{0.1}Co_{2.9}O_4$ to Ni_2CoO_4 were prepared and the amount of NiO phase increased although always remaining a minor component. With increasing nickel content, the lattice parameter for the unit cell increased slightly from 0.809 to 0.814 nm and the average crystallite size dropped from about 17.5 to 10 nm. Most work used a $NiCo_2O_4$ coating which had a lattice parameter value 0.812 nm and the average crystallite size was 15 ± 2.5 nm.

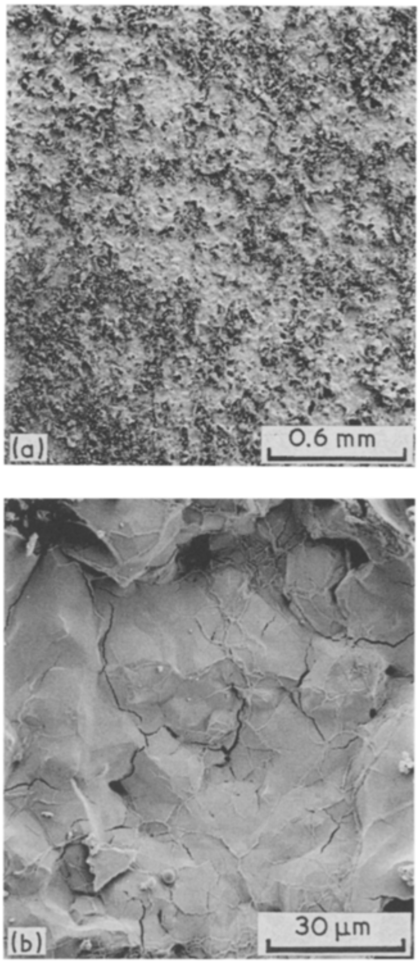

Fig. 1. Scanning electron micrographs of $NiCo_2O_4$ prepared by thermal decompositions of Ni/Co nitrates at 573 K on a Ti substrate.

4. Results

Cyclic voltammograms were run for each of the spinels using a range of potential scan rates and also concentrations of aqueous potassium hydroxide. Figure 2 shows one typical cyclic voltammogram run for $NiCo_2O_4$ in 2.5 mol dm^{-3} KOH at 25 mV s^{-1}. It shows two anodic peaks at + 0.16 V and + 0.33 V against SCE and a single broad reduction peak at + 0.1 V. The peak current densities are proportional to the potential scan rate (25–200 mV s^{-1}) and the charges associated with the oxidation and reduction appear to be the same when allowance is made for the charging current. The value of 60 mC cm^{-2} would be consistent with the peaks being due to the oxidation of

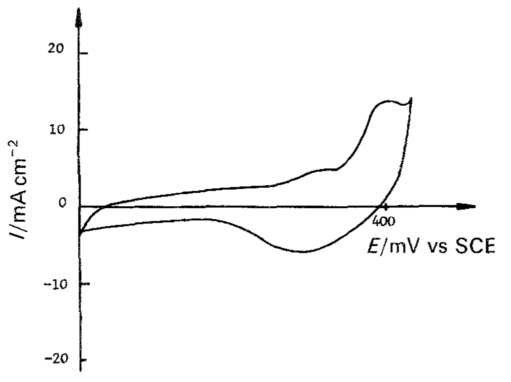

Fig. 2. Cyclic voltammogram for $NiCo_2O_4$ (fired at 573 K) in 2.5 mol dm^{-3} KOH. Potential scan rate 25 mV s^{-1}.

metal ions in the surface layers of a very rough deposit. When the potential is taken positive to + 0.4 V, a very large current is observed and oxygen can be seen evolving from the electrodes. The details of the voltammograms (for example, the quality of the peak shapes and the current densities) were, however, very dependent on the pretreatment steps and all parameters in the preparation of the layers, in addition to the potential scan rate, potential limits and the concentration of KOH. Indeed, we had some difficulty in obtaining totally reproducible voltammograms even under nominally identical conditions. This was not the case with other data reported later in this paper and we conclude that the cyclic voltammetry of the spinel surfaces is unusually sensitive to some parameters; this makes it a less useful technique for ‘quality control’ of spinel electrodes. These conclusions are not at variance with the literature [15–19] which reports a strong variation in the response with experimental conditions and also differences in the voltammograms reported by various groups.

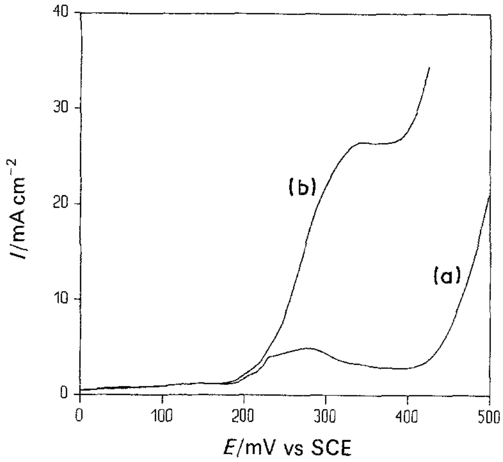

Fig. 3. I-E characteristic recorded at 1 mV s^{-1} for $NiCo_2O_4$ in (a) 2.5 mol dm^{-3} KOH (b) 2.5 mol dm^{-3} KOH + 0.1 mol dm^{-3} C_2H_5OH.

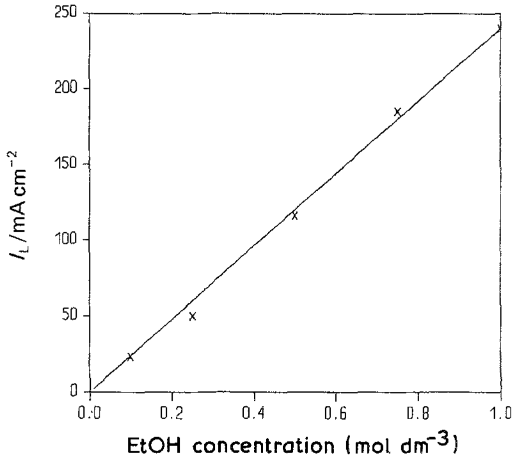

Fig. 4. Variation of the limiting current density for the oxidation of ethanol with the concentration of ethanol. $NiCo_2O_4$ anode in 2.5 mol dm^{-3} KOH. I-E curves recorded at 1 mV s^{-1}.

Figure 3 reports I-E characteristics recorded using a very slow potential scan rate, 1 mV s^{-1}, for a $NiCo_2O_4$ coated Ti disc electrode in 2.5 mol dm^{-3} potassium hydroxide before and after the addition of 0.1 mol dm^{-3} ethanol. In the KOH solution only two low current density peaks are observed at + 0.23 V and + 0.30 V prior to the commencement of oxygen evolution at + 0.4 V. Presumably these anodic peaks again result from the conversion of the metals in the spinel to a higher oxidation state. With ethanol present in the solution, a well formed oxidation wave is observed at $E_{1/2}$ = 0.28 V. The limiting current density was found to be 24 mA cm^{-2}. As with the oxidation of ethanol at nickel in aqueous base the potential for the oxidation wave seems to coincide with that for the change of oxidation state of a metal ion within the surface metal oxide. This suggests that a similar mechanism is operating, that is, a chemical reaction occurs between the higher metal oxide and the ethanol, but the limiting current density is much higher indicating that the rate of the chemical step is considerably enhanced at the spinel. Indeed, the plateau current observed at $NiCo_2O_4$ is a significant fraction of that expected for a diffusion controlled $4e^-$ oxidation of the ethanol to acetic acid (in Part 2 of this series it is shown that this reaction occurs with excellent selectivity and good current efficiency even at high current density). Further experiments showed that the limiting current density for the oxidation of ethanol is proportional to the concentration of ethanol, see Fig 4, but is independent of the KOH concentration (0.25–5 mol dm^{-3}). On the other hand, the half wave potential for the oxidation of ethanol does vary with hydroxide ion concentration; for example, the values were + 0.37 V and 0.22 V for 0.25 and 5 mol dm^{-3} respectively.

The oxidation of ethanol at $NiCo_2O_4$ was also (examined using rotating disc electrode techniques. Figure 5 shows steady state I-E curves (obtained using a point by point procedure) for the oxidation of 0.1 mol dm^{-3} ethanol in 2.5 mol dm^{-3} KOH at rotation rates between 4–30 Hz. It can be seen that the limiting current clearly increase but it is not proportional to the square root of rotation rate, confirming that the reaction is partially mass transport controlled at these potentials. It was also considered of interest to investigate a simple electron transfer couple at the

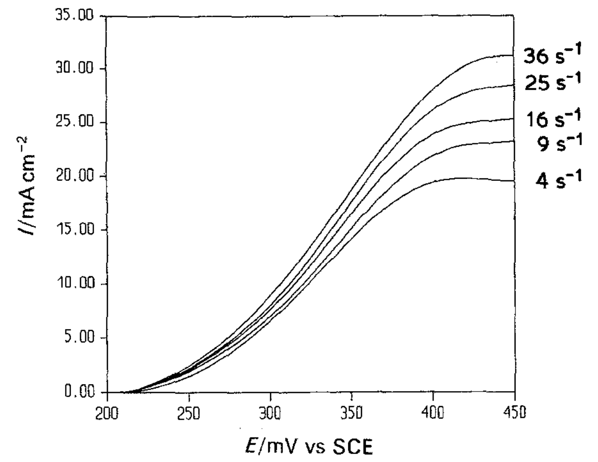

Fig. 5. I-E characteristics as a function of rotation rate for $NiCo_2O_4$ in a solution of ethanol (102 mmol dm^{-3}) + KOH (2.5 mol dm^{-3}). Data obtained using a point by point technique.

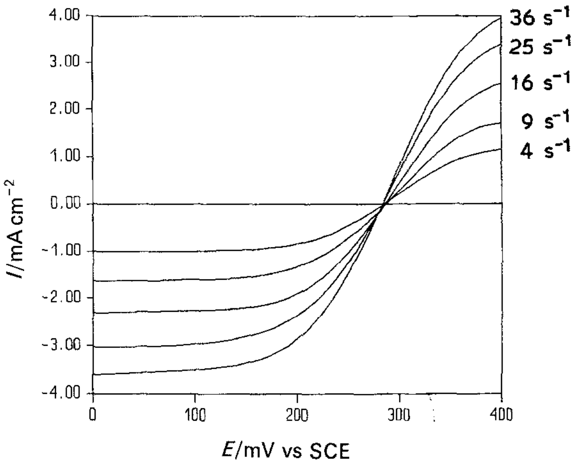

Fig. 6. I-E characteristics as a function of rotation rate for $NiCo_2O_4$ in a solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (each 5 mmol dm^{-3}) + KOH (2.5 mol dm^{-3}). Data recorded using a point by point technique.

spinel electrode. Hence I-E curves were constructed for an equimolar solution of ferrocyanide and ferricyanide at five rotation rates, see Fig. 6. With this couple the limiting currents for both oxidation and reduction are equal and proportional to the square root of rotation rate, confirming that, as expected, the reactions become mass transport controlled at high overpotentials. Moreover, it is apparent from the shape of the curves close to zero overpotential that the standard rate constant for the couple is high at the spinel surface. Hence, at least under some conditions, it is possible for outer sphere electron transfer reactions to occur rapidly at spinel surfaces.

Temperature has a considerable influence on the I-E curves for ethanol oxidation at the spinels, see Fig. 7. With increasing temperature the limiting current increases markedly (for example, the limiting current approximately doubles as the temperature is raised from 292 K to 330 K) although the energy of activation estimated from the limiting currents was only 19 kJ mol^{-1}. This again reflects the partial mass transport control. The half-wave potential also shows a substantial shift to less positive potentials (as does the potential for oxygen evolution); over the range of temperature studied (273–329 K), the half-wave potential shifts 160 mV while the reference electrode shifts only 42 mV.

The Co/Ni ratio in the spinel had some effect on their catalytic activity. Table 1 compares the limiting currents for the oxidation of 0.1 mol dm^{-3} ethanol at six spinel compositions and it can be seen that $NiCo_2O_4$ gives the highest rate of ethanol oxidation. Also in the table for comparison are entries for Co_3O_4, a Zn/Co spinel and three nickel surfaces (a) a polished nickel electrode (b) an electrode prepared by the cathodic deposition of nickel hydroxide from a nickel nitrate solution followed by polarisation at positive potentials in aqueous KOH (c) a high surface area nickel electrode prepared by the deposition of the metal onto copper from a Watt's bath at high current density [29]. The final electrode is capable of giving current densities similar to those obtained with $NiCo_2O_4$ but we believe the stability, robustness and long term performance of the spinel are very superior. During constant potential experiments, there was no decrease in current density over several hours and electrodes could be used for several experiments.

The influence of the preparation conditions of the spinel was then tested. It was found that more stable and reliable electrodes were obtained if the spinel layers was built up slowly using repeated application of thinly sprayed nitrate solutions. On the other hand, at least the short term activity of the anodes did not depend on the weight of the final coating; similar current densities were observed with $NiCo_2O_4$ electrodes with coatings in the range 2 – 20 mg cm^{-2}. Figure 8 shows the influence of the firing temperature for the thermal decomposition of the nitrates. Clearly, low temperatures are advantageous from the viewpoint of catalytic activity although 573 K was, in fact, used for most electrodes as it led to surfaces of higher stability.

Table 1. Limiting current densities for the oxidation of 0.1 mol dm^{-3} ethanol in 2.5 mol dm^{-3} aqueous KOH at various anode materials

Electrode	I_L *(mA cm^{-2})*	*Electrode*	I_L *(mA cm^{-2})*
$Ni_{0.1}Co_{2.9}O_4$	3.3	Co_3O_4	6.8
$Ni_{0.5}Co_{2.5}O_4$	13	$ZnCo_2O_4$	4.2
$Ni_{0.75}Co_{2.25}O_4$	13	Polished Ni	0.24
$NiCo_2O_4$	24	Electrodep. Ni	23
$Ni_{1.25}Co_{1.75}O_4$	19	Electrodep. Ni $(OH)_2$	9.7
$Ni_{1.5}Co_{1.5}O_4$	19		

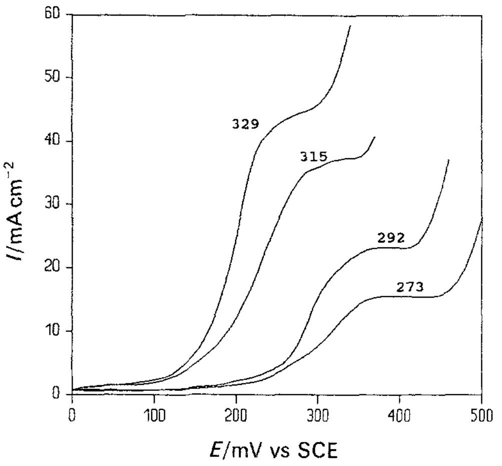

Fig. 7. I-E curves as a function of temperature for the oxidation of ethanol (0.1 mol dm^{-3}) in 2.5 mol dm^{-3} KOH at a $NiCo_2O_4$ anode. Curves recorded using a potential scan rate of 1 mV s^{-1}.

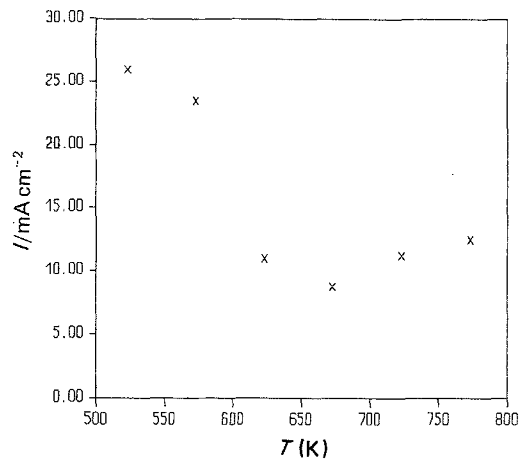

Fig. 8. Limiting current density for the oxidation of ethanol (0.1 mol dm^{-3}) in 2.5 mol dm^{-3} KOH at $NiCo_2O_4$ as a function of the temperature for the thermal decomposition of the nitrates during the preparation of the spinels.

5. Discussion

The Co/Ni spinels are clearly very effective electrocatalysts for the oxidation of ethanol to acetic acid (and a later paper will show that the conversion of alcohols to carboxylic acids is a general reaction). This oxidation takes place at several metal oxide anodes (such as Ni, Co, Cu, Ag) in aqueous base [8, 30, 31]; in all cases the mechanism of the reaction involves a rate determining chemical reaction between a higher oxidation state metal oxide on the anode surface and the organic substrate. Hence although the selectivity and current efficiency for these oxidations are frequently high, the rate of conversion is uncomfortably low for practical synthesis. This has led to several attempts [8, 29, 32–35] to prepare high surface area nickel oxide electrodes which would give the same performance at enhanced current densities. No reported nickel oxide electrodes combine the activity and stability shown by the cobalt spinels in this study. The most active spinels give limiting currents two orders of magnitude larger than that at polished nickel while experience shows that the spinel electrodes may be used for many experiments without change of behaviour. The spinel surfaces are certainly very rough but it is not clear whether their high activity results only from this high area or whether there are also specific chemical catalytic effects as well. The variation of limiting current density with the spinel composition argues either for a change in surface area or for some change in rate of the chemical step. Although scanning electron microscopy showed no obvious evidence for a change in surface area, it is difficult to distinguish the two possibilities conclusively.

It is also interesting to note that the most active spinel for the oxidation of ethanol, $NiCo_2O_4$, is also the best catalyst for oxygen evolution. Moreover, the temperature for the decomposition of the nitrates during the preparation of the layers also influences the activity for both reaction in the same way. The most active electrodes are prepared at lower temperatures. Haenen *et al.* [16] believe that the main effect of the lower firing temperature is to increase the surface area but Trasatti [36] suggest that lower crystallinity and an excess of oxygen in the lattice may be other important factors resulting from a lower firing temperature. He also believes that higher firing temperatures lead to the formation of a poorly conducting oxide layer between the spinel and the metal substrate.

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