

Derivatised nickel and cobalt oxide modified electrodes: effect of surfactant

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Abstract

The oxide/oxyhydroxide electrodes of nickel and cobalt have been prepared by cycling the respective metal hexacyanoferrate modified electrodes in alkali. The voltammetric behaviour of these derivatised electrodes prepared in the presence and absence of surfactant is described. The results reported pertain to the effects noticed in the presence of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB). Enhanced film growth and improved electrochemical reversibility observed for metal hexacyanoferrate modified electrodes in the presence of CTAB are inherited and retained by the derivatised electrodes during treatment with alkali. Cyclic voltammetry and scanning electron microscopy techniques are used to substantiate the results observed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chemically modified electrodes; Cyclic voltammetry; Hexacyanoferrate of cobalt and nickel; Oxide derivatives; Surfactant

1. Introduction

The nickel oxide electrode system has been the object of extensive study [1] in regard to both electrochemical and structural aspects. Information is scarce for obtaining modification with nickel hydroxide on a glassy carbon (GC) surface [2,3]. In one of the methods Ni(OH)₂ is formed on the surface by ex situ chemical precipitation [2], which involves immersion of the GC substrate in 0.01 M NiNO₃ and then in 0.01 M NaOH for about 3 s. The thickness of the modifying layer was controlled by the number of immersions. In another method the Ni(OH)₂ is formed from 10 µl of 50 mM NiNO₃ solution on the surface of a GC electrode [4]. A novel procedure for the preparation of Ni(OH)₂ by surface derivatisation of NiHCF on GC was reported by Joseph et al. [5–7].

The electrochemical behaviour of cobalt oxyhydroxide compounds is reported to be complex in comparison with nickel oxyhydroxide compounds, since higher oxidation states can be attained in the former case

[8–10]. The behaviour is also dependent on the experimental conditions, such as potential limits or scan rates in cyclic voltammetric experiments [8]. A recent publication [11] reported that cobalt oxide films were grown anodically on transparent/conducting glass from a 0.01 M Co(NO₃)₂ and 0.1 M sodium acetate aqueous solution using a current density of 76 µA cm⁻². The possible electron transfer reaction at $E = -0.175$ V versus the standard calomel electrode (SCE) in 0.1 M KOH corresponds to the Co(OH)₂ → Co₃O₄ transition according to Ref. [8] followed by another peak at $E = 0.2$ V corresponding to the Co(OH)₂ → CoOOH and Co₃O₄ → CoOOH transitions.

A third oxidation reaction peak, hidden by the oxygen evolution reaction curve and corresponding to the transition CoOOH → CoO₂, is frequently cited in the literature [8–10]. On scan reversal, three reduction peaks corresponding to the three oxidation peaks are reported corresponding to the peak potentials at $E = 0.45$, 0.15 and about -0.15 V versus SCE. The latter peak is less intensive. These potential values clearly indicate that the two sets of redox peaks prior to oxygen evolution are associated with good reversibility. Reversibility of the cobalt oxide/oxyhydroxide system is also well referenced in Refs. [8,10,12].

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A similar response as in Refs. [11,12] was obtained in our earlier work [7], wherein the electrochemical response of GC coated with CoHCF (cobalt hexacyanoferrate) in 1.0 M NaOH is associated with two sets of redox peaks at about -0.175 and $+0.40$ V versus SCE. The possible use of a counter electrode of cobalt oxide/oxyhydroxide in the nickel oxide/oxyhydroxide electrochromic system is discussed in this paper.

The effect of surfactants on the modification of electrodes with various metal hexacyanoferrates and their oxide derivatives has been investigated by us for the first time [13–15]. The novel and interesting possibility of derivatisation of some metal hexacyanoferrates, especially NiHCF and CoHCF, to their oxide derivatives, with the added beneficial effects noticed in the presence of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) for metal hexacyanoferrates, has made it inevitable that the oxide derivatisation studies should be performed in the presence of added surfactant. It is pertinent to mention here that the parent compound Prussian blue (PB) dissolves in alkali and is not derivatised to its corresponding oxide. The interesting cyclic voltammetric properties of these novel derivatised surface films and the scanning electron micrographic results of cobalt oxide film are discussed in this paper.

2. Experimental

A three-electrode cell, assembled with a platinum counter electrode, standard calomel reference electrode and platinum working electrode (2 cm^2), was used. All cyclic voltammetric experiments were carried out with a potentiostat (Wenking Model LB 75) coupled to a Wenking voltage scan generator VSG 72 and X - Y recorder (Rikadenki — RW 201). All chemical substances were of analytical grade and used without fur-

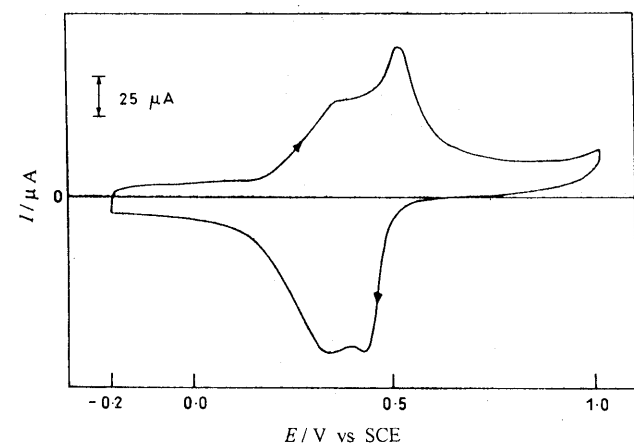


Fig. 1. CV response of a NiHCF modified GC electrode in 0.1 M KCl at 100 mV s^{-1} .

ther purification. Doubly distilled water was used for preparing solutions. Solutions for modification were prepared fresh each time. Prior to modification, the platinum electrodes were subjected to ultrasonic cleaning and flame treatment. All the potentials reported are measured with respect to an SCE unless specified otherwise. The potential of the SCE is $+0.24$ V versus the standard hydrogen electrode (SHE).

The modification of the electrodes with NiHCF/CoHCF film involved potential cycling of the electrode in the modifying mixture, which contains, as the case may be, $0.5\text{ mM NiCl}_2/\text{CoCl}_2 + 0.5\text{ mM K}_3\text{Fe}(\text{CN})_6$ in $0.1\text{ M KCl} + 0.02\text{ M HCl}$ from -0.2 V to 1 V, at a sweep rate of 0.1 V s^{-1} for 15 min. 0.92 mM of CTAB was added to the modifying mixture whenever required. The optimum concentration of CTAB solution to be added to the modifying mixture was found to be 0.92 mM by trial experiments; this corresponds to its critical micelle concentration (cmc), and beneficial effects are noticed only at this concentration.

3. Results and discussion

3.1. Nickel oxide films

Fig. 1 shows the usual cyclic voltammetry (CV) response of the NiHCF modified GC electrode in 0.1 M KCl at a scan rate of 100 mV s^{-1} . The CV exhibits two sets of reversible redox peaks, one at 0.35 V and the other at around 0.48 V.

Fig. 2 shows the response of the NiHCF modified electrode in 0.1 M NaOH at 100 mV s^{-1} . The electrode becomes derivatised to the oxide species quantitatively, as reported earlier [5,6]. The anodic and cathodic peaks occur at ~ 0.38 V and 0.24 V respectively. The redox reaction of this derivatised oxide electrode is represented as follows:



At potentials positive of 0.45 V there is a sharp rise in anodic current due to oxygen evolution.

In a subsequent experiment, modification of the electrode with NiHCF was carried out in the modifying solution to which 0.92 mM of CTAB was also added.

Fig. 3 shows the CV response of this NiHCF + CTAB modified electrode in 0.1 M KCl at a scan rate of 100 mV s^{-1} .

It is noted that two sets of redox peaks are obtained with the NiHCF film electrode, also prepared in the presence of CTAB. In this case the first set of redox peaks appear at ~ 0.32 V and the second at ~ 0.45 V. The striking feature observed in the CV obtained for the films prepared in the presence of CTAB is the highly reversible nature of the redox peaks, which are sharp and show exact symmetry over the X -axis; this

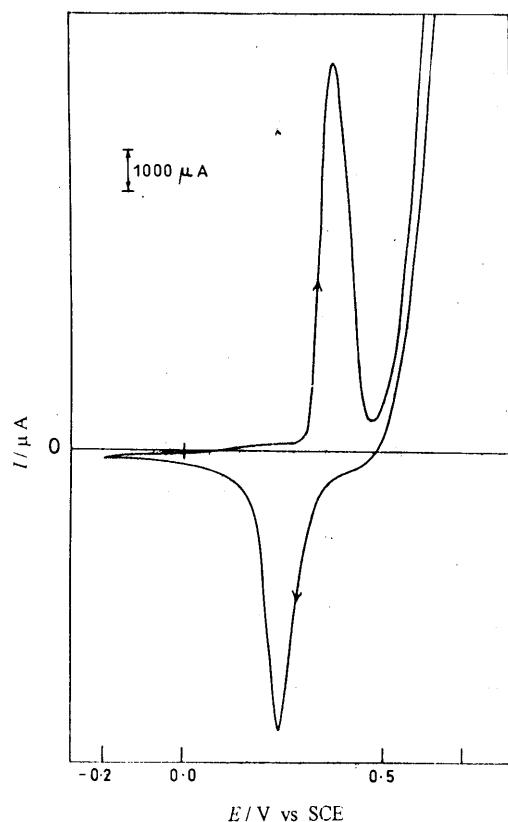


Fig. 2. CV response of a NiO-modified electrode in 0.1 M NaOH at 100 mV s^{-1} .

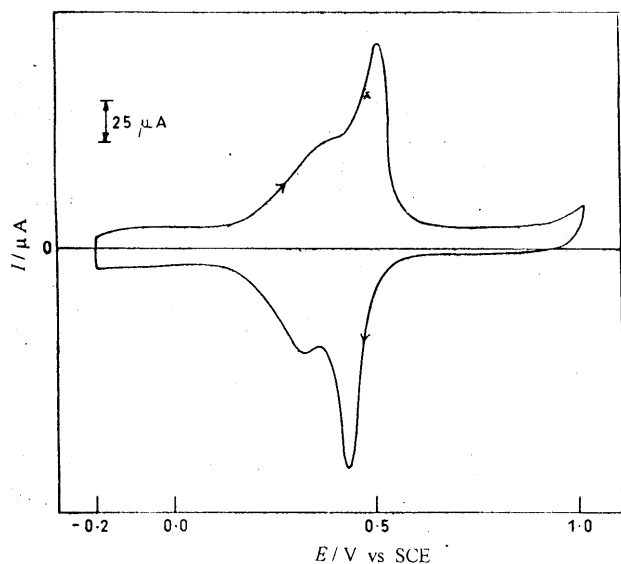


Fig. 3. CV response of a NiHCF + CTAB – modified GC electrode in 0.1 M KCl at 100 mV s^{-1} .

can be easily appreciated by a comparison of Figs. 1 and 3. It is clear from the cyclic voltammetric response that addition of CTAB does not cause any change in peak potential values, whereas peak current values are enhanced as observed for PB + CTAB films.

NiHCF + CTAB film on further cycling in 0.1 M NaOH yields the CV response presented in Fig. 4. By comparing Figs. 2 and 4 one can see that there is no change in the shapes of the CVs. An enhancement of cathodic and anodic currents can immediately be noticed in 0.1 M NaOH for NiO + CTAB film, as observed for the parent NiHCF + CTAB film in 0.1 M KCl. Table 1 shows the cyclic voltammetric parameters of NiO, and NiO + CTAB modified electrodes in 0.1 M NaOH at scan rates of 5, 100 and 200 mV s^{-1} .

It can be seen from Table 1 that there is no significant change in the peak potential parameters due to the addition of CTAB. However, considerable enhancement can be seen in the anodic and cathodic peak currents, particularly at higher sweep rates, in the case of the NiO modified electrode prepared in the presence of CTAB. Further, the Q_a/Q_c ratio is much closer to unity in the case of the NiO films formed in the presence of CTAB, in comparison with the Q_a/Q_c ratio obtained with NiO films formed without CTAB. The NiO films formed both in the presence and absence of CTAB were extremely stable and they lasted for several

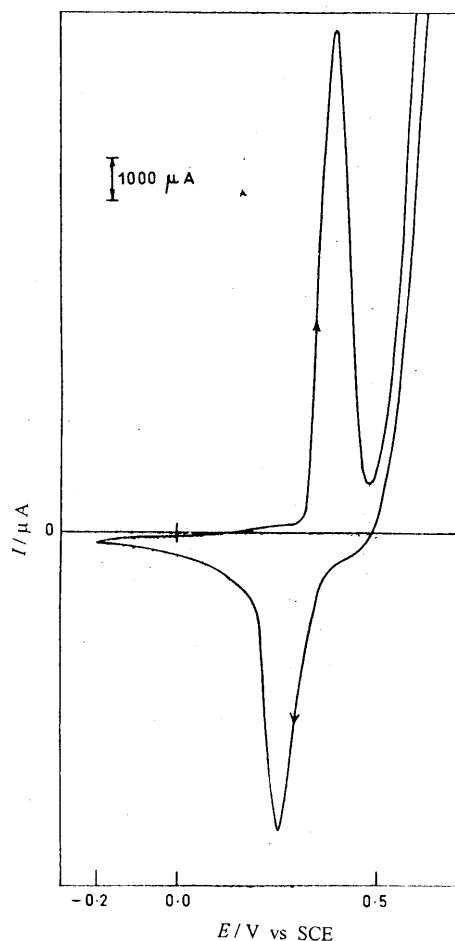


Fig. 4. CV response of a NiO + CTAB – modified electrode in 0.1 M NaOH at 100 mV s^{-1} .

Table 1
CV parameters of NiO, and NiO+CTAB-modified electrodes in 0.1 M NaOH at scan rates 5, 100 and 200 mV s⁻¹ (Pt area: 2 cm²)

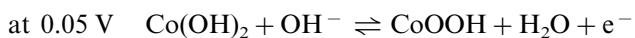
	Scan rate/mV s ⁻¹	E _{pa} /V	E _{pc} /V	ΔE _p /V	10 ⁴ I _{pa} /A	10 ⁴ I _{pc} /A	Q _a /mC cm ⁻²	Q _c /mC cm ⁻²
NiO	5	0.34	0.26	0.08	20.5	9.50	3.2	3.7
	100	0.38	0.23	0.15	99.0	55.00	3.2	3.6
	200	0.40	0.23	0.17	139.0	82.00	2.7	2.9
NiO+CTAB	5	0.35	0.27	0.08	22.0	10.00	4.9	4.7
	100	0.40	0.25	0.15	124.0	74.00	3.9	3.9
	200	0.42	0.25	0.17	182.0	112.50	3.3	3.2

hundreds of cycles without reduction of charge under the redox peaks.

3.2. Cobalt oxide films

Fig. 5 depicts the typical CV response of the CoHCF modified electrode in 0.1 M KCl + 0.1 M HCl at 100 mV s⁻¹. At this scan rate only one broad peak (a₁) appears on the anodic side at about 0.45 V, and on the cathodic side one sharp peak (c₂) appears at ~0.5 V and one broad peak (c₁) at ~0.3 V. It is assumed that two peaks (a₁ and a₂) have merged into one broad peak (a₁) on the anodic side under our experimental conditions.

Fig. 6 gives the stabilised cyclic voltammetric response of a CoHCF derivatised CoO modified electrode in 0.1 M NaOH at 50 mV s⁻¹. The CV shows two sets of redox peaks: one at a formal potential of ~0.05 V (a₁c₁) and the other at ~0.25 V (a₂c₂). The redox reactions occurring at the two formal potentials are represented as follows [7]:



At potentials positive of 0.5 V there is a sharp rise of anodic current due to the evolution of oxygen.

In a subsequent experiment, modification of the electrode with CoHCF was carried out in the modifying solution to which 0.92 mM of CTAB was also added.

Fig. 7 shows the CV response of the CoHCF + CTAB modified electrode in 0.1 M KCl + 0.1 M HCl at a scan rate of 100 mV s⁻¹. In this case too, as in the case without CTAB, the anodic peak a₁ and the cathodic peak c₁ appear at about 0.45 V and 0.3 V respectively (at more negative potentials). At the second redox centre, at more positive potentials, an anodic wave a₂ appears at ~0.58 V and its corresponding cathodic peak c₂ appears at 0.5 V, as in the case without CTAB. An additional prewave appears on the anodic side before a₁, whose origin is not clear at the moment. At a glance one can notice the great enhancement of the currents at the first redox centre a₁c₁ due to the addition of CTAB. (cf. Figs. 5 and 7).

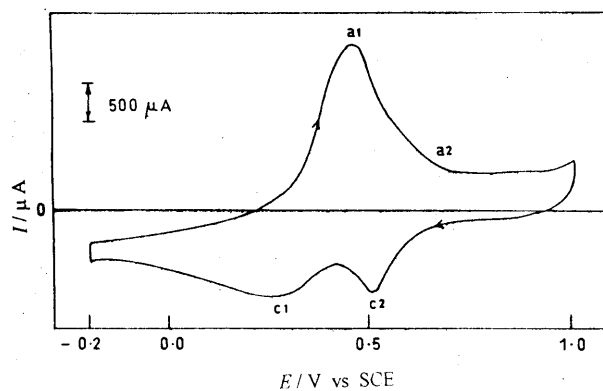


Fig. 5. CV response of a CoHCF – modified electrode in 0.1 M KCl + 0.1 M HCl at 100 mV s⁻¹.

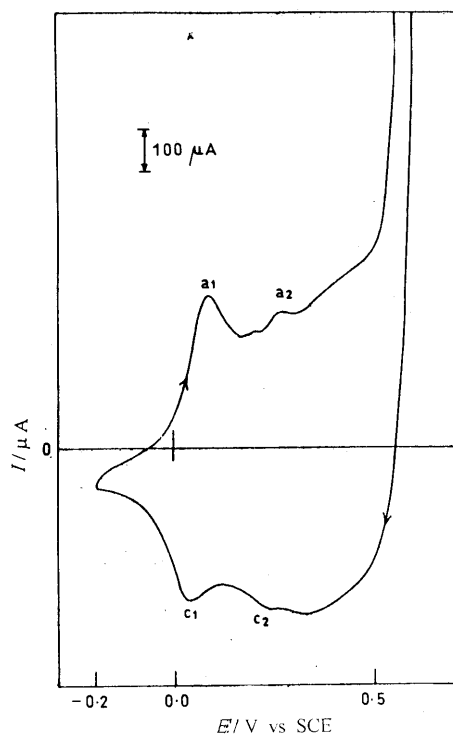


Fig. 6. CV response of a CoO – modified electrode in 0.1 M NaOH at 50 mV s⁻¹.

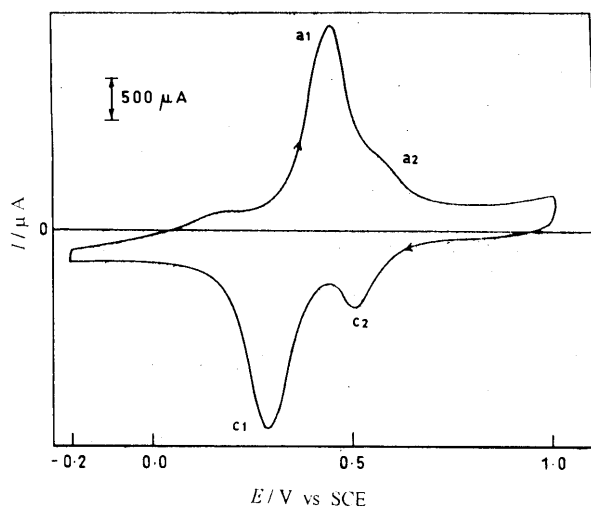


Fig. 7. CV response of CoHCF + CTAB – modified electrode in 0.1 M KCl + 0.1 M HCl at 100 mV s^{-1} .

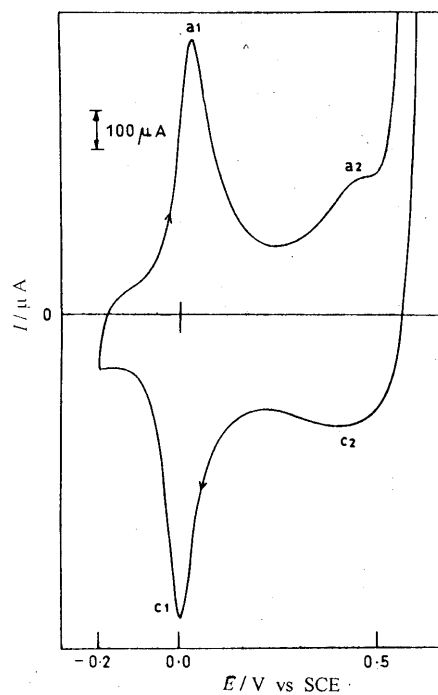


Fig. 8. CV response of a CoO + CTAB modified electrode in 0.1 M NaOH at 50 mV s^{-1} .

Now the resulting CoHCF + CTAB modified electrode is derivatised to a CoO + CTAB electrode in the same way as described above for the NiO + CTAB electrode. Fig. 8 illustrates the CV response of the CoO + CTAB modified electrode in 0.1 M NaOH at 50 mV s^{-1} .

It is very interesting to note that one set of sharp reversible redox peaks a_1 c_1 now appear at $\sim 0.03 \text{ V}$, at a slightly less positive potential (as against 0.05 V in the absence of CTAB). A second set of redox waves a_2 c_2

can also be noticed at $\sim 0.43 \text{ V}$ (at more positive potentials compared with a_2 c_2 of Fig. 6), however, with much smaller currents than those for the first set of redox peaks. Thus the addition of CTAB also resulted in sharper redox peaks being obtained (Fig. 8), with enhanced currents in the first redox centre.

Figs. 9 and 10 show the CV behaviour of CoO, and CoO + CTAB modified electrodes respectively in 0.1 M NaOH at different scan rates and illustrate more clearly the above-mentioned aspects. Table 2 shows the cyclic voltammetric parameters of CoO, and CoO + CTAB modified electrodes in 0.1 M NaOH at sweep rates of 5, 100 and 200 mV s^{-1} . In the case of CoO films formed in the absence of CTAB, peak current and peak potential values are given for both the redox centres and values of total charge under the anodic peaks a_1 and a_2 and total charge under the cathodic peaks c_1 and c_2 are given, corresponding to each scan rate in Table 2. The origin of the large capacitance observed in the voltammograms in Figs. 6–10 is not immediately clear. This is probably associated with the complex nature of adsorption of cobalt hexacyanoferrate film on Pt surface and its subsequent derivatisation behaviour in alkali, with the complexity being enhanced further in the presence of added surfactant CTAB.

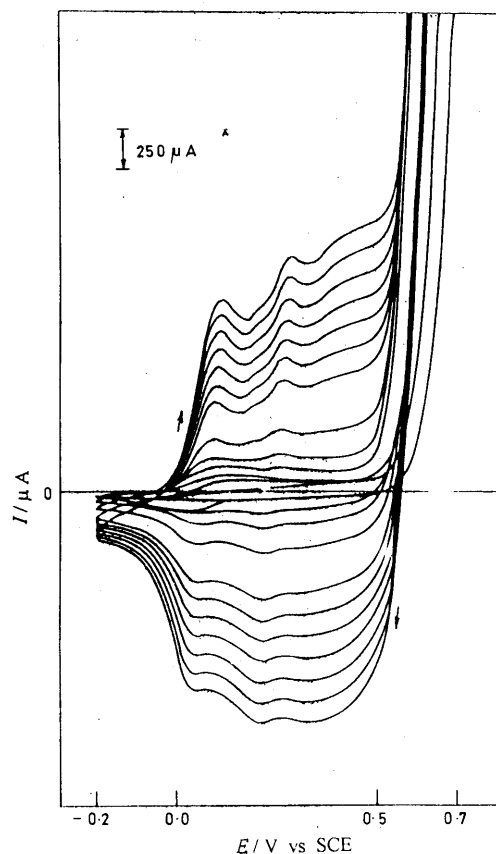


Fig. 9. CV response of a CoO – modified electrode in 0.1 M NaOH at 5, 10, 20, 40, 80, 100, 120, 140, 160, 180 and 200 mV s^{-1} .

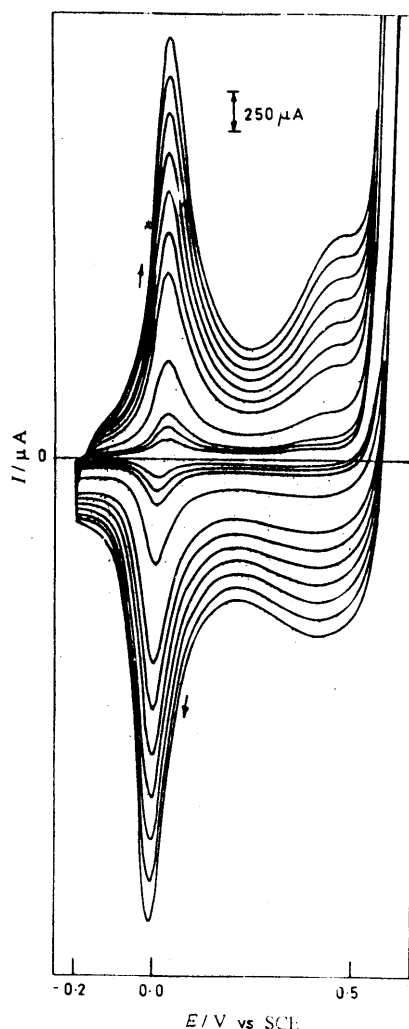


Fig. 10. CV response of a CoO+CTAB – modified electrode in 0.1 M NaOH at 5, 10, 20, 40, 80, 100, 120 140, 160, 180 and 200 mV s^{-1} .

In the case of CoO film formed in the presence of the CTAB addition, analysis of the CV data is restricted to the reversible redox peaks at ~ 0.03 V, as a similar analysis for the second redox centre is not easy as it appears as a voltammetric wave. From the charge

values of films, formed with and without CTAB, it can be seen that there is an enhancement of the charge of three to four times at higher scan rates, due to the addition of CTAB during modification of the electrodes.

The reversible redox centre of CoO + CTAB film at the formal potential 0.03 V was analysed for its CV parameters. Table 3 depicts the cyclic voltammetric parameters of a CoHCF + CTAB derivatised CoO + CTAB modified electrode in 0.1 M NaOH at different scan rates. It can be seen from the table that the ΔE_p ($E_{pa} - E_{pc}$) value becomes as low as 20 mV at slow scan rates. This tendency for $\Delta E_p \rightarrow 0$ mV as v reaches 0 mV s^{-1} indicates a reversible charge transfer process involving a surface redox reaction. The I_{pa}/I_{pc} ratio is also seen to be nearly unity at all the scan rates and conforms to the above conclusion. Values of Q_a and Q_c are nearly equal at different scan rates, as required for the reversible redox process on the surface of the modified electrode. Finally, I_p/v for both anodic and cathodic peaks is also noted to be nearly constant, independent of sweep rate, as per the above scheme.

The CoO and CoO + CTAB films are highly stable against prolonged cycling of the electrode potential, i.e. no reduction of charge under the anodic and cathodic peaks was observed after cycling for a long period of about 2 h.

3.3. Spectral studies

Cataldi et al. [16] reported X-ray photoelectron spectroscopy (XPS) in ultrahigh vacuum (UHV) and CV results to characterise the NiHCF deposit on GC electrodes before and after treatment in high pH solutions. The results indicate that NiHCF films undergo profound and chemically irreversible alterations in alkaline solutions. Even though slight alterations were observed in Ni 2p signals, the iron present in the film suffered the most changes with final dissolution in the supporting electrolyte. The differences between a typical nickel oxide electrode and a derivatised nickel oxide electrode have been elucidated by X-ray diffraction, impedance

Table 2
CV parameters of CoO and CoO+CTAB-modified electrodes in 0.1 M NaOH at sweep rates 5, 100 and 200 mV s^{-1} (Pt area: 2 cm^2)

	Scan rate/ mV s^{-1}	E_{pa}/V	E_{pc}/V	$\Delta E_p/\text{V}$	$10^4 I_{pa}/\text{A}$	$10^4 I_{pc}/\text{A}$	$Q_a/\text{mC cm}^{-2}$	$Q_c/\text{mC cm}^{-2}$
CoO a_1c_1 centre	5	0.11	0.05	0.06	1.00	1.25	0.95	0.93
	100	0.11	0.04	0.07	6.50	6.75	0.19	0.19
	200	0.11	0.04	0.07	12.00	12.50	0.14	0.14
a_2c_2 centre	100	0.27	0.21	0.06	8.25	8.25		
	200	0.28	0.21	0.07	14.75	14.75		
CoO+CTAB	5	0.03	0.01	0.02	1.25	1.25	0.60	0.58
	100	0.04	0.00	0.04	14.25	15.75	0.58	0.55
	200	0.05	-0.01	0.06	26.25	29.00	0.56	0.54

Table 3
CV parameters of CoHCF+CTAB-derivatised CoO+CTAB-modified electrode in 0.1 M NaOH (Pt area: 2 cm²). Data for the redox peaks at 0.03 V

Scan rate/mV s ⁻¹	E_{pa}/V	E_{pc}/V	$\Delta E_p/V$	$10^4 I_{pa}/A$	$10^4 I_{pa} b^{-1/2}/A V^{-1/2}$	$10^4 I_{pc}/A$	$10^4 I_{pc} b^{-1/2}/A V^{-1/2}$	I_{pa}/I_{pc}	$Q_a/mC cm^{-2}$	$Q_c/mC cm^{-2}$
5	0.03	0.01	0.02	1.25	250.00	1.25	250	1.00	0.60	0.58
10	0.03	0.01	0.02	2.00	200.00	2.00	200	1.00	0.54	0.52
20	0.03	0.01	0.02	2.75	137.5	3.00	150	0.92	0.50	0.48
40	0.03	0.01	0.02	6.25	156.0	6.75	169	0.93	0.44	0.42
80	0.04	0.00	0.04	11.75	147.0	12.75	159	0.92	0.56	0.54
100	0.04	0.00	0.04	14.25	142.5	15.75	157	0.91	0.58	0.55
120	0.04	0.00	0.04	16.75	139.6	18.50	154	0.91	0.51	0.50
140	0.05	0.00	0.05	19.25	137.4	21.25	151	0.91	0.57	0.55
160	0.05	-0.01	0.06	21.75	136.0	23.75	148	0.92	0.55	0.53
180	0.05	-0.01	0.06	24.00	133.0	26.50	148	0.91	0.52	0.51
200	0.05	-0.01	0.06	26.25	131.2	29.00	145	0.91	0.56	0.54

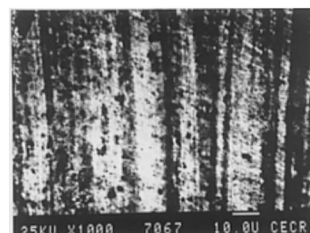
spectroscopy and scanning electron microscope (SEM) studies [17]. These studies indicated the derivatised nickel oxide electrode to be more electroactive, having a uniform surface structure and facilitating electron transfer at a faster rate.

SEM studies of cobalt hexacyanoferrate film before and after cycling in alkali, at magnifications of 100, 500, 1000 ×, etc., are presented in Fig. 11(a)–(e) [18]. It is very clear from Fig. 11(d) and (e) (after treatment in alkali) and Fig. 11(b) and (c) (before treatment with alkali) that profound structural changes accompany the transformation of CoHCF film to its oxide/oxyhydroxide film in alkali. From the SEM images it is also clear that cobalt hexacyanoferrate has an amorphous nature, whereas the CoHCF film cycled in alkali has developed an orderly dendritic structure. The structural pattern of cobalt oxide/oxyhydroxide is entirely different from that of the oxide/oxyhydroxide of nickel reported earlier [17]. The SEM images of NiHCF in alkali revealed only reactivity differences. Not much information as to the structural changes could be obtained from the SEM images [17]. The present results are in tune with XPS studies on NiHCF film in alkali reported by Cataldi et al. [16], wherein profound and chemically irreversible alterations in alkaline solutions are reported.

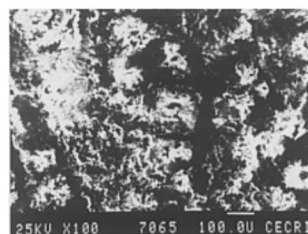
From a literature survey it is clear that already some attempts have been made in modelling the surfactant adsorption [18–21]. The cyclic voltammetric measurements performed on monolayers of a surfactant derivative of Ru(bpy)₃²⁺ at an indium tin oxide electrode revealed information about structural features of the molecular organisation, the electron transfer properties and other chemical characteristics [18]. These studies mainly belong to the field of electrochemistry in ordered systems. The stability of nitrobenzene in anionic micelles arises from a relatively strong surface interaction. From suitable models it has been proposed that nitrobenzene reacts with sodium dodecyl sulphate in

a surface process at the Stern layer of this system. Residence of the anion radicals of nitrobenzene in this same region results in enhanced stability of these species with respect to consumptive homogeneous chemical reactions [20].

The tentative thinking on the effect of surfactant in the case of NiHCF formed in the presence of CTAB is



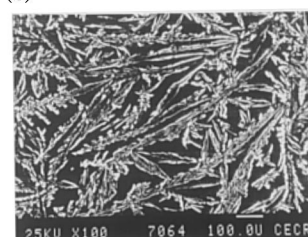
(a)



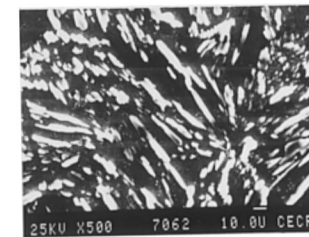
(b)



(c)



(d)



(e)

Fig. 11. SEM micrographs of: (a) SnO₂ surface at ×1000; (b) CoHCF film on SnO₂ at ×100; (c) CoHCF film on SnO₂ at ×1000; (d) CoHCF film on SnO₂ after cycling in NaOH at ×100; (e) CoHCF film on SnO₂ after cycling in NaOH at ×500.

discussed in another publication [15]. The beneficial effects noticed in the presence of CTAB (facilitating the entry of K^+ ions into the channels) only at a specific concentration corresponding to its cmc add support to the thinking that the effects observed are, by and large, attributable to the specific orientation of the surfactant molecule at the electrode surface. This view gains support from a recent demonstration [22] that, on RPG and GC surfaces, the surfactant polar head groups interact with hydrophilic groups at the surface leading to the formation of hemimicelles at the interface. Moreover, the surfactant addition seems to contribute more towards altering the structure of the double layer. Concerted efforts to evolve suitable models for the systems under study in combination with contributions by surface analytical techniques will help in enhancing the understanding in this new area of research.

4. Conclusion

The beneficial effects noticed due to the addition of CTAB during modification of electrode surfaces with hexacyanoferrates of nickel and cobalt are manifested by increased peak current, charge and improved electrochemical reversibility. These effects are reflected by the respective oxide derivatives in alkaline media as revealed by the cyclic voltammetric response. The present approach offers a novel route for the preparation of catalytic nickel and cobalt oxides with improved qualities. Studies on the electrocatalytic performance of these derivatised oxide electrodes are in progress.

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