

TRANSITION METAL OXIDE ANODES AND THEIR APPLICATION IN THE SYNTHESIS OF ORGANIC COMPOUNDS

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The transition metal compounds are well known for their catalytic activities in the redox process. In electrochemical synthesis of organic and inorganic compounds the transition metal anodes are widely used. It is supposed that these anodes under alkaline conditions are covered with their oxides, hydroxides and oxyhydroxides.

In this communication, we are reporting an entirely new electrochemical method for the preparation of cobalt and nickel oxyhydroxide anodes on substrates of stainless steel, graphite and titanium and their application for the oxidation of organic compounds.

Keywords : Transition Metals; Oxide Anodes; Synthesis of Organic Compounds; Redox Process; Anodic Deposition; Ion Concentration; Effect of pH ; Current Density

INTRODUCTION

THE transition metals or their compounds are well known for catalytic activity in the redox processes. For electrochemical oxidations, anodes having an oxide layer have been reported to be suitable. Since these electrodes have low oxygen over-voltage they can be used for controlled oxidation in an alkaline medium. Literature survey shows that the number of anodes of practical use at higher pH values are restricted to few in numbers. The cobalt and nickel electrodes which are generally used as anodic materials in an alkaline solution are supposed to be covered with their respective oxides (Galizziali *et al.*, 1974; and Conway *et al.*, 1969). Very few papers have appeared on the preparation of cobalt-oxide electrode (Wishvender & Jorge, 1971; Grube & Feuchit, 1922; Wernicke, 1870; Coehn & Glaser, 1903; Elsemongy *et al.*, 1977; and Cowling & Riddiford, 1969) and nickel oxide electrode (Benson *et al.*, 1964; Miles *et al.*, 1978; Jones *et al.*, 1978; Briggs *et al.*, 1955; Wertes *et al.*, 1972; Fioshim *et al.*, 1971; and Pechatnova *et al.*, 1978).

Remnev *et al.* (1974) and Shub *et al.* (1978) reported the thermal coating of spinel cobalt oxide from cobalt nitrate on titanium substrate at 350 °C. Recently, Klepikov and Syseeva (1978) have shown that cobalt oxide can be deposited electrophoretically from 40 per cent suspension of cobaltous oxide hydrate in isopropyl alcohol medium on a platinum support.

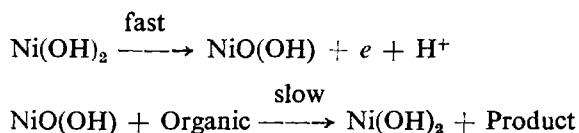
Briggs *et al.* (1955) have investigated the deposition of nickel oxide from an alkaline bath containing nickel sulphate. Other investigators (Fioshim *et al.*, 1971;

and Pechatnova *et al.*, 1978) have shown that nickel oxide can be deposited by the thermal method.

In the present study, cobalt and nickel oxides were deposited from a bath containing simple metal amine complexes. The procedure involved herein is very simple and avoids the complication of maintaining *pH* and metal ion concentration, because here the complex ions which are larger in size than simple aquaions maintains the requisite metal ion concentration and *pH* at the electrode surface. It has been observed that the deposition can be obtained even from the $1 \times 10^{-2}M$ solution of the complex.

The most of the reported studies of partial oxidation of organic compounds have been carried out on the platinum, graphite or on other noble metal anodes (Sato *et al.*, 1908; Conway & Vijh, 1967; Parker, 1968; Sundholm, 1971; Fleischmann *et al.*, 1971*a, b*, 1972; Weinberg & Weinberg, 1968; Mann & Barnes, 1970; and Vertes *et al.*, 1972).

Fleischman *et al.* (1971*a, b*, 1972) have reported the oxidation of aliphatic alcohols and amines on nickel hydroxide electrode. These workers have given the following reaction mechanism for the organic oxidation on the nickel hydroxide electrode.



The similar reaction was proposed for the oxidation of aliphatic amines at silver electrode in an alkaline solution (Hampson *et al.*, 1969). In this work, the investigators have observed that amines were found to be oxidised at the potential where silver (II) oxide was formed on the electrode surface.

Similar type of reaction mechanism has been reported on the cobalt oxide electrode by Cowling and Riddiford (1969).

Thus the foregoing survey of the literature clearly indicates that higher oxidation states of cobalt and nickel are the active species which takes part in the electrochemical reactions. Therefore, the oxidation of methanol, ethanol, *n*-butanol, *n*-pentanol, furfural, benzyl alcohol and mandelic acid under different conditions has been carried out and reported in this communication.

For the purpose of simplicity, the paper has been divided into two parts. Part A describes the studies on the preparation of cobalt and nickel oxide anodes and the structure of oxides as revealed by physico-chemical methods. Part B describes the application of these anodes for the oxidation of organic compounds.

Part—A

EXPERIMENTAL

The standard solutions of nickel sulphate (1M), cobaltous sulphate (1M) and ammonia (5M) were prepared from the Analar materials dissolved in a double

distilled water and their concentrations were determined as described by Vogel (1968). 1cm dia \times 10cm long graphite and stainless steel rods and a strip 1cm \times 7.5cm \times 0.156cm of titanium were used for the deposition. Before use the graphite, stainless steel and titanium were pre-treated in the usual manner.

Cobalt Oxide Anode

The 1M solution of cobalt sulphate (100ml) was taken and stoichiometric amount of ammonia was added with continuous stirring, thereby the Co(II) hexamine is formed which subsequently oxidised to Co(III) hexamine by auto-oxidation. The cobalti-hexamine species thus formed hydrolyses under the influence of dissolved oxygen in the solution to pentamine species. This solution on electrolysis gives a smooth adherent black deposit on the anode and cobalt metal on the cathode. It was observed that a current density between 0.5Amp/dm² to 2Amp/dm² favours the smooth deposition.

Nickel Oxide Anode

The nickel tetramine complex was prepared by adding the stoichiometric amount of ammonia to the 100ml solution of 1m nickel sulphate. The smooth and adherent deposit of nickel was obtained on the anode and the nickel metal on the cathode. The anodic current density was maintained between 0.5Amp/dm² to 2.0Amp/dm² for the smooth deposition.

Factors affecting the Anodic Deposition

Several experiments of various nature were carried out to reach the best conditions for the deposition of oxides.

The factors studied were :

- (i) Current density on anode.
- (ii) Effect on concentration of components.
- (iii) Effect of pH.
- (iv) Effect of foreign ions.
- (v) Effect of organic materials.
- (vi) Effect of temperature.

(i) *Current Density* : It was observed that the low current densities favour the deposition of the oxide of low oxygen contents, whereas at high current densities the deposition was found to be of labile nature, but at the same time the oxide obtained was rich in oxygen content. The best deposition obtained when the anodic current density is maintained between 0.5Amp/dm² to 2Amp/dm² in both the cases.

(ii) *Effect of Concentration of Components* : It has been found that a concentration of 10⁻²M of metal ion is required for the good deposition below which the efficiency falls. Similarly, if there is excess of ammonia more than the stoichiometric amount, the efficiency decreases perhaps due to the formation of a complex of higher NH₃ : M ratio.

(iii) *Effect of pH* : The pH 8 to 10 favours the anodic deposition. At pH more than 10, the rate of deposition was found to be very low, whereas at lower pH (below 8) deposition of hydroxide of normal valence state occurs, probably due to the non-availability of hydroxyl ion.

(iv) *Effect of Foreign Ions* : The presence of Fe^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Cr^{3+} in minute quantity (10^{-4}M) in the electrolytic bath has no effect on the deposition whereas Cl^- inhibits the deposition and causes the corrosion of substrate material. NO_3^- , SO_4^{2-} , SO_3^{2-} , HCOO^- , ACO^- favours the deposition of oxide. The presence of boric acid was found to be unfavourable, because of formation of borate complex.

(v) *Effect of Organic Materials* : It was observed that the presence of 1 per cent ethanol, or acetone, or formaldehyde favours the smooth deposition whereas high concentration of these reductants favours the deposition of lower oxides.

(vi) *Effect of Temperature* : It was observed that 30 °C temperature favours the adherent and smooth deposition on stainless steel and graphite substrate whereas at high temperature i.e., above 50 °C the deposits obtained on the stainless steel substrate peel off quickly, whereas on graphite substrate the hydroxide contents were found more, probably due to the hydrolysis of metal ions in the pores of graphite, but if glossy graphite is taken then in that case deposition of oxide takes place but of labile nature. The peeling off of the oxide at higher temperature is due to the hydrophobic nature of the deposit. In the case of titanium substrate the higher temperature has the favourable effect on the deposition.

Oxygen Overpotential Studies

These experiments were carried out using a V. T. V. M. (G. M. 6020 Philips model) and a solid state direct current source. The three compartment cell was used, the working and secondary electrodes were oxide deposited stainless steel or graphite rods of an apparent area of 30cm^2 and platinum foil respectively, separated by glass frit. The reference electrode (Hg/Hgo) was separated from the working electrode by luggin capillary. Current-potential curves were obtained by applying different current densities and noting the potential. These studies were carried out at different pH values. Results are plotted in Fig. 1.

RESULTS AND DISCUSSION

The results of the gravimetric and volumetric analysis of anodically deposited cobalt and nickel oxide are recorded in Table I. The possible composition of oxide as revealed by the analysis has also been indicated.

The X-ray diffraction studies confirm the findings obtained by chemical methods. The results are tabulated in Tables II to V.

The complexing agents play the important role in maintaining the pH of the solution and in supporting the presence of small metal ion concentration at the electrode surface.

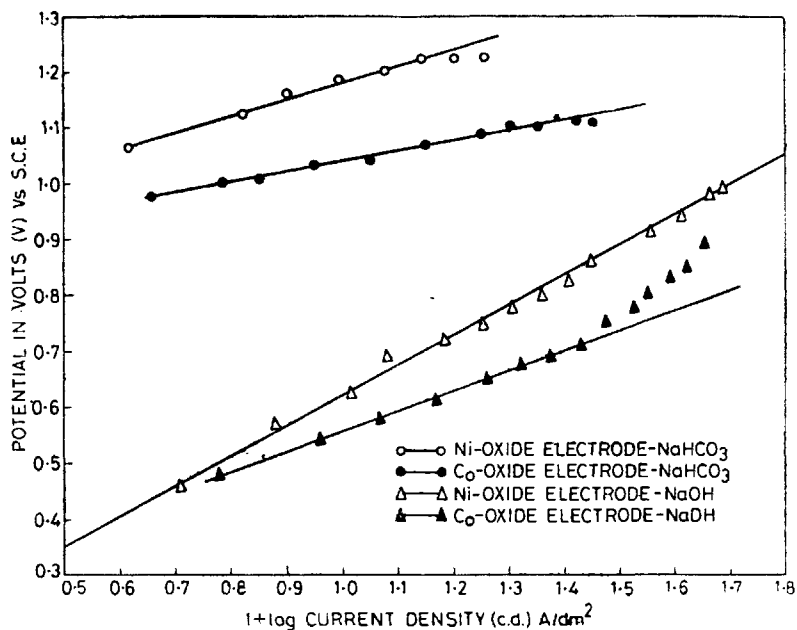


FIG. 1.

TABLE I

Electrolyte	Substrate material	Current density (Amp/dm ²)	The possible composition of deposit
Tetramine nickel complex	Stainless steel	1	NiO(OH)
	Graphite	1	NiO(OH).4Ni(OH) ₂
Cobalti penta amine complex	Stainless steel	1	CoO(OH)
	Graphite	1	Co ₂ O(OH) ₃ .CoO(OH) Co(OH) ₂

TABLE II

Nickel oxide deposited on graphite substrate
(114.6mm X-ray powder pattern)

Before heating the sample			After heating the sample to 400 °C for 2hrs		
<i>d</i> -Spacing in Å	Assignment	Literature value 6-0044	<i>d</i> -Spacing in Å	Assignment	Literature value-835
7.6954	4Ni(OH) ₂ NiO OH	7.7	2.4102	NiO	2.4190
3.87659	"	3.85 ₀₀	2.0829	"	2.09
2.5984	"	2.56 ₀₀	1.478	"	1.48 ₀₀
1.53765	4Ni(OH) ₂ NiO OH	1.53 ₀₀			

TABLE III

Nickel oxide deposited on stainless steel substrate

114.6mm X-Ray powder pattern

Before heating the sample			After heating the sample to 400 °C for 2hrs		
<i>d</i> -Spacing in Å	Assignment	Literature value	<i>d</i> -Spacing in Å	Assignment	Literature value
4.8347	NiO(OH)	4.83(6.141)	2.4102	NiO	2.41 ₉₀ (4.835)
2.698	Ni(OH) ₂	2.70(14-117)	2.08296	NiO	2.09 _x (4.835)
2.3678	NiO(OH)	2.41 ₈₀ (6-0075)	1.478	NiO	1.48 ₆₀ (4.835)
1.5607	Ni(OH) ₂	1.56(14-117)			
1.49570	Ni ₃ O ₂ (OH) ₄	1.52(6-0144)			

TABLE IV

Cobalt oxide deposited over stainless steel substrate

114.6mm X-ray powder pattern

Before heating			After heating at 400 °C for 2 hours		
<i>d</i> -Spacing in Å	Assignment	Literature value	<i>d</i> -Spacing in Å	Assignment	Literature value
4.589	CoO(OH)	4.55	5.3784W		
			4.3408M	CoHO ₂	4.38(7-162)
2.3740	CoO(OH)	2.36	3.97908M	Co(OH) ₂	4.00(2-0925)
			3.57VW		
			2.8966	Co ₃ O ₄	-2.86 ₄₀ (9-418)
			2.4208	Co ₃ O ₄	2.438(9-418)
			(Broad and diffuse)		
			2.2652VW		
			1.9973BM	Co ₃ O ₄	2.02 ₂₅ (9-418)
			1.8654M		
			1.5615BM	Co ₃ O ₄	1.55 ₃₅ (9-418)
			1.4300M	Co ₃ O ₄	1.43(9-418)

TABLE V

Cobalt oxide deposited on graphite substrate

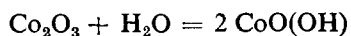
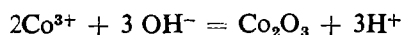
114.6mm X-Ray powder pattern, Broad and diffuse

13.867Å Inner radius, 10.586Å outer radius

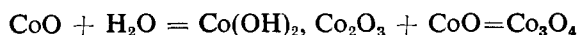
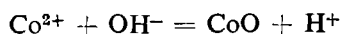
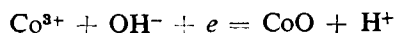
<i>d</i> -Spacing in Å	Assignment	Literature value	<i>d</i> -Spacing in Å	Assignment	Literature value
			2.506	- Co O	2.46 (9-402)
			2.2721	CoHO ₂	2.31 (7-169)
			2.088VW	CoO OH	2.10
4.5484	CoO(OH)	4.55(2-0214)			
4.0557	Co(OH) ₂	4.00(2-0925)			
2.87729	Co ₃ O ₃	2.87(2-0770)	1.8163	-CoHO ₂	-1.80(7-169)
2.69678	Co(OH) ₂	2.68(2-925)	1.5743	Co(OH) ₂	1.58(2-0925)

The oxidation of cobalt (II) ammonia complex (cobalt hexamine) to cobalt hexamine (Cobalt III — ammonia or possibly a pentamine hydroxo complex) is followed by the dissociation of the latter complex.

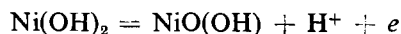
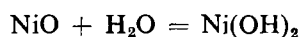
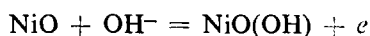
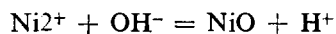
The possible reaction mechanism of the cobalt oxide formation can be represented as follows:



or



Similarly reaction mechanism for nickel oxide deposition can also be written as :



The X-ray diffraction studies indicates that on stainless steel substrate the CoO(OH) species formed in case of cobalt while in the case of nickel NiO(OH) is deposited. But when the stainless steel is substituted by graphite anode the picture is different, in case of cobalt the deposit obtained consists of CoO(OH) , Co(OH)_2 and Co(OH)_2 and in case of nickel it was $4\text{Ni(OH)}_2\text{NiO(OH)}$.

The reason for getting the lower oxides on graphite substrate can be attributed to the porosity of graphite, where the metal ion in solution will be interlocked and gets precipitated as hydroxide of lower valency state. But on smooth surface the percolation of solution particles is not possible and therefore only higher oxide formation predominates.

The oxygen overpotential studies for cobalt oxide and nickel oxide with graphite as well as of stainless steel substrate were carried out at different $p\text{H}$ values. Herein we are reporting the studies made in 1M NaHCO_3 and 1M NaOH because at lower $p\text{H}$ values the oxygen overvoltage is raised and mechanical strength of oxide on substrate is weakened by anodic polarisation in an acidic solution and hence these electrodes are not stable in acidic $p\text{H}$ range.

The anode potential curves in both the cases (nickel oxide and cobalt oxide) gives one arrest; this shows that at least one oxidising species is produced electrolytically like hydrogen peroxide. Latimer(1952) has reported that at 0.4V in H_2SO_4 medium the hydrogen peroxide is formed at platinum electrode and at 0.7V Pt(OH)_2 formation takes place.

Matsumoto *et al.* (1977a, b) have shown that the σ^* band formation at an oxide, which is dependent on the magnitude of the overlap integral between an *eg*-orbital of a metal ion, *M* and *Sp*-orbital of an oxygen ion. O of the oxide is a major factor in determining the electrocatalytic activity of the oxide for oxygen reduction. This suggests not only that *d*-orbitals of *M* must not be localised but form a band in order for the oxide to have a high catalytic activity, but also that the nature of the band influences the catalytic activity. According to Goodenough (1966) there are three kinds of *d*-band in transition metal oxides; a π^* band formed by interaction of a *t_{2g}* orbital of *M* with a *p π* orbital of O in M-O-M and the σ^* band by an *eg*-orbital of M with a *Sp σ* orbital of O in M-O-M.

The nickel oxide and cobalt oxides are well known *p*-type of semi-conductors, the *eg*-orbitals in these cases are localised (Goodenough, 1971).

If the end-on type adsorption takes place in these cases, then the overlapping of π^* orbital of an oxygen molecule, whose orbital is half occupied by electrons and energetically highest (Olive & Olive, 1974) with the orbital of a transition metal ion of the oxide will be very weak on adsorption. Therefore, electrons in σ^* band rather than in the π^* band seem to be more easily transferred to π^* orbital of an oxygen molecule (Matsumoto *et al.*, 1977a, b). This is one of the possible reasons why a transition metal oxide having the σ^* conduction bands shows a high catalytic activity for oxygen reduction.

The oxygen overpotential studies indicate that oxide electrode is usable to carry the high current densities as the alkalinity of the solution increases. This phenomenon can be attributed to the process of promotion of σ^* band formation which brings the increase of the catalytic activity of the oxide ion. Studies on the oxidation of organic systems using these oxide electrodes revealed interesting results and are described in the second part of this paper.

Part-B

The oxygen overpotential studies have been carried out using the same set-up as used in Part A of this paper.

The oxidation of methanol, ethanol, *n*-butanol, *I*-pentanol, ethylene glycol, glycerol, furfural, benzyl alcohol and mandelic acid were carried out in the following way :

The one mole of aqueous solution of organic substrate was prepared in one mole of supporting electrolyte (NaOH, NaHCO₃) and this solution (100ml) was used as anolyte and catholyte was 1M solution of a supporting electrolyte. The anodes were either nickel oxide or cobalt oxide deposited over stainless steel or graphite rods of 30cm² apparent area and cathode in all the cases was a stainless steel strip of 10cm² area. The anolytes and catholytes were separated by a glass frit.

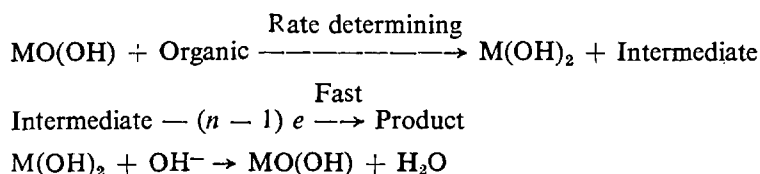
It was observed that in the oxidation of aliphatic alcohol the use of either divided or undivided cell is immaterial apparently because of an irreducible nature of oxidation product at cathode.

It was observed that the black colour of the nickel oxide electrode changes to greenish colour in the presence of organic substrate. However, if we impress an anodic current, the greenish colour turns to black indicating that the nickel is oxidised to higher valency state. In the case of cobalt oxide anode, the colour change was not pronounced.

In all the oxidation studies the theoretical current was passed, the current density was maintained at 10 Amp/dm^2 . The oxidation products were extracted with petroleum ether after neutralisation with dilute H_2SO_4 and the organic layer obtained was subjected to distillation and the fractions at different temperatures were collected. The products were identified by mass spectrum, infrared spectrum and elemental analysis and usual qualitative and preparative tests.

RESULTS AND DISCUSSION

The anode potential graph gives the one arrest, indicating that at least one oxidising species is produced electrolytically. The mechanism of anodic oxidation can be written as



where M is Ni or Co.

It was observed that the current shows a first order dependence on both hydroxide ion and alcohol concentration in the Tafel region (Fig. 2). The curves in presence of 1M ethanol in 1M NaOH show the Tafel slope of 0.26V. At higher potentials, the current is independent of the potential and depends only on the substrate concentration.

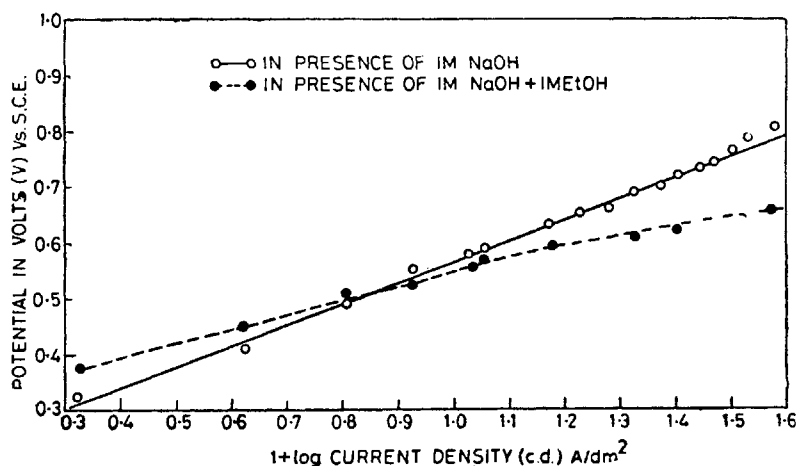


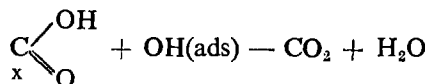
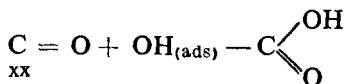
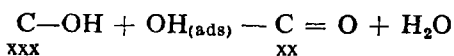
FIG. 2.

The electrochemical studies (Masui *et al.*, 1968; and Smith & Mann, 1969) and ionization potential data (NSRDS-NDS) suggest that in these cases the rate controlling step cannot be an electron transfer process between organic substrate and metal oxide anode. The oxide layer of the electrode contains the trapped hydroxyl radicals and that is the rate controlling step in the anodic oxidations. It was observed that current carrying capacity of oxide electrode decreased with the decrease in hydroxyl ion concentration (Fig. 1). Fig. 1 reveals that the current at cobalt oxide electrode is substantially lower than at a nickel oxide anode. The less current carrying capacity of cobalt can be attributed due to the partial decomposition of oxide layer (CoO(OH)) to Co₂O₃ and CoO. The results of the oxidation of various alcohols are given in Table VI.

TABLE VI

Substrate	Supporting electrolyte medium	Product obtained
Methanol	NaOH NaHCO ₃	Sodium formate Formaldehyde
Ethanol	NaOH NaHCO ₃	2,4 hexadinenal, ethyl acetate Acetaldehyde
<i>n</i> -Butanol	NaOH NaHCO ₃	<i>n</i> -Butyric acid, butyl butyrate <i>n</i> -Butanal
1-Pentanol	NaOH	<i>n</i> -Valeric acid
Ethylene glycol	NaOH	Glycolic acid, Glycolaldehyde
Glycerol	NaOH	Glyceraldehyde, Meso oxalic acid
Furfural	NaOH	2-Furoic acid, resin
Benzyl alcohol	NaHCO ₃	2-Furoic acid
	NaOH	Benzoic acid
	(NaHCO ₃)	Benzaldehyde
Mandelic acid	(Na ₂ CO ₃)	Benzyl benzoate
	NaOH	Benzoic acid

In an alkaline solution the oxidation of the adsorbed organic species occurs *via* an electrochemically generated adsorbed hydroxyl radical



The adsorbed organic moiety ($\underset{\text{xxx}}{\text{C}}-\text{OH}$) was considered to exist in equilibrium with bulk organic substrate (Bagotskii & Vassil'ev, 1967). It was observed that

increasing the chain length of the alcohol from C₂ to C₅ leads to reduction in the current efficiency for the oxidation, probably due to the formation of heterogeneous system.

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Discussion

G. A. TEDORADZE (*Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow*) :

1. Were your anodes stable in the organic substance solutions ? 2. Whether any organometallic compounds detected in the products ? 3. Will these anodes be more economical than the conventional graphite anodes ? 4. Do adsorption of organic substances take place at your anodes ?

K. S. UDUPA : 1. It is found to be stable. 2. We have not been able to identify any such intermediates or final products. 3. Graphite anodes get disintegrated during electrolysis and cannot be used in alkaline medium. These oxide electrodes can be used for selective oxidations. 4. We have not carried out any such studies with these anodes.

L. I. KRISHTALIK (*Institute of Electrochemistry, Academy of Sciences of USSR, Moscow*) :

1. What is the advantage of using this complex bath for the deposition of oxide electrodes ? 2. Whether any heat treatment is given before it is used for oxidation reactions ?

K. S. UDUPA : 1. We can make use of a dilute solution for deposition. 2. No heat treatment is necessary before it is used for oxidation studies.