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# ELECTROCHEMICAL BEHAVIOUR OF TITANIUM SUPPORTED SPINEL TYPE ANODES

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## ABSTRACT

Studies on the cobalt based spinel compounds coated titanium anodes (for example, cobalt-nickel and cobalt-zinc systems) by galvanostatic polarisation technique have been carried out under various experimental conditions. The influence of the incorporation of nickel or zinc as oxides to cobalt spinel has also been studied and the results compared. In addition, data obtained from x-ray and SEM studies are presented.

**Key words: Cobalt spinels, Ti anode, polarisation**

## INTRODUCTION

The study of electrochemical and physicochemical properties of transition metal oxides, in particular cobalt (II-III) oxide ($Co_3O_4$), is of paramount importance in view of their promising use as active catalysts and electrode materials for the synthesis of organic and inorganic chemicals. Cobalt oxide catalyst can be prepared by thermal decomposition of a number of its salts [1-3] like hydroxide, carbonate,nitrate, acetate, oxalate. However, the nitrate seems to be the best source [4] for the preparation of oxide electrodes from the view point of practical application. Considering the breakdown potential and stability in acidic environment, titanium is a more suitable substrate metal for the preparation of oxides coated anodes.

The starting materials, solvent taken for the preparation of chelates and its concentration, the rate of heating and decomposition temperature, all have a marked influence on the structure, morphology and hence the catalytic activity of the oxides coated anodes [5]. All these properties are interrelated and interdependent. Hence, rigorous control of the conditions of preparation is a prerequisite.

It is known that the cobalt based spinel anodes have been used in water electrolysis under alkaline condition and in brine electrolysis [6-9]. Its application as a nonconsumable anode in molten salt electrolysis has also been reported [10]. A few references [11,12] are available wherein the behaviour of spinel anodes has been studied in acidic conditions, that too, with limited objectives of corrosion rate and mechanistic aspects. Fixing up of optimum conditions of the anode possessing longest life and lowest anode potential has not been extensively studied. Some results of the electrochemical behaviour of the cobalt based spinel anodes are briefly presented in this paper and discussed with special reference to the results published by other workers.

## EXPERIMENTAL

Titanium, cold rolled, annealed and expandable sheet of M/s Titanium Metals and Alloys Ltd., U.K. was cut into small pieces of size 1cm x 8 cm. It was polished with emery papers upto 4/0 and washed with isopropanol. Subsequently thick films of oxides of cobalt, cobalt + nickel, and cobalt + zinc were deposited onto titanium by decomposing the corresponding nitrates dissolved in isopropanol (0.5 to 0.6 mol $dm^{-3}$). The chelate was brushed onto titanium test electrodes at room temperature, dried at ~ 100°C, baked in air at 200-400°C for 5 minutes and later cooled to ambient. The procedure of coating, baking and cooling is repeated till all the chelates are loaded and finally annealed at 400°C for an hour. Depending upon the starting chemicals and composition the decomposition temperature is controlled. A constant load of 10 $g/m^2$ of Co was maintained in all the experiments, unless otherwise mentioned. A geometrical area of 1 $cm^2$ was used by stopping off the rest. In case of Co-Zn system, additions of oxide of tantalum or titanium were done by taking appropriate quantities of the chlorides in the chelate, whereas nitrate salt has been used in the case of zirconium. The experimental setup used for galvanostatic experiments was essentially similar to that already reported [13]. AR sulphuric acid (0.5 M) has been used in all experiments unless otherwise stated.

## RESULTS AND DISCUSSION

### Influence of incorporation of nickel or zinc into cobalt on life and anode potential

Fig. 1 indicates the plot of logarithmic service life vs composition, keeping total load (Co + Ni) as constant. It is seen that the service life increases exponentially with increase in cobalt oxide. This observation is similar to the one observed in case of Ti/($RuO_2$ + $TiO_2$) electrode [14]. From the figure, one is led to conclude that cobalt oxide plays the major role for acting as electrocatalyst. Fig. 2 represents the electrochemical behaviour of the anodes having different compositions of cobalt in the Co-Ni system keeping the load of cobalt oxide as constant.

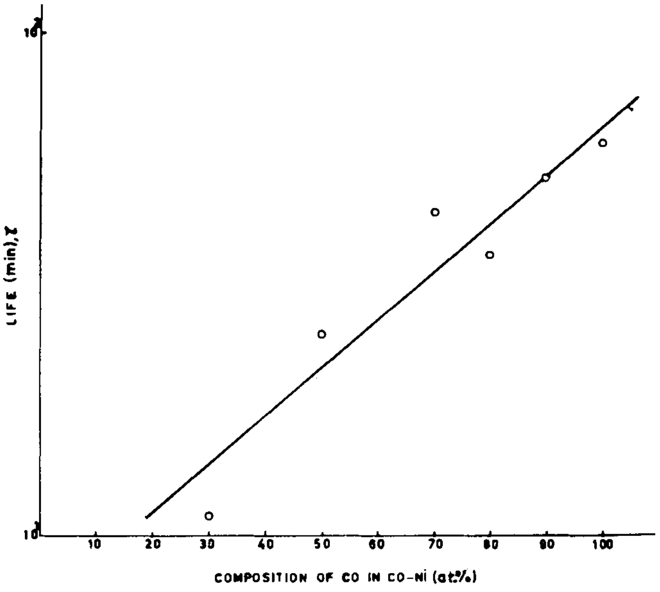

Fig. 1. Dependence of service life on cobalt content for Ti/Co-Ni spinel
Total load : 10 $g/m^2$
c.d. : 500 $mA/cm^2$
Electrolyte : 0.5M $H_2SO_4$

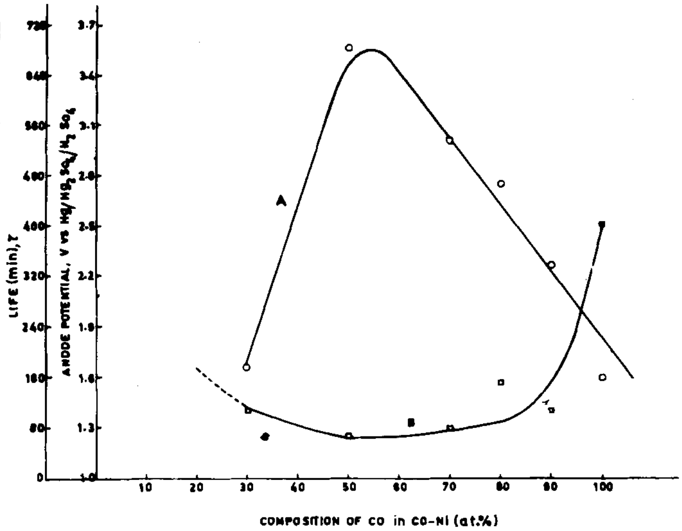

Fig. 2. Dependence of service life on composition for Ti/Co-Ni spinel
Load of Co : 10 g/m$^2$
C.d. : 200 mA/cm$^2$
Electrolyte : 0.5M $H_2SO_4$

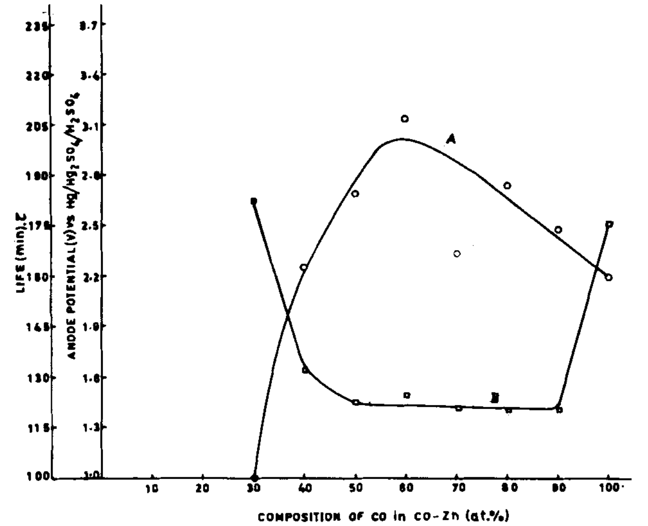

Fig. 3. Dependence of service life on composition for Ti/Co-Zn spinel
Load of Co : 10 g/m$^2$
C.d. : 200 mA/cm$^2$
Electrolyte : 0.5M $H_2SO_4$

From curve A, it is clear that the life of the anode increases as the percentage cobalt content decreases and it reaches the maximum around 50 at. % Co + 50 at. % Ni, other experimental conditions being kept constant. Similarly, from curve B, it is seen that the anode potential abruptly decreases from 2.52 V to ~ 1.45 V and later remains more or less constant with an indication for further increase with increase in Ni content. This behaviour is expected due to the fact that nickel oxide would also show high polarisation in view of its poor conductivity. The electrochemical behaviour is similar at higher anodic current densities also. The present observations run parallel with the data on electrical conductivity as well as electrochemical activity vs composition [15].

Fig. 3 shows the relationship between (i) service life τ and (ii) anode potential vs composition for Co-Zn system keeping the load of cobalt as constant. The other experimental conditions are the same as in the case of Co-Ni. The service life is maximum in the region 50-80 at. % Co, as revealed by curve A. Curve B points out that the anode potential falls steeply from 100% $Co_3O_4$ to 90 at.% Co, remains the same upto 50 at.% and later increases, as was found in the case of Co-Ni. Taking into consideration the life and anode potential, the optimum composition lies at 50 at.% Co in both the spinel systems. This is in accordance with the results reported [16,17] based on specific conductivity measurements. However, stoichiometric spinel will be formed at 67 at.% Co and this is reported to have the maximum conductivity and carrier concentration [15]. The curves 2A and 3A are unsymmetrical about the respective peaks and this may be explained as due to the higher conductivity reflected by the manifestation of lower anode potentials on the cobalt rich side.

On comparing the two systems, it is clear that the role of the incorporating element is significant. The life of the anode having 100% $Co_3O_4$ is short with higher anode potential (cf. figs. 2 & 3). At the optimum composition, the addition of nickel increases the life by two times while that with zinc by ⅓. Nickel simultaneously lowers the anode potential by 1.28 V whereas zinc decreases the potential by 1.07 V. Hence the two fold advantages of incorporating nickel is clear. The longer life may be explained as due to the fact that ionic radius of $Ni^{2+}$ (0.69 A) is close to that of $Co^{2+}$ (0.72 A) whereas that of $Zn^{2+}$ (0.83A) is higher, thereby facilitating the formation of compatible mixed crystal oxide coating. In case of Co-Zn a progressive decay of electrocatalytic activity with increase in Zn content above 35 at.% has already been observed [18]. The present observations to the one already reported [18].

**Effect of temperature of preparation of coating on anode potential**

From Figs. 2 and 3 it is observed that with 100% $Co_3O_4$ the potential is high. This may be attributed to the poor conducting normal spinel of $Co_3O_4$ (15). In addition the formation of high resistance barrier film of $TiO_2$ at the interface between the substrate titanium and $Co_3O_4$ layer cannot be ruled out [19] due to the porous nature of the coating. On the other hand the bimetal spinel of $NiCo_2O_4$ and $ZnCo_2O_4$ are good

Table I :Influence of temperature of preparation on anode potential

| Systems | Conditions of preparation on Ti substrate | Anode potential * V, vs. $Hg/Hg_2SO_4/H_2SO_4$ |
|---|---|---|
| 1. $Co_3O_4$ | (A) Heated at 200°C for 35 minutes | 1.846 |
| | (B) Heated at 200°C for 35 minutes and annealed at 400°C for 1 hr. | 2.870 |
| | (C) Heated at 400°C for 40 minutes | 2.130 |
| | (D) Heated at 400°C and annealed at 400°C for 1 hr. | 2.760 |
| 2. (a) Co-Zn spinel | Prepared by (B) or (D) route | 2.140 |
| (b) Co-Ni Spinel | | 1.618 |

* at 5 KA/m$^2$

conductors and hence exhibit lower anode potentials. This is illustrated in Table I. Furthermore, from Table I it is observed that the anode potentials of titanium specimens prepared under conditions 1B and 1D have the same value of ∾ 2.8 V as compared with 1.85 V for samples prepared under 1A viz. at 200°C. Experiments (1A and 1B) were carried out with a view to have uniform habitat of cobalt oxide crystal [20] covering the entire surface with minimum macro, micro and meso pores and pore size distribution. The increase in anode potential for higher temperature of heat treatment may be due to (i) change in the electrochemical properties of the oxide (ii) formation of barrier $TiO_2$ film or (iii) cumulative effect of (i) and (ii) [21]. For test electrodes prepared under 1C, higher potentials are obtained with respect to 1A. This leads one to conclude that the barrier film formation is dependent both on temperature of decomposition and duration of heating. The increase in anode potential at higher temperature of the formation of the compound is more due to the bad conducting $TiO_2$ as revealed by XRD studies. Based on this conclusion, all test electrodes have been prepared by coating the entire chelate first at 200-250°C (each coating being heated for five minutes) and subsequently annealed at 400°C for an hour.

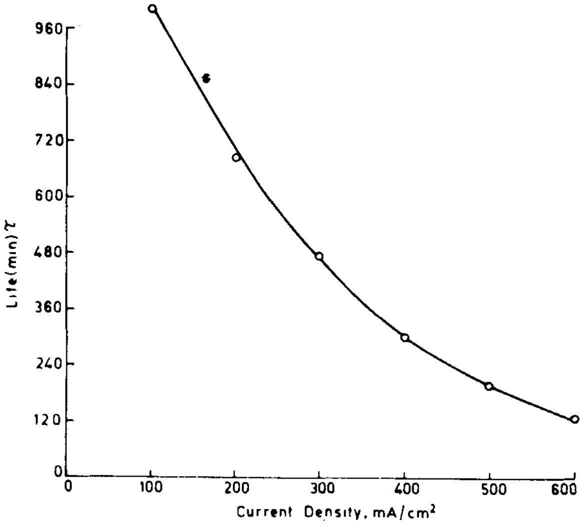

Fig. 4. Dependence of service life on current density
Composition of Co-Ni = 50 : 50 at.%
Electrolyte : 0.5M $H_2SO_4$

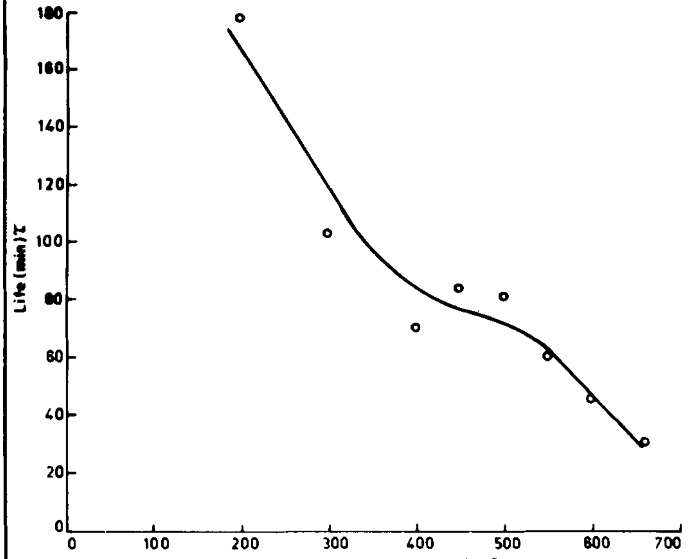

Fig. 5. Dependence of service life on current density
Composition of Co-Zn = 50 : 50 at.%
Electrolyte : 0.5M $H_2SO_4$

### Dependence of service life on current density

Figs. 4 and 5 show the influence of current density on useful life. It is observed that the service life of the Co-Ni spinel anode increases regularly with decrease in current density whereas that of the Co-Zn system shows two different behaviours in the current density range studied. Elucidation of this requires further study.

### Effect of concentration of chelate and additives

The addition of 5 at.% of Ti, Ta or Zr to Co-Zn system decreases the life at all concentrations investigated.

### Performance in different electrolytes

Curves a, b and c of Fig. 6 show typical potential-time curves obtained in potassium hydroxide, sulphuric acid and ammonium sulphate solutions respectively. The life of the anode is in the order: ammonium sulphate < sulphuric acid < potassium hydroxide. The service life depends on the nature of electrolyte and is maximum in potassium hydroxide.

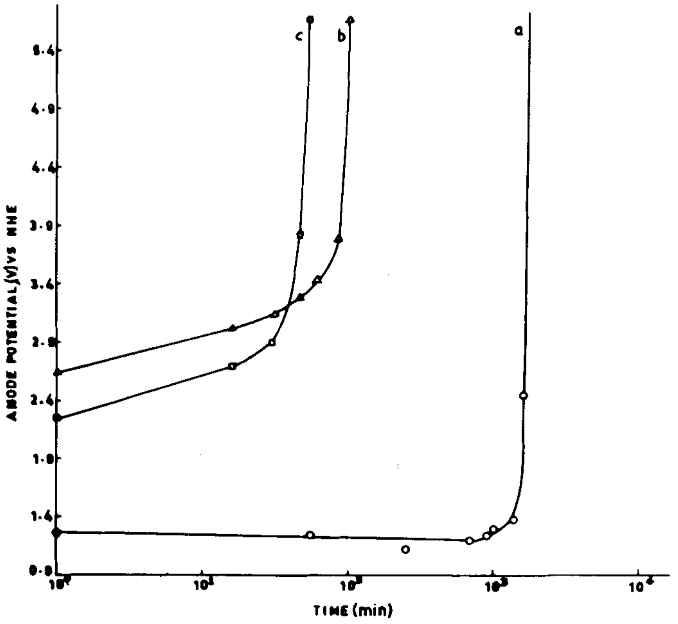

Fig. 6. Dependence of anode potential vs time
C.D. : 500 mA/ $cm^2$
Anode: Ti/Co-Ni (50 : 50 at.%)
a : 1.0M KOH
b : 0.5 M $H_2SO_4$
c : 0.5 M $(NH_4)_2SO_4$

### X-Ray diffraction (XRD) studies

Figs. 7 and 8 represent the XRD patterns for various compositions of oxides of Co-Ni and Co-Zn systems at different experimental conditions, in addition to cobalt oxide.

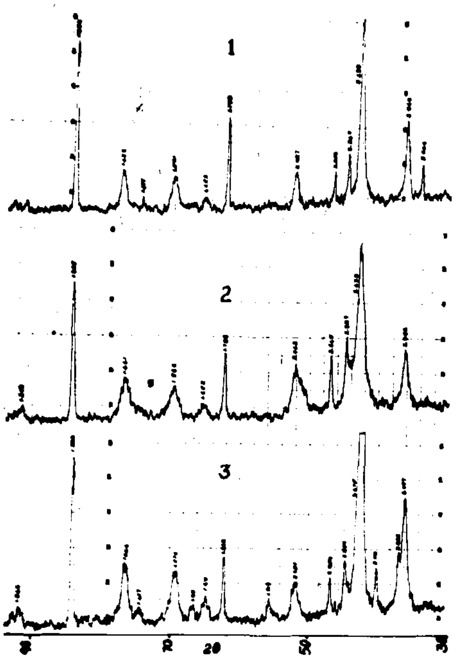

Fig. 7. X-ray diffraction patterns
(1) Cobalt oxide at 400°C
(2) Co-Ni (50 at.% Co)
(3) Co-Zn (50 at.% Co)

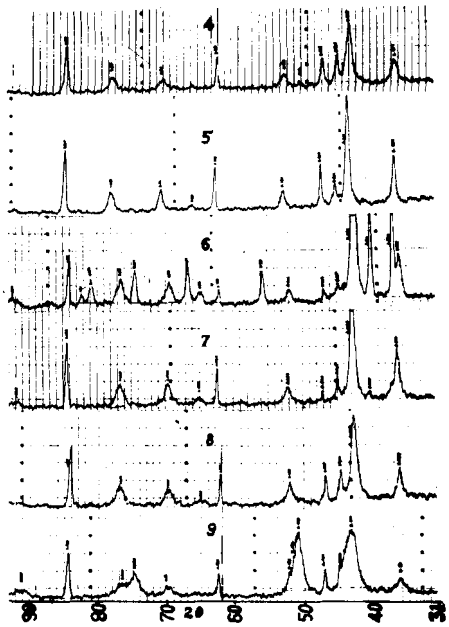

Fig. 8. X-ray diffraction patterns
(4) Cobalt oxide at 200°C
(5) Co-Zn (90 at.% Co)
(6) Co-Zn (30 at.% Co)
(7) Co-Zn-Zr
(8) Co-Ni (70 at.% Co)
(9) Co-Ni (30 at.% Co)

*Co - Ni*

The crystal structure of single metal oxide spinel and that of bimetals $NiCo_2O_4$ are very similar. From Fig. 7(2) it is observed that incorporation of Ni upto 50 at.%, mixed spinels are generally coexisting. In addition, incipient formation of cubic NiO is indicated because of the appearance of a peak at d = 1.25 Å. At 70 at.% Ni Fig. 8(9) cubic NiO is predominant due to the appearance of a well defined peak at 2.088 Å. Since the d-values of spinel and NiO are very close (and the peak θ width of NiO is large) they merge and become indistinguishable.

*Co-Zn*

From the Figs. 7(1) and 7(3) again crystal structure of single metal spinel and the structure of bimetal spinel are essentaily similar upto 50 at.% Zn, the characteristic being shifting of the d values to the higher side. The characteristic shifts are observed in all cases studied and they become greater as the quantity of zinc is increasing. At 50 at.% Zn it is observed that segregation of ZnO starts and develops appreciably at 70 at.% Zn, Fig. 8 (6) (d = 2.82 Å, 2.61 Å).

*Co - Zn - Zr*

Addition of 5 at.% Zr to Co-Zn does not alter the crystal structure except suppressing the excess zinc completely.

*Comparison of Co-Ni and Co-Zn*

The deviation of d-values during incorporation of Ni into cobalt oxide spinel is absent or not appreciable, whereas that of Zn increases the d-values.

Incorporation of Zn into cobalt oxide system increases the amplitude of the d lines, whereas the converse is true in the case of Ni.

Addition of Ni to cobalt system on Ti substrate affects the d-values of Ti-Co compounds, as it forms Ti-Ni compounds.

In the case of Co-Zn system the formation of Ti-Zn compound is not revealed by XRD presumably due to the greater affinity of titanium towards Co in relation to Zn.

*Influence of temperature*

The observation of the presence of CoO at 400°C in all cases is, at the first instance, rather strange. But similar findings have been reported elsewhere [6,17].

It is evident that Ti substrate is not inert, but it also takes part in the compound formation especially at 400°C, due to the appearance of additional peaks of $TiO_2$ at d = 1.477 Å and 3.044 Å. This supports the explanation offered for increase in anode potential at higher temperature for $Co_3O_4$ system.

In addition the absence of titanium oxide peak (d = 3.044 Å 1.477 Å) in the case of Co-Ni and Co-Zn system suggests that the formation of the same is suppressed even at 400°C because of nickel or zinc addition.

Thus XRD studies facilitate one to understand that the bimetallic spinel precursor elements (Ni or Zn) of the present study form a continuous series of *solid solutions with single metal spinel* $Co_3O_4$. *In both the systems* spinels are preponderant at 70: 30 at.%.

**Scanning Electron Microscopic (SEM) studies**

Figures 9 (a)-(e) illustrate the morphology as observed with SEM. In case of 100% $Co_3O_4$ a homogeneous phase with compact coating of normal spinel with porosity in between grains is observed. A gradual incorporation of nickel increases the inverted spinel phase $NiCo_2O_4$ upto 80 at.% Co. But, at around 70 at.% Co there is a tendency towards the formation of a homogeneous phase of inverted spinel. On further increase of nickel, a heterogeneous phase is again observed which may be due to the presence of inverted spinel and cubic nickel oxide.

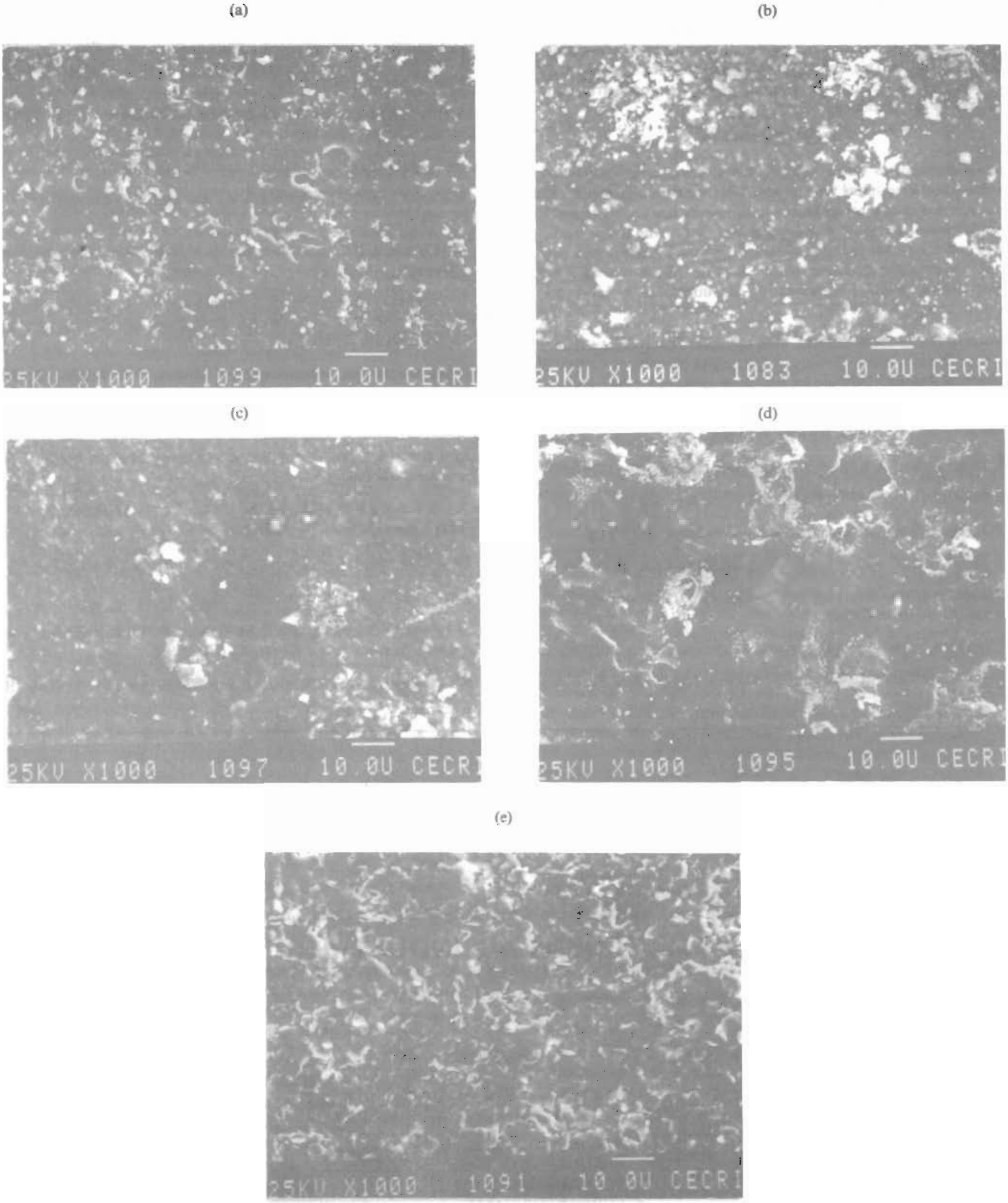

Fig. 9 Scanning Electron Micrograph of spinel compounds on titanium
(a) 100% $Co_3O_4$ (b) Co-Ni (80 at.% Co) (c) Co-Ni (70 at.% Co) (d) Co-Ni (50 at.% Co) (e) Co-Ni (30 at.% Co)

Although 70 at.% Co (and 30 at.% either Ni or Zn) results in a homogeneous phase with good coverage as evidenced both by XRD and SEM data, yet 50 at.% Co system exhibits the maximum life from polarisation measurements. This observation is supported by the explanation found elsewhere [18] that the breakdown of the stoichiometric spinel is necessary to get maximum activity.

## CONCLUSIONS

These measurements throw light on the electrochemical behaviour of titanium supported spinel type anodes. The present study facilitates one to fix up the optimum compositions of the anode from the points of view of lowest anode potential with longest life. Out of the two systems viz. Co-Ni and Co-Zn studied, it is observed that the beneficial influence of nickel is appreciable than that of zinc. Further work is necessary before a final picture could be evolved for its utilization as an anode in electrowinning.

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