ELECTROMETALLURGY AND THERMICS

ANODES FOR ELECTROWINNING — POLARISATION CHARACTERISTICS

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ABSTRACT

Study is made on oxygen evolving electrode from the stand point of the development of electrodes based on the use of noble metal oxides/spinel type oxides either singly or jointly coated over titanium having a suitable inner layer. The significance of the part played by oxygen evolving electrocatalysts is examined.

Key words: Electrocatalysts, cobalt spinels, polarisation, Ti anodes

INTRODUCTION

Electrowinning of zinc, copper and manganese normally involves sulphate electrolytes, whereas nickel and cobalt are electrowon from chloride and/or sulphate media [1]. The process demands employment of insoluble or permanent anode. The development of such a long life anode for use in high acidic electrolytes seems to be rather difficult. The fundamental requirement for this purpose is that the efficiency of the reaction $M \longrightarrow M^+ + e$ should be zero. In other words, the intended reaction of oxygen evolution from sulphate electrolyte or chlorine evolution from chloride solution in the case of electrowinning of metals should occur to the extent of one hundred percent. This is the crucial point to be borne in mind, besides the electrocatalytic nature, the electrode stability in presence of the electrolyte, the product of electrolysis [2] etc. The potential of the anode which accounts for a large proportion of the total cell voltage and the life of anode are the prime factors where significant improvements could be effected, thereby resulting in overall economy. Noble metal oxides-coated titanium anodes are being tested commercially in electrowinning of zinc [3] and copper [4].

The current trend in developing new catalytic materials for anodes seems to be directed towards the use of active, reasonably selective and less expensive transition metal oxides with good conductivity equal to that of noble metal oxides. Of the known electrode materials, cobalt based complex oxides with spinel structure are promising in view of their desirable electrocatalytic properties.

Based on approaches similar to long life anode (LLA) [5] and bilayer coating [6], work has been reported on titanium supported Co_3O_4 catalytic anodes [7,8]. From the literature it is observed that the influence of (i) an interlayer of mixed crystal oxides of ruthenium and titanium (ii) long term polarisation at high anodic current densities (iii) sulphuric acid and (iv) other spinels based on Co_3O_4 has not been studied in detail. In addition, it is generally stated [9] that as a rule simple oxides and some complex-spinel type oxides are unstable in acids. Hence is the necessity to study in detail the electrochemical behaviour of such systems in order to get a fresh insight into the problem and make a comparison with bilayer electrodes consisting of noble metal oxides.

EXPERIMENTAL

Details of the preparation of titanium test electrodes of bilayer type consisting of noble metal oxides and/or valve metal oxides and experimental set up for accelerated polarisation experiments were essentially the same as described elsewhere [6].

In case of systems with spinel oxides supported on Ti, the procedure described earlier [10] has been adopted. As regards bilayer spinels with titanium support, the above two procedures have been combined.

AR sulphuric acid (0.5 M) and an anode current density of 500 mA/cm^2 have been employed.

RESULTS AND DISCUSSION

Accelerated polarization tests

Bilayer anode with noble metal oxides

Fig. 1 shows the composition of outer layer vs (i) life and (ii) potential of anode having the intermediate layer of a fixed composition of RuO_2 + TiO_2 (1:3).
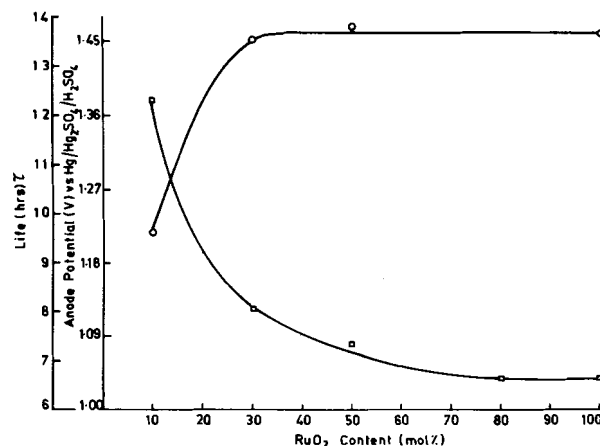

Fig. 1: Influence of RuO_2 content in the outerlayer on life and anode potential

It is clear that as the composition changes from 10 to 30 mole % RuO_2 the life of the anode increases and remains constant above 30 mole %. At the same time, the anode potential decreases from 1.38 V (10 mole % RuO_2) to 1.06V (50 mole % RuO_2) and therefore gradually decreases reaching constancy around 80 mole % and above. From the points of view of low anode potential, longest life and saving in consumption of the chemicals, employment of 100 mole % RuO_2 as an outer layer is advantageous.

In Fig.2, 'A' represents the anode potential vs time curve of outer layer (100% RuO$_2$) coated Ti, 'B' represents that of Ti substrate coated with the inner layer of RuO$_2$ + TiO$_2$ (1:3) and curve 'C' represents Ti substrate coated with both inner and outer layers.
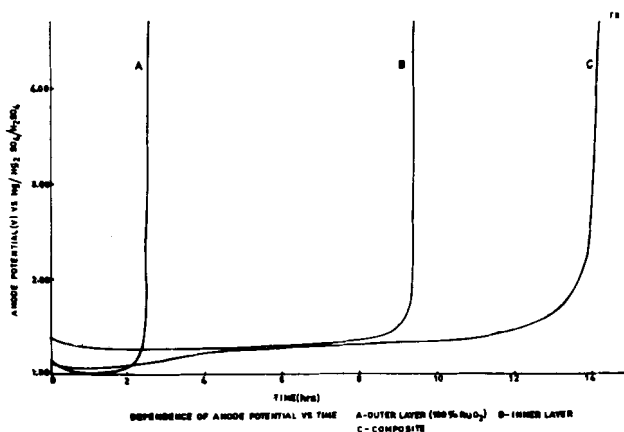

Fig. 2 Dependence of anode potential vs time
A - Outer layer (100% RuO$_2$)
B - Inner layer
C - Bilayers
Current density : 500 mA/cm^2
Electrolyte : 0.5M H$_2$SO$_4$

The role of the inner layer on the modifications of the outer layer is very important. The life of bilayer coated anode is more than the summation of the individual lives of the anodes having either inner or outer layer alone indicating that the inner layer modifies the outer layer so as to give a longer life in addition to substrate protection.

Spinel systems (Co - Ni and Co - Zn)

Table I gives the data on the influence of the inner layer on the life and potential of the spinel compounds coated Ti anode.

It is observed that the introduction of an inner layer leads to lowering of anode potential in all the cases studied. Furthermore, with respect to the life of the anode it plays a significant role by way of increasing the life markedly in the case of Co - Ni. The results could be explained based on the dual role of the inner layer viz., protection of the substrate titanium metal by prolonging the time of failure of the anode and modification of the spinel layer appropriately so as to result in a change in life.

On comparing the service lives of anodes (Fig.2 and Table I), wherein the fixed composition of mixed-crystal oxides of Ru and Ti used as a common inner layer on titanium over which either spinel compounds or noble metal oxide is coated as an outer layer, it is seen that the performance of an anode with Co - Ni (90:10) as an outer layer is comparable with that of the same electrode substituted with RuO$_2$ as an outer layer. Among the spinel systems studied, anodes with Co-Ni show synergetic effect positively whereas Co-Zn exhibits the reverse trend. This could be explained as follows.

If one considers the ionic radii of the elements present in the composite electrode viz. Ru^{4+}, Ti^{4+}, Co^{2+}, Co^{3+}, Ni^{2+}, Ni^{3+} and Zn^{2+}, they are more or less the same, except Zn^{2+}. The latter has the largest ionic radius leading to distortion of the inner layer, the distortion being aggravated during anodic polarisation which becomes even more when O$_2$ is freely liberated. In addition X - ray data [6] indicate that Co-Zn system is more prone to segregation.

On the other hand in case of Co - Ni as well as RuO$_2$ the same size of ionic radii of Ru^{4+}, Ti^{4+}, Co^{2+}, Co^{3+}, Ni^{2+} and Ni^{3+} favours interdiffusion without affecting the inner layer and hence exhibits positive synergetic effect.

The performance of a composite electrode comprising the inner layer plus Co-Ni spinel system is comparable with that of a composite electrode made up of noble metal oxides. Of course the quantity of 10g Co vs 3g of Ru is to be borne in mind.

CONCLUSION

From the study on the electrochemical behaviour, it is inferred that an improved spinel viz. Co-Ni with inner layer supported on titanium exhibits a life longer than the summation of the individual lives, whereas the reverse is the case with Co-Zn system. Further work relating to rate of build up of species of cobalt and nickel in acidic electrolyte during long term polarisation and their control, and their influence on current efficiency for metal deposition, is necessary before a clear picture could be evolved as to their suitability as anodes in electrowinning.

Table I: Influence of inner layer on anode potential and life

Conditions: Electrolyte 0.5M H$_2$SO$_4$: Ambient Temp., C.d. 500mA/cm^2,
Load of electrocatalyst (Ru = 3g/m^2, Co = 10g/m^2); Anode potential (V) vs Hg/Hg$_2$ SO$_4$/H$_2$SO$_4$

Systems (Atom %)	Ti/Outer layer - (Spinel)		Ti/Inner layer (RuO$_2$ + TiO$_2$)		Ti/Bilayer composite			Remarks	
	Anode potential (V)	I Life (min)	Anode potential (V)	II Life (min)	Anode potential (V)	III Life (min)	Anode potential (V)	I + II ≤ III Life (min)
Co-Ni(90:10)	1.700	80	1.415	546	1.145	810	Decreases	Positive
Co-Ni(50:50)	1.640	200	1.254	539	1.161	753	Decreases	≃
Co-Zn(50:50)	2.120	83	1.249	519	1.133	500	Decreases	Negative

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