

ELECTROCHEMICAL PREPARATION AND BEHAVIOUR OF MIXED OXIDE OF COBALT, NICKEL AND MANGANESE

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An attempt has been made to prepare the mixed cobalt oxide by codeposition of nickel and manganese oxides. It was observed that the inclusion of nickel or manganese enhances the life of the cobalt oxide anode and electrocatalytic properties get improved considerably.

Key words: Mixed oxides of Co, Ni, Mn, Electrocatalysis, electrodeposition

INTRODUCTION

The enzymes are most efficient catalysts for reactions involving oxygen. Studies have revealed that homogeneous catalysis in living cells can be accomplished by metal complexes which are relatively simple yet can compete with the enzymes. The activation of oxygen is one of the complicated tasks in homogeneous and heterogeneous catalysis due to the exceptional stability of oxygen molecule in ground state.

The formation of surface oxides at noble metals is well known [1,2]. The transition metals and their compounds are known for catalytic activity in redox process. Anodes having oxide layers have been reported [3,4] to be suitable for electrochemical oxidation reactions. The cobalt and nickel electrodes which are generally used as anode materials in alkaline solutions are reported to be covered with their respective oxides [5-7]. The preparation of cobalt and nickel oxides from ammoniacal bath was earlier reported [8,9]. The electrochemical dissolution and vibrational spectra of NiOOH were studied in detail [10] and the use of the same in alkaline water electrolyser was also reported [11].

At present no suitable electrochemical method is available for the preparation of mixed transition metal oxide anodes. This communication reports the preparation of Co-Ni and Ni-Mn oxide anodes with the aim to see the effect of nickel and manganese metal ions on the behaviour of cobalt oxide anodes. The electrochemical characterization of these anodes by studying their polarization behaviour under different experimental conditions has also been carried out.

EXPERIMENTAL

The electrochemical bath for the deposition studies was prepared as reported earlier [3,4]. For the codeposition of nickel, cobalt and manganese, the different molar ratios of these solutions were used. The effect of the following factors on the anodic deposition of these oxides was studied: (i) Current density of anode (ii) Concentration gradient (iii) pH (iv) Addition of organic materials and (v) Temperature.

The polarisation studies during deposition and after deposition were carried out in a 3-compartment cell. In all the cases, the anode

substrate was either 1 cm foil of platinum or stainless steel, and cathode was 1 cm foil of stainless steel. The potentials were recorded against saturated calomel electrode (S.C.E.)

RESULTS AND DISCUSSION

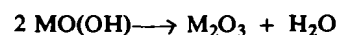
The results of polarization studies of these anodes in 0.1M KOH medium are shown in Fig. 1. The polarization studies in KOH in presence of ethanol are given in Fig. 2.

As reported earlier [3,10], the complexing agents play an important role in maintaining the pH of the solution as well as the metal ion concentration at the electrode surface. Thus the deposition of these oxides is smooth and adherent on electrode surface and achieving high current efficiency (approx. 90%) for the deposition.

The study on the effect of current density on the deposition revealed that the low current density favoured the deposition of oxides of low oxygen content. The deposited oxide was found to be highly adherent and uniform whereas at higher current density, a coarse and powdery deposit was obtained.

It was found that 1×10^{-2} M metal concentration was suitable for getting the smooth and adherent deposit. It was observed that pH 8-10 was suitable for the deposition while at higher pH the deposited metal oxides dissolved away in ammoniacal solution [10]. The studies on the effect of temperature showed that the ideal temperature for the deposition was 318K. Above 318K, the deposition was not stable, perhaps due to the high reactive nature of the deposited oxide and also due to the dehydration in oxy-hydroxide matrix.

The possible reaction can be written as



where M is either cobalt or nickel. This mechanism seems to be most suitable. If one puts forward the hypothesis that solvent molecules can get oxidized by MO(OH), the present studies on deposited metal oxides reveal that MO(OH), cannot oxidize H₂O as such without the presence of OH⁻ ions when they are placed in hot water at a temperature of 353K. Hence it is presumed that if the dehydration of MO(OH) occurs during the formation, it may distort the symmetry of metal oxides.

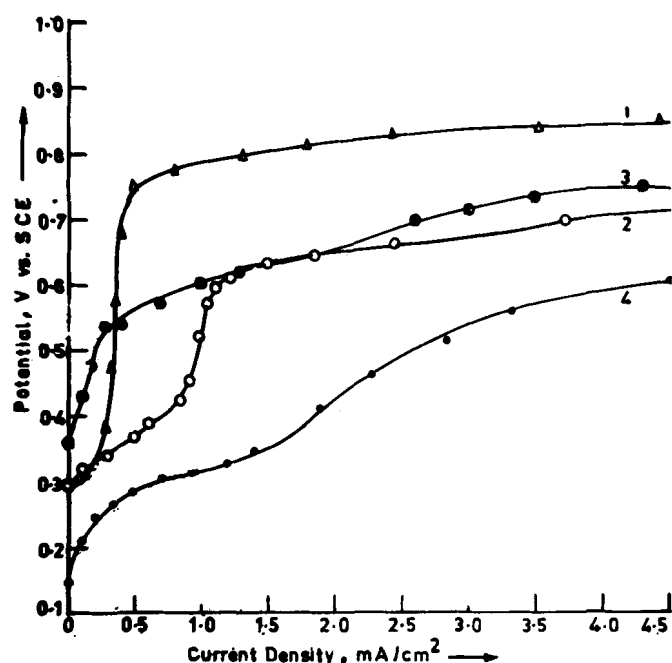


Fig. 1: Polarization curve in 0.1M KOH. 1 = Mn oxide; 2 = Co-Ni oxide; 3 = Mn-Ni oxide; 4 = Co oxide

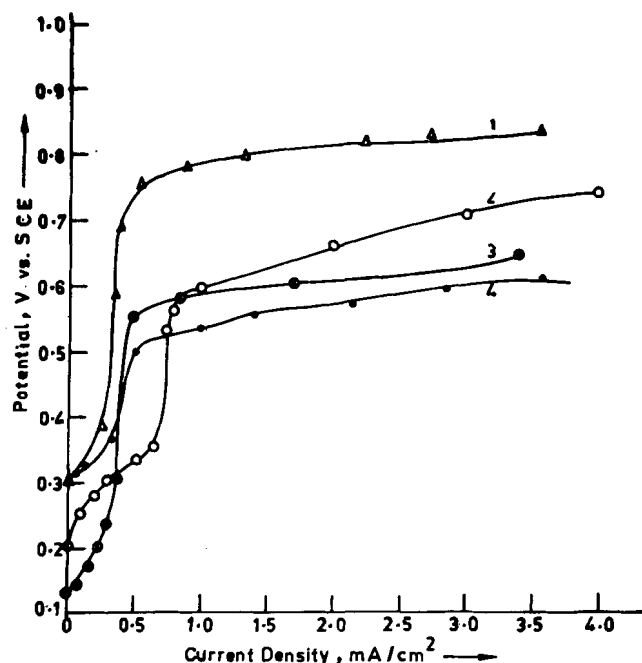
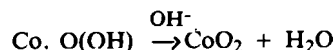


Fig. 2: Polarization curve in 0.1M KOH + 0.036 M in ethyl alcohol 1 = Mn oxide; 2 = Co-Ni oxide; 3 = Mn-Ni oxide; 4 = Co oxide

The polarization studies in presence of 0.1M KOH (Fig. 1) reveal that the formation of Co-oxide has two breaks in the curve, thereby indicating that at lower current density (1mA cm^{-1}) lower valent Co-oxide prevails at the electrode surface upto 0.3V vs SCE). By comparing with the earlier reported value, this oxide is CoOOH and increasing the current density results in the oxidation of Co(III) to Co(IV) . The curve at higher current densities does not show any limiting potential, which suggests the formation of inactive Co(IV) oxide. The reaction can be represented as



This reaction is irreversible in nature and hence this does not work as a good electrocatalyst as revealed in Fig. 2 (where studies were carried out in 0.036M EtOH). The behaviour of Co-oxide electrode is improved in presence of 5% nickel, where there is a smooth increase in potential, reaching the limiting value.

However, if Co is substituted with manganese, then the results are highly discouraging. Though pure manganese gives a smooth polarization curve in 0.1M KOH, yet the potential required is quite high. It is interesting to note that mixed Ni-Mn gives a good performance in presence of organic substrate like EtOH, which is due to the fact that manganese in presence of organic substrate remains in Mn(III) state and does not get oxidised to Mn(IV) . However, the potential required is quite high.

CONCLUSION

The study on the mixed oxides has revealed that it is possible to improve the performance of Co oxide and Mn oxide anode by suitably doping with nickel. If one can afford to carry out the oxidation studies of organic substrate at higher potential and low current density, then the mixed Ni-Mn oxide and mixed Co-Ni oxide anodes are suitable.

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