

Kinetics of deposition and dissolution of cobalt using cobalt amalgam

N G Renganathan and V K Venkatesan

Central Electrochemical Research Institute, Karaikudi - 230 006, INDIA

Kinetics of cobalt on cobalt amalgam electrodes are discussed in the present investigation. The preparation of the cobalt amalgam by a simple and *insitu* method employing rotating platinum based mercury film electrode has been indicated. The amalgam thus prepared was subjected to anodic and cathodic polarisation. The linear sweep voltammogram obtained for the reduction of Co(II) ion and the anodic dissolution of cobalt from amalgam electrode in solutions containing different concentrations of sodium sulphamate and sodium chloride at the sweep rate of 0.01 V.s^{-1} shows one pair of cathodic and one pair of anodic peaks. With increase in concentration of anions, in general, peak height decreases and at the highest concentration, it gets flattened. The peaks are absent in sodium sulphate solution. From the sweep rate dependence, the anodic and cathodic transfer coefficient values are calculated. Probable mechanism for the deposition and dissolution of cobalt from cobalt amalgam electrodes has been suggested.

Key words: Mercury film electrodes, cobalt amalgam, cyclic voltammetry

INTRODUCTION

Kinetics of deposition and dissolution of Co on and from cobalt amalgam has not been studied in detail. In the present study, an attempt has been made to study the kinetics of deposition and dissolution of cobalt using cobalt amalgam.

EXPERIMENTAL

Cobalt amalgam was prepared by depositing cobalt onto platinum based mercury film electrode from solutions of NaCl, NaNH_2SO_3 , containing 0.01 M cobalt at -1.52 V for 3 minutes. It was then allowed to undergo oxidation and reduction in the same solution.

RESULTS AND DISCUSSION

Preconcentration has been carried out and the scheme is given in Fig. 1. The details are available in [1].

A typical Lscv obtained is shown in Fig. 2. In general, there are one pair of cathodic and one pair of anodic peaks. The peaks are reported for the first time in this communication and not observed earlier. The peak height decreases with increase in concentration of anions and gets flattened at the highest concentration. Peaks were observed only in NaCl and NaNH_2SO_3 medium and absent in Na_2SO_4 . As discussed in [2], the electroactive species being $\text{Co}[(\text{H}_2\text{O})_5\text{L}]^+$ and the mode of reduction and oxidation is stepwise as in the case of nickel [3]. The absence of peaks in SO_4^{2-} medium and the presence of peaks in Cl^- and NH_2SO_3^- medium suggest that cobalt

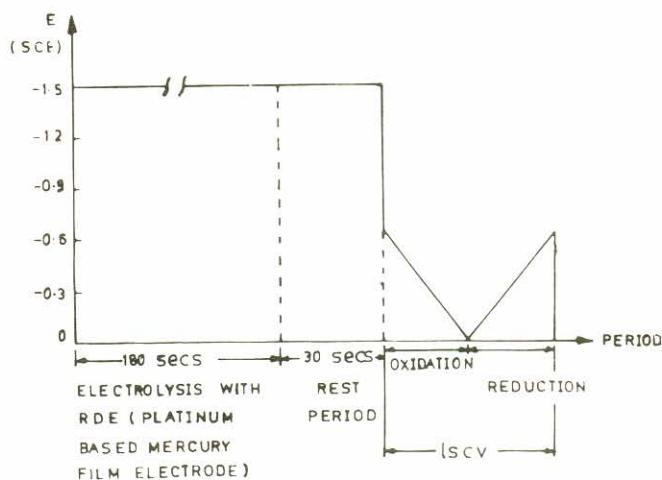
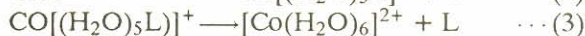


Fig. 1: Scheme for preconcentration of cobalt on PtBME and for getting Lscvs for oxidation of cobalt from PtBCAFE and reduction of Co(II) on PtBCAFE

microcrystals are responsible for the peaks. Microcrystals floating over mercury were photomicrographed and are available in [1]. The crystals are held in active condition by occluded hydrogen. Peaks are not due to oxide formation since they are not so reversible and not stable in the complex forming medium. Probable scheme for oxidation of cobalt from and reduction (reverse of the following) of Co(II) on PtBCAFE may be (L stands for Cl^- or NH_2SO_3^-)



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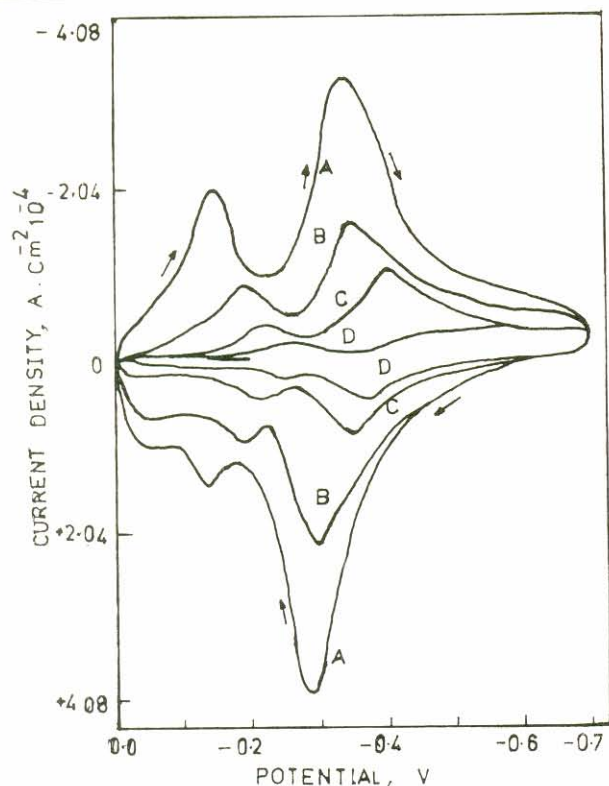


Fig. 2: LSCVs for cathodic reduction on and anodic oxidation of cobalt from stationary PtBCAFE at the $v = 0.01 \text{ V.s}^{-1}$ from solutions of pH 4.5 containing A = 0.05M NaNH_2SO_3 ; B = 0.1M NaNH_2SO_3 ; C = 0.5M NaNH_2SO_3 ; D = 1.5M NaNH_2SO_3 (0.01M $\text{Co}(\text{NH}_2\text{SO}_3)_2$ and 0.5M boric acid are used in all the cases A to D)