

# Electro-oxidation of formaldehyde and glycol on silver alloys in alkaline solutions

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Silver and silver alloys have been studied as catalysts for the electro-oxidation of formaldehyde and ethylene glycol in alkaline medium. Sb was found to increase the oxidation rate of formaldehyde and Bi that of ethylene glycol. This was correlated with the electronegativity difference between silver and alloying element.

**Key words:** Electro-oxidation, silver alloys, formaldehyde, fuel cells

## INTRODUCTION

The electro-oxidation of formaldehyde and ethylene glycol is important in view of the applications in the field of soluble organic fuel cells. The ease of handling and stability of these organic chemicals favour their use in fuel cells.

Pure metals of group I Band VIII B elements are good electrocatalysts for their oxidation [1]. Alloys among these groups have also been reported recently [2,3]. Parsons has recently reviewed the various catalysts used and mechanistic aspects of the study [4]. In this paper, the electro-oxidation on silver based alloys has been reported.

## EXPERIMENTAL

Ag-Sb 2%, Ag-Bi 2% alloys have been prepared by vacuum arc melting. Smooth polished electrodes were used for electrochemical studies. 6.0M KOH was the electrolyte. The concentration of the organic chemical was 1.0M and the temperature of the cell was maintained at 298K. Steady state polarisation and cyclic voltammetry studies were employed.

For comparison, the following catalysts were also studied. Ag-Pd, Pd-Ni, Pd-Cu, Pd-Ru alloys were electrodeposited [5] on smooth electrodes, their quantity being proportional to the charge used up for deposition.

## RESULTS AND DISCUSSION

The exchange current density values obtained for electro-oxidation of formaldehyde and glycol are given in Table I. The Tafel slope is in the range of 120-135 mV/decade and the reaction order is found to be close to unity for both the compounds. From the cyclic voltammetric studies, it is inferred that the oxidation of organic starts at a potential when the surface silver is covered with OH adsorption

layer. For Ag-Sb system, the peak for oxidation of HCHO occurs at  $-0.600$  mV vs Hg/HgO, OH<sup>-</sup> reference electrode and for Ag-Bi system, it is shifted to positive potential beyond  $+0.05$  V.

TABLE-I: The exchange c.d. values from steady state measurements

Temp. 298K      6.0M KOH + 1.0M organic

System	$i_0$ in formaldehyde (A.cm <sup>-2</sup> )	$i_0$ in glycol (A.cm <sup>-2</sup> )
Ag-Sb	$9.6 \times 10^{-5}$	$8.3 \times 10^{-6}$
Ag-Bi	$8.7 \times 10^{-3}$	$9.1 \times 10^{-5}$
Pd-Ni	$8.7 \times 10^{-6}$	$3.1 \times 10^{-3}$
Pd-Ni	$7.5 \times 10^{-4}$	—
Pd-Cu	$1.1 \times 10^{-3}$	$1.7 \times 10^{-5}$
Pd-Ag	$8.0 \times 10^{-5}$	$9.6 \times 10^{-4}$
Pd-Ru	$3.7 \times 10^{-4}$	$5.1 \times 10^{-4}$

The difference in the electrocatalytic behaviour can be explained due to favouring of OH adsorption on Ag by Sb in Ag-Sb system rather than in Ag-Bi system. This is due to the synergistic effect on the alloy surface caused by the difference in the electronegativity values in Ag-Sb system. Since the mechanism involves HCHO adsorption M-OH—H<sub>2</sub>COOH<sup>-</sup> adsorption as intermediate step, the oxidation is favoured in Ag-Sb system.

But in Ag-Bi system, the enhancement in the rate of oxidation of ethylene glycol can be explained as due to the electrocatalytic activity of the individual constituent element and that of Bi being greater than Ag itself [4,6].

The rates of electro-oxidation on electrode surfaces codeposited with other alloy electrocatalysts were compared by the c.d. values at constant  $\eta = 100$  mV. For formaldehyde

oxidation, the rate was in the order Pd-Cu > Pd- Ru > Pd-Ni > Pd-Ag and for ethylene glycol Pd-Ag > Pd-Ru > Pd-Ni > Pd-Cu systems.

### CONCLUSION

The rates of electro-oxidation of formaldehyde and ethylene glycol on Ag-Sb system were comparable with those of alloys of group VIIIIB and IB metals.

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