

ELECTRO-OXIDATION OF BENZYL ALCOHOL AT COPPER OXIDE ANODE

S. XAVIOR RAJA RATHINAM

Sacred Heart College, Tiruppattur - 635 601, INDIA and

DINESH CHANDRA TRIVEDI

Central Electrochemical Research Institute, Karaikudi - 636 006, INDIA

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The copper anode, under alkaline conditions, acts as a copper oxide anode, but the problem associated with this anode is the stability of an oxide layer on the substrate. Hence, the various methods, viz, electrochemical, chemical and thermal methods under various conditions were tried to obtain the stable oxide layer. After obtaining the stable copper oxide anode, selective oxidation of benzyl alcohol to benzaldehyde was studied.

Key words: Benzyl alcohol, copper oxide anode, benzaldehyde, electro-oxidation

INTRODUCTION

The preparation of surface structure and material of electrode are of prime importance in electrosynthesis, as the mechanism and the final products of many electrode reactions are known to depend on electrode material [1]. CuO coated copper electrode has low oxygen overvoltage. They can be used for controlled oxidation in an alkaline medium. Literature survey shows that number of anodes for practical use at alkaline pH are restricted to a few [2-8]. It has been observed that electrochemically generated copper oxide on copper does not work as an efficient anode. Hence a study was undertaken to examine different aspects of CuO formation on Cu substrate, namely (i) chemical oxidation of Cu substrate (ii) electrochemical formation of CuO on Cu and (iii) thermal oxidation of Cu surface to CuO. Studies of the surface structure were carried out by scanning electron microscope (SEM). Electrochemical characterization of these three different oxides was also carried out under identical conditions using galvanostatic technique in presence and absence of benzyl alcohol.

EXPERIMENTAL

Electrochemical formation of copper oxide

The copper plate was anodically polarised in 1M NaOH solution at a controlled potential of 0.67V (corresponding to a current density of 20 mA cm⁻²) for 20 minutes when the surface was coated with copper oxide. It was observed that at higher current density the dissolution of copper occurred which could be seen from the blue colour of the solution due to the formation of copper hydroxide in NaHCO₃ and Na₂CO₃ medium and a blue mass was deposited on the surface of the copper plate.

Formation of copper oxide by thermal and chemical oxidation of copper

The copper plate was washed and degreased using trichloroethylene and then heated in a furnace up to 623K for 2 hours. It was allowed to cool within the furnace, and then used as electrode. In the chemical method 250 ml of 0.1N NaOH was heated in a beaker to 363K and 3g of ammonium persulphate was added and stirred well. On dipping copper plate in this solution, formation of copper oxide took place instantaneously.

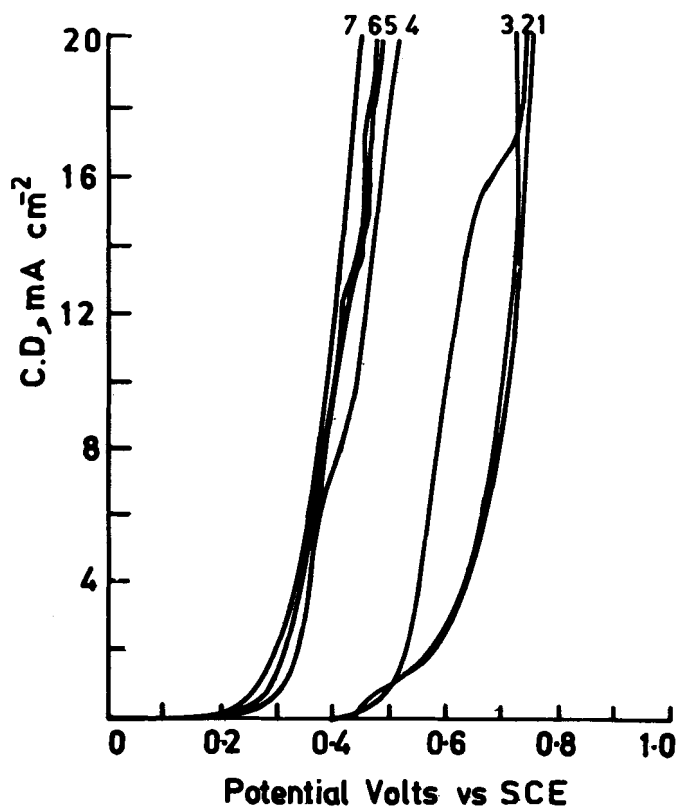


Fig.1: Polarisation studies on electrochemically prepared copper oxide anode in 1N NaOH (curves 1-3) and with benzyl alcohol ($1 \times 10^{-2}M$) (curves 4 to 7). From higher to lower C.D.: (1) and (5) without agitation (3) and (4) with agitation; From lower to higher C.D.: (2) and (6) with agitation; (7) without agitation

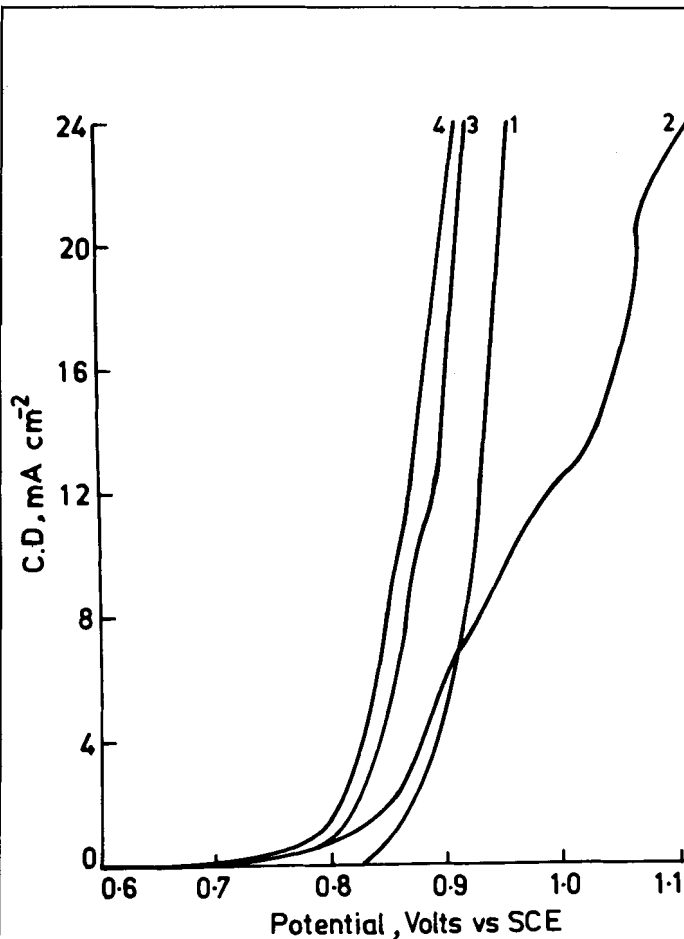


Fig.2: Polarisation studies on electrochemically prepared copper oxide anode in 1M Na₂CO₃ (curves 1 & 2) and with benzyl alcohol (1 × 10⁻²M) (curves 3 & 4); 1 and 3 – without agitation; 2 and 4 with agitation

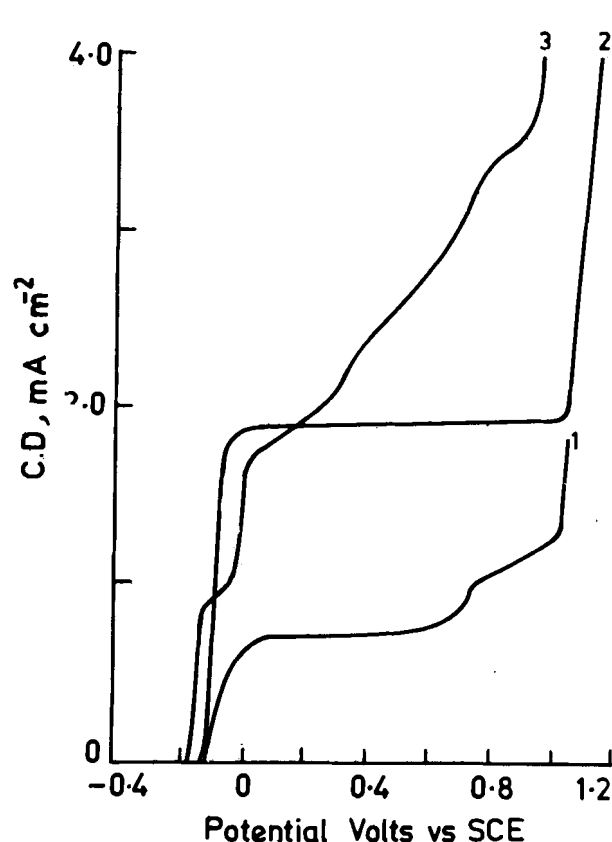


Fig.3: Polarisation studies on electrochemically prepared copper oxide anode in 1M NaHCO₃: 1 – without agitation; 2 – with agitation; 3 – with benzyl alcohol (1 × 10⁻²M) and without agitation

The electrochemical measurements were carried out, in a three compartment cell, using galvanostatic mode (ECO instrument model 550) and employing copper oxide anode prepared by aforesaid three methods. The reference electrode was standard calomel electrode (SCE). The working electrode was separated from the stainless steel cathode by a glass frit. The polarisation studies were carried out by two methods using agitation and without agitation: (i) The electrode was pre-polarised at higher current density for 30 minutes and then by decreasing current density the potential was noted (ii) By slowly increasing the current density the potential change was noted. Between each reading the time interval was 2 minutes.

The electrode potential was measured using a digital multimeter. It was observed that there were slight changes in the electrode potential with agitation. However changes in electrode potential from lower to higher and higher to lower current density readings was negligible. The current potential curves are plotted in Figs. 1-3.

SEM photographs (Fig. 4) indicate the differences in the structure of CuO prepared by the three methods.

Synthesis of benzaldehyde

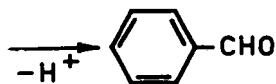
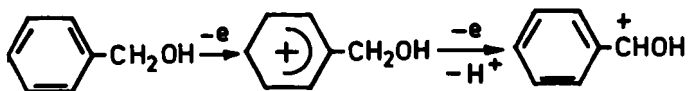
Saturated solution of Na₂CO₃ was used as electrolyte. Thermally coated copper oxide over copper plate was used as anode and a stainless steel rod was used as cathode. 25ml of benzyl alcohol was added and the mixture was stirred constantly by a mechanical stirrer. At a current density of 19 mA cm⁻², the whole solution turned blue due to the dissolution of electrode indicating that sodium carbonate medium was unsuitable for oxidation studies.

On carrying out the synthesis using 0.5N NaOH solution at an initial current density of 19 mA cm⁻² (with the electrode potential of 0.76 V) for five hours and extracting the solution with benzene, benzaldehyde could be collected at 349K and the same was estimated as semicarbazide derivative. The same synthesis was

carried out using chemically and electrochemically coated copper oxide electrodes.

RESULTS AND DISCUSSION

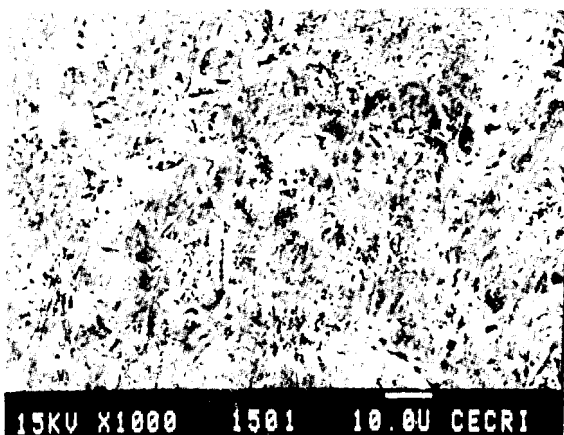
In the electrochemical method during the anodic polarisation of the metal the change is Cu to Cu(I) and then to Cu(II) [9-10]. The inflection in the curve (in Fig.1) at 0.65V corresponds to the Cu(II) - Cu(III) change and is too close to the oxygen evolution potential. The mechanism proposed for oxidation of benzyl alcohol involves the rapid loss of a proton and an electron from the initially formed cation radical, since the oxidation potential of the aldehyde is higher than that of alcohol.



When NaHCO₃ and Na₂CO₃ were used, the solution turned into blue due to the dissolution of CuO. This is due to the low availability of OH⁻ ions and consequently the formation of oxyhydroxide of copper.

Interpretation of SEM (Fig. 4)

The SEM photomicrographs (1501 & 1502) reveal that copper



4 (a)

Fig. 4 (a) & (b): SEM photomicrographs for CuO prepared electrochemically

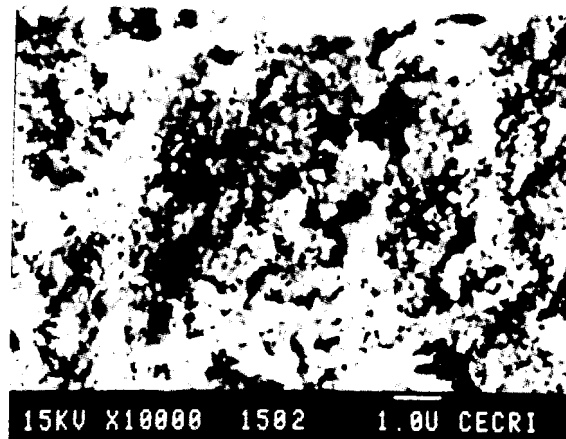


Fig.4(b)

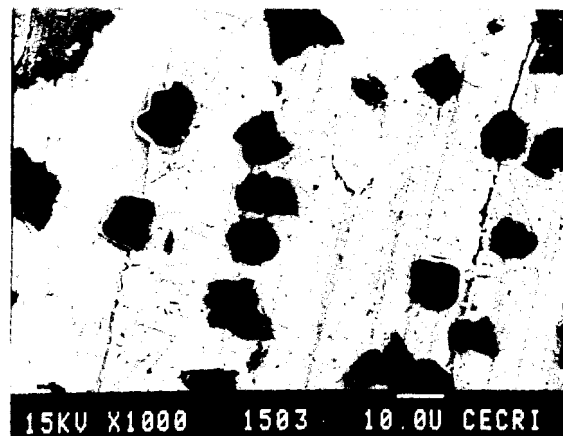
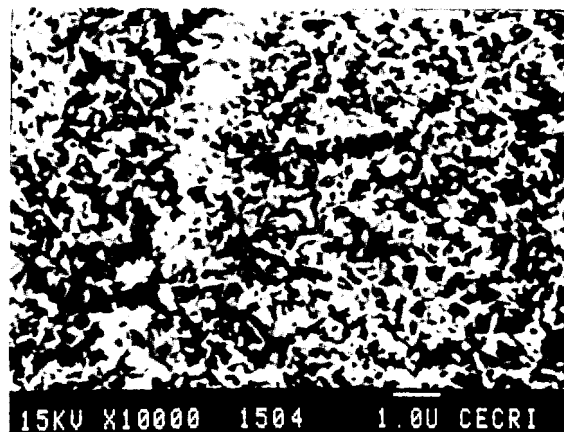


Fig.4(c)



4 (d)

Fig.4 (c) & (d): SEM photomicrographs for CuO prepared chemically

oxide formed electrochemically consists of two different phases as can be seen from different shadows.

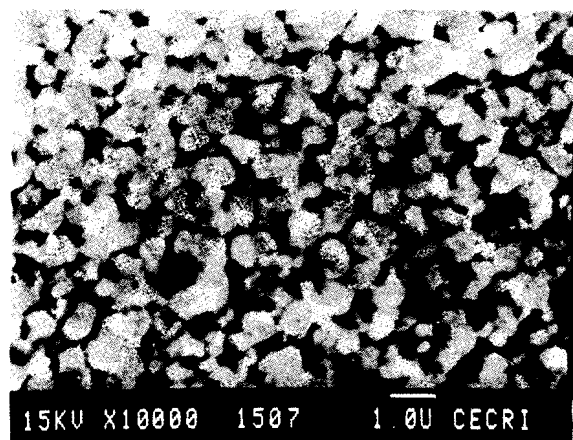


Fig.4(e): SEM photomicrographs for CuO prepared thermally

The SEM micrographs (1503 & 1504) for copper oxide prepared by chemical method show that nucleation for the copper oxide starts at different points and the points where nucleation occurs has dense growth of copper oxide. The SEM micrograph (1507) for thermally prepared copper oxide reveals that crystals are hexagonal in shape and uniform without any surface fission. A better catalytic activity towards the oxidation of organic compounds under alkaline medium is achieved by thermally formed copper oxide anode. Recent studies on the oxidation of benzyl alcohol under different pH conditions at copper oxide anodes (prepared by three different methods) indicate that benzaldehyde forms in NaOH medium does not get further oxidized at these anodes, because of higher ionisation potential. Thus this method allows a selective oxidation of benzyl alcohol to benzaldehyde.

Mechanism of catalysis at copper oxide anode

In oxidation catalysis the surface must provide sites for many functions. One function is oxygen exchange and its conversion to active part and its removal as a part of the product [2]. The second function is electron exchange and third function that provides bonding sites for the reactants and intermediate sites and that bond should be strong enough to activate the absorbent but should not be very strong to form a stable complex. If there is an isolated site offering a single oxygen atom the reaction will stop after that atom is extracted from the catalyst. Therefore, during experiments exclusively benzaldehyde is obtained without any traces of benzoic acid.

In the present case the cation vacancy becomes electron exchange centre [1]. If atom is removed bearing a anion vacancy, the vacancy is promptly annihilated by two cation vacancies (for cuprous oxide) at the surface leading to perfect lattice. The reoxidation of Cu_2O involves the formation of new cation vacancy.

Metal oxides where oxidation state of bulk cation can vary by one oxidation number (like Cu_2O , CuO) are very common as active oxidation catalysts, when cations of both oxidation states are available on the surface. One of them will have unpaired electrons and carries adsorption sites forming covalent bonds with the adsorbent. For the best catalytic activity the ratio of cuprous to cupric should be 1:1.



The concentrations of Cu(I) and Cu(II) oxides were determined spectrophotometrically. The IR spectroscopy indicates that these oxides have linear structure.

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