CHAPTER - V

THE ELECTROCHROMIC PROPERTIES OF COPPER OXIDE (CuO) THIN FILMS

5.1 INTRODUCTION

Intercalation compounds can be formed through the uptake or exchange of guest molecules, atoms, or ions by host lattices having suitable structures. These processes are well known examples of solid-state reactions that can occur at low temperatures. The books edited by Mandel Corn [1] and by Whittingham and Jacobson [2] may serve as standard texts for intercalation phenomena. The hosts can be of different types, including framework lattices and layer structures. The guest species can also show a large variety, but the types of interest for electrochromism are almost exclusively H^+ (protons) and the alkali ions Li^+, Na^+, K^+ etc. these mobile ions can be co-ordinated to water molecules. Among the possible reaction mechanisms, the partinent one for electrochromism are related to host lattices with some electronic conductivity, for which an effective lattice charge can be accomplished by the intercalation. Thus the intercalation proceeds under synchronous uptake of ions and electrons into the solid. From a chemical point of view, the intercalation process can be considered as a topotactic redox reaction by electron and ion transfer [3]. The reaction is reversible, and the host lattice retains its basic structural integrity during the course of forward and backward reaction. Anion intercalation is unfavourable under most conditions, which can be understood from steric and energetic argument [4].

In cyclic voltammetry, a voltage is applied between the copper oxide film and a counter electrode. The voltage is swept back and forth between two set points, usually in a triangular manner, alternatively, the voltage is pulsed between two levels. The current flowing into and out of the film in conjunction with the ion intercalation/ deintercalation is measured. Cyclic voltammetry can be used nonquantitatively to give a 'fingerprint' of the electrochemical processes, to trace reversible and irreversible effects, and to ascertain voltage levels that yield stable operation. Voltages outside the stability range can lead to gas evolution, metal electroplating etc. quantitative cyclic voltammetry is also possible [5], for example for measurements of charge densities associated with intercalation/ deintercalation processes. Commercial potentiostats can be used for cyclic voltammetry, an alternative low-cost system particularly suitable for electrochromics was described recently by Kirkup et al. [6].

The anodic formation and complex electrochemical properties of copper oxide films on bulk copper electrodes in alkaline electrolytes have been studied extensively [7-13]. Due to the poor electronic conductivity of stoichiometric Cu_2O, the two oxides can coexist with copper. Both oxides are semiconductors, Cu_2O having a direct bandgap of about 2.1 eV [14, 15] and therefore strongly absorbing at wavelengths below 600 nm, with a reddish appearance. CuO, with Eg = 1.3 eV is absorbing throughout the visible spectrum [16]. While thin

Cu_2O films with high transparency can easily be made by a variety of routes, and electrochromic behaviour has been reported [17-19] on lithium intercalation of Cu_xO films, electrochromic devices based on interconversion of Cu and Cu_2O, or of Cu_2O and CuO do not appear to have been investigated.

Transparent thin films of copper(I) oxide prepared on conductive SnO_2/F glass substrates by anodic oxidation of sputtered copper films or by direct electrodeposition of Cu_2O transformed reversibly to opaque metallic copper films when reduced in alkaline electrolyte. Due to their large electrochemical storage capacity and tolerance for alkaline electrolytes, these cathodically colouring films may be useful as counter electrodes for anodically colouring electrode films such as nickel oxide or metal hydrides.

Electrochromism is a phenomenon related to a persistent and reversible optical change induced electrochemically, whose macroscopic effect is a change in colour [20]. A copper oxide film shows a brownish to pale brown (transparent) electrochromism with ion injection. The quality of an EC material is measured by its colouration efficiency, which is its transmittance contrast between coloured and bleached states relative to injected charge, response time, and chemical stability.

Very few studies have been reported on the electrochromic properties of copper oxide. Metallic copper films were prepared by DC magnetron sputtering from an oxygen free high conductivity Cu target in an argon atmosphere at a pressure of 10 mTorr by T. J. Richardson, et al. [21] for study of electrochromism in copper oxide thin films [21]. They reported that the dark state produced by anodic polarization, referred to as "CuO" begins to appear at 0.2 V. Despite the black colour of CuO, the switching was limited to about 20%. Polarization beyond 0.7V resulted in oxygen evolution and no further darkening of the film. Sputtered Cu_2O films contained small amounts of Cu and had a deep copper colour. Oxidation following reduction of the entire film to copper produced a clear, highly transparent and strongly adherent Cu_2O film, which exhibited superior cycling stability to the mainly metallic precursor films. Electro-deposited Cu_2O was less uniform and adherent, but could be cycled several times over a wide range of visible transmittance [21].

M. T. San Jose, et al. [22] studied electrochemical behaviour of copper oxides at a carbon paste electrode. They carried out several experiments to elucidate the electrochemical transformation of copper oxide in 10 M KOH medium occuring at +300 to -1400 mV (sce). The voltammograms have been employed to propose several charge transfer mechanisms.

5.2 EXPERIMENTAL PROCEDURE

Copper oxide thin films were prepared by spray pyrolysis technique. Copper acetate solution was prepared as described in Chapter III, Section 3.3.3 and was used as a precursor solution. Copper oxide films were deposited onto fluorine doped tin oxide (F.T.O.) coated glass substrates maintained at various temperatures from 250 to 350^0C in the interval of 50^0C. These samples were annealed at 500^0C for half an hour in air, which then used as working electrode in a three electrode EC cell. Graphite was a counter electrode and 0.1 N NaOH was an electrolyte. The voltages were measured with respect to the standard calomel electrode (SCE).

Cyclic voltammetry (CV) was carried out using computer controlled Versastat-II model equipped with electrochemistry software, M270. For CV, a cyclic potential sweep is imposed on an electrode and the current response was observed at different scan rates. Stability of copper oxide films in 0.1N NaOH was tested by repeating CV for several times. Chronoamperometry (CA) studies were carried out using X-Y (t) recorder in conjunction with scanning potentiostat and the variation of colouration and bleaching current with respect to time at fixed potential was recorded. Optical transmittance spectra of coloured and bleached films, in the range 350 to 850 nm wavelength, were recorded by using Hitachi-330 spectrophotometer.

5.3   RESULTS AND DISCUSSION

This chapter is devoted to electrochemical measurements of copper oxide thin films and testing of electrochromism in these films. This has been done by employing electrochemical characterization techniques such as cyclic voltammetry, chronoamperometry and spectrophotometric measurements.

During rudimentary experiments it was found that all the un-annealed samples (C_{250} to C_{350}) get dissolved in 0.1 NaOH electrolyte. Therefore electrochemical measurements of the un-annealed samples were not possible. However, annealed samples (C_{A250} to C_{A350}) were quite adherent and withstood electrochemical characterizations for prolonged period. Therefore, these samples were subjected to the characterizations without further problems.

5.3.1   Electrochemical Characterization

5.3.1.1   Cyclic voltammetry (CV)

If the potential of an electrode in the electrochemical cell is controlled externally, the solution can be made to 'adjust' by electron transfer to approach equilibrium with the electrode potential. In many electrochemical experiments, the solution initially has only form of a redox couple present and the electrode is initially set at a potential such that this form does not undergo electron transfer. This ensures that the experiment begins at zero faradaic current. The electrode potential is

then to a position that favours electron transfer. The manner in which the potential is changed gives rise to a profusion of electrochemical controlled potential techniques.

CV is a potential controlled 'reversal' electrochemical experiment. A cyclic potential sweep is imposed on electrode and current response is observed. Analysis of the current response can give information of the thermodynamics and kinetics of electron transfer at the electrode-solution interface, as well as the kinetics and mechanisms of solution chemical reactions indicated by the heterogeneous electron transfer. Fig. 5.1 shows the overall view of the CV experiment. A potentiostat system sets the control parameters of the experiment. Its purpose is to impose on an electrode (the working electrode) a cyclic linear potential sweep and to output the resulting current-potential curve. This sweep is described in general by its initial (E_i), switching (E_s), final (E_f) potentials, and sweep (or scan) rate. The potential as a function of time is;

$$E = E_i + Vt \qquad \text{(forward sweep)} \qquad \dots (5.1)$$

$$E = E_s - Vt \qquad \text{(reverse sweep)} \qquad \dots (5.2)$$

More complicated sweeps are possible such as the option of a second potential multiple cycles are sometimes used, but in many instances these will not be more informative than a single cycle. However, the electrochromic stability of an EC electrode in an

electrolyte can be studied by repeating these cycles several times. The term 'Linear Sweep Voltammetry' (LSV) is used for a half cycle CV. Fig. 5.2 illustrates various possible cycles.

The electrochemical reaction of interest takes place at the working electrode (WE). Electrical current at the WE due to electron transfer is termed as 'Faradaic current'. An auxiliary or counter electrode (CE) is driven by the potentiostatic circuit to balance the faradaic process at the WE with an electron transfer of opposite direction (e.g. if reduction takes place at the WE, oxidation takes place at the CE). The process at the CE is of not interest, and in most experiments the small current observed mean that the electrolytic products at the CE have no influence on the processes at the WE. The faradaic current at the WE is transduced to a potential output at a selected sensitivity, expressed in amperes per volt, and recorded in digital and analog form. The CV response is plotted as current versus potential.

In this study a three-electrode EC cell has been studied. The configuration of the cell was as follows :
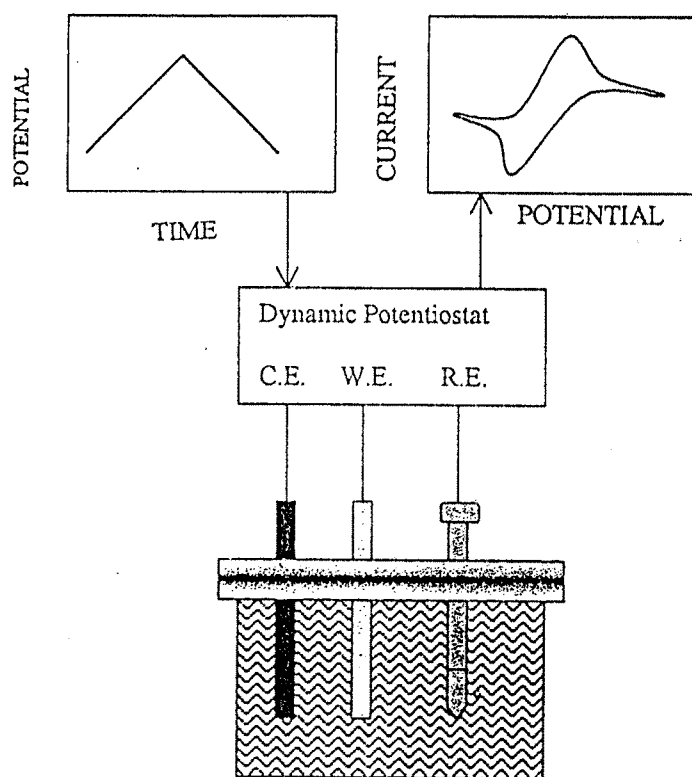
FTO/ CuO/ 0.1N NaOH/ C; SCE
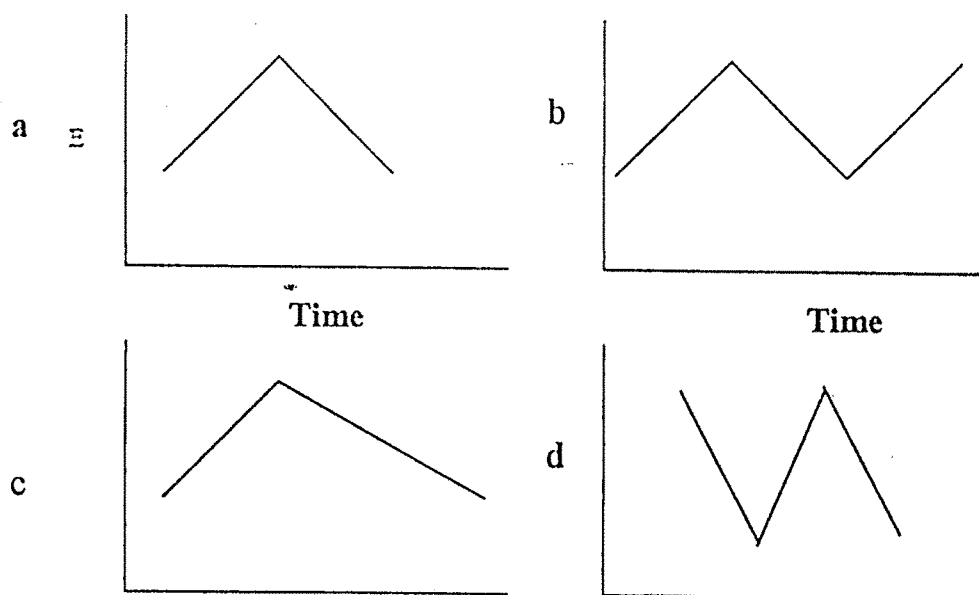
Fig. 5.1   Overall view of the CV experiment.

Fig. 5.2   CV waveforms.

Cyclic voltammetry (CV) was performed for all the annealed samples, C_{A250} to C_{A350} in an aqueous hydroxyl ions containing electrolyte, 0.1 N NaOH. In figure 5.3 (a to c) CVs of these samples at 50 mV/ sec. scan rate are plotted. Copper oxide voltammograms are plotted starting from zero current potential, O.O V (SCE), scanning upto -1V (SCE) and reverse towards + 1V (SCE).
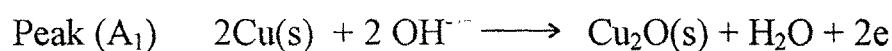
In the voltammogram we observe in the cathodic scan, the peak C_1 (-700 mV), which may be due to the reduction of copper oxide to metallic copper.

Reduction :

Peak (C_1) $Cu^{2+} + 2e^- \longrightarrow Cu^0$
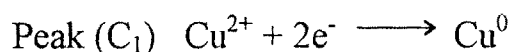
In the anodic scan, the peaks A_1 (-75 mV), and A_2 (+650 mV) are observed which may be due to oxidation of copper to copper oxide.

Oxidation :

Peak (A_1) $2Cu(s) + 2\,OH^- \longrightarrow Cu_2O(s) + H_2O + 2e$

Peak (A_2) $Cu_2O(s) + 6\,OH^- \longrightarrow 2CuO + 3H_2O + 2e$

CVs of the sample C_{A250} to C_{A350} are similar to that reported for conventionally deposited copper oxide thin films [21]. During the potential sweep, the current resulting from ion intercalation and deintercalation was measured. A cathodic scan to the extreme potential
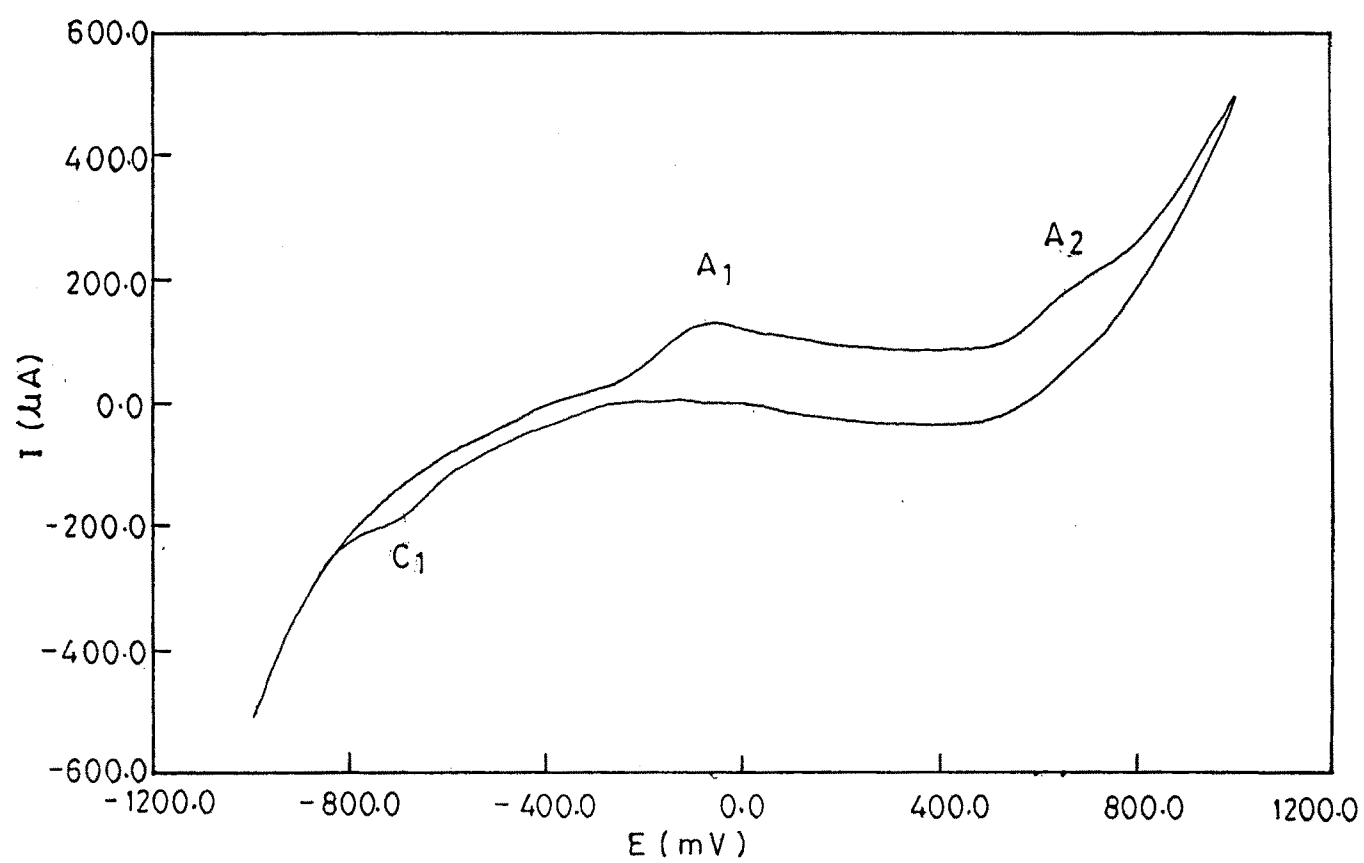
Fig. 5·3(a)-Cyclic voltammogram of the sample deposited at 250 °C and heat treated at 500 °C for 1 hr recorded at 50 mV/s in 0·1 M NaOH solution.
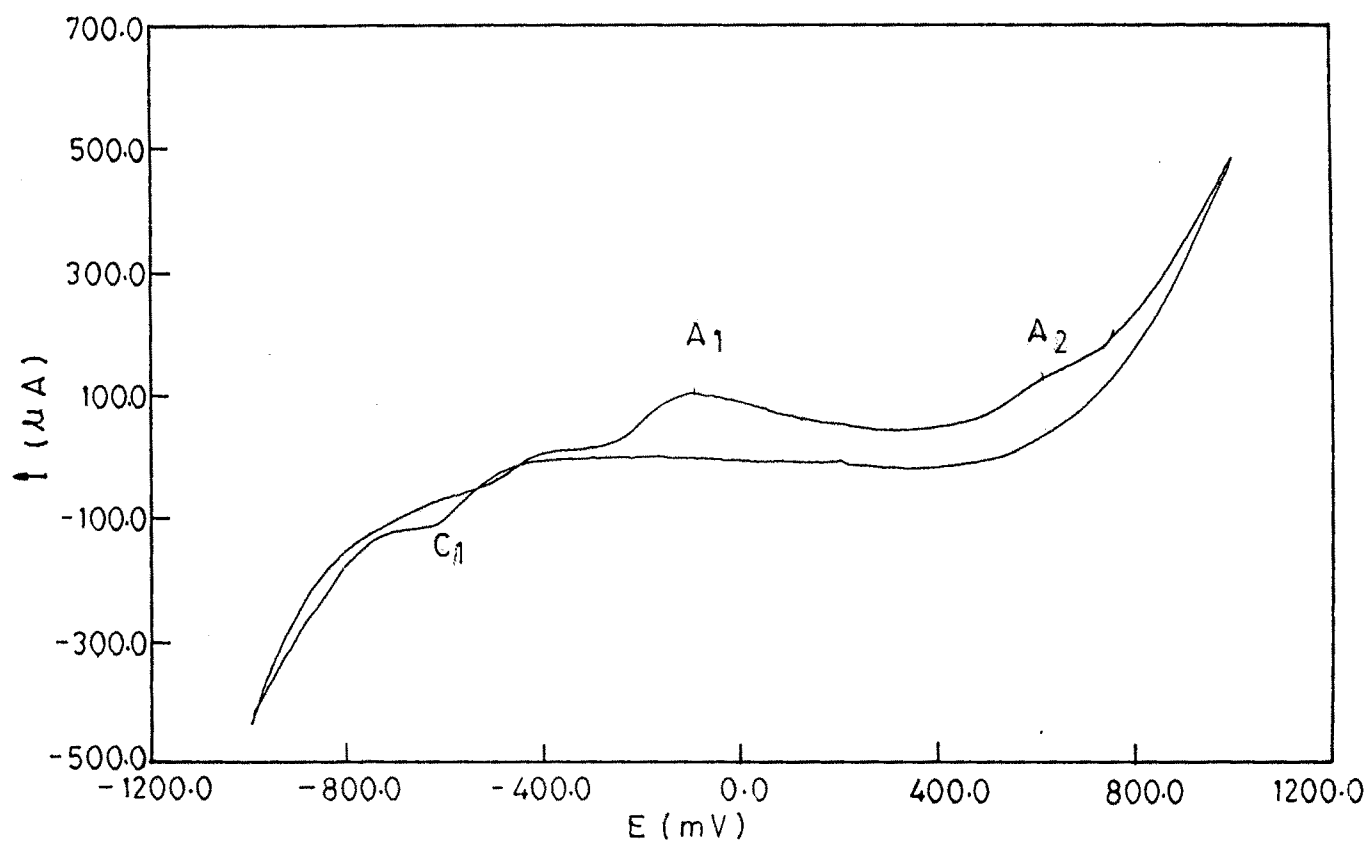
Fig. 5·3(b)-Cyclic voltammogram of the sample deposited at 300 °C and heat treated at 500 °C for 1 hour recorded at 50 mV/s in 0·1 M NaOH solution.
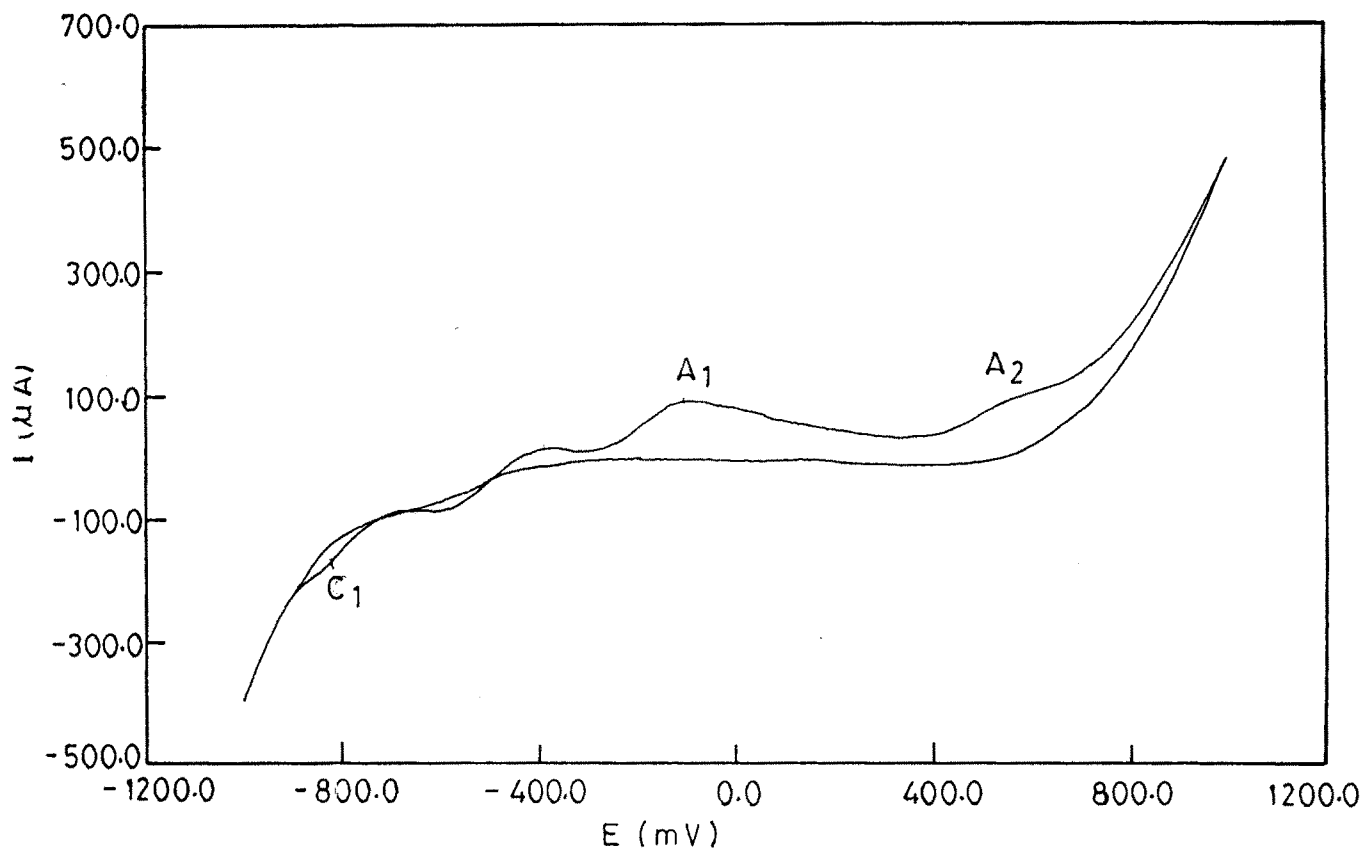
Fig.5·3(c)-Cyclic voltammogram of the sample deposited at
350 °C and heat treated at 500 °C for 1 hour recorded
at 50 mV/s in 0·1 M NaOH solution.

of -1V (SCE) caused the films to turn brownish and at an anodic scan to + 1.0V (SCE), the films became pale brown. If the colour bleach cycles are repeated similar CVs, with no much change in shape and size are observed. This evinces that all the annealed samples exhibit electrochromism. The curves show a single oxidation-reduction cycle, with oxidation and reduction peaks. The colouration and bleaching of the Cu_2O film is associated with intercalation (insertion) and deintercalation (egress) of OH⁻ ions.

Thus the film can be reversibly made relatively transparent by electrochemical oxidation and coloured by reduction in a hydroxyl ion containing electrolyte. From (Fig. 5.3) different parameters associated with OH⁻ ion intercalation and deintercalation into and out of Cu_2O host lattice were calculated and are given in Table 5.1.

Table 5.1 : Different parameters associated with intercalation and deintercalation of OH⁻ ions from NaOH electrolyte into and out of sprayed copper oxide thin film samples

Sample	Structure	E_{pa} (mV)	I_{pa} (μA)	D cm²/ sec	t_c sec	t_b sec	ΔOD	% CE (cm²/C)
C_{A250}	CuO	-65	140	53×10^{-16}	4	2.5	0.51	32
C_{A300}	CuO	-100	115	3.58×10^{-16}	3.9	3.4	0.39	25
C_{A350}	CuO	-95	100	2.7×10^{-16}	2.5	8	0.46	29

E_{pa} : Anodic peak potential; I_{pa} : Anodic peak current;
D   : Diffusion coefficient; t_c : Colouration time;
t_b : bleaching time and   CE : Colouration efficiency

The magnitude of anodic peak current is maximum for sample C_{A250} among all the samples. This suggests that extent of OH^- ion intercalation as well as deintercalation is maximum for amorphous samples, which wanes for other samples. The diffusion constant of OH^-+ ions is calculated from the Randell-Sevcik equation;

$$i_p = 2.72 \times 10^5 \times n^{3/2} \times D^{1/2} \times C_o \times v^{1/2} \qquad \ldots 5.3$$

where D is the diffusion constant, C_o is the concentration of active ions in the solution, v is the scan rate, n is the number of electrons and is assumed to be 1, i_{pa} is the anodic peak current density. The values of i_p have been taken from Fig. 5.3. By substituting all the values, diffusion constants were calculated and are listed in Table 5.1. It is observed that for sample C_{A250}, D is minimum. It is known that large film thickness and high intercalation level gave minimum diffusion constant. This evokes that sample C_{A250} has high OH^- intercalation level, which decreases with decreasing film thickness i.e. from sample C_{A250} to C_{A350}.

5.3.1.2   Chronoamperometry (CA)

CV is a powerful technique because the CV wave-shape is sensitive to all the parameters of the electrochemical mechanism. For the same reasons, however, a full quantitative analysis with CV can be difficult. It is usually helpful if qualitative or quantitative information can be obtained from other sources. Potential step methods can play a

complimentary role to CV in the analysis of electrochemical mechanism. This is because they can be performed under conditions of a fast and irreversible forward heterogeneous rate constant. The overview of CA experiment is shown in Fig. 5.4. The potential waveform imposed at the WE for the double potential step (DPS) is also shown in Fig. 5.4. The characteristics of the wave form are the initial potential E_i, the step potential E_s, the step time t and final potential E_f. Here we consider only the case of $E_s = E_f$. Normally electrolysis occurs at the initial potential setting and the potential is stepped to a voltage well beyond the formal reduction potential of the principal electro-active species, that undergoes reduction or oxidation.

In this study chronoamperometry (CA) was used to measure the speed of electrochromic response and to apprehend intercalation and deintercalation mechanisms. To examine chronoamperometric response, initially an external voltage of -200 mV (SCE) was applied between Cu_2O film and counter electrode and variation in intercalation current (j_i) was monitored with respect to time. Fig. 5.5 (a to c) shows CA response for all the samples In response to this intercalation, current (J_i) increases rapidly upto its maximum and decays further to a constant value. The colouration time 't_c' (time required for intercalation current to stabilize at its lowest value) is estimated to be 4 sec for sample C_{A250}. The applied voltage was then switched to + 200 mV (SCE), which results into rapid increase in deintercalation current
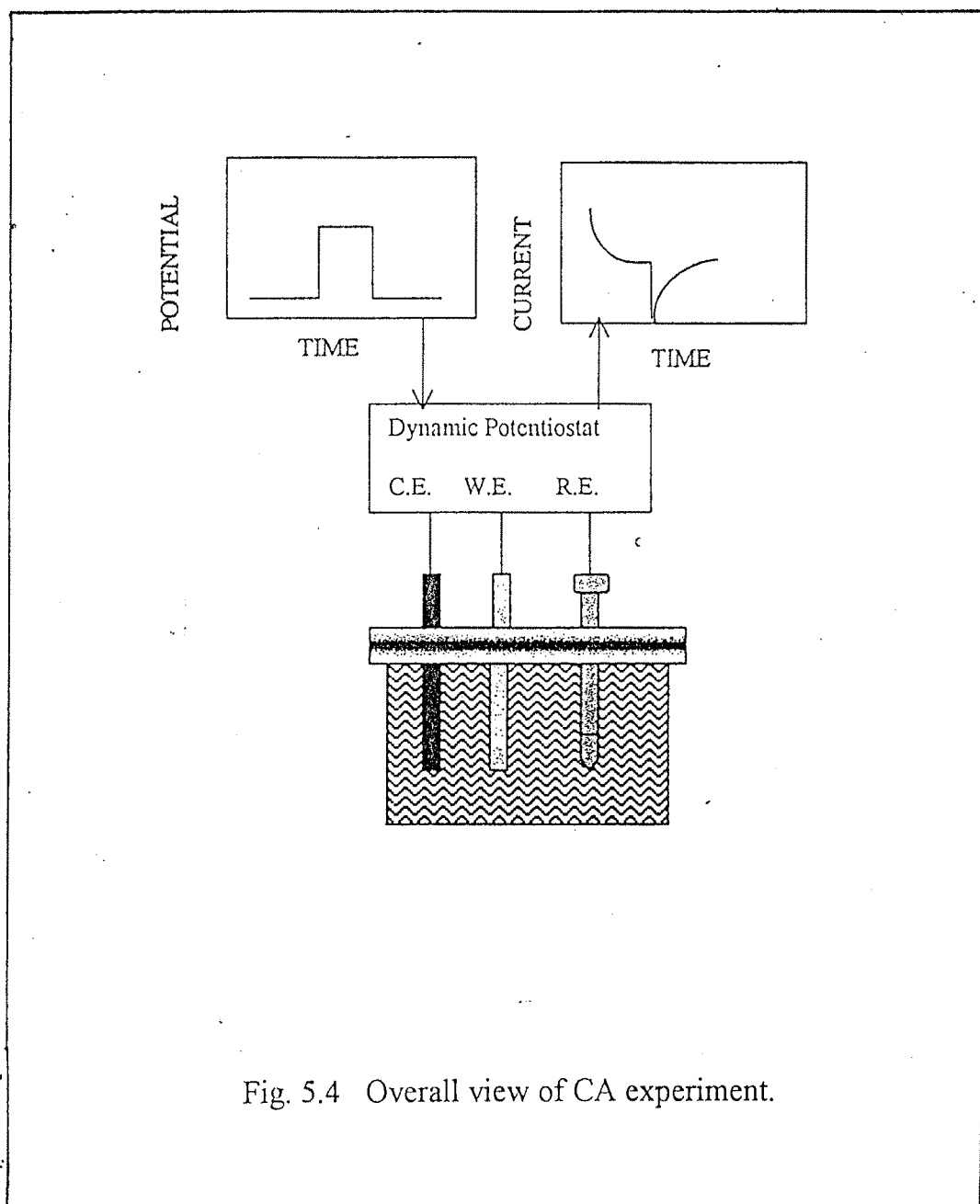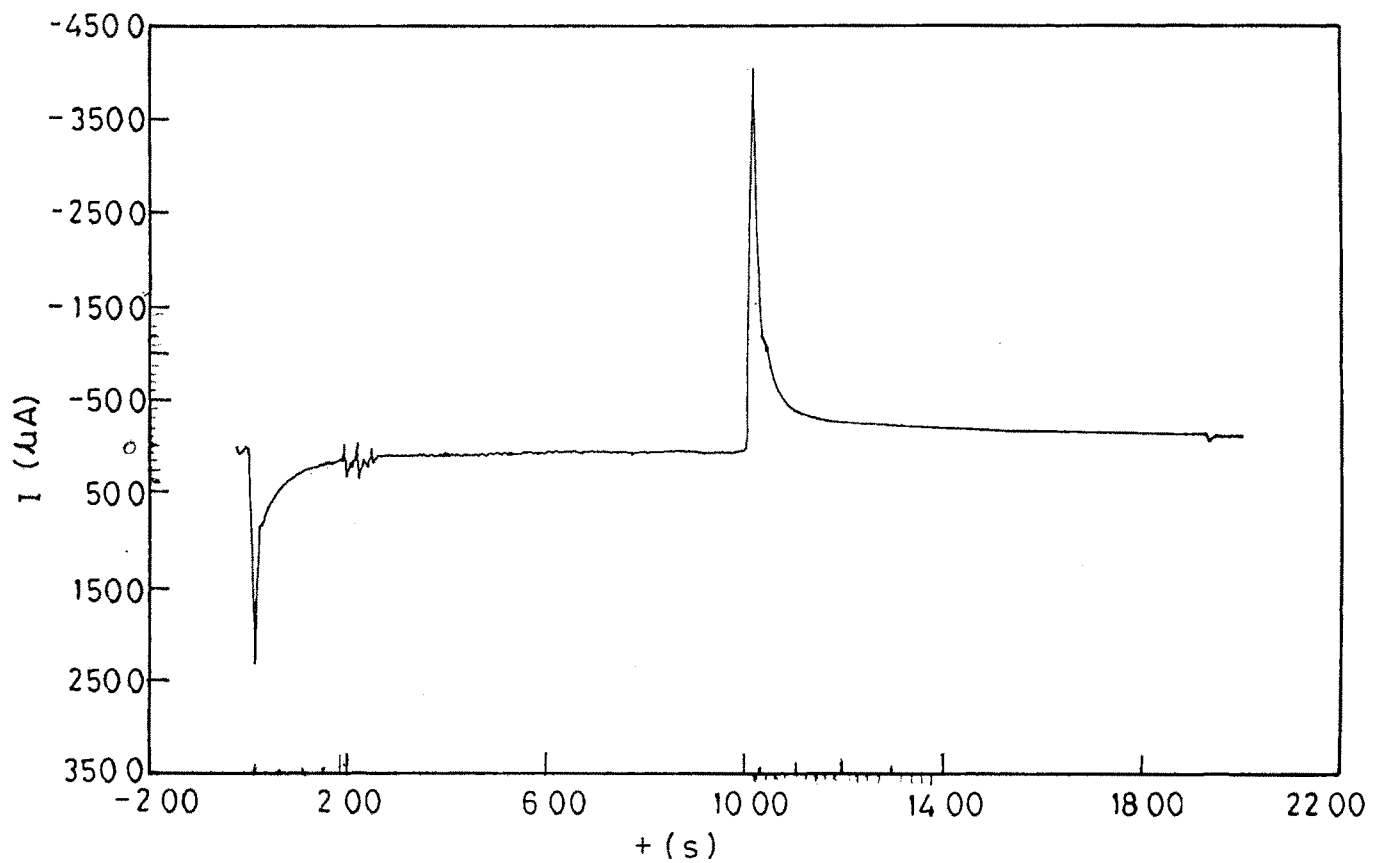
Fig. 5.4 Overall view of CA experiment.

Fig. 5·5(a)-Chronoamperometric curve for the sample dep at 250°C and heat treated at 500 °C at 1 hour.
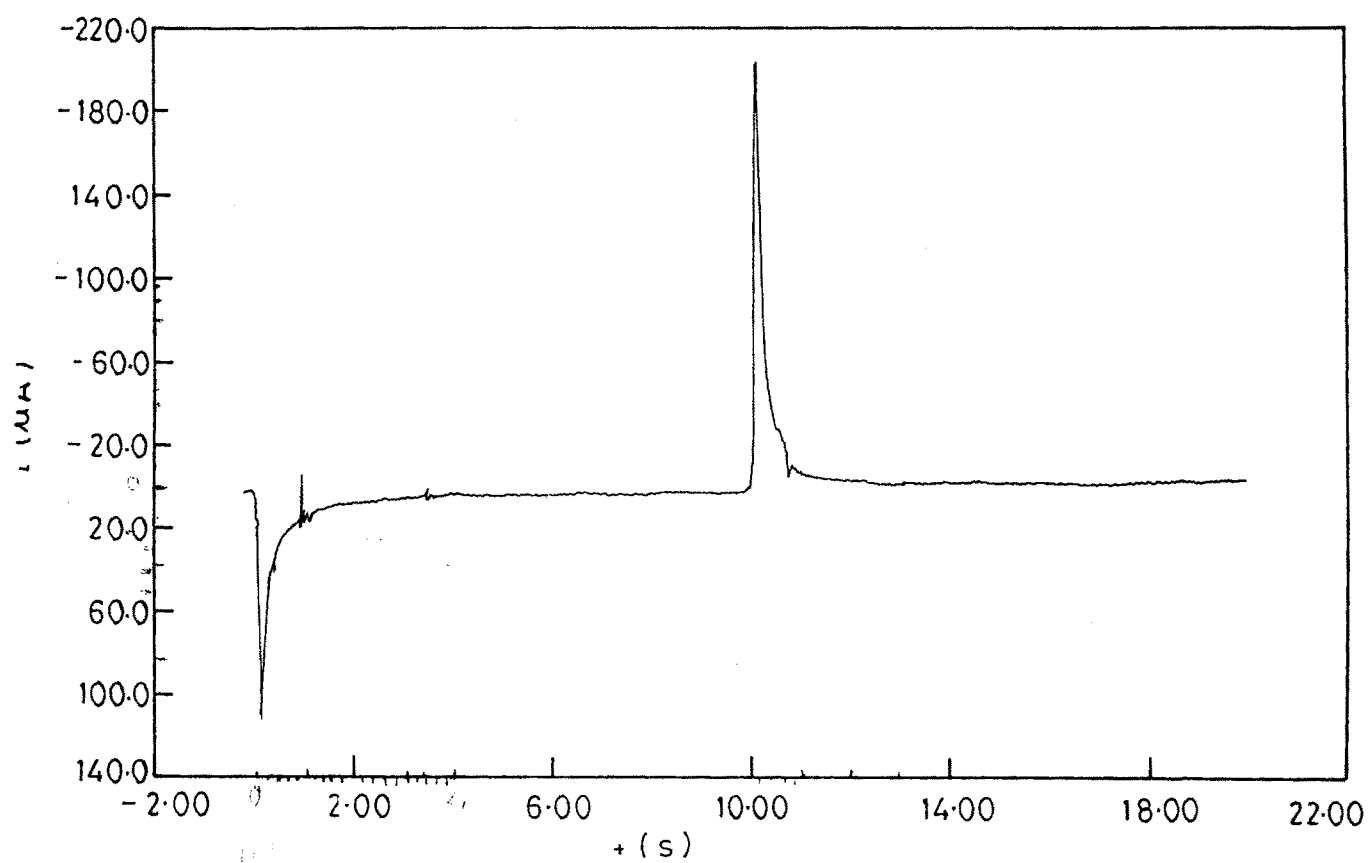
Fig.5·5(b)-Chronoamporometric curve for the sample deposited at 300 °C and heat treated at 500 °C for 1 hour.
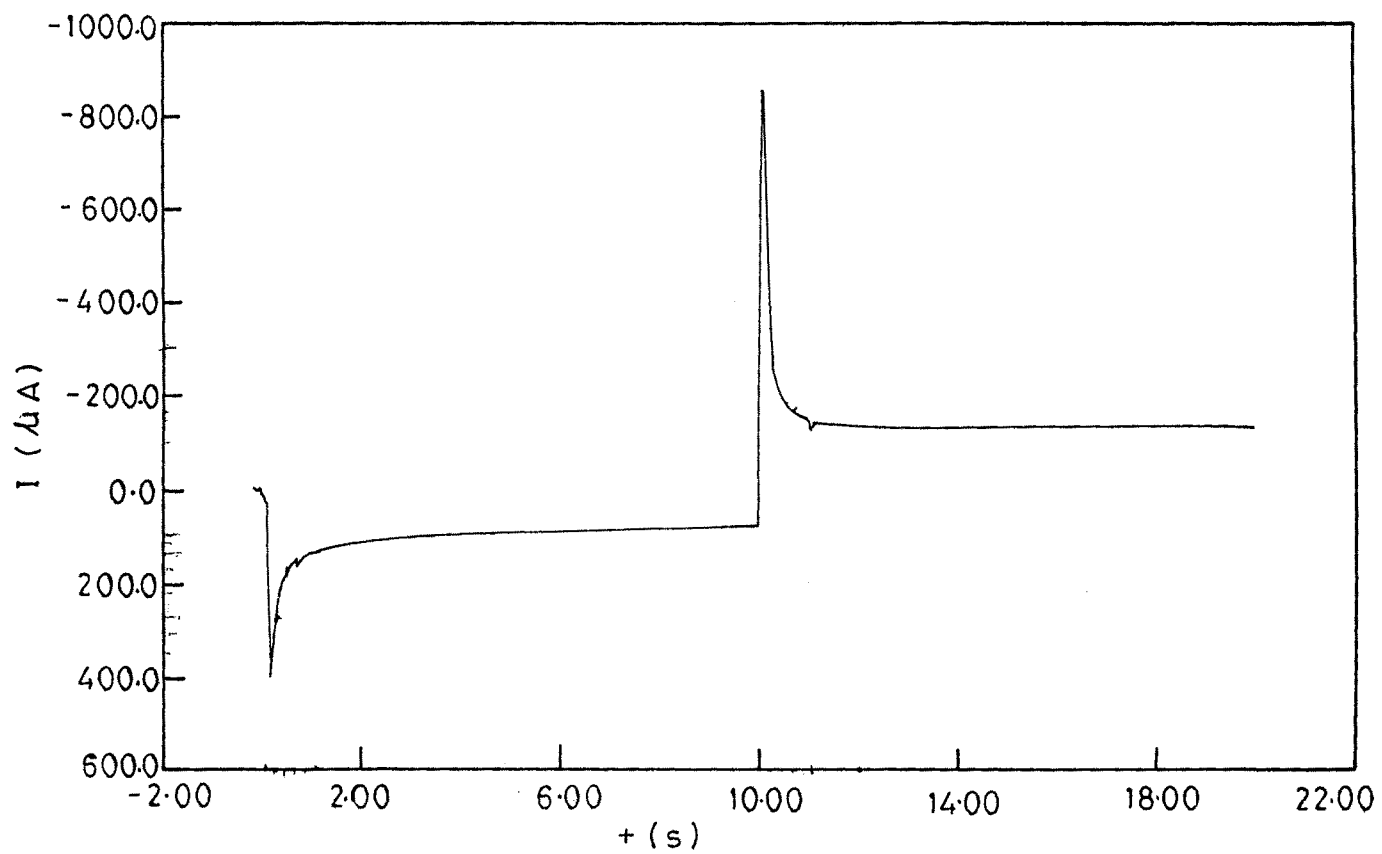
Fig.5·5(c)-Chronoamperometric curve for the sample deposited at 350 °C and heat treated at 500 °C for 1 hour.

followed by sharp decay to a constant value. The bleaching time 't_b' (time required for the deintercalation current to stabilize at its lowest value) is estimated to be 2.5 sec., for sample C_{A250}. The values of 't_c' and 't_b' are given in table 5.1.

The asymmetry in current response is typical for materials, which exhibit different conductivity, in different oxidation states. The higher bleaching current arises from good conductivity of copper and rapid decay in current is due to conductor-to-insulator transition. On the other hand insulator-to-conductor transition has slower transient. Intercalation is largely governed by the properties at the boundary between the electrolyte and the copper oxide film, whereas deintercalation is mainly influenced by ion transport in the film. For asymmetric barrier the time dependance J_i (t) can be obtained from following equation (25)

$$J_i (t) = t^{-1/2} \exp (E_i/R_g T) \qquad \qquad \dots (5.4)$$

where E_i is the voltage applied during intercalation process, $J_i(t)$ is intercalation current density, R_g is gas constant and T is the inverse temperature. Fig. 5.6(a) shows a plot of log J_i versus log t for intercalation, typically for a potential step of $\pm 1V$ (SCE). The slope was calculated to be 0.063, 0.037 and 0.056 for C_{A250}, C_{A300} and C_{A350} samples respectively.
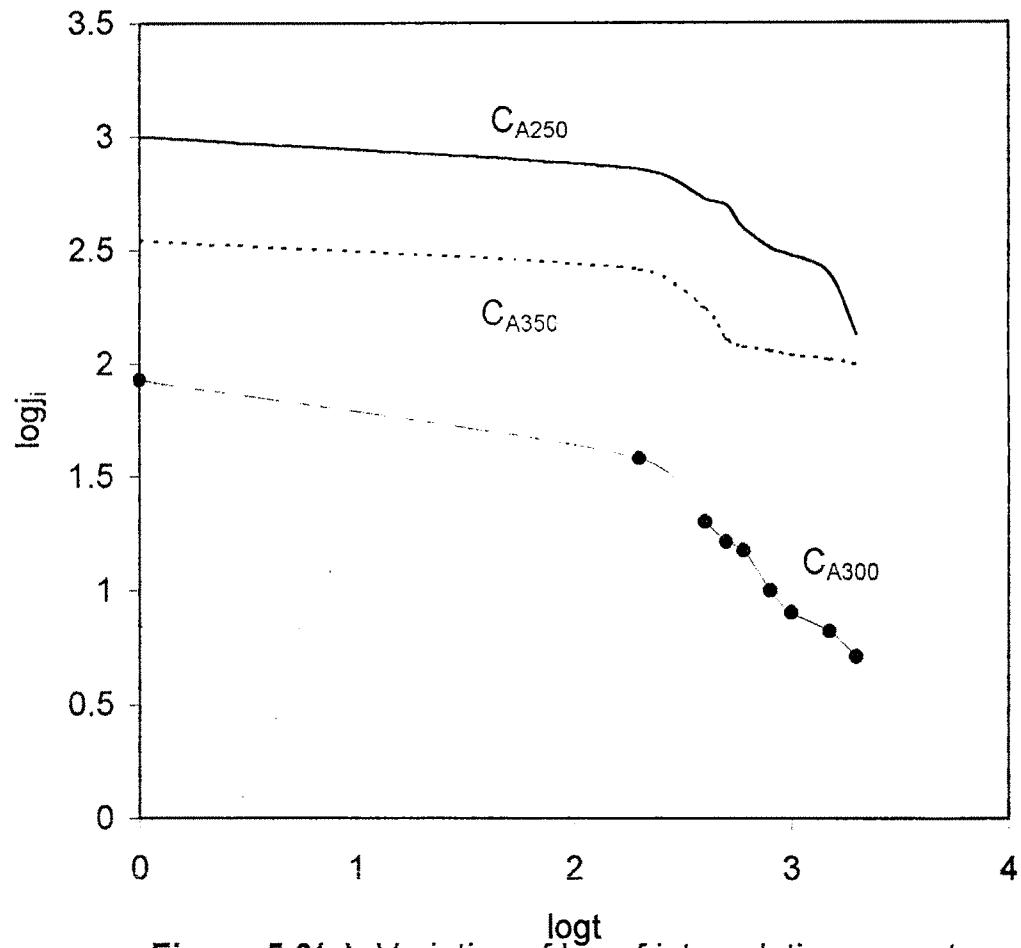
Figure 5.6(a): Variation of log of intercalation current (Ji) versus log of time (t).

Faughnan et al. [23] have shown that the time dependance $J_{di}(t)$ (deintercalation current density) can be obtained by using following equation

$$J_{di}(t) \quad \alpha \; Dm^{1/4} \; E_d^{1/2} \; t^{-3/4} \qquad \qquad \ldots (5.5)$$

The slope of log J_{di} versus log (t) plot for de-intercalation (Fig. 5.6b) was calculated to be 1.70, 2.10 and 1.82 for the samples C_{A250}, C_{A300} and C_{A350} respectively.

The cathodic charge densities (ΔQi), resulted from OH⁻ ion intercalation into CuO, were measured from integration of colouration currents for all the samples. Fig. 5.7 shows the OH⁻ ion charge densities inserted in samples C_{A250} to C_{A350}.

5.3.2 Optical Transmittance Study

Initially the C_{A250} was coloured (reduced) by applying + 100 mV (SCE) for about 2 seconds, withdrawn from the EC cell and immediately submitted for spectroscopic measurements. The transmittance spectrum in the range of wavelength between 350 to 850 nm was recorded. Afterwards the sample was again placed in EC cell and bleached (oxidized) by applying -100 mV (SCE), for about 12 seconds, and its transmittance spectrum was recorded. Similar procedure was adopted for other samples. Fig. 5.8 (a to c) shows transmittance spectra for all the samples.
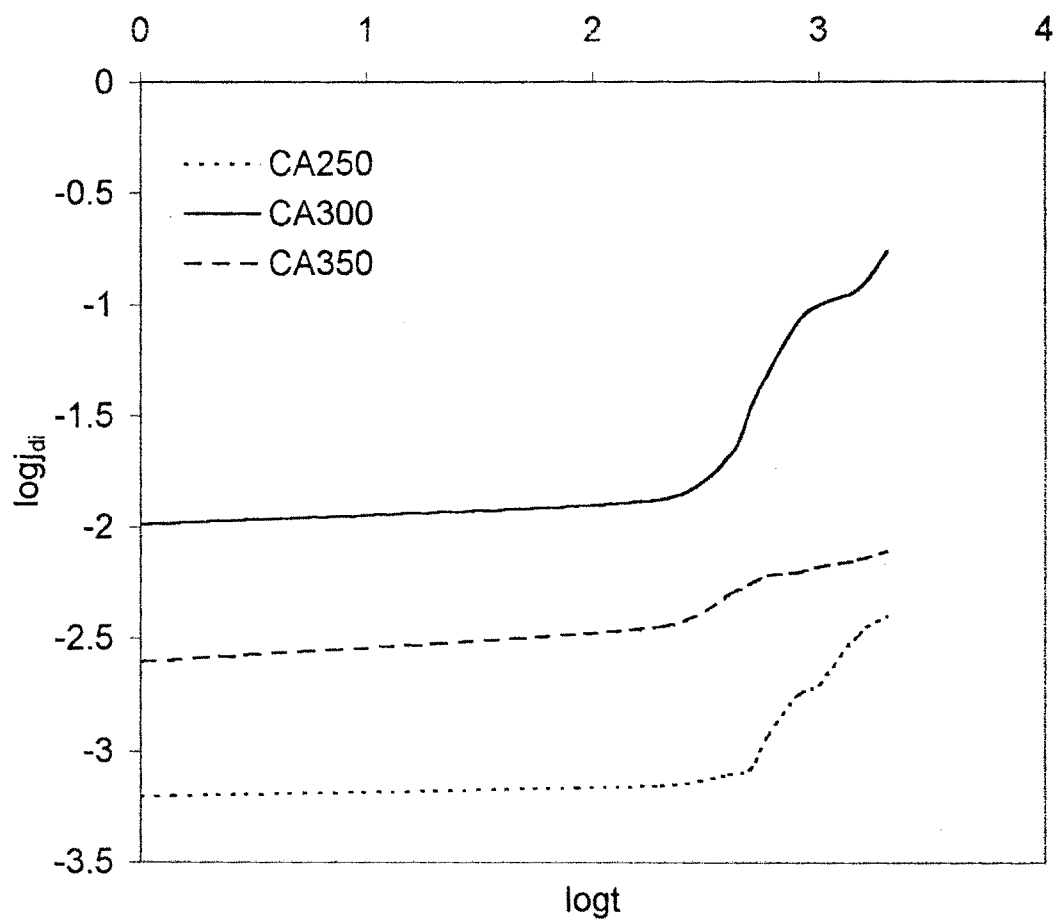
Figure 5.6 (b): Variation of log of deintercalation current (Jdi) versus log of time (t)
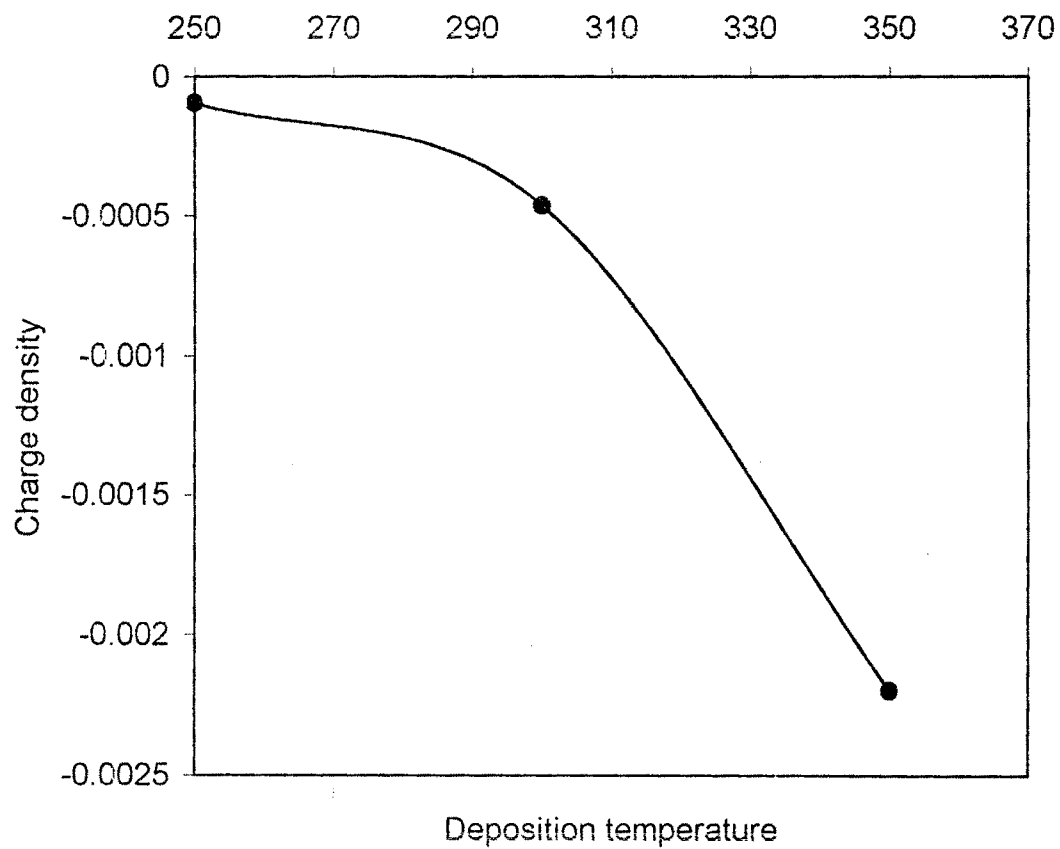
Figure 5.7: The OH charge densities inserted in samples C_{A250}, C_{A300} and C_{A350}.

Fig.5·8 (a)- Variation of transmittance with wavelength for the
          sample deposited at 250°C & heated for half an hour
          in air at 500°C in its pristine state (T-250 H-A),
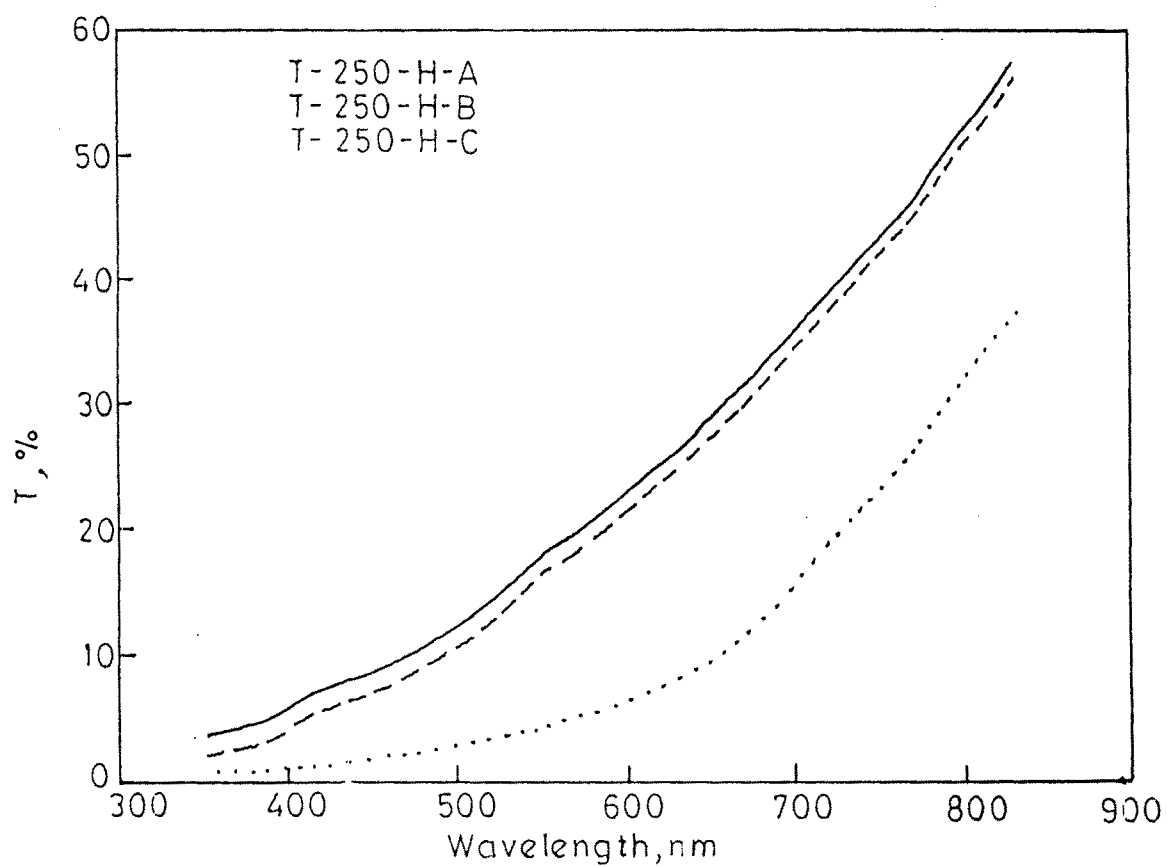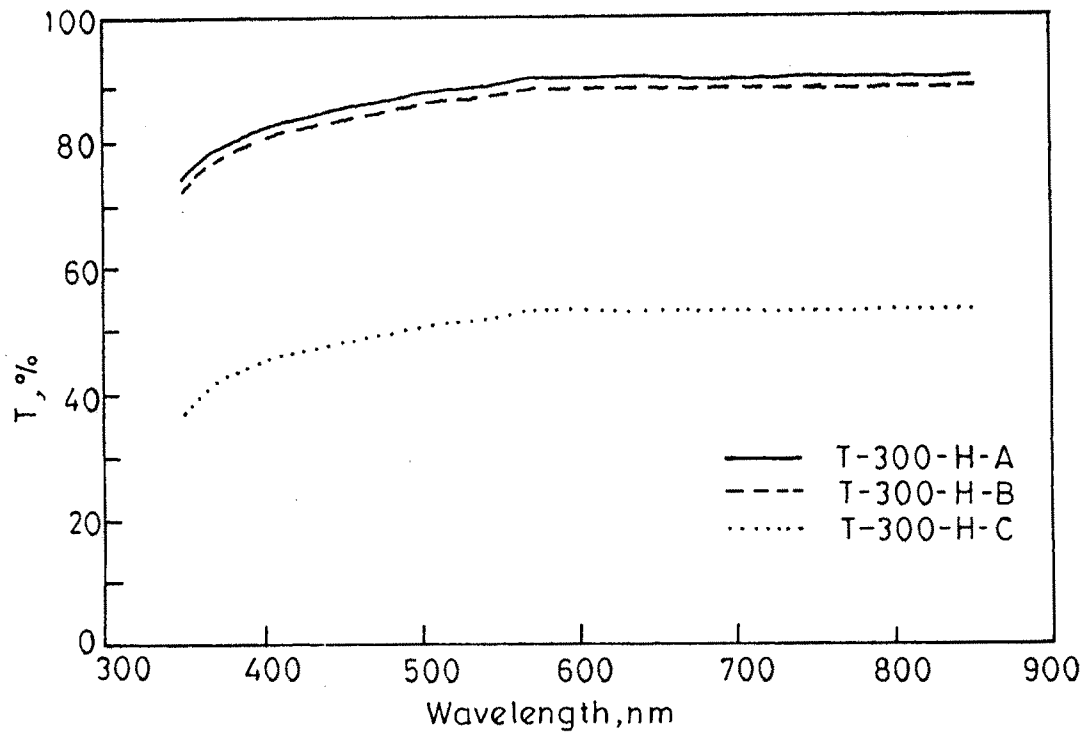   Bleached state (T-250 H-B) & coloured state (T-250-H-C).

Fig.5·8(b)- Variation of transmittance with wavelength for the
sample deposited at 300 °C & heated for half an hour
in air at 500 °C in its pristine state (T-300 H-A),
Bleached state (T-300-H-B) & coloured state (T-300 H-C).
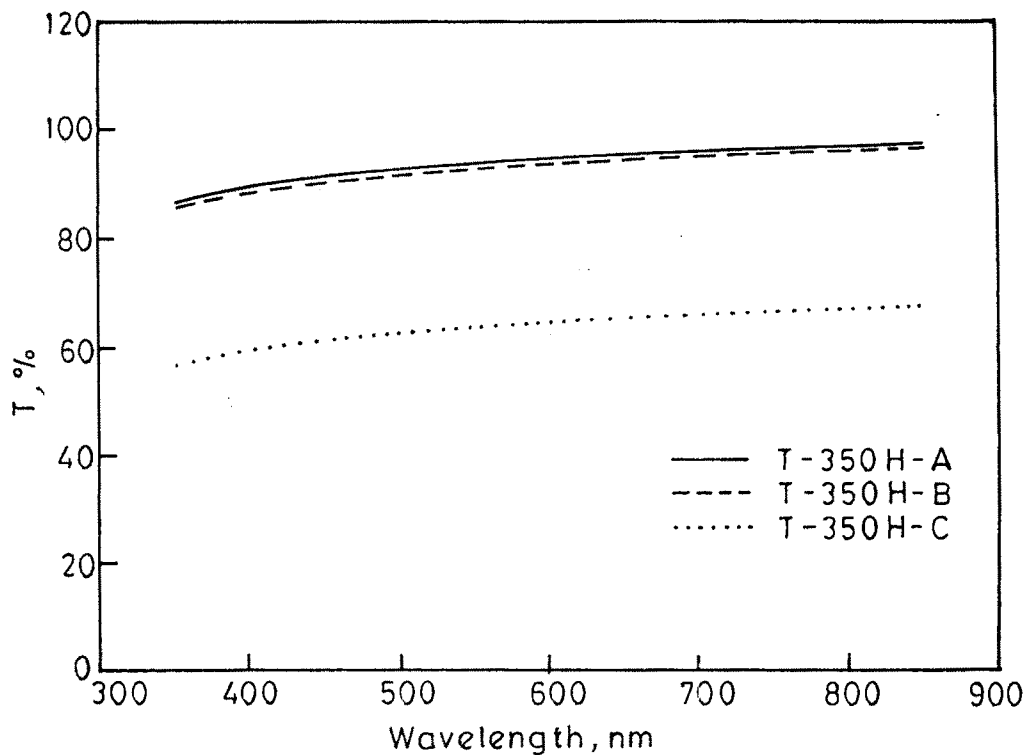

Fig.5·8(c)- Variation of transmittance with wavelength for the
sample deposited at 350 °C and heated for half an
hour in air at 500 °C in its pristine state (T-350 H-A),
Bleached state (T-350 H-B) and coloured state (T-350 H-C).

The colouration efficiency (CE) was calculated using following equation

$$CE = \Delta OD / \Delta Q \qquad \qquad \dots (5.6)$$

is an important parameter to probe the potential of a material as an electrochromic material. It is defined as the ratio of optical density (ΔOD) of the film in its coloured state and bleached state at a certain wavelength (λ) and corresponding injected (or ejected) charge density (ΔQ). The optical density change is obtained by the following equation.

$$\Delta OD\ (\lambda) = \ln\ [To(\lambda) / Tx(x)] \qquad \qquad \dots (5.7)$$

where $To(\lambda)$ is transmittance of the bleached state and $Tx\ (\lambda)$ is the transmittance of the coloured state at particular wavelength (λ).

After substituting values of all the parameters the colouration efficiency for all the samples were calculated, and are listed in table 5.1. Sample C_{A250} exhibit maximum CE than other samples. T. J. Richardson, J. L. Slack, M. D. Rubin have studied electrochromism in copper oxide thin films. They reported that Cu_2O to Cu switching covered a large dynamic range, from 85 to 10% photopic transmittance with colouration efficiency CE = 32 cm^2/C. Switching between two copper oxide was more stable and more efficient with maximum CE = 60 cm^2/C. The values in this study are in good agreement with the reported values.

5.3.3 Electrochemical Stability

The films C_{A250} to C_{A350} were coloured and bleached (c/b) by applying $\pm$ 1V (SCE) for several times in 0.1 N NaOH electrolyte. The insertion (reduction) and extraction (oxidation) processes were found to be stable and fully reversible upto about 5000 c/b cycles, indicating that all the samples have appreciable stability in liquid electrolyte. After these cycles both anodic and cathodic currents start decreasing rapidly indicating deterioration of the samples.

Both the parameters CE and electrochemical stability are of fundamental importance for eventual industrial development.

5.4 CONCLUSIONS

Electrochemical behaviour of CuO films deposited by spray pyrolysis technique in NaOH electrolyte is almost quite similar to the films deposited by other conventional techniques. The onset of ionic intercalation into host lattice depends on crystallinity of the films, for amorphous samples it is high whereas for crystalline samples it is low. The diffusion constant D was found to lie between 53×10^{-16} cm^2/sec and 2.7×10^{-16} cm^2/sec for C_{A250} to C_{A350} samples. The response time for colouration was about 4 seconds and for bleaching was about 3 seconds. The colouration efficiency was found to lie between 32 cm^2/C to 25 cm^2/C for samples C_{A250} to C_{A350}. All the films are found to be stable upto about 5000 c/b cycles.

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