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Experiments on the Peeling of Copper Coating Deposited Via the Electroless Method on Glass Beads

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In this communication we are reporting, for the first time, results of peeling experiments carried out on spherical glass beads coated with an (approximately) micron-sized thin layer of copper. The glass beads, after a due process of pretreatment, sensitization and activation, are coated with copper via an electroless deposition method from a standard electroless bath. In each experiment, a copper coated bead is suspended in an agar gel medium and subjected to electrolysis using electrolyte solution containing copper sulphate. As the electrolysis proceeds, the coating starts peeling at the hemisphere facing the cathode, and the extent of peeling is measured by measuring the progress of the critical angle with time. The factors influencing the progress of the critical angle, namely, the applied voltage, electrolyte concentration, and bead size are varied and the resulting profiles are presented and discussed.

Keywords: Electroless deposition, core/shell particles, peeling

1. INTRODUCTION

Electroless deposition of copper on glass and other surfaces has been well studied in the literature (Ohno [1], for instance, gives a review of the scientific aspects). The present study focuses, for the first time, on how the resulting coating can be peeled by electrolysis when the coated bead is suspended between two electrodes (see Figure 1). In particular, it is desired to experimentally determine the progress of the critical angle of peeling with time and elucidate the parameters that influence the progress. This involves the principle of bipolar electrolysis [2]. At present, no practical application exists for such a peeling phenomenon, but Gurumoorthy [3] has proposed a novel technique by which such peeling phenomenon can be exploited to make so-called “Janus beads” [4].

2. EXPERIMENTAL PROCEDURE

The experimental procedure is divided into the following steps:

(i) Electroless coating of glass spheres,
(ii) Bipolar electrolysis in rectangular cells,
(iii)Measurement of critical angle from captured images.

2.1 Electroless coating

Glass spheres, procured from a local supplier, were of diverse sizes. Beads of identical size were selected by measuring the diameter using a micrometer screw gauge. The selected glass spheres had diameters that fell in two size ranges: 3.5 - 4.0 mm and 7.0 - 7.5 mm. These selected glass spheres first had to be pretreated, and then had to be sensitized and activated before the electroless coating step.

2.1.1 Pretreatment

For increasing the surface roughness and improving the adhesiveness of coating to the glass substrate, the glass spheres are etched in HF solution (10% vol/vol).

The glass beads are then degreased with 2M NaOH at ambient temperature and then rinsed in distilled water and dried at 100^{o} C. The initial weight of the sphere is measured using an electronic balance.

2.1.2 Sensitization and Activation

The sensitization step helps make the surface of the glass sphere sensitive to the attachment of activators. By far the most commonly used sensitizer is stannous chloride. Goldie [5] supplies the formula for a good sensitizer and is given below:

Stannous chloride: 10 gm/l
Hydrochloric acid: 40 gm/l
pH: > 1
Temperature: Room
Time for sensitization: 1 – 2 minutes.

After this procedure, the glass sphere is taken out and washed thoroughly with distilled water before the activation step.

In the activation step, the surface of the glass sphere is exposed to a solution containing a noble metal to ensure the presence of a thin, catalytic layer on the surface. A typical formula [5] for the activator is given below:

Palladium chloride: 0.1 – 1.0 gm/l
Hydrochloric acid: 5 – 10 ml/l
Temperature: Room
Time for activation: 1 – 2 minutes

2.1.3 Electroless deposition bath

The bath composition used for electroless coating is given below [5]:
Copper sulphate, pentahydrate: 5 gm/l
Sodium hydroxide: 7 gm/l
Formaldehyde (37-41% vol/vol): 7 gm/l
Sodium potassium tartarate: 25 gm/l
pH: 12.0 – 12.5
Temperature: Room

35-40 minutes of mild mechanical agitation is sufficient to get nearly $1\mu m$ thick coating. The coating thickness is measured as follows: The coated bead is dried thoroughly in an oven at 100^0C and its final weight is measured by means of an electronic balance. The difference in initial and final weights gives the weight of the coating. This weight divided by the density of copper and the surface area of the sphere gives the coating thickness.

The uniformity of the coating can be qualitatively judged by careful visual examination. Only those beads with uniform coating were selected for further peeling experiments.

2.1.4 Mechanism of electroless deposition

The overall reaction taking place during electroless deposition of copper may be represented in the following form:

$$\begin{aligned} &Cu^{2+} + 2e \rightarrow Cu^0 \\ &HCHO + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e \end{aligned} \qquad (1)$$

The individual steps of the overall mechanism is as shown below [5] :
Activation:

$$\begin{aligned} &Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0 \\ &(SnCl_2 + PdCl_2 \rightarrow SnCl_4 + Pd^0) \end{aligned} \qquad (2)$$

The Pd^0 deposited on glass surface acts as catalyst for the electroless step.

Electroless coating:

$$\begin{gathered} HCHO + OH^- \xrightarrow[\text{catalyst}]{Pd^0} H_2 + HCOO^- \\ (HCHO + NaOH \xrightarrow[\text{catalyst}]{Pd^0} H_2 + HCOONa) \end{gathered} \qquad (3)$$

$$\begin{gathered} Cu^{2+} + H_2 + 2OH^- \rightarrow Cu^0 + 2H_2O \\ (CuSO_4 + H_2 + 2NaOH \rightarrow Cu^0 + Na_2SO_4 + 2H_2O) \end{gathered} \qquad (4)$$

$$\begin{gathered} HCHO + OH^- \xrightarrow[\text{catalyst}]{Cu^0} H_2 + HCOO^- \\ (HCHO + NaOH \xrightarrow[\text{catalyst}]{Cu^0} H_2 + HCOONa) \end{gathered} \qquad (5)$$

It may be seen that Equation (5) is identical to Equation (3), the difference being only that copper replaces palladium as the catalytic metal and the reaction proceeds autocatalytically.

2.2 Bipolar electrolysis in rectangular cells

Rectangular quartz cells of dimensions 25mm x 25mm x 40mm were used to conduct the bipolar electrolysis experiments. The schematic is shown in Figure 1.

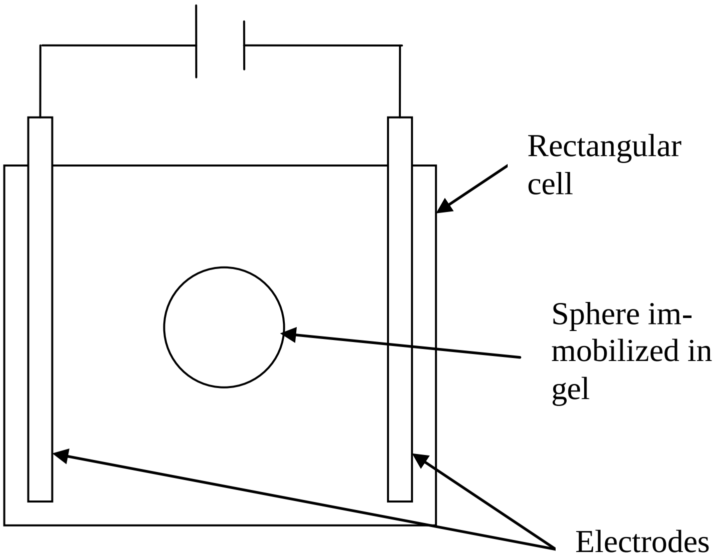


Figure 1. Schematic of experimental set-up

The copper coated glass sphere was immobilized in a block of agar gel. The agar gel was prepared as follows: 80 ml of distilled water is heated to 95^0C and 0.64g of agarose powder is dissolved in it. The resulting clear solution is poured into the rectangular quartz cell to half its height. Then it is allowed to cool to around 40^0C when it forms a clear gel.

Then the copper coated glass sphere is placed in the centre of the gel surface and more hot agar solution is poured to cover the cell to its brim. This solution is then allowed to gel. In this manner the copper coated glass sphere is placed in the center of the gel block.

Two narrow slit-like compartments are cut into the gel at two opposite edges. In these compartments, 0.1M $CuSO_4$ solution is introduced. Copper electrodes of dimensions 16mm x 40 mm were inserted into the compartments and connections made to a DC power supply (BK Precision 1623A). Oil was spread on the surface to prevent any evaporation of $CuSO_4$ solution.

Constant DC voltage was applied and electrolysis carried out with snapshots taken every few minutes through the transparent walls of the quartz cell using a Nikon COOLPIX990 digital camera.

2.3 Measurement of Critical Angle

The critical angle, θ_c, is the angle which demarcates the coated portion of the sphere (after electrolysis) from the uncoated exposed portion. As shown in Figure 2, the sphere becomes progressively bare as the electrolysis proceeds. The τ-line which is the boundary of demarcation between the coated and peeled regions moves from left to right. As this happens, we expect the critical angle to progressively increase.

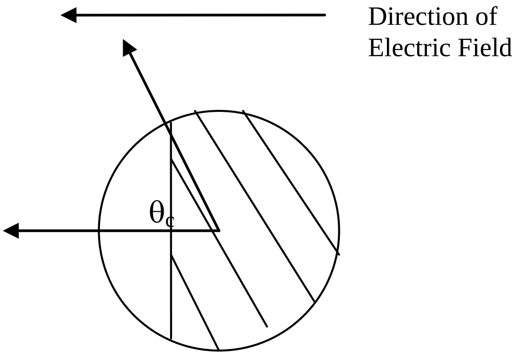


Figure 2. Schematic of partially peeled sphere with critical angle θ_c.

The snapshots that captured the progress of peeling front with time were analyzed using the UTHSCSA Image Tool software version 3.00 to measure the critical angle θ_c.

3. RESULTS AND DISCUSSION

Figures 3a to 3h show the representative set of images showing the progress of the peeling front with time. The brown part is the copper coated portion of the sphere whereas the dark green part is the exposed glass sphere. Applied voltage was 0.5 V and the size of the glass bead was 7.26 mm. The different snapshots clearly show the progress of the τ -line from left to right with time.

(a) Time = 0 min (b) Time = 30 min

(c) Time = 1 hour (d) Time = 1 hour 30 min

(e) Time = 2 hours (f) Time = 3 hours

(g) Time = 4 hours (h) Time = 5 hours

Figure 3. Camera images showing the progress of peeling of copper shell from glass spheres. Applied voltage = 0.5 V; size of glass sphere = 7.26 mm.

In Figures 4 to 6, the various experimental trends are captured. In Figure 4a, the advancement of the peeling front, as characterized by the increase in critical angle, θ_c, for varying applied voltages is plotted. In these experiments the $CuSO_4$ concentration is kept constant at 0.1M. The bead sizes used in the experiments were in the range 7.0-7.5 mm. The amount of copper deposited in each of the beads was in the range 0.4-0.6 mg (as measured by an electronic balance). The interelectrode (IE) spacing was 1.5 cm. As can be seen from Figure 4a, there is an induction period before peeling begins to occur and this induction period decreases with increase in applied voltage. This induction is explained as follows:

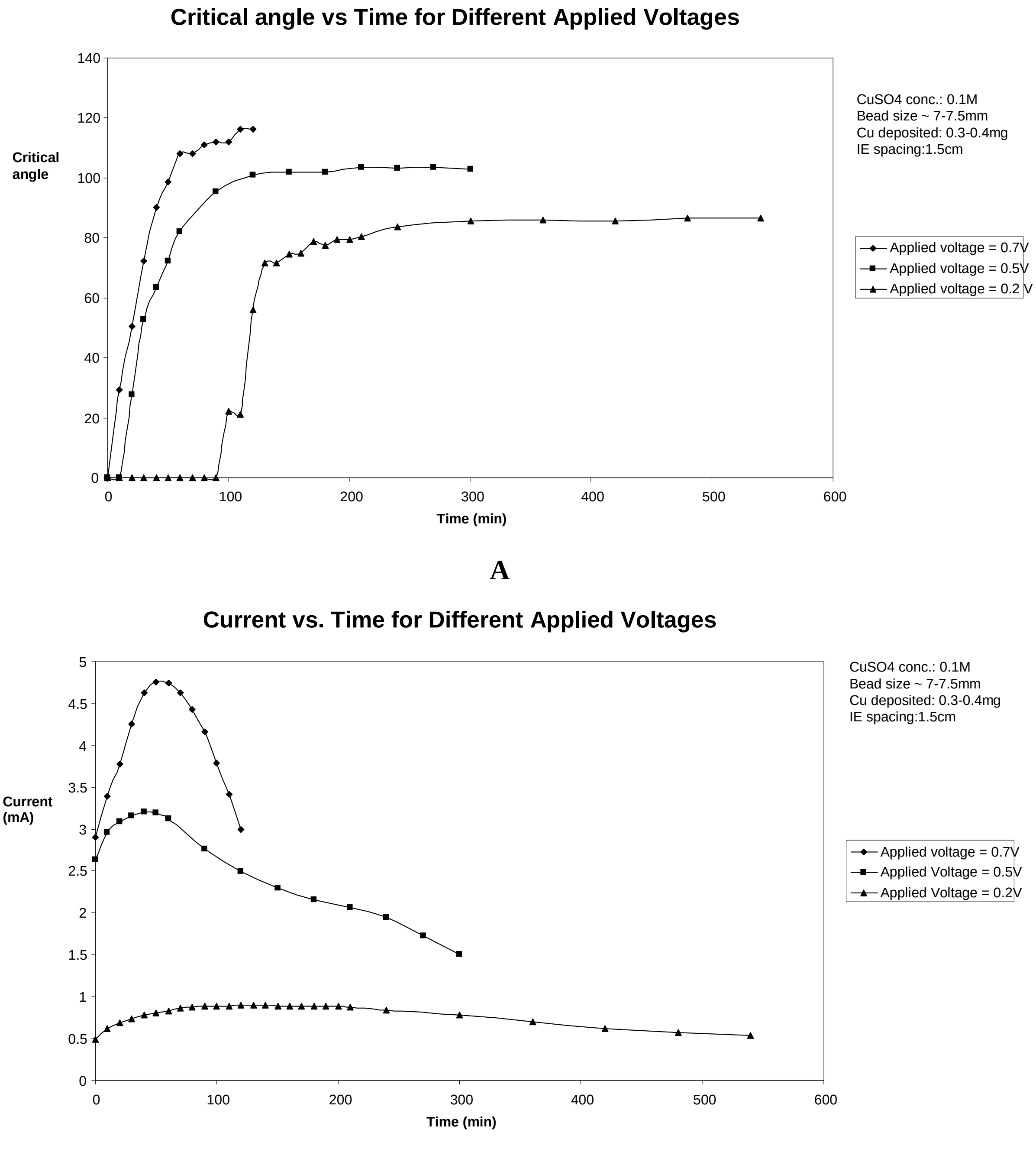


Figure 4. (a) Advancement of peeling front for different applied voltages. (b) Current passing through the cell with time for different applied voltages

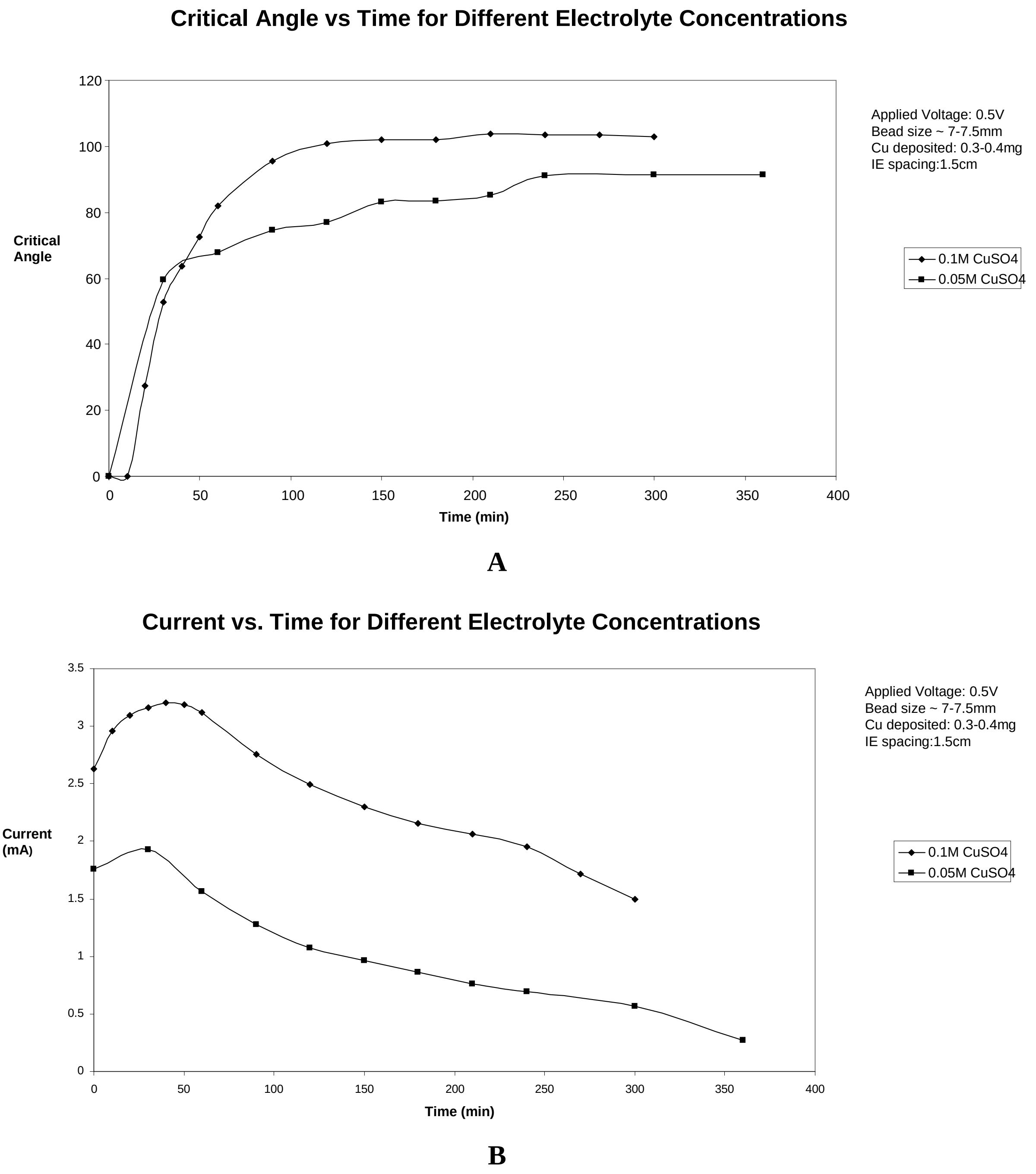
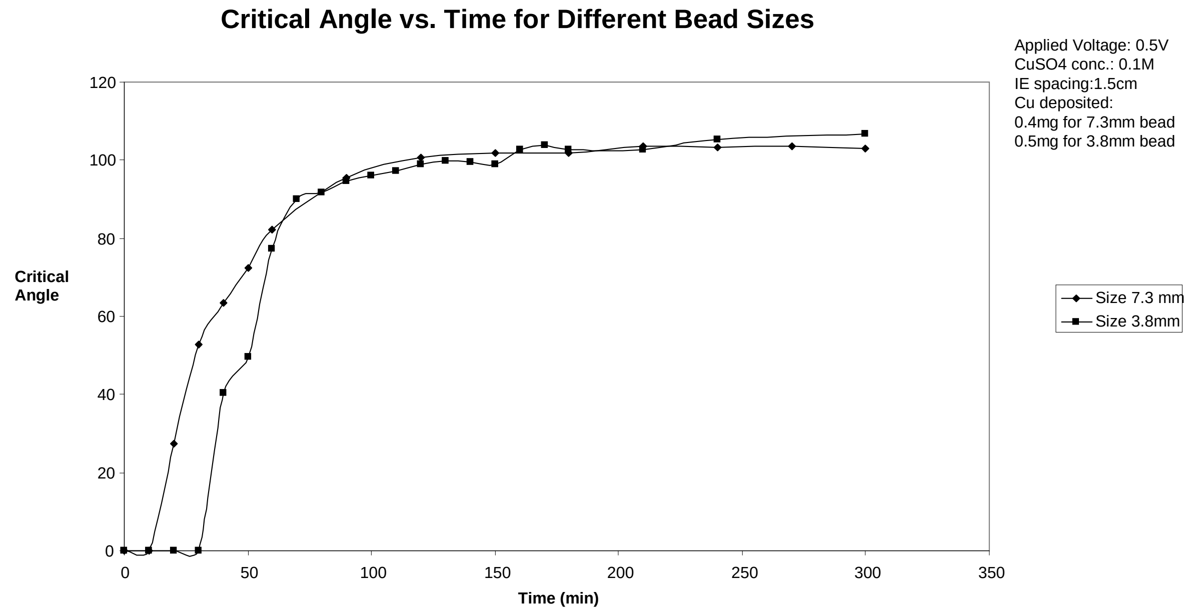
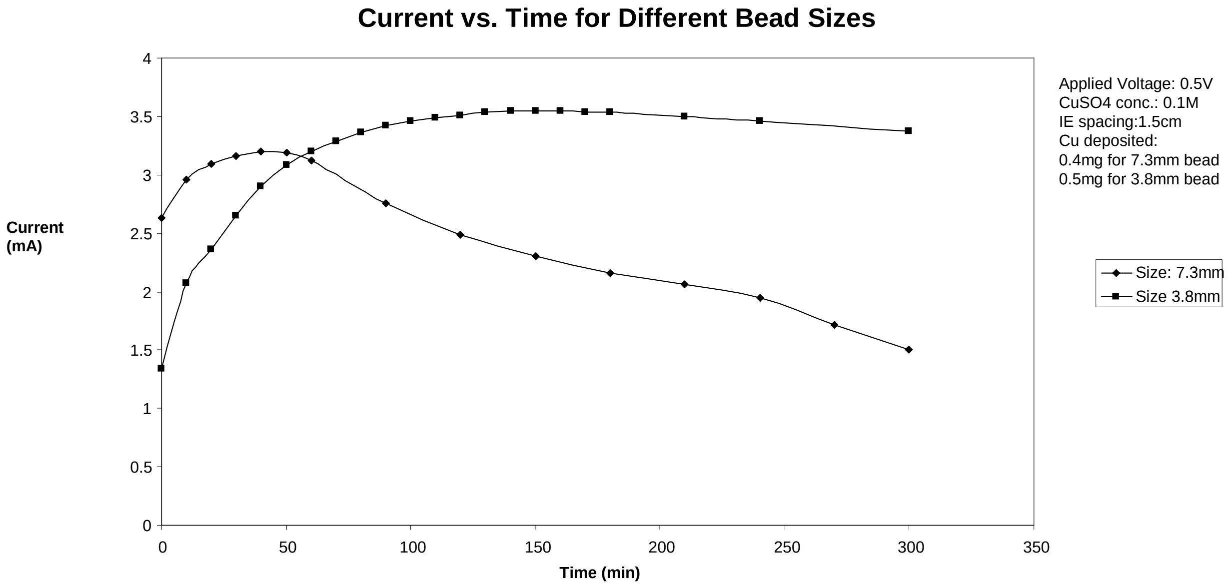


Figure 5. (a) Advancement of peeling front for different electrolyte concentrations. (b) Current passing through the cell with time for different electrolyte concentrations.

As the electrolysis proceeds, the coating first begins to thin at the hemisphere facing the cathode. It is only after the thinning process is completed at the region of the sphere closest to the cathode that the peeling starts taking place. The experiments reveal that at higher voltages the thinning is faster and the induction period is shorter. Furthermore, peeling is seen to be faster as applied voltage increases. Also the peeling rate decreases with time so that the θ_c-time curve plateaus after some time. The plateau effect occurs as the peeling front moves towards the shadow region of the sphere.



A



B

Figure 6. (a) Advancement of peeling front for different bead sizes. (b) Current passing through the cell with time for different bead sizes.

Figure 4b shows the corresponding current profiles as the electrolysis occurs. The surprising feature is the initial increase in current and then an occurrence of a maximum and subsequent decrease. This behavior of current is found to occur in all the experiments (see Figures 5b and 6b). The initial increase can be attributed to the fact that new current pathways are formed through the gel as bipolar electrolysis progresses (i.e. conductivity of the gel progressively increases). The subsequent decrease seems trickier to explain.

It was initially suspected that this could be due to evaporation of solvent. It was found, however, that the decrease occurs even when oil is poured on the gel surface to retard evaporation. This decrease could be attributed to diffusional limitations on electrode surface.

Figures 5a and 5b show the critical angle and current profiles as time progresses for different electrolyte concentrations (0.1M $CuSO_4$ and 0.05M $CuSO_4$). The applied voltage was kept constant at 0.5 Volts and the glass beads used in the experiments were in the size range 7.0-7.5 mm. The amount of copper deposited on each of the beads was in the range 0.3-0.4 mg. As expected, Figure 6a shows that the rate of peeling is faster at higher concentration than at lower concentration. The τ-line crosses the equator significantly faster at the higher electrolyte concentration. This suggests that one can use the electrolyte concentration as a handle for controlling the τ-line evolution.

Figures 6a and 6b show the advancement of the peeling front with time and the current profiles for different bead sizes (3.8mm and 7.3 mm) keeping the applied voltage at 0.5 V and the electrolyte concentration at 0.1M $CuSO_4$. One can infer from Figure 6a that the peeling is more or less independent of bead size. It is worth noting that such a conclusion may be valid at macroscopic bead sizes but not in the submicron domain since there the basic electrochemical behavior itself changes [6]. In the nanoscale, the diffusion layer and the double layer are of comparable sizes and hence one cannot ignore diffusion within the double layer.

While no analogous peeling experiments have been reported in the literature, similarities can be observed with the experiments of Duval et al [7]. Duval et al report bipolar behavior on a supported thin planar aluminium surface in a thin-layer cell. Just as we have visually observed a “peeling edge”, these authors have followed visually a “corroding edge”. It was found that as applied voltage is increased, the corroding edge moves faster initially before decelerating. This is found to happen in our case also: as voltage is increased, the peeling occurs at a faster rate initially before slowing down in the shadow region. Duval et al have gone further and developed a model for the movement of the corroding edge. Such a model can be extended to the spherical case that we have considered.

4. CONCLUSIONS

Experiments have been devised to study the peeling of copper coated on a glass sphere via the electroless method. Peeling is seen to occur faster with increasing applied voltage and at higher concentrations. The size of the bead does not appear to affect the peeling rate but the case may be different at submicron domains. A model to explain these experimental trends has been presented in the thesis by Gurumoorthy [3] . It is found that the qualitative trends are well captured by this model but an exact comparison was precluded by the nonavailability of accurate parameter values (such as exchange current densities and transfer coefficients) for this system.

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