Supplement 1

Protocol employed for standardization, calibration and estimation of copper plated on untreated and coated Al

Plating of Cu on the surface of Al is driven by the potential difference between Al and Cu and it is a spontaneous process on untreated Al. However, on coated Al the electrolyte has to penetrate through the pores and voids in the coating to reach the base metal (Al) before the Cu is getting plated out. This principle was used to estimate the porosity and surface coverage of manganese phosphate coated Al.

In the present study, the porosity and surface coverage of the coatings deposited on Al was determined by immersion plating of Cu [29] using the untreated Al as control. The plating solution consists of 99.8 g/l of $CuSO_4.5H_2O$ and 99.8 g/l of ethylenediamine. The total area of the untreated and coated Al used for Cu plating was 50 cm^2. Since the time lag for plating of Cu varies with porosity and surface coverage of the manganese phosphate coated Al, a longer time period of 2 h was selected in this study. Once the uncoated surface of Al was plated with Cu, further deposition would not be possible due to the lack of driving force for plating of Cu on Cu by immersion plating. After Cu plating, the samples were washed thoroughly to remove the excess electrolyte present on their surfaces, dried using a stream of compressed air and photographed.

Quantitative estimation of the amount of Cu plated on untreated and coated Al was also made to enumerate the surface coverage of coatings. Sodium diethyldithiocarbamate (DEDTC) was chosen as the complexing agent following its very high sensitivity towards copper. Before determining the amount of Cu plated on untreated and coated Al, copper solutions with known concentrations were prepared for standardization and calibration. A stock solution of 0.0393 g/l of $CuSO_4.5H_2O$ was prepared and 1 to 8 ml (containing 10 to 80 μg of Cu) of this solution was pipetted into a beaker. Subsequently, 5 ml of 25% citric acid was added. To render the solution slightly alkaline, dilute ammonia solution was added and the excess ammonia was boiled off. Later, 15 ml of 4% ethylenediaminetetraacetic acid solution was added and it was allowed to cool to room temperature. The solution mixture was transferred to a separatory funnel followed by the addition of 10 ml of 0.2% DEDTC and shaken for 45 s until a yellow brown colour develops (formation of Cu-DEDTC complex). After this, 20 ml of chloroform was dropped down into the separatory funnel and shaken for 30 s until the organic layer acquires a yellow colour. The aqueous solution-chloroform mixture was shaken

for another 15 s and the phases were allowed to separate well. The aqueous layer was removed and 20 ml of 5% H_2SO_4 was added, shaken for 15 s and the organic phase was separated. The optical density of the organic layer was determined at 435 nm using diode array spectrophotometer (Agilent 8453). Based on the measured absorbance values of the standard copper solutions, a calibration plot was constructed. The calibration curve exhibits a liner fit with a correlation coefficient of 0.998 and a standard deviation of 0.02 for the working range of 10 to 80 µg of Cu. The amount of Cu plated on untreated and manganese phosphate coated Al was estimated after stripping the plated Cu in dilute HNO_3 using a similar experimental procedure used for standardization and calibration.

The UV-visible spectrum of Cu-DEDTC complex prepared using 10 to 80 µg of Cu (as $CuSO_4.5H_2O$) along with its calibration curve is shown in Fig. Supplement 1.
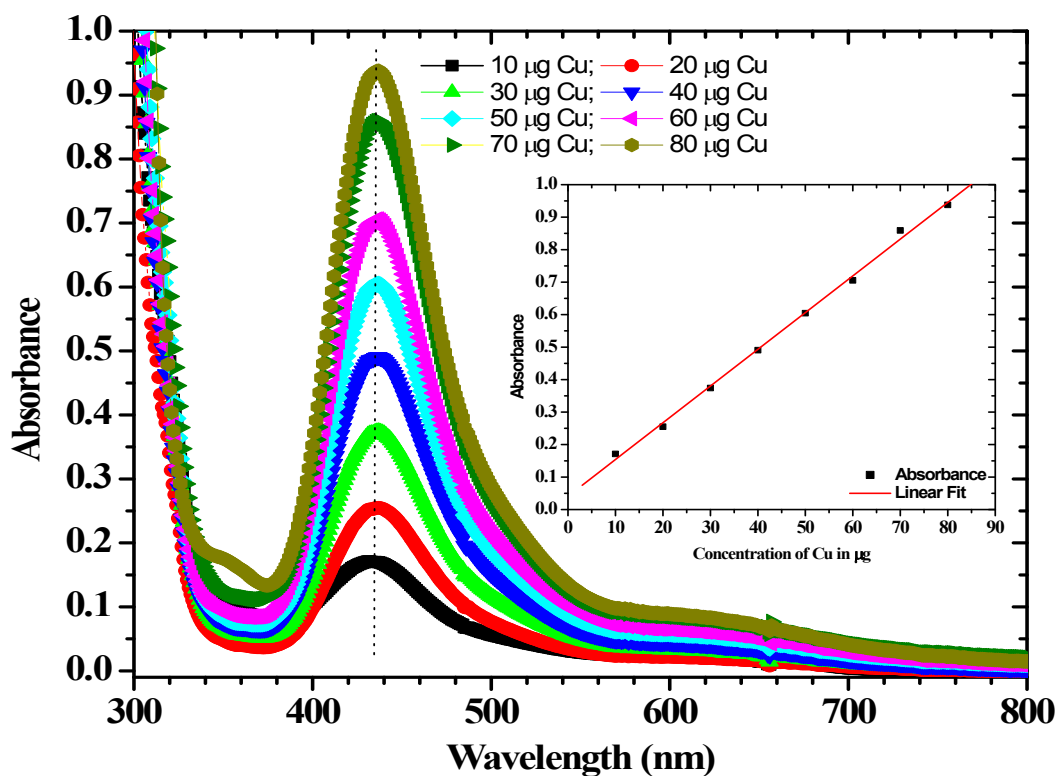

Fig. Supplement 1: UV-Visible spectra of copper-diethyldithiocarbamate complex
(inset: Standard calibration curve of Cu)