

# Electrodeposition of Sn, In and Cu from Citrate Electrolytes, Part I. Electrolyte Characterization

Salem S. Zahmi and Elizabeth J. Podlaha  
*Department of Chemical Engineering  
Northeastern University  
Boston, Massachusetts 02115, USA*

## Introduction

Both copper zinc tin sulfide (CZTS) and copper indium gallium selenide (CIGS) are thin film photovoltaic absorber materials that have components that can be electrodeposited, making it possible to develop an alternative fabrication process for solar panels that is lower in cost than vapor phase technologies. The advantage of the CZTS system is that non-abundant elements (*i.e.*, In and Ga) found in the CIGS compounds are replaced with Zn and Sn having a similar band gap,<sup>1-7</sup> but without the non-abundant elements, such as In, they have lower efficiencies.<sup>6-7</sup> This work is an effort to find an electrolyte common to both systems that can be used to electrodeposit CZTS, CIGS or any combinations of the two. The citrate complexing agent has been used with many of the elements in the electrodeposition of these two systems,<sup>8-9</sup> and has been examined here to meet the needs in creating a common electrolyte. Towards this end, a citrate electrolyte is used to compare the electrodeposition of Sn, In, InSn, InCu, SnCu and CuInSn.

## Experimental

Voltammetry was used to compare the reduction of Sn, In, InSn, InCu, SnCu, and InSnCu in a three electrode configuration with a Solartron SI 1287 potentiostat. The counter electrode was carbon, the working electrode was carbon, and the reference electrode was silver/silver chloride. As a pretreatment, a layer of copper was first deposited onto carbon for 10 min using constant applied current density of  $-10 \text{ mA/cm}^2$  for deposits without Cu. The In and Sn electrolytes contained 0.05 M indium chloride (or tin chloride) and 0.7 M sodium citrate. All film depositions were performed at room temperature. The InSn electrolyte contained the same concentration of citrate, and equimolar amounts of the metal ions: 0.05 M indium chloride and 0.05 M tin chloride. The addition of 0.03 M Cu was added to the In, Sn, and InSn electrolytes and the deposition was done directly onto the carbon electrode. The natural pH was used, and not adjusted. Deposits were fabricated at constant potential for 30 min, and the composition characterized using X-ray fluorescence spectroscopy. Surface morphology was inspected using a Field Emission Scanning Electron Microscope (FE-SEM).

## Modeling

A comprehensive mass balance model has been developed to assess the different complexed species with variable combinations of the metal ions and citrate ligand. The complexation of different metal species with citric acid was simulated using literature equilibria values. There are 24 unknowns which include not only the complexed metal species, but also the different citrate species. Different combinations of Cu, In, Sn, Zn and Ga species were predicted at different electrolyte pH.

## Results

The current-potential behavior of three electrolytes with In, Sn, and InSn in an excess of citrate shows a change in the deposition behavior when the Sn and In are combined that is not related to complexation. Also in the case when Cu is added to the solution, the current-potential behavior was

different for InCu, SnCu, and InSnCu deposition. The deposition efficiency was calculated and there is a large improvement in the deposition efficiency when Cu is present in the solution. There is also a change in the In:Sn composition in the deposit when Cu is deposited as a ternary alloy. The partial current densities were determined for the three electrolytes. There is little change in the Sn partial current density when co-deposited with In, but a large enhancement in the Sn rate when co-deposited with Cu, with or without In. In turn, the presence of Sn enhances the reduction rate of In, amplified in the presence of Cu. This enhancement is in part due to an increase in the deposit surface area as shown in Table 1. The SEM images shows an increase in the surface area when Cu is add to the solution, also there is an increasing in the surface area when the In with Sn in the solution, However, the increased surface area does not account for a change in the ratio of Sn:In in the deposit.

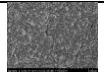
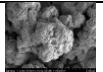
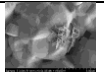
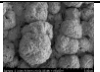
Materials	Sn	SnCu	InSn	InSnCu
E (V)	-0.75	-0.75	-0.75	-0.75
$i_j$ (A/cm <sup>2</sup> )	1.729 E-5	1.062 E-3	4.773 E-5	7.535 E-4
SEM Image				

Table 1. Sn partial current densities when co-deposited with In, Cu and InCu and its corresponding SEM image.

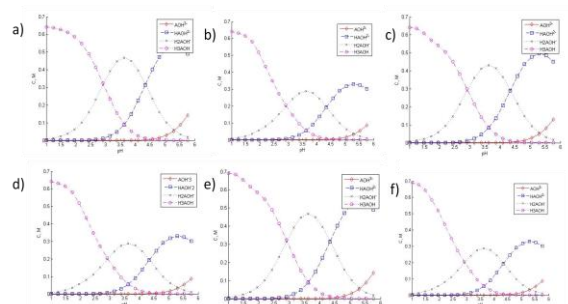


Figure 2. Concentrations of citric acid complexes from a) Sn b) SnCu c) SnIn d) SnInCu e) In f) InCu

Modeling equilibrium species showed that Sn and In complexes were the same with or without the addition of Cu in an electrolyte with excess citrate. However, Citric acid species were affected by the addition of Cu in the solution. Figure 2 shows  $\text{HAOH}^{2-}$  and  $\text{H}_2\text{AOH}^-$  concentrations were lower in the presence of Cu in the solution. There was no significant change in the ratio of  $\text{H}_2\text{AOH}^-/\text{HAOH}^{2-}$

### Conclusion

The reduction rate of Sn was enhanced in the presence of Cu in the solution, altering the In:Sn ratio in the deposit. An improvement of the deposition efficiency was observed when Cu is added to the solution despite an increase in the side reaction rate. In was also enhanced when co-deposited with Cu but was significantly enhanced when codeposited with SnCu.

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