Electrodeposition of CIGS/CZTS Components from Aqueous Electrolytes

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Thin films for solar panels can be made more cost-effective if they can be produced by electrodeposition, and this exploratory work aims to develop an electrolyte to be used for a variety of photovoltaic devices, including Cu-In-Ga-Se (CIGS), Cu-In-S (CIS) and Cu- Zn- Sn – S (CZTS) materials, and any combination of them. In particular, two important subset alloy systems were examined in detail: CuSnIn and CuSnZn. The latter alloy combination was then studied with different sources of sulfur in the electrolyte to produce CZTS. To complement and help interpret the electrochemical experiments a complexation model was developed. A variety of electrochemical techniques was used to inspect the polarization behavior, and deposits were fabricated at constant potential. The composition was analyzed by x-ray fluorescence (XRF) spectroscopy and the surface structure inspected by scanning electron microscopy (SEM).

A comparison of the electrodeposition of CuSn with and without In was examined in a citrate electrolyte, with excess citrate in an effort to fully complex the species to promote electrolyte stability. The current potential behavior of each reacting species, Cu, Sn and In, and their alloy combinations SnIn, CuSn, CuIn, CuSnIn, was studied. The most significant results were that when Sn is codeposited with Cu or CuIn there is an enhancement in the partial current densities of Sn. Also, the reduction rate of In(III) was observed to be accelerated, but only when both Cu and Sn were present. The In(III) reduction enhancement on stationary electrodes occurred when Cu(II) reduction was under mass transport control. In order to evaluate if the In(III) rate was a consequence of the mass transport effect, an upside down rotating disk electrode was used. Even when the deposition occurs in the kinetic range of the codepositing species, the In(III) rate is still enhanced. No change in the surface morphology and roughness occurred when CuSn is codeposited with In, thus the enhancement of In(III) was not due to a change of surface area. An unwanted result was that precipitation in CuSn and CuSnIn electrolytes have been observed after a couple days of preparing the solutions, but could be circumvented at low pH, by changing the type of complexed Sn species.

The effect of Zn concentration in the current potential behavior of Zn, CuZn, SnZn, and CuSnZn was studied in a mixing environment using the upside down rotating disk electrode at pH 2. A shift to more negative potential was observed on the CuZn (or SnZn) polarization when Zn concentration was increased in the electrolyte. A first order reaction order of Zn was found when Zn was singly deposited. The effect of co-depositing Zn with Cu (or Sn) on the reaction order of Zn was studied by varying the Zn concentration in the electrolyte and an increased in the apparent reaction order of Zn was observed when Zn was codeposited with Cu (or Sn) and was found to be related to displacements reactions occurring during deposition, and consistent with EIS measurements.

Based on knowledge gained in the CuSnIn and CuSnZn experiments, an electrolyte for depositing CZTS was developed using different sources of sulfur where thiourea and thiosulfate were examined. The presence of thiourea (or thiosulfate) in the electrolyte was found to have an inhibiting effect on the reduction rate of Sn for the first time. This result is a step towards creating CZTS by electrodeposition in a one-step process without the need for a secondary sulfurization step.