

Liquid Metal Salts: High Current Density  
Electrodeposition of Cu-Sn-Zn Metal Stacks from Ionic  
Liquids for Kesterite based Thin Film Photovoltaics

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Liquid metal salts (LMS) are ideal electrolytes for high-speed metal electroplating [1,2]. In these ionic liquids, the metal ions are the main component of the cations, leading to very high metal concentration, specifically when compared to common metal salts dissolved in conventional ionic liquids. LMS present good mass transport properties and allow high current densities during electroplating. Furthermore, no decomposition reactions are observed at high cathodic overpotentials, as the cathodic limit of the LMS corresponds to the metal deposition.

In this work, we report on the synthesis of new cationic zinc(II) and tin(II) complexes with bis(trifluoromethylsulfonyl)imide (Tf<sub>2</sub>N) anions and their application to the high-speed electrodeposition of metal stack precursors for the rapid and low-cost fabrication of earth-abundant and non-toxic Cu<sub>2</sub>ZnSnSe<sub>4</sub> (kesterite) based thin film solar cells.

The new LMS have been characterized by differential scanning calorimetry, single-crystal X-ray diffraction, thermogravimetric analysis, rheology, elemental analysis and Fourier transform infrared spectroscopy.

In the case of the Zn-LMS, the cations consist of six-coordinate Zn(II) centers ligated by one or two different *N*-alkylimidazole ligands (*N*-methylimidazole, MeIm; *N*-ethylimidazole, EtIm). Depending on the ligand composition, the melting point of the heteroleptic Zn(II)-LMS [Zn(MeIm)<sub>6-x</sub>(EtIm)<sub>x</sub>][Tf<sub>2</sub>N]<sub>2</sub> can be tuned, ranging from 65 °C to 20 °C.

Oxygen-donor ligands, like diglyme (G2, 1-methoxy-2-(2-methoxyethoxy)ethane), ethanol (EtOH) and pyridine-*N*-oxide (pyO) were found to form stable Sn-LMS with low melting temperatures, below 80 °C. Single-crystal X-ray diffraction revealed that the cations contain Sn(II) centers that are tri- or tetra-coordinate.

The electrochemical behavior of the liquid metal salts has been evaluated by cyclic voltammetry, chronopotential- and chronoamperometry on platinum and molybdenum electrodes. [Zn(EtIm)<sub>6</sub>][Tf<sub>2</sub>N]<sub>2</sub> and [Sn(G2)(EtOH)][Tf<sub>2</sub>N]<sub>2</sub> have been used together with [Cu(MeCN)<sub>4</sub>][Tf<sub>2</sub>N] [1] for the rapid electrodeposition of stacked Cu-Sn-Zn metal precursor layers on molybdenum substrates. High current densities above 200 mA cm<sup>-2</sup> allowed short metal deposition in less than one minute. The metal precursors were annealed by Rapid Thermal Processing (RTP) under selenium and tin selenide atmosphere at high temperature and converted to the p-type semiconductor absorber Cu<sub>2</sub>ZnSnSe<sub>4</sub>.

The low-cost fabrication process of chalcogenide absorbers in ionic liquids by electrodeposition and annealing (EDA) takes normally up to 60 minutes [3].

With this new EDA process, device-quality Cu<sub>2</sub>ZnSnSe<sub>4</sub> absorber layers can be formed in a total processing time of less than five minutes. In combination with long up-times of the deposition baths, the short processing times are important for large-scale PV module production.

The morphology and composition of the Cu-Sn-Zn metal precursors and the absorber layers were analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX). The crystallinity was analyzed by X-ray diffraction. The optoelectronic properties of the absorbers were evaluated by photoluminescence, Raman and absorption spectroscopy. Latest results on Cu<sub>2</sub>ZnSnSe<sub>4</sub> solar cells, formed via this high-speed EDA process will be presented.

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