# 1. INTRODUCTION

Tin is a technologist's metal, in the sense that whilst its manifold applications reach into all aspects of life, nevertheless, most people are usually unaware of its presence. Long before history came to be written, tin was associated with the technological advance of mankind and archaeological evidence confirms that tin was one of the earliest metals known to human society. From early Bronze Age to Space Age of today, tin has continued to play an important role out of proportion to the gross tonnage produced and used [1]. In 2007, the People's Republic of China was the largest producer of tin, where the tin deposit are concentrated in the southeast Yunnan tin belt, with 43% of the world's share, followed by Indonesia and Peru [2]. The main physical properties of tin are listed as **Table 1.1**[1]:

| Properties | Values and Units |
|---|---|
| Atomic Number | 50 |
| Atomic mass | 118.710 g. $mol^{-1}$ |
| Electron configuration | [Kr] 4 $d^{10}$ $5s^2$ $5p^2$ |
| Electron per shell | 2, 8, 18, 18, 4 |
| Appearance | Silvery lustrous gray |
| Density at 298K | 7310 $kg/m^3$ |
| Melting Point | 231.93 ºC |
| Boiling Point | 2602 ºC |
| Specific heat capacity at 298K | 27.112 $J \cdot mol^{-1} \cdot K^{-1}$ |
| Electrical resistivity at 273K | 115 nΩ·m |
| Thermal conductivity at 300K | 66.8 $W \cdot m^{-1} \cdot K^{-1}$ |
| Thermal expansion at 298K | 22.0 $\mu m \cdot m^{-1} \cdot K^{-1}$ |
| Young's modulus | 50 GPa |
| Shear modulus | 18 Gpa |

**Table 1.1:** Main physical properties of Tin

Tin has many industrial applications and is widely used in tin plating, solder manufacturing, chemical production, brass and bronze fabrication and variety of other application. The main objective of tin plating is to:

1. Increase resistance to wear,
2. Increase electrical conductivity,
3. Improve surface reflectivity especially for decorative purposes.

Tin and its alloys can be electrodeposited from various electrolytes including aqueous fluoroborate, sulfate and methane sulfonate solutions. The sulfate electrolyte is generally adopted as a first choice of plating electrolyte due to its low cost and long history. The fluoroborate bath is used when high current density is required. The methanesulfonate- based electrolyte is favored for its environmental benefits and it facilitates higher stannous ion saturation solubility with a low oxidation rate to stannic ions [3]. However, hydrogen evolution reaction often occurs in the aqueous based electrolyte electrodeposition resulting in profound effect on current efficiency and quality of the tin deposits. As a result, different additives may be needed to suppress such difficulties [4].

In contrast, a fundamental advantage of using ionic liquid electrolytes in electroplating is that, since these are non-aqueous solutions, there is negligible hydrogen evolution during electroplating and the coatings possess the much superior mechanical properties of the pure metal. Hence essentially crack-free, more corrosion-resistant deposits are possible. This may allow thinner deposits to be used, thus reducing overall material and power consumption [5]. Electrodeposition in ionic liquids was rarely studied in the past. In 1992, Wilkes and Zaworotko reported the first air and moisture stable imidazolium based ionic liquid with either tetrafluoroborate or hexafluorophosphate as anions. Then, several, liquids consisting of 1-ethyl-3-methylimidazolium, 1,2-dimethyl-3-propylimidazolium, or 1-butyl-l-methyl-pyrrolidinium cations with various anions, such as tetrafluoroborate ($BF_4^-$), tri-fluoro-methanesulfonate ($CF_3SO_3^-$), bis(trifluoromethanesulfonyl)imide [$(CF_3SO_2)_2N^-$] & tris (trifluoromethanesulfonyl)methide [$(CF_3SO_2)_3C^-$], were found and received much attention because of low reactivity against moisture [6].

Few studies were reported on the electrodeposition of Tin(II) in ionic liquids. The first was done by Hussey and Xu [7] in an $AlCl_3$ mixed in 1-methyl-3-ethyl imidazolium chloride melt. W. Yang *et al.* [8] has done Tin and Antimony electrodeposition in 1-ethyl-3-methylimidazolium tetrafluoroborate, and N. Tachikawa *et al.* [9] has done electrodeposition of Tin(II) in a hydrophobic ionic liquid, 1-*n*-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide.

In view of the advantages of the air and water stable ionic liquids, the aim of this study is to investigate the electrochemical behavior of the Tin electrodeposition from a mixture of an ionic liquid, 1-butyl-1-methyl-pyrrolidinium trifluoro-methanesulfonate, (BMPOTF) with Tin(II) Methane Sulfonate in Methane Sulfonic Acid (MSA).