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A review of developments in the electrodeposition of tin

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ABSTRACT

The importance of tin and its electrodeposition are summarised and the scope for plating tin is outlined. Established applications of electroplated tin include corrosion protection, electronics fabrication and cooking utensils. The past 20 years have seen developments in the science and technology of tin plating, including research into nanostructured deposits, adoption of environmentally friendly methanesulfonic acid baths and more ambitious coatings including multi-layers and composites. Our ability to tailor deposit structure and composition has been improved by newer electrolytes, pulse plating and electrolyte additives. The diversity of tin applications has extended to lithium batteries using newer structures (such as composites, multi-layers and nanostructures), electrical control (*e.g.*, pulsed current) and relative bath/electrode movement (including the use of rotating electrodes). Electrochemical aspects of modern tin deposition are illustrated by data from the authors' laboratory which highlights the versatility of methanesulfonic acid electrolytes. A wide range of deposit morphology, colour and surface finish are possible by the use of suitable addition agents and control of electrode/electrolyte movement and operating conditions. Subject areas needing further research work are identified.

Contents

Abbreviations: ENSA, ethoxylated α-naphthol sulfonic acid; MSA, methanesulfonic acid; PEG, polyethylene glycol; POELE, polyoxyethylene lauryl ether; PPG, polypropylene glycol; PTFE, polytetraflouroethylene; RCE, rotating cylinder electrode; RCH, rotating cylinder Hull; RDE, rotating disc electrode.

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List of symbols

c	concentration of stannous ions	mol cm^{-3}
D	diffusion coefficient of Sn^{2+} ions	cm^2 s^{-1}
E	electrode potential	V
dE/dt	linear potential sweep rate	V s^{-1}
F	Faraday constant	C mol^{-1}
j	current density	A cm^{-2}
j_{ct}	charge transfer current density for tin deposition	A cm^{-2}
j_L	limiting current density for tin deposition	A cm^{-2}
j_{max}	maximum current density	A cm^{-2}
j_p	peak current density	A cm^{-2}
q	electrical charge under the current *vs.* potential curve	C
t	time	s
t_{max}	time corresponding to the maximum current density	s
ν	linear potential sweep rate	V s^{-1}
z	number of electrons involved in the electrode process	dimensionless

Greek

ν	kinematic viscosity of the electrolyte	cm^2 s^{-1}
ω	electrode rotation speed	rad s^{-1}

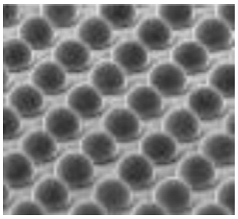
1. Electrodeposition of tin

Tin is a soft, ductile and silvery white metal which can be deposited as a matte or bright finish. General applications of tin electroplating are listed in Table 1[1,2]. Pure tin coatings have been used to form a protective surface to resist air oxidation, to enhance corrosion resistance and to improve solderability. Bright tin coatings also provide decorative finishes that can be aesthetically pleasing even when exposed to air and moisture. The electrodeposition of tin has a long history and a good summary of its established science and technology is given in the book by Jordan [3], while the protective coatings for metals book by Gabe [4] provides a useful treatment of tinplate as a metallic coating. Tin is one of the very few metals suitable for contact with foodstuffs during cooking. Pure tin and its alloys have received increasing attention as anode materials for Li-ion batteries as alternatives to graphite due to their high specific capacity and energy density.

Electrolytes for tin deposition can be acidic or alkaline. Tin is normally deposited from divalent stannous ions, Sn^{2+} in an acidic bath and *via* tetravalent stannate ions, SnO_4^{4-} in an alkaline one. The choice of bath is usually governed by the operating parameters and the required physical properties of the deposit. Important factors may include the range of applied current density, electrolyte throwing power, cathode current efficiency, surface morphology, texture and appearance, deposit uniformity, speed of deposition, use of bath additives and electrolyte stability, solubility of tin compounds, stability of electrolytes, solderability and possible reflow of deposits on heating.

Alkaline baths are usually hydroxide based and acidic baths have sulphate or sulphonate based compositions. Alkaline baths can be operated without additives since the stannate ion appears as a soluble complex. In acidic baths, the addition of additives is required for electrolyte stability. A low maximum current density is achieved in alkaline baths and they may suffer from losses in current efficiency [3]. Acidic baths can offer faster deposition rates at ambient temperature but are more complicated to maintain [2–5]. Their operation is largely determined by the type of additives. This review emphasises aqueous, acidic electrolytes, particularly those based on modern methanesulphonic acid, using data from the authors' laboratory to illustrate their electrochemistry and the importance of additives.

Table 1
Applications of tin and tin–copper alloy electrodeposition. Images courtesy of Enthone Inc. [1].

Industrial sector	Initiatives and modern developments
Microelectronics 	• Lead-free compliance • Miniaturisation of wafer bumping • Improved whisker-free deposits • Enhanced flip–chip bonding
Printed circuit boards 	• Lead free directives • Miniaturisation of high aspect ratio microvias • High throwing power deposition • Nanoscale semiconductor wafers and lead outs • Possible replacement for Ni-Au coating
Automotive and industrial 	• Improved corrosion resistance and tribology • Meeting new regulations for hazardous plating • Partial replacements for Pb-, hexavalent Cr- and Cd-free coatings • Improved coating properties
Jewellery and decorative 	• Allergy-free coatings • Build-up of metallised layers on plastics • Reduced cost • Substitute coatings for nickel
Batteries for electrochemical energy storage 	• Anodes for rechargeable Li-ion battery • Improving battery cycle life • Theoretical capacity: 992 mA h g^{-1} Sn

Recently, deep eutectic solvents have been studied as a new class of electrolytes for the electrodeposition of metals. Such electrolytes can be formed between a variety of quaternary ammonium salts and carboxylic acids. Their physical properties, such as viscosity, conductivity, and surface tension are similar to ambient temperature ionic liquids, rendering them suitable for developing uses in electrodeposition of tin. Abbot et al. [6] have described the electrolytic deposition of Sn and Zn/Sn alloys from a solution of the metal chloride salts in urea and ethylene glycol/choline chloride based ionic liquids. The kinetics and thermodynamics of deposition differed from aqueous processes and different phases, compositions and morphologies were obtained for the metal coatings in various ionic liquid systems. Anodic stripping was studied by cyclic voltammetry together with compositional analysis using SEM/EDX and X-ray diffraction. The differences in electrochemical