Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

A Block Copolymer as An Effective Additive for Electrodeposited Ultra-low Sn Coatings

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Experimental details

A conventional three electrode cell with Luggin-Haber capillary to minimize IR_{drop} was used in all electrochemical experiments. The electronic system used in the experiments was an EG&G Princeton Applied Research potentiostat/galvanostat, Model 2273. Prior to each experiment, a Pt disk (RDE) as working electrode (0.1639 cm^2) was gradually polished to mirror finish using 3.75 μm and 1.87 μm alumina powders and then ultrasonically rinsed with de-ionised water for 2 min. The reference electrode was $Hg/HgSO_4$/saturated K_2SO_4 solution (SMSE). All electrode potential were versus to SMSE in this paper. A Pt plate (1 cm^2) was employed as the counter electrode. The potential sweep rate was 50 $mV \cdot s^{-1}$ for voltammogram measurements. The 45℃ plating bath were employed for all tests and plating samples.

The tin MSA plating electrolyte was made of 0.1 $mol \cdot L^{-1}$ $Sn(MSA)_2$, 50 $ml \cdot L^{-1}$ MSA and 2 $g \cdot L^{-1}$ catechol as anti-oxidant. All solutions were prepared using deionized water. The substrate is WTRS which the roughness is 300-600 nm (Figure 1a and b). The rotating cylinder electrode was employed for preparing the tinplate at line speed 400 $m \cdot min^{-1}$. The 15$A \cdot dm^{-2}$ is used for electrodepositing a thin coating of 0.7$g \cdot m^{-2}$. An electromagnetic induction equipment was used for heating the tinplate to alloy treatment, and the process is 320℃, 0.5 s. To investigate the intermetallic layer, the tinplate was immersed in solution containing 50 $g \cdot L^{-1}$ NaOH and 10 $g \cdot L^{-1}$ KIO_3 to remove free-tin layer. For the imaging and element analysis of samples, a field-emission-gun scanning electron microscope (FEI Quanta 200 F) was used. Tin contents in both platform and pit (**Figures. 1**(c) and (d)) were also analyzed by energy dispersive spectrometer (EDS) by 10 kV (accelerating voltage). In order to analysis three dimensional profile image, a firstly calibration was essential by standard polysilicon with roughness 5nm using photoelectric profiler (WGL Shanghai).

Cloud point tests: two tubes contained 25 ml plating bath with additive were heating-up at 2℃$\cdot min^{-1}$ in water bath. Later, the cloud point temperature was recorded when the bath became turbid.

The surface tension for control of additives in plating bath were measured using stalagmometers (Kocour, Model 075920), the droplet numbers of 5 ml plating solution was recorded, the value bigger, and the wettability is better.

The covering power is the ability of deep plating ability, which were evaluated by the inner hole method. The blind copper pipes (diameter 10mm×length 50mm)

with external insulation treatment, were faced to tin anode and electrodeposited at 1A, 5min. Then, cutting the pipe from cross direction, and measuring the length of tin coating.

Cathode current efficiency was analyzed by weighing method. The samples were prepared by $3A \cdot dm^{-2}$ electrodepositing 20min on wet temper rolling steel (WTRS). According to Faraday's law, the current efficiency is the ratio between practical and theoretical amount of tin coating. The porosity for a 0.7 $g \cdot m^{-2}$ tin tinplate were tested with the method in accordance with the guide to the tin plate [1]

Hull cell Tests were experimented in 250 mL volume. The anode is tin plate with thickness around 3mm. The cathode is WTRS (100mm×70mm×0.18mm). The samples were prepared under d 2A, 3min, in stationary bath.

Supplemental Results

Table S1 the performance comparison of tin MSA plating bath with 1 $g \cdot L^{-1}$ PE9400 and 45 $ml \cdot L^{-1}$commercial TPG7 additive respectively

Additive	Cloud Point	Surface Tension	Color of Bath	Covering Power (cm)	Current efficiency	Porosity ($mgFe \cdot dm^{-2}$)
PE9400	79±3℃	73.5±2	colorless	5±0.01	86.9±2%	5.49±0.5
TPG7	58±3℃	66±2	light gray	2.1±0.01	86.4±2%	9.0±0.5

Notes: All the conditions are within the scope of operation manual of commercial TPG7 additive.

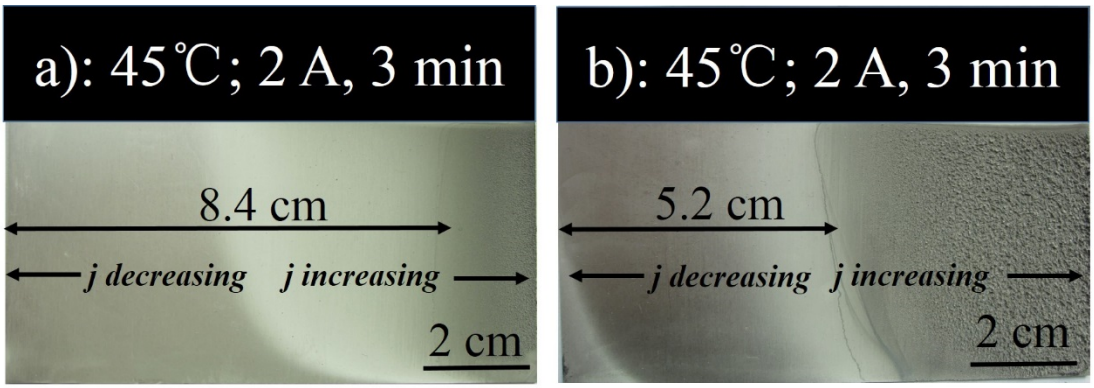

Figure S1 the Hull cell test comparison of samples from tin MSA plating bath a) with 1 g·L^{-1} PE9400; b) with 45 ml·L^{-1}commercial TPG7 additive

(2A, 3min, in stationary 45℃ bath)