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

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Abstract: In this work, a new type of block co-polymer additive, PE9400, was investigated for electrodepositing an ultra-low Sn coating in methanesulfonic acid (MSA) electrolyte. A thin coating with a loading of 0.7 $g \cdot m^{-2}$ tin was fabricated with excellent uniformity and coverage on wet temper rolling steel (WTRS), when PE9400 was used as an additive in the plating bath. Electrochemical measurements, real electroplating experiments, and SEM analysis, coupled with elemental qualification, indicated that the PE9400 additive results in a strong cathodic polarization with a wide operating current density range, resulting in fine grain size with even Sn distribution. These results confirm that PE9400 is able to significantly improve the quality of ultra-thin tin coating, giving rise to superior properties such as cloud point, surface activity, covering power and porosity compared to currently used Commercial TPG7 additive. Thus, this work may provide a new electrodeposition formulation to produce ultra-low Sn coating with sufficient quality for the Sn electroplating industry, which will significantly save tin source for food packaging applications.

Tinplate has been successfully applied as food and drink packaging over the past century. With an increase in tin source consumption and price, a decrease in tin coating weight has become a topic of high popularity.[1-3] However, producing a uniform thin coating of tin (<1.1 $g \cdot m^{-2}$) with uniform coverage during high speed electrodeposition is technologically difficult, and few satisfied experimental results are reported in the literature so far.[4] Most of the current research only achieves a loading above 1.1 $g \cdot m^{-2}$ in order to yield a uniform Sn distribution as a protective coating. On the other hand, saving the limited Sn sources has become an urgent need. Generally, to solve this problem, there are two feasible strategies in experimental efforts. One is to search for better additives that will lead to a lower coating weight, and the other is to develop novel materials instead of tinplate such as: tin free steel,[5] plastic and aluminum plate[6]. However, the reliable tin-free coating technologies still are not available yet. Hence, development of an efficient additive to improve the coating quality is the only feasible solution to solve this practical problem.

As for the electroplating formulation there are two main additives, besides tin salt and acid, in the methanesulfonic acid (MSA) electrolyte. An antioxidant is used to stabilize the rate of Sn^{2+} oxidation and hydrolysis, such as hydroxyl-phenol, catechol etc[7, 8]. Also, a grain refiner is required to improve the cathode polarization and refine grain, such as polyethylene glycol (PEG) or nonionic surfactant etc[9-11]. Grain refiner can also directly affect the quality of the tin coating. Though much

research is devoted to tin deposition[12-15], few report on additive studies for tin MSA electrolyte. Methanesulfonic acid as an electrolyte has been used for tin electrodeposition for over a decade. Basic properties of MSA have been reported.[16] Because the pH of tin methanesulfonic acid plating bath is below 1, no suitable complexing agent for Sn^{2+} has been developed for electrodepositing smooth and compact tin coating.[17, 18]

In this work, we discovered a new type of block copolymer (PE9400) that can be used as an effective additive in Sn electrodeposition to realize the ultra-low loading (0.7 $g \cdot m^{-2}$). Importantly, PE9400 plays a significant role in improving the coating quality even with such a low loading. Electrochemical and physical characterization further provides a mechanism in understanding about the role of the additive, which significantly increases the cathodic polarization during the electrodeposition process. Furthermore, the studied additive is capable of working in a wide range of operating current densities, when a forced convection environment was employed.

PE9400 is a block copolymer made of 40% ethylene oxides (EO) and 60% propylene oxides (PO). PE9400 (trade name Pluronic® PE9400, molecular weight: 4600) is environment friendly and has a high cloud point, demonstrating excellent stability in MSA electrolyte under strong forced convection conditions. The molecular structure of PE9400 is shown as follows[19]:

$$HO\text{-}(CH_2CH_2O)_x\,[CH\,(CH_3)\,CH_2O]_y\,(CH_2CH_2O)_z\text{-}OH$$

According to its molecular structure the reactivity of PE9400 is stronger than polyoxyethylene ether and other surfactants. The PO groups aid PE9400 in adsorbing on a surface with sizeable roughness[20]. Using WTRS as a substrate for tinplate[21, 22] results in special rolling surface morphology, which is studied by SEM and Photoelectric Profiler shown in **Figures** 1(a) and 1(b), respectively. As illustrated, the WTRS surface has different shapes and sizes of the pit, and its rolling lines are not continuous with drop heights of the peaks in the range of 500-2000 nm. These images also imply that the high specific surface area would lead to relatively lower real current density. Tin MSA plating bath, with PE9400 and Commercial TPG7, additive was used to prepare the thin Sn coating by using rotational cylinder electrodes (with 15 $A \cdot dm^{-2}$ at line speed 400 $m \cdot min^{-1}$) as shown in **Figures** 1(c) and (d), respectively. During the electroplating experiments, we can get a thin and high coverage, and uniform coating with an ultra-loading of 0.7 $g \cdot m^{-2}$ tin on wet temper rolling steel (see in Fig. 1c). With the addition of PE9400 into the tin MSA plating bath, lower porosity and finer grain coating, with matt brightness, were obtained when compared to the coatings obtained from a bath with TPG7 additives.

Tin contents in both platform and pit (**Figures. 1**(c) and (d)) were also analyzed by energy dispersive spectrometer (EDS). The tin contents in platform and pit of thin coating produced with PE9400 were 60.88% and 56.88%, respectively. As for the TPG7 additive, Sn contents in platform and pit were 53.06% and 40.11%,

respectively. Figure 1d's region 5, there is no virtually apparent tin coating, but a tin content as low as 9.5% was detected by using EDS. SEM and EDS results further confirm that the PE9400 containing tin base plating electrolyte possesses remarkably uniform coverage. The molecular structure of PE9400, with 60 weight % PO, plays a pivotal role in the enhancement of surface activity, the increase in uniformity of the deposits, and decrease in the wettability difference between platform and pit on the WTRS substrate. In addition, we performed a performance comparison between PE9400 and TPG7 additives in terms of their bath properties including cloud point, surface activity and covering power (Table S1). The cloud point and surface tension results indicate that PE9400 can increase the bath working temperature and the wettability. The covering power demonstrates that PE9400 is more favorable in coverage and uniformity for thin coating, in according with the low porosity value (5.49 ± 0.5 mgFe·dm^{-2}) on an ultra-low loading (0.7 g·m^{-2}) tin tinplate.

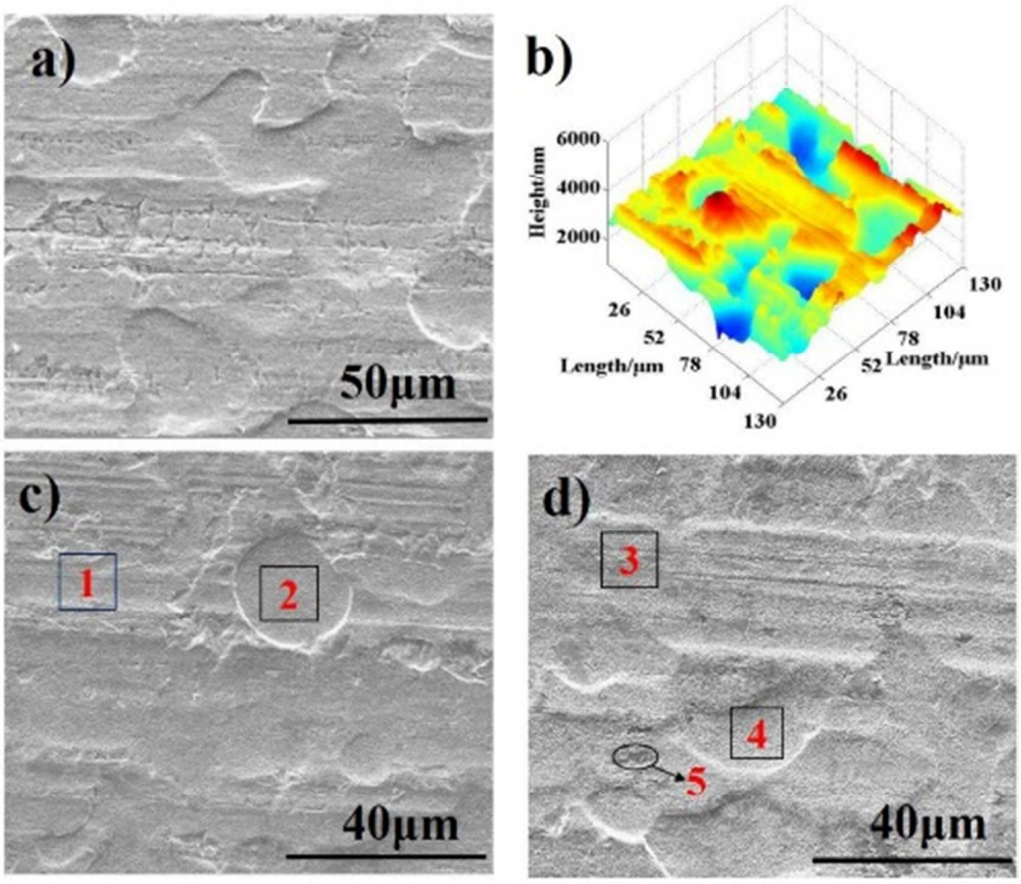

Figure 1. a, b) the SEM image and surface morphology of WTRS; c) and d) were SEM images of tin coatings with a loading of 0.7 $g \cdot m^{-2}$ on WTRS substrate using PE9400 and TPG7 additives, respectively. The mass percentages of tin in Fig. 1c and d pointed region 1, 2, 3, 4, 5 were 60.88%, 56.88%, 53.06%, 40.11% and 9.54%, respectively.

We then studied the electrochemical behavior of PE9400 using cyclic voltammograms (CV) measurements in MSA tin plating bath containing 0.1 $mol \cdot L^{-1}$ $Sn(MSA)_2$, 50 $ml \cdot L^{-1}$ MSA and 2 $g \cdot L^{-1}$ catechol at a scan rate of 50 $mV \cdot s^{-1}$ in a

three-electrode cell (**Figure 2**). These CVs consist of a cathodic peak, a hydrogen evolution area, and a tin stripping area. During the initial scan along the negative direction, the CV of the tin MSA plating bath, in the absence of PE9400, rises around -0.9 V, signifying the reduction of Sn^{2+} to Sn and a weak adherence of spongy tin on the Pt electrode surface. With addition of 1.0 $g \cdot L^{-1}$ of PE9400 into the plating bath, the onset potential for Sn^{2+} reduction occurs at around -0.97 V, 70 mV more negative than that of additive-free tin MSA plating bath. Furthermore, the CV of the blank tin MSA plating bath indicates a cathodic current density peak of -4.0 $A \cdot dm^{-2}$ at -1.0 V, much higher than that of the electrolyte in the presence of PE9400 (-1.9 $A \cdot dm^{-2}$ at -1.07 V). The onset potentials corresponding to hydrogen evolution are around -1.1 V for the electrolyte without PE9400, and -1.53 V with PE9400. These results indicate that PE9400 leads to a larger initial nucleation overpotential, larger negative overpotential for hydrogen evolution, and stronger cathodic polarization than that of the blank tin MSA plating bath. This behavior may be explained by the very strong adsorption of PE9400 and the formation of a thin adsorbed film on tin/iron cathode surfaces[23], which leads to uniform interfacial free energy all over the exposed deposit surface, facilitating lateral diffusion of Sn adatoms until they reach growth sites.[24]

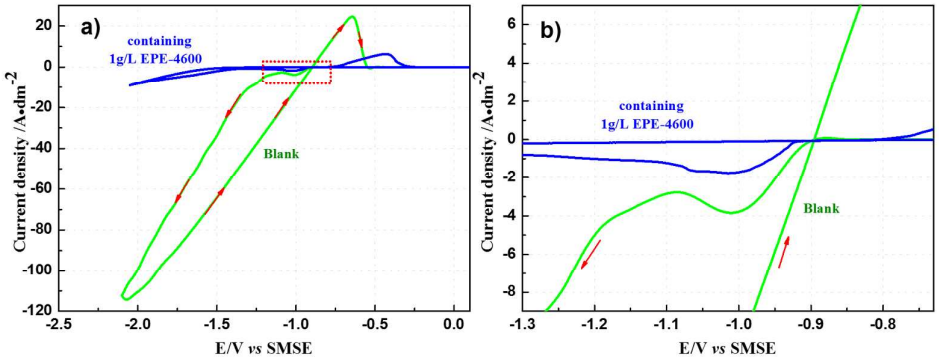

Figure 2.Cyclic voltammogram performance of PE9400 in tin MSA plating bath containing 0.1 mol·L^{-1} Sn $(MSA)_2$, 50 ml·L^{-1} MSA and 2 g·L^{-1} catechol at scan rate of 50 mV·s^{-1}.

Cathodic polarization measurements were performed at a scan rate of 50 mV·s^{-1} with different rotational speeds using a Pt-RDE. This is to analyze the cathodic process of Sn^{2+} reduction at different forced convection conditions in the presence of PE9400. **Figure 3** shows the polarization curves from the tin MSA plating bath containing 1.0 g·L^{-1} PE9400. The reduction process started occurring at -0.99 V with a sharp increase at approximately -1.17 V. The sharp rise in the polarization curves likely results from the forced convection effect on tin electrodeposition by increasing rotating speed. When the rotational speed starts from 0 to 1500 rpm, the current densities have a significant rise in the potential range from -1.1 V to -1.8 V. *vs* SMSE. That may be due to the diffusion layer thickness of the Sn^{2+} becoming thinner under the enhanced forced convection. With an increase of rotational speed (>1500 rpm), the curves tended to be overlapped, which would result from the diffusion layer

thickness of Sn^{2+} quickly stabilizing. This unique property of PE4900 is very important for tinplate production process, because the running speed of WTRS is normally above 200 $m \cdot min^{-1}$ and the residence time of WTRS in the plating bath is less than 10 s. Thus, these results revealed that the electroplating bath containing PE9400 can build up a mass transfer equilibrium stably with a quick electrode interface response to changes in solution convection.

In addition, we determined the operating current range of the plating bath by using a Hull cell test (Fig S1). A qualified tin coating with a length of 8.4 cm was prepared from a bath with an addition of 1.0 $g \cdot L^{-1}$ PE9400, which is longer than the coating obtained from the TPG7 additive (5.2 cm). This illustrates that the tin bath with PE9400 has a larger operating current density range then compared to the TPG7 additive. And the appearance comparison of testing samples reveal that PE9400 has a strong inhibition impact on Sn^{2+} reduction and increase in cathodic polarization, which is in agreement with the electrochemical measurements.

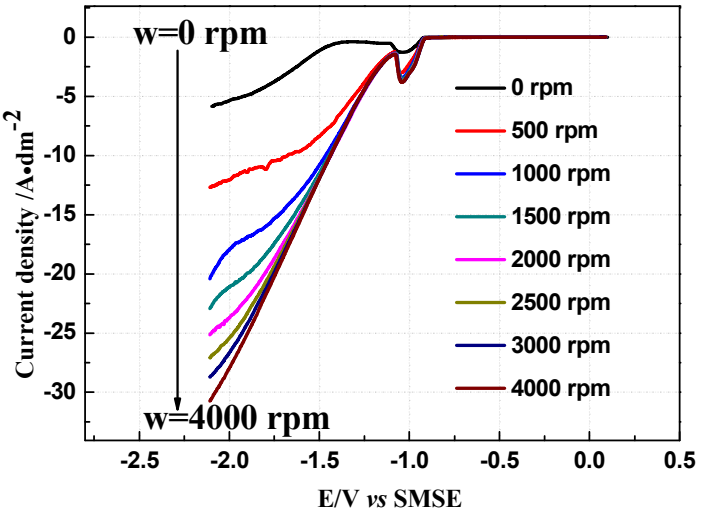

Figure 3. Effect of hydrodynamic modulation on linear sweep voltammetry performance in plating solution containing 0.1 mol·L^{-1} Sn $(MSA)_2$, 50 ml·L^{-1} MSA, 2 g·L^{-1} catechol and 1.0 g·L^{-1} PE9400 at scan rate of 50 mV·s^{-1}.

The intermetallic $FeSn_2$ layer produced by a reflowing process for thin tin template is equally important as that of the bath electrochemical behavior of plating pure tin coating. In particular, **Figure 4a** is an SEM image of tinplate with a loading of 0.7 g·m^{-2} subjected to a reflowing treatment (320^{o}C, 0.5 s). This image illustrates that a pore-free and uniform surface has been observed after the pure tin coating was melted under high temperature and spread on the substrate. As a result, a new $FeSn_2$ intermetallic layer was developed on the interface of the Sn and Fe. After removal of the free tin by immersing in a solution containing 50 g·L^{-1} NaOH and 10 g·L^{-1} KIO_3 (supporting information), the intermetallic layer was exposed as shown in the SEM images (**Figure 4b**). The $FeSn_2$ intermetallic layer appears as densely populated

needle-like structures on the steel surface. Some $FeSn_2$ crystal was even inclined to grow on the WTRS in Figure 4b (expanded view). According to the corrosion behavior of tinplate, initial pore-free tin coating and a pore-free intermetallic layer would result in excellent anticorrosion properties. This is resultant of the individual tin, intermetallic layers, and steel substrates being fabricated orderly. Such a multi-layered configuration would significantly improve the corrosion-resistance in an oxygen-free environment, which is a typical convention of tin-coated steel can for use as food and drink storage.[25-27] Thus, PE9400, as a suitable additive, is able to produce a high-quality ultra-low loading thin-tinplate to improve the corrosion resistance to tinplate products.

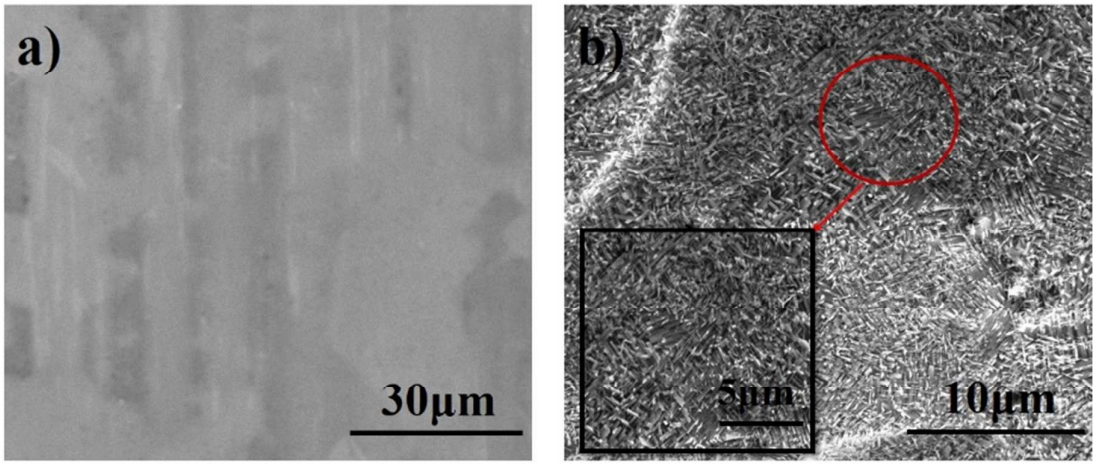

Figure 4. The SEM images of 0.7 $g \cdot m^{-2}$ thin tin tinplate after reflowing. a) The free tin layer; b) $FeSn_2$ intermetallic layer (reflowing process parameters: 320^{o}C, 0.5 s).

Conclusions

In summary, we reported a novel block copolymer additive (PE9400) in MSA electrolyte to electrodeposit an ultra-low loading (of 0.7 $g \cdot m^{-2}$ tin) thin coating on wet temper rolling steel. The electrochemical behavior of tin MSA plating bath containing PE9400 was investigated by cyclic voltammetry and linear voltammetry measurements on Pt-RDE. The results illustrate that PE9400 has tendency towards strong adsorption on the electrode surface, which increases the cathodic polarization and decreases the current of Sn^{2+} and H^{+} reduction. Besides the extension of the operating current density range, the mass transfer equilibrium can be built quickly at the electrode/electrolyte interface with an increase of rotating speed in the presence of PE9400.

Using the additive, tin electrodeposits obtained from the electrolyte were smooth and compact with uniform elemental distribution throughout the substrate surface. After an important post high-temperature treatment, a new intermetallic layer $FeSn_2$ was generated, also showing uniform and high coverage on steel substrates. These results further solidify evidence that the block copolymer (PE9400) can be an effective electrolyte additive for fabricating ultra-low Sn coating for tinplate, thereby significantly reducing loss and saving the limited tin sources.

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References

1. W. Waddell, D. Thomas and N. Williams, *Met. Constr.*, 1986, 18, 156-161.
2. S. Vitkova, V. Ivanova and G. Raichevsky, *Surf Coat Tech*, 1996, 82, 226-231.
3. D. Salm, A. Towers and D. Kaan, *2nd Inter Tinplate Conference*.1980.
4. K. Marsh and B. Bugusu, *J Food Sci*, 2007, 72, R39-R55.
5. J. Z. Li, Y. C. Wang, Y. W. Tian, Y. Li and X. L. Sun, *Advanced Materials Research*, 2012, 396, 336-339.
6. R. C. Griffin, *Principles of package development*, Springer Science & Business Media, 2012.
7. C. T. J. Low and F. C. Walsh, *Electrochimica Acta*, 2008, 53, 5280-5286.
8. M. Jordan, *The electrodeposition of tin and its alloys*, Leuze, 1995.
9. M. Fukuda, K. Imayoshi and Y. Matsumoto, *Surface and Coatings Technology*, 2003, 169-170, 128-131.
10. J. W. Gallaway and A. C. West, *J Electrochem Soc*, 2008, 155, D632.
11. N. Xiao, D. Li, G. Cui, N. Li, D. Tian, Q. Li and G. Wu, *Electrochimica Acta*, 2013, 109, 226-232.
12. S. Wen and J. A. Szpunar, *Electrochimica Acta*, 2005, 50, 2393-2399.
13. C. Han, Q. Liu and D. G. Ivey, *Electrochimica Acta*, 2009, 54, 3419-3427.

14. X. Huang, Y. Chen, J. Zhou, Z. Zhang and J. Zhang, *J Electroanal Chem*, 2013, 709, 83-92.

15. F. C. Walsh and C. P. de León, *Surface and Coatings Technology*, 2014, 259, 676-697.

16. M. Canales and C. Aleman, *J Phys Chem B*, 2014, 118, 3423-3430.

17. J. D. (Ed.), *Lange's Handbook of Chemistry (16th edition)*, McGraw-Hill, New York, 2005.

18. M. R. Buchner, F. Kraus and H. Schmidbaur, *Inorg Chem*, 2012, 51, 8860-8867.

19. A. R. K. C. H. Lee, H-C Koo, J. J. Kim, *J. Electrochem. Soc*, 2009.

20. T. Franklin, *Surf Coat Tech*, 1987, 30, 415-423.

21. H. Kijima, *J Mater Process Tech*, 2015, 216, 1-9.

22. M. G. A. Benabida, A. Zarrouk, *Der Pharma Chemica*, 2014, 6, 9.

23. N. Xiao, D. Li, G. Cui, N. Li, Q. Li and G. Wu, *Electrochimica Acta*, 2014, 116, 284-291.

24. L. M. L. Oniciu, *J Appl Electrochem*, 1991, 10.

25. K. Wang, J.-h. Wang, H.-h. Wang, C.-w. Fu, D.-h. Xia, X. Zheng, L.-h. Dang and J.-b. Shi, *Journal of Central South University*, 2014, 21, 76-82.

26. Y. Che, Z. Han, B. Luo, D. Xia, J. Shi, Z. Gao and J. Wang, *Int. J. Electrochem. Sci*, 2012, 7, 9997-10007.

27. D. Tošković, M. Rajković, L. Vasiljević and D. Stanojević, *Zbornik radova Tehnološkog fakulteta, Leskovac*, 2005, 58-72.