

Electro-deposition for Foamed Zinc Material from Zinc Sulfate Solution

Qinghua Tian^a, Xueyi Guo^b, Ping Xue^c, Yu Song^d, and Lian Duan^e

School of Metallurgical Science & Engineering, Central South University, Changsha, China

^aqinghua@mail.csu.edu.cn, ^bxyguo@mail.csu.edu.cn, ^cxueping20011982@163.com,
^dfreefish_sy@163.com, ^edl_wolf@163.com

Keywords: Electro-deposition; Foam zinc; Electroless plating; Polyurethane; Foam metal.

Abstract. It is very possible for the foam zinc materials to take the place of zinc powder and become a new ideal material of electrode for zinc-air battery, because of its excellent three dimensional reticulated structure, high porosity, high specific surface area and uniform quality, and was widely used in many other fields. A novel method for preparing very porous zinc foam was proposed, in which the polyurethane foam as substrate was processed by degreasing process, roughening process, activation, electroless plating and zinc electrodeposition. Then, experiments were carried out to explore the effects of the solution composition(concentration of $ZnSO_4$)and the operation conditions (such as the interelectrode distance; current density, temperature, pH value of electroplating solution and so on) on the morphology of the foam zinc and the current efficiency. The optimum experimental conditions were determined by optimizing the factors. On these conditions the foam zinc presents a three-dimensional reticular structure with high porosity, and uniformity, and the outward appearance of the coating is bright.

1 . Introduction

Zinc-air batteries employ oxygen from the air to their cathode, using an anode primarily composed of zinc and an alkaline electrolyte. The advantages of zinc-air batteries consist of include flat discharge voltage, safety and environmental benefits, good shelf life, and low cost. In addition, zinc-air batteries have high volumetric energy density compared to most primary batteries. Large format and high power zinc-air systems are being developed for portable and motive power applications such as scooters, bicycles and buses. Due to the high power requirement, the anode in these systems uses zinc powder of dendritic form electroplated from alkaline electrolyte. Dendritic zinc powder has quite a high specific surface area, it is about 100 times higher than that of atomized zinc powder, which is the material used for anode in small zinc-air batteries such as the button cells used for hearing aids.

In order to improve the volumetric energy density and power of Zinc-air batteries, we introduced foam zinc to replace conventional zinc powder, which has higher specific surface area. There are many ways to manufacture foam metallic materials, such as Gas injection, Vapour deposition, Solid-gas eutectic solidification, Powder compact melting technique, et al. Foam metallic materials produced by Electro-deposition technique have an excellent three dimensional reticulated structure, high porosity, high specific surface area and uniform quality. In this paper, The Electro-deposition technique of foam zinc is introduced in detail.

2. Experimental

2.1 Chemicals and solutions. Polyurethane foam was obtained from the Bridgestone Corp. (Japan). Formaldehyde, oxalic acid, absolute ethanol, NaOH, Na_2CO_3 , Na_3PO_4 , $KMnO_4$, H_2SO_4 , $CuSO_4 \cdot 5H_2O$, $PdCl_2$, HCl (37%), $SnCl_2 \cdot 2H_2O$, NaCl, $ZnSO_4$, $Al_2(SO_4)_3$, $KAl(SO_4)_2$, Na_2SO_4 were all of analytical grade.

2.2 Experimental procedure. The experimental procedure of the preparation of foam zinc: Polyurethane foam → Organic solvent degreasing → Chemical degreasing → Chemical roughening → Film removing → Activation → Electroless plating → Electro-deposition → Foam zinc

3. Results and discussion

3.1 Pretreatment. As a nonconductor, polyurethane foam can't been electrodeposited directly. Electro-deposition on a polymer foam requires some electrical conductivity of the initial polymer foam. This can be achieved by conductive treatments, which is also known as surface metallization. This method is based on four major steps: degreasing process, roughening process, activation and electroless plating.

3.1.1 Degreasing process. Degreasing process is also called oil-removing; the objective of it is to remove the dirt and release agent on the surface of polyurethane foam, to ensure the activation of substrate surface can carry out uniformly on Nonmetallic Materials. Organic solvent degreasing means to remove the oil stain on the surface of polyurethane foam by organic solvent, which can dissolve the saponified oil and unsaponifiable oil. The main characteristics of organic solvent degreasing are that it can remove various oil fast, and there is little corrosion of the substrate material. The oil still stayed on the surface of polyurethane foam after some organic solvents had volatilized, and would form a layer of oil film. Consequently the substrate foam material need supplementary treatment with chemical degreasing.

Organic solvent degreasing and chemical degreasing were used in the present work. Absolute ethanol was used as organic degreaser at first. Then the reticulated polyurethane foam was dipped into the organic degreaser at room temperature and kept for 60 seconds. After water washing for 5 minutes, the polyurethane foam was placed into the chemical degreasing solution for 5 minutes, the composition of it was as following: NaOH (35 g/L) ,Na₂CO₃ (25 g/L) ,Na₃PO₄ (10 g/L) and Emulsifying Agent OP (0.5ml/L) ,then clean water washing for 5 minutes again. The combined degreasing process helped to ensure the thoroughness of oil-removing and the service life of activating solution in next step.

3.1.2 Roughening process. Chemical roughening is also called chemical etching, which has a lot of advantages, such as high speed of roughening, wide range of available field, convenient preparation of solution and so on. Chemical roughening is the key procedure of surface metallization, with an important effect on coating adhesion.

This roughening solution is composed of KMnO₄ (1g/L) and H₂SO₄ (0.05ml/L) under the conditions of solution temperature 45°C and pH value from 2 to 3. The foam after degreasing process was dipped into the roughening solution for 5 minutes. Fig.1 and Fig.2 are the microphotographs of foam substrate before and after roughening process, respectively. The result shows that the roughening process makes the surface coarser. The adhesion between Metal Cladding and Non-metal substrate was improved effectively. Oxalic Acid (10g/L) was used as film removing agent to remove the residues(such as KMnO₄) stayed on the surface of the foam.

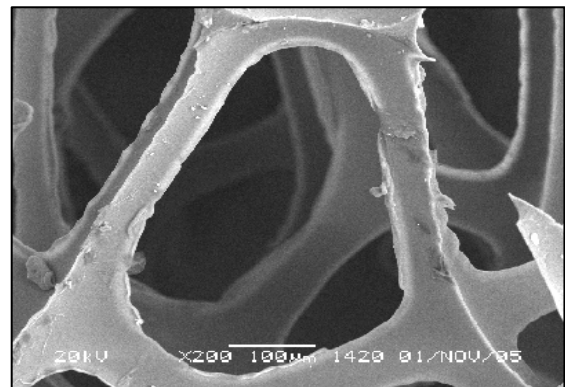
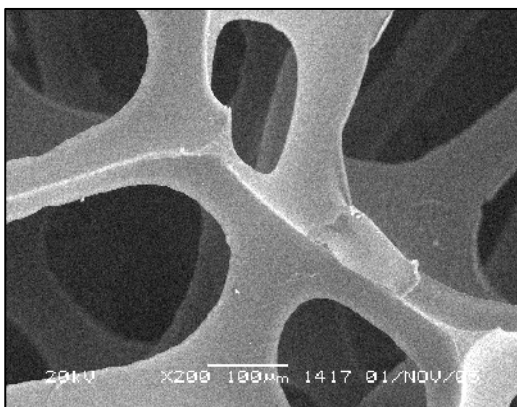


Fig. 1. The SEM of polyurethane foam before roughening Fig. 2. The SEM of polyurethane foam after roughening

3.1.3 Activation processes. The aim of activation processes is to get a effectively catalytic active layer of pellet catalysts, which can induce the electroless process as following. It would influence not only the quality of electroless plating deposits but also the quality of electrodeposited layer.

In this experiment, the beaker with activation solution was placed in the water bath of constant temperature water bath under certain temperature for 10 minutes. The foam after roughening process was dipped into the activation solution and kept for 5 minutes, clean water washing for 5 minutes and then dipped the foam into accelerator at 30°C for 5 minutes. After water washing 5 minutes, the polyurethane foam was placed into the pre-dip solution under room temperature for 1 minute,

The salt-based palladium colloid activation solution was compared with acid palladium colloid activation solution. Tab.1 shows that the salt-based palladium colloid activation solution presented fairly high activity, All property parameters of it were better than acid palladium colloid activation solution. Therefore, it was chosen as activation solution in the optimality conditions.

Table 1 the comparison of two activation solution

	acid palladium colloid	salt-based palladium colloid
activation temperature (°C)	35	30
activation time (s)	6	9
inducement time (s)	50	5
coating time (s)	60	50
service life (times)	15	6
cost (\$/L)	11	3

3.1.4 Electroless Plating. Electroless plating is a kind of surface treatment technology which produces metal plating coating on the substrate surface by chemical deposition in the absence of applied current, according to the principle that the autocatalytic redox reaction between the metal salts and the reducing agent in the same solvent occurs on the catalytically active surface of the substrate. As the conventional cathode materials for zinc-air batteries compact the zinc powders onto the copper plate current collector, the present work utilized the electroless copper plating to electrodeposite zinc on the substrate of chemical copper deposition.

Based on the comparative experiments of the present work, the optimum formula and the technical conditions for the electroless copper plating were determined as follows:

Copper Sulfate	16 g/L		
Potassium Sodium Tartrate	30 g/L		
Na ₂ EDTA	20 g/L	pH Value	12.5
Formaldehyde(HCHO)	5 ml/L	Temperature	50°C
α , α' -Bipyridine	25 mg/L		
Potassium Ferrocyanide	25 mg/L		
PEG-1000	1 g/L		

Electroless copper plating for 10min under such conditions can produce bright and uniform copper coating which accords with the requirement of the subsequent electrodepositing.

3. 2 Electrodeposition. Because of the complex structure, high porosity and flexibility of the foam substrate materials, the conventional technologies of planar or liner zinc plating are unable to deposit zinc onto the surface of the foam substrate. The present work studied the electrodepositing of zinc on the foam substrate from the selection of the laboratory equipment to the determination of the technical parameters.

Through the Hull Cell experiment of three conventional systems of zinc plating, i.e. zincate, chloride and sulfate, the present work found the widest range of current density and the best brightness in the sulfate plating bath. As a result, the sulfate plating bath was selected for the

electrodepositing of the conductive foam substrate, and the influence of various additions on the electrodepositing effect was studied, according to which three kinds of additions were finally determined to increase the stability of the plating bath and the brightness of the plating coating. Meanwhile, based on the flexibility and movability of the polyurethane foam substrate, the four sides contact conductive racks for cathode were designed.

The various technical parameters, such as the pH value and temperature of the electroplating bath, the concentration of the sulfate, the cathode current density and the interelectrodes distance of the electrodepositing process, were all examined in probing experiments to determine the optimum range of various parameters for the electrodepositing of zinc on the foam substrate.

Concentration of Zinc Sulfate(g/L)	200 ~ 300
Current Density of Cathode(A/dm ²)	0.03k ~ 0.06k
Temperature of Plating Bath(°C)	25 ~ 40
pH Value of Plating Bath	3.0 ~ 4.0
Electrodes Distance(cm)	3 ~ 5

According to the optimum conditions, the foam zinc material of complete coating, uniform structure and high porosity was prepared by the electrodepositing in the present work(Fig.3).

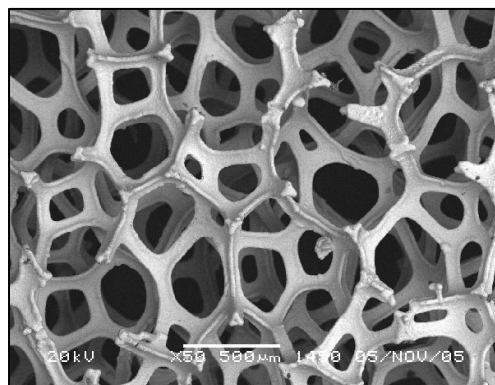


Fig. 3. The SEM image of the foam zinc prepared by optimum experimental conditions

4. Conclusion

The foam zinc, prepared by electro-deposition technology, presented a three-dimensional reticular structure with high porosity, high specific surface area, uniform distribution, and the outward appearance of the coating is bright, the porosity of it is greater than 90%. Consequently, the foam zinc is suitable for use as anode material in zinc-air batteries.

References

- [1] J. Goldstein, I. Brown, B. Koretz. *Journal of Power Sources*. Forum Vol. 80 (1999) , p. 171-179
Information on <http://www.powerzinc.com>
- [2] H.P Degischer, Kriszt B. . *Handbook of Cellular Metals : Production, Processing, Applications*(Wiley-VCH, Weinheim2002)
- [3] P. S. Liu, B. Yu, A. M. Hu, et al . *J Mater Sci. Technol*, Forum Vol. 18 (2002) , p. 299-305
G.J. Davies, Shu Zhen . *Journal of Materials Science* , Forum Vol. 18 (1983), p.1899-1911
- [4] J. Banhart . *Progress in Materials Science*, Forum Vol. 46 (2001) , p. 559-632
- [5] Z. M Tu, S. M. Han, Z. L. Yang, et al.. *Ornamental Electroplate Coating*(Chemistry Industry Press, Peking 2004)
- [6] Hajdu J. *Plating & Surface Finishing*, Forum Vol. 83 (1996), p. 29-33
- [7] Y. F. Zhang, Z. X. Cui, L. J. Ma. *New Technologies and Processes*, Forum Vol. 8 (2001), p. 38-39
- [8] Q. H. Tian, J. F. Yan, X Y Guo, *Electroplating & Finishing*, Forum Vol. 26 (2007), p. 38-4