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The Effect of Suspended Particles on the Corrosion Resistance of Electrodeposited Zinc Powders①

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Abstract Zinc powders were electrodeposited from $ZnCl_2$ baths with containing suspension of unsoluble particles such as graphite, PbO_2, SnO_2, TiO_2, SiO_2 etc.. The structure, morphology and corrosion behavior of zinc powder were analyzed. SEM results showed that the dendritic growth of zinc can be inhibited by applying the suspension method. Suspension of PbO_2, SnO_2, TiO_2, SiO_2 and In_2O_3 could greatly improve the corrosion protection of zinc powder in 5 mol/L KOH. In addition, fractal theory is employed to further explain the results.

Key words Electrodeposition, Zinc powder, Suspension, Microstructure, Corrosion resistance

1 Introduction

Zinc powder is a popular anode material used in many rechargeable and primary batteries. Since the corrosion behavior of zinc powder is important to battery performance, many attempts in recent years have been made to prepare Hg-free zinc with better corrosion resistance, such as adding some effective inorganic and/or organic corrosion inhibitors into the electrolyte, controlling the particle sizes and morphology of zinc, and preparing zinc alloys[1～3]. Based upon the fact that zinc powder can be electrodeposited from $ZnCl_2$ bath or alkaline bath[4], the properties of zinc powder were likely to be controlled under certain electrolytic conditions such as electrolysis ways, current density, solution concentration and the type of additive etc..

Suspended electrolysis is a method in which electrolysis is carried out with suspended species under mechanical stirring or ultrasonic dispersion. Compared with conventional electrolysis, it has the following advantages: 1) to hinder the passivation of anode even at high current density[5], 2) to prevent dendritic growth[6]; 3) to modify the properties of deposits such as microstructure, particle size etc.[7]. Therefore this method has gained much interest in recent years. As we have known that electrodeposition of zinc often leads to four kinds of deposits: spongy, compact, boul-

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der and dendritic. Being harmful to the reversibility of batteries, dendritic deposits of zinc should be avoided during the course of electrodeposition. Thus use of the technology of suspended electrolysis could not only prevent the formation of dendritic zinc, but also introduce additives into zinc powders to modify their corrosion behaviors at the same time. So in this paper, we attempt to employ this method to prepare some zinc powders, and discuss the effects of suspended particles on the morphology and corrosion behavior of zinc.

2 Experimental

Zinc deposits were obtained under galvanostatic conditions with or without mechanical strring. The bath solutions were made of 30 g/L $ZnCl_2$ and 100 g/L NH_4Cl, suspended species which included graphite, In_2O_3, TiO_2, SiO_2, SnO_2, PbO_2, Ge_2O_3, MoO_3 etc. were added to the bath in amounts between 0 and 1.0 g/L. All the reagents used were of analytical grade.

The electrodeposition of zinc was carried out at 25 ℃, the anode was zinc plate with an exposed area of 10 cm^2, the cathode material was Pb, and current density was selected at 20 - 100 mA/cm^2. After 2 hours deposition, the deposits were removed and washed with ethanol, then dried and kept in the vacuum drier.

The deposit phases were analyzed by X-ray diffraction and the morphology was observed by scanning electron microscopy (SEM). The corrosion behavior in 5 mol/L KOH was analyzed with EIS spectra. The AC impedance experiment was performed using PAR. m 378 system with ac signal of 5 mV and frequency range between 100 KHz and 0.01 Hz, where working electrode was made by pushing the mixture of zinc powder with a little PTFE onto a stainless steel web, Pt wire was served as counter electrode and Hg/HgO, KOH(5 mol/L) was as reference electrode.

3 Results and discussion

3.1 The morphology and microstructure of the deposits

The zinc deposits were electrodeposited from conventional bath (i.e. without stirring) and suspension baths. The morphology of various zinc powders was examined by SEM, from Fig. 1 and Fig. 2, it could be observed that electrodeposition of zinc from conventional bath led to the dendritic zinc, but dendritic growth of zinc was limited from suspention baths. In addition, the morphology of zinc powder prepared with suspended method varied according to the kinds of suspended particles. The results indicated that the existence of stirring which caused the flowing of solution did not help the growth of dendritic, and also the existence of suspended species might act as crystal nuclei to

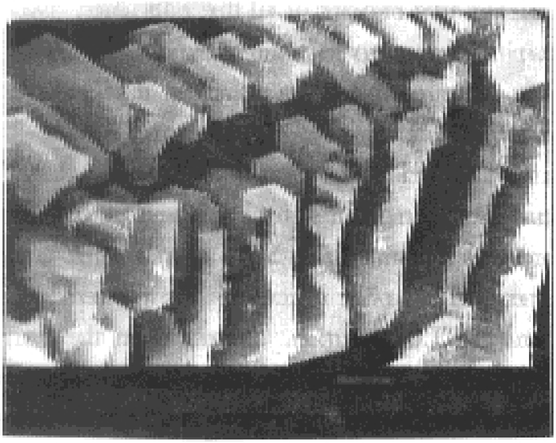

Fig. 1　SEM picture of zinc powder electrodeposited from conventional $ZnCl_2$ bath at 10 mA/cm^2

induce the electrocrystallization of zinc.

Fig. 3 showed the X-ray diffraction patterns of zinc powders deposited from suspension baths of graphite and PbO_2. From Fig. 3, we found the characteristic diffraction peak of C at $d = 3.34$, an increase of amount of suspended graphite gave rise to the increase of the height of diffraction peak at $d = 3.34$. However, suspension of other species only caused some changes in the height of certain peaks and the appearance of new peak out not the characteristic diffraction peak of suspended species. Therefore, we could draw a conclusion that the suspended particles were codeposited with zinc powders, and we called these powders the composite zinc powders.

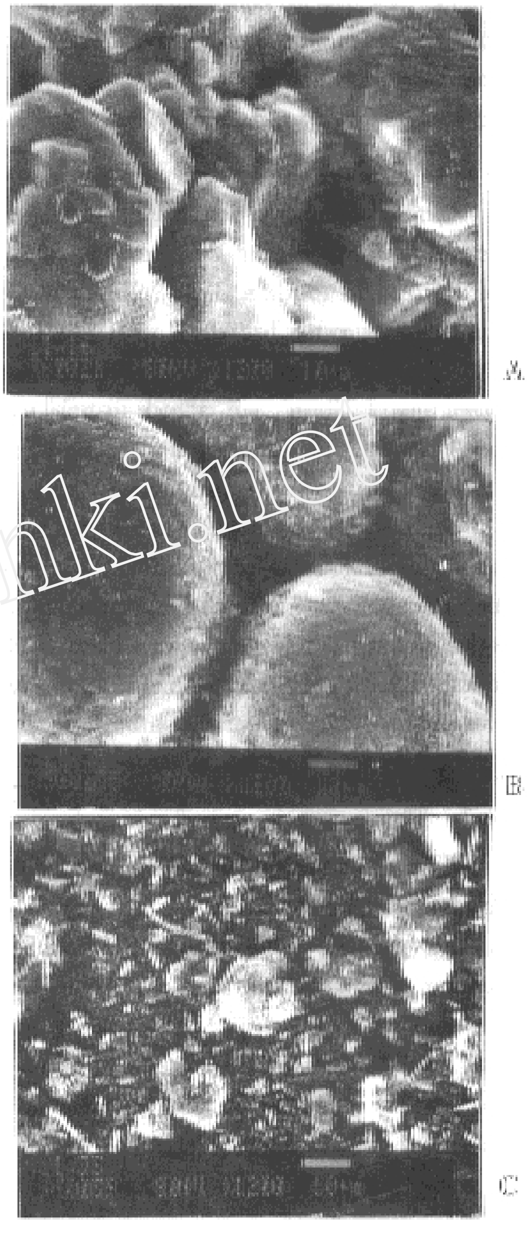

Fig. 2 SEM picture of zinc powder from suspension baths at 100 mA/cm^2, a) graphite, b) PbO_2, c) ultra-fine $Ni(OH)_2$

3.2 Effect of the amount of suspended species on the corrosion properties of zinc powder

It has been reported that mixing certain amount of graphite with zinc powder was beneficial to decrease the corrosion rate of zinc electrode in alkaline media[8]. So graphite was chosen as the first suspended substance. 0～1.6 g/L amounts of C were suspended in the baths and the effect of the amount of C on the corrosion behavior of zinc deposits electrodeposited at 100 mA/cm^2 was examined by EIS measurements. Fig. 4 showed the Nyquist plots for composite zinc powders with different amount of C. There existed two regions in all the EIS plots, two capacitive loops at high frequencies and inductive one occurred at low frequencies, it indicated the existence of passive film at zinc surface in 5 mol/L KOH. The corresponding equivalent circuit consisting of resistors, capacitors and inductor was shown in Fig. 5. to simulate the electrochemical behavior of composite zinc elecrode in 5 mol/L KOH solution. Elements in the equivalent circuit respectively reporesented as: R_1-solution resistance; Q_1-film capacitance; R_2-film resistance; Q_3-double-layer capacitance; R_3-charge-transfer resistance; R_4-film resistance; L-inductor. If regardless of the existence of inductive loop, the polarization resistance R_p was the sum of R_2 and R_3, otherwise R_p was calculated by the equation

$$R_p = (1/R_4 + 1/(R_2 + R_3))^{-1}$$

Tab. 1 Electrochemical parametres simulated from EIS plots of composite zine with suspension of different amount of C(0～1.6 g/L)

amount	Q_2	N_2	R_2	R_3	Q_3	N_3	R_4	L_7	R_p	R_p'
0	1.02E-4	1	0.34	1.06	5.10E-2	0.54	2.58	0.01	1.40	0.91
0.04	1.52E-4	1	0.58	3.55	1.85E-2	0.56	6.00	0.50	4.12	2.44
0.2	1.75E-4	1	0.59	1.60	6.84E-2	0.74	8.08	0.30	2.19	1.72
0.4	1.71E-4	1	0.55	1.08	7.51E-2	0.73	8.32	0.32	1.63	1.37
1.0	1.66E-4	0.80	0.68	0.84	2.46E-2	0.80	4.91	0.10	1.52	1.16
1.6	1.28E-4	0.83	0.51	0.78	1.58E-2	0.82	5.91	0.39	1.29	1.06

Q_2, Q_3: (Fcm^{-2}); R_2, R_3, R_4, R_p, R_p': (Ωcm^2); L: (Hcm^2)

As shown in Table 1, an increase in C amount led to the decrease of charge-transfer resistance R_3 and also the decrease of R_p. Compared with the EIS data of zinc without graphite, it indicated that the existence of a little C was effective to the corrosion protection of zinc electrode. However, excess C would cause zinc electrode to become more unstable in 5 mol/L KOH. The reason could be attributed to that better conductivity of graphite made the loss and winning of electrons in zinc electrode become easier.

3.3 Effect of current density on the corrosion behavior of zinc

At fixed amount of C(1.0 g/L), zinc deposits were prepared at current density range from 20 mA/cm^2 to 200 mA/cm^2. The simulated EIS data were shown in Table 2. From Table 2, we found that zinc anode electrodeposited at lower current density showed higher corrosion resistance.

3.4 Effect of kinds of suspended species

Different kinds of particles (0.1～0.5 g/L) were suspended in the electrolytic bath. The experiment curves were showed in Fig. 6 and simulated

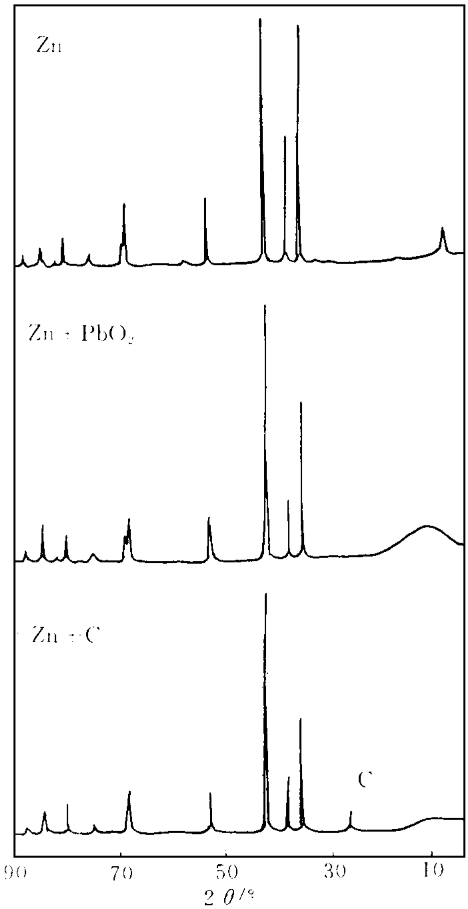

Fig. 3 X-Ray diffraction profiles of zinc powders obtained from a bath with different suspension species

Tab. 2 Electrochemical parametres simulated from EIS plots of composite zinc with C at different current density (mA/cm^2)

Current density	Q_2	N_2	R_2	R_3	Q_3	N_3	R_4	L_7	R_p	R_p'
20	9.88E-5	0.99	0.73	2.84	2.09E-2	0.54	8.74	0.29	3.56	2.53
50	1.90E-4	1.00	0.30	1.25	1.92E-2	0.60	8.10	0.27	1.54	1.30
100	1.66E-3	0.80	0.68	0.84	2.46E-2	0.80	4.91	0.10	1.52	1.16
200	1.83E-4	1.00	0.37	1.34	4.84E-2	0.50	7.29	0.41	1.72	1.39

Q_2, Q_3: (Fcm^{-2}); R_2, R_3, R_4, R_p, R_p': (Ωcm^2); L: (Hcm^2)

Tab. 3 Electrochemical parametres simulated from EIS plots of zinc (powders) with different kinds of suspention species

species	Q_2	N_2	R_2	R_3	Q_3	N_3	R_4	L	R_p	R_p'
——	1.02E-4	1.00	0.34	1.06	5.10E-2	0.54	2.58	0.01	1.40	0.91
C	1.66E-3	0.80	0.68	0.84	2.46E-2	0.80	4.91	0.10	1.52	1.16
TiO_2	2.02E-3	0.69	1.37	3.32	1.21E-2	0.85	6.57	0.56	4.96	2.83
In_2O_3	7.21E-5	0.96	1.62	3.38	1.45E-3	0.78	20.19	1.89	5.00	4.01
SiO_2	1.65E-2	0.60	1.41	3.53	3.54E-3	0.52	8.42	0.12	4.94	3.11
GeO_2	1.07E-4	1.00	0.46	1.46	2.13E-2	0.51	——	——	1.92	——
MoO_3	3.08E-4	0.93	0.71	1.17	1.70E-2	0.65	——	——	1.89	——
SnO_2	4.17E-5	1.00	1.21	3.05	1.14E-3	0.75	6.85	0.26	4.26	2.79
PbO_2	2.61E-4	0.85	1.17	6.57	7.29E-3	0.71	13.84	4.08	7.75	5.00

Q_2, Q_3: (Fcm^{-2}); R_2, R_3, R_4, R_p, R_p': (Ωcm^2); L: (Hcm^2)

EIS data shown in Table 3. The results indicated that suspension of PbO_2, SnO_2, In_2O_3, TiO_2, SiO_2 could obviously increase the value of R_p, suspension of C, GeO_2, MoO_3 only had slight improvement on corrosion resistance of zinc. As we could see, there might have 3 aspects about the effect of suspended species on the electrodeposition process of zinc. 1) suspended species could act as crystal nuclei to change the mophology of zinc deposits; 2) suspended species might absorb charged particles to produce additional electric-field and affect the deposition of zinc.

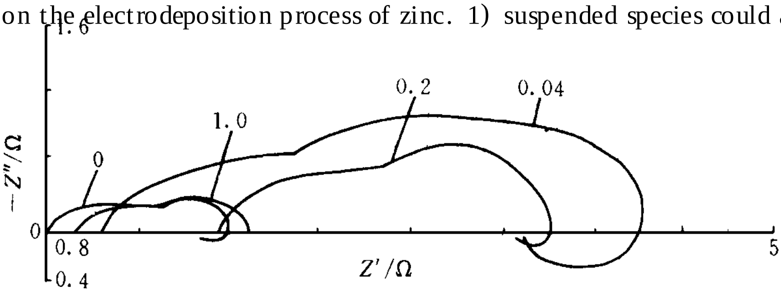

Fig. 4 Nyquist plots for zinc powders with different amount of C in 5 mol/L KOH

3) suspended species might codeposit with zinc , As the deposition potentials of PbO_2 , SnO_2 and In_2O_3 were near to that of zinc , it has the possibility for the formation of zinc alloy powders. The introduction of Pb , Sn or In in zinc would greatly improve the corrosion protection of zinc anode owing to the high overpotential of hydrogen on them. In addition , they could also act as crystal nuclei[9]. In the case of TiO_2 , SiO_2 , C , GeO_2 , MoO_3 , their influence may take place in the manner of 2) and/ or 3) .

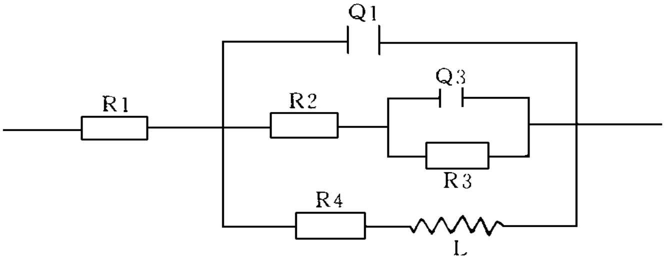

Fig. 5　Equivalent circuit for simulating EIS plots

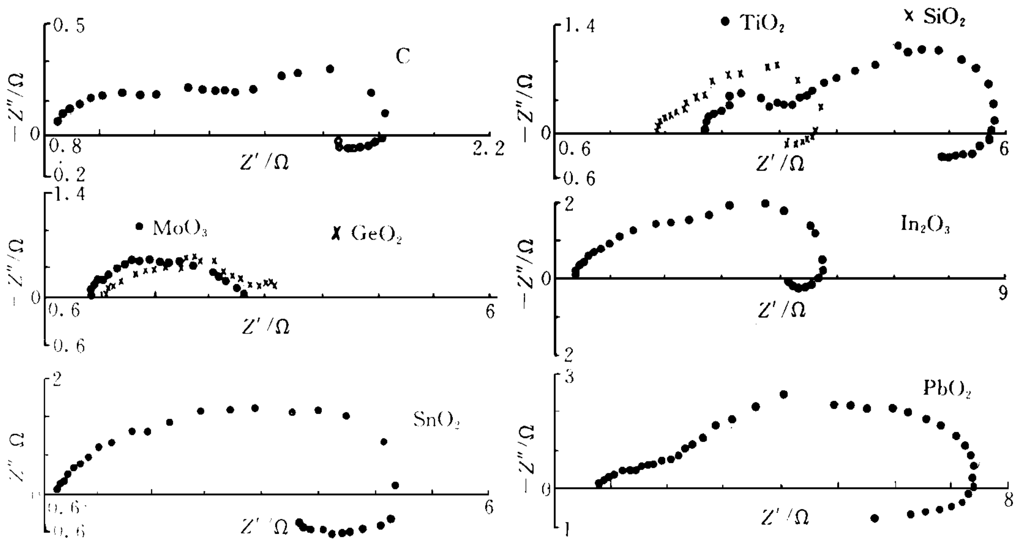

Fig. 6　Nyquist plost of zinc powders with suspension of different kinds of species

3.5　Fractal theory on the corrosion behavior of zinc

When zinc powder was used for anodes in many batteries , the surface of zinc anode is porous and rough and therefore fractal. In recent years , fractal theory has been introduced into the field of electrochemistry such as the electrodeposition of metal , the redox behaviors of electrode and corrosion properties of materials etc. [10,11]. The fractal dimension (Df) of an electrode surface can be determined by the measurement of impedance spectroscopy[12].

In fractal theory , if an electrode is a blocking electrode or ideally polarized electrode , its impedance Z can be represented as:

$$Z = K(j\omega)^{-\alpha} \tag{1}$$

where α is CPE exponent ($0 < \alpha < 1$) , ω is the angular frequency applied , $j = \sqrt{-1}$, and K is a constant.

Another form of equation(1) can be rewritten as:

$$\log|Z| = C - \alpha \log f \quad (2)$$

here C is a constant, and f is frequency. A plot of $\log|Z|$ vs $\log f$ gives a straight line whose slope can be used to obtain the value of α, this can be easily carried out with the help of Bode plot. With Sirepinski Carpets model, the relationship between α and Df exists the following equation(3):

$$\alpha = 3 - Df \quad (3)$$

Based upon the equation (2) and (3), the effects of the amount and kinds of suspension species on Df were shown in Table 4 and Table 5. From Table 4, it was found that higher Df gave rise to lower R_p. As we could see that the value of Df revealed the disorder of an electrode surface, higher Df i.e. higher disorder resulted in higher activities. So the zinc powder with lower Df should have high corrosion resistance. This conclusion can be verified by the results of SEM. The same rules can also be found in Table 5, especially in the case of PbO_2, SnO_2, and In_2O_3, their Df values were much lower than other's, which revealed that suface status of zinc electrode with suspention of PbO_2, SnO_2 or In_2O_3 was greatly modified. Of course, as the fractal theory had not been developed too perfectly, its application in some fields is worthy of disputing.

Tab. 4 Fractal dimensions of composite zinc with suspension of different amount of C(g/L)

amount	0	0.04	0.2	0.4	1.0	1.6
R_p	1.40	4.12	2.19	1.63	1.51	1.29
Df	2.904	2.817	2.854	2.875	2.876	2.896

Tab. 5 Fractal dimensions of zinc(powders) with different kinds of suspension species

	——	C	TiO_2	SiO_2	GeO_2	MoO_3	In_2O_3	SnO_2	PbO_2
R_p	1.40	1.52	4.96	4.94	1.92	1.89	5.00	4.26	7.75
Df	2.90	2.88	2.82	2.83	2.83	2.83	2.68	2.64	2.68

4 Conclusions

From the experiment results, it may be concluded that suspended electrodeposition method is an available way to obtain nondendric deposits of composite zinc with improved corrosion behavior. The result of SEM has revealed that the morphology of zinc can be affected according to the kinds of suspended species. The results of EIS measurements indicated that zinc deposits with better corrosion resistance could be electrodeposited at suitable current density and with the existence of certain suspended species.

Acknowledgements

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References

1 J P 02 ,270 ,265(1990) , Alkaline zinc batteries containing corrosion inhibitors

2 Kordesch. Batteries. Vol. 1 , chapter 3 , 1980

3 Feng S B. A sutdy of electrolytic technology for corrosion-resistant zinc-alloy powder. Dianchi , 1993 , 23 : 55

4 Jean St-pirrer , Dominique Pirow. Electrowinning of zinc powder from alkaline bath. J. Appl. Electrochem. , 1986 , 16 : 447

5 Shudong , Xia Xi. Preparation of electrolytic MnO_2 from suspended bath. Master Thesis , 1992

6 Fautrat S , Mills P. Electrochemical deposition with a forced fluid flow inducing a transition from dendritic to disordered ramified morphologies. Phys. Rev. 1996 , 53(E) : 4 990

7 Jaksic M M , Komnenic V P. Hydrodynamic effects of hydrophilitic alconox surfacant on the macromorphology of electrodeposited zinc and flow visualization. J. Electroanal. Chem. , 1995 , 397 : 127

8 You J K, Chem S P and Lin Z G. Studies on porous zinc electrodes without Hg additives for secondary alkaline batteries. Xiamen DaXue XueBao , 1989 , 28 : 44

9 Mansfield F and Gilman S. The effect of lead ion on the dissolution and deposition characteristics of a zinc single crystal in 6 N KOH. J. Electrochem. Soc. , 1970 , 117 : 588 & The effect of tin and tetraethylammonium ions on the characteristics of zinc deposition on a zinc crystal in aqueous KOH. J. Electrochem. Soc. , 1970 , 117 : 1 158

10 Sagues F and Lilopeztomas et al. Disordered grown systems , generation and fractal analysis on electrodeposition , Phys. Rev. Lett. , 1994 , 72 , 3 848

11 Liu R Q , Zhang X G and Xi Xia. Study on the CPE behavior of zinc powder. Dian Yuan Jishu , 1996 , 6 :1

12 Delevie R. The influence of surface roughness of solid electrodes on the electrochemical measurements. Electrochim. Acta , 1965 , 10 : 113

13 Sapaval B , Chzulciel J N , Peyriere J. Electrocal response of fractal and porous interface. Phys. Rev. A , 1988 , 38 , 5 867

悬浮粒子对电沉积 Zn 粉缓蚀性能的影响

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摘要　在 $ZnCl_2$ 镀槽中悬浮一定量的不溶性粒子,如石墨, PbO_2 , SnO_2 , TiO_2 , SiO_2 等,电沉积制备 Zn 粉,并对其结构、形貌及腐蚀行为进行分析. SEM 的结果表明使用悬浮法可阻止 Zn 枝晶生长. 悬浮 PbO_2 , SnO_2 , TiO_2 , SiO_2 或 In_2O_3 等能明显地提高 Zn 粉在 5 mol/L KOH 溶液中的缓蚀能力,此外,文中还应用分形理论对结果作了进一步的讨论.

关键词　电沉积, Zn 粉, 悬浮, 微观结构, 缓蚀