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ORIGINAL PAPER

Effects of 1-butyl-3-methylimidazolium hydrogen sulfate-[BMIM]HSO_4 on zinc electrodeposition from acidic sulfate electrolyte

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Abstract A comparative study of the effect of 1-butyl-3-methylimidazolium hydrogen sulfate-[BMIM]HSO_4 and gelatine on current efficiency (CE), power consumption (PC), deposit morphology, and polarization behaviour of the cathode during electrodeposition of zinc from acidic sulphate solutions were investigated. Compared with the traditional industrial additive, gelatine, the addition of [BMIM]HSO_4 was found to increase current efficiency, reduce power consumption, and improve the surface morphology. Maximum CE and minimum PC were obtained at the addition dosage of 5 mg dm^{-3}. Meanwhile, simultaneous addition of the two additives induced a blocking effect of the zinc reduction and led to more leveled and fine-grained cathodic deposits. Moreover, cyclic voltammetry results and kinetic parameters such as Tafel slope, transfer coefficient, and exchange current density obtained from Tafel plots led to the conclusion that both additives have a pronounced inhibiting effect on Zn^{2+} electroreduction. The data obtained from X-ray diffractogram revealed that the presence of additives did not change the structure of the electrodeposited zinc but affected the crystallographic orientation of the crystal planes.

Keywords Additives · Zinc · Deposit morphology · Crystal orientation · Ionic liquids

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1 Introduction

More than 80% of the world's primary zinc is produced by roast-leach-electrowin processes. Sulfide mineral concentrates are oxidized to oxides during high temperature roasting in air. The metal oxide product is then leached with aqueous sulfuric acid. Leaching results in the formation of zinc sulfate in the aqueous sulfuric acid and the metal is then produced by electrodeposition [1]. However, electrodeposition of zinc is extremely sensitive to the presence of certain metallic impurities [2–5] in the electrolyte. Although high purity zinc metal can be electrodeposited from ultrapure zinc sulphate solutions, rigorous electrolyte purification is economically non viable.

To counteract the harmful effects of these metallic impurities, additives like glue [6–8] and gum arabic [9] are most commonly used, however, the search for better additives is continuing. For example, 2-butyne-1, 4-diol [10], nonylphenoloxylethelene [11] and a combination of nonylphenol-polyethylene glycol, dinaphthylamine-4,4′-disulphuric acid and polyethelene glycol [12, 13] have been reported to be superior to glue or gum arabic. In addition, 2-picoline and 4-ethylpyridine [14, 15], sodium lauryl sulphate [16], triethylbenzylammonium chloride, and cetyltrimethylammonium bromide [17, 18], and perfluorinated carboxylic acids [19] as alternatives to glue or gum arabic to improve the electrodeposition characteristics of zinc from acidic sulphate electrolytes have been investigated.

Ionic liquids (iLs) as a kind of novel green solvents with many attractive properties, such as chemical and thermal stability, non flammability, very low or negligible vapour pressure, high ionic conductivity, and a wide electrochemical potential window [20, 21], have been widely investigated for a variety of applications [22–28]. Currently, scientists are interested in the applications of ionic liquids as additives; reports on ionic liquids used as lubricant additives [29, 30], organic synthesis and catalytic reactions [31, 32], mobile phase additives in liquid chromatography [33], the effect in the detection of paraoxon [34], etc. In particular, the most extensively studied iLs is based upon the imidazolium cation.

The present study investigates the effects of 1-butyl-3-methylimidazolium hydrogen sulfate-[BMIM]HSO_4 on the morphology of cathodic deposits and evaluates the kinetic parameters of the cathodic process in presence of this additive. The effect of [BMIM]HSO_4 on the kinetics and mechanism of the cathodic process as well as upon the quality of zinc deposits were compared with those exerted by gelatine which is used as levelling additive [35] in zinc electrodeposition from acidic sulphate solution.

2 Experimental details

2.1 Apparatus and materials

Small-scale galvanostatic electrolysis experiment was performed in a 250 cm^3 plexiglass cell. A pure aluminum sheet (>99.95%) and two parallel Pb–Ag (Ag, 1%) plates were used as the cathode and anode, respectively. The interelectrode distance was 2.5 cm. Zinc was deposited on both sides of the cathode onto a total area of 4.5 cm^2.

Zinc electrolyte was prepared by dissolving AnalaR zinc sulfate in doubly distilled water and purified by adding 2 g dm^{-3} zinc dust, heating to boiling point with stirring for about 30 min and then filtering. Then analytical grade H_2SO_4 was added in the purified neutral zinc sulfate solution, to obtain the electrolytic solution contained 55 g dm^{-3} zinc and 150 g dm^{-3} H_2SO_4. Reagent grade gelatine was obtained from Chemical Reagent Co., Shanghai, China. The 1-butyl-3-methylimidazolium hydrogen sulfate-[BMIM]HSO_4 was laboratory synthesis and the specific synthetic method was similar to those described previously [36]. The synthetic products were characterized by NMR (Bruker Avance DPX-300) and IR (Bio-Rad FTS-40, sample dispersed between KBr plate), and the corresponding spectral characteristics were described as following.

2.1.1 1-Butyl-3-methylimidazolium chlorides-BMIC

The H NMR spectrum for BMIC (300 MHz; $CDCl_3$; Me_4Si) consists of the following peaks: δ_H 10.0756 (1H, m, Im), 7.2975 (1H, m, Im), 7.0721 (1H, m, Im), 3.9256 (2H, s, NCH_2–), 3.3106 (1H, s, NMe), 1.9642 (2H, m, NCH_2CH_2–), 1.4659 (2H, m, $NCH_2CH_2CH_2$–), 0.9496 (3H, m, NBu); ν_{max}(film)/cm^{-1} 3,139–3,082, 2,959.9, 2,938.6, 2,873.1, 1,570.1–1,464.8, 1,423–1,382, 1,170, 752.9.

2.1.2 1-Butyl-3-methylimidazolium hydrogen sulfate-[BMIM]HSO_4

Analysis of [BMIM]HSO_4 by H NMR (300 MHz; $CDCl_3$; Me_4Si) produced a spectrum similar to that for BMIC, although it has another a singlet at δ 3.1937 (1H, s, HSO_4); ν_{max}(film)/cm^{-1} 3,141.8, 3,066.4, 2,960.3, 2,936.4, 2,873.2, 1,571.9, 1,465.3, 1,171.9, 1,090.3.

2.2 Electrolysis and electrochemical measurements

All electrolysis and electrochemical measurements were carried out by using a CHI760C electrochemical workstation from Shanghai CH Instruments Company in China.

Chronopotentiometry was utilized to observe the effect of electrolyte additives on the zinc electrowinning. All the electrowinning experiments were conducted for 2 h at a constant current density of 400 A m^{-2} and at 40 ± 1 °C. After electrolysis, the cathode was removed from the cell and washed thoroughly with distilled water and dried. The current efficiency was calculated by weight according to Faraday's law.

Electrochemical studies were based on the analysis of cyclic voltammetric measurements and potentiodynamic polarization texts. A conventional three-electrode cell was used for these experiments. Cyclic voltammetric experiments were carried out at 30 °C under atmospheric condition and scanned at a constant scan rate of 20 mVs^{-1} from the initial potential of-0.70 V to the final potential of -1.30 V. A graphite rod was used as counter, a saturated calomel (SCE) as the reference electrode and a pure aluminum (>99.95%) sheet (0.3 mm thick) as working electrode. Every sheet was sealed with epoxy resin, with the remaining portion as the efficient working area (0.28 cm^2). The potentiodynamic polarization studies were carried out, after the cyclic voltametric tests, the potential was scanned from ca.-1.05 V to-1.30 V at a constant scan rate of 5 mVs^{-1} at 30 °C under atmospheric condition. All potentials were recorded with respect to the saturated calomel electrode (SCE). Before each experiment, the aluminum sheet electrode was polished successively with fine grade emery papers, degreased with anhydrous alcohol in an ultrasonic bath for 10 min, washed with doubly distilled water and finally dried.

2.3 Deposit examination

The surface morphology of the deposits was examined by scanning electron microscopy (SEM) using a Tescan VEGA II XMH microscope. The preferential orientation of the crystals was determined by using a Rigaku D/max 2200 X-ray diffractometer comparing with ASTM standard zinc powder.

3 Results and discussion

3.1 Current efficiency and power consumption

The effects of [BMIM]HSO$_4$ and gelatine, in the concentration range of 1–50 mg dm^{-3} in the acidic sulphate bath on current efficiency (CE) and power consumption (PC) of zinc electrodeposition were studied. The results are listed in Table 1. As shown in this table, the current efficiency increases with the initial addition of additives, but at higher concentrations the current efficiency drops. This increase can be attributed to the suppression of hydrogen evolution during zinc electrodeposition by blocking the active sites through cathodic adsorption of additives [19]. For [BMIM]HSO$_4$, the maximum in CE (92.7%) occurs at 5 mg dm^{-3}, whereas for gelatine the maximum in CE (89.5%) occurs at around 1 mg dm^{-3}. The combined addition of 5 mg dm^{-3} [BMIM]HSO$_4$ and 1 mg dm^{-3} gelatine increases the CE by 2.5% in comparison to additive-free solution. Moreover, it can be seen from Fig. 1 that CE drops off much more rapidly at high concentrations of gelatine than [BMIM]HSO$_4$, at 50 mg dm^{-3} of the additive the CE is only 81.6% for gelatine as compared to 87.8% for [BMIM]HSO$_4$. Such decreases in current efficiencies on increasing additive concentrations have also been observed by other workers [14–19] and are generally attributed to the surface coverage of the cathode by a strongly adsorbed additive layer with an excess addition of additives, which decreases the zinc deposition rate and inhibits the electroreduction of zinc.

The power consumption in the absence and in presence of additives in the electrolyte during the electrodeposition of zinc is also given in Table 1. As can be seen, with the addition of [BMIM]HSO$_4$, the PC decreases at the initial addition, a maximum reduction in PC of ~142 kWht^{-1} is obtained at an additive concentration of 5 mg dm^{-3}. With increasing the concentration up to 50 mg dm^{-3}, a PC ~54 kWht^{-1} more is needed for the electrodeposition process. The similar law can be found in the addition of gelatine where the maximum reduction in PC is ~52 kWht^{-1} at an additive concentration of 1 mg dm^{-3} and further reduction in PC of 56 kWht^{-1} is obtained if 5 mg dm^{-3} [BMIM]HSO$_4$ is also present in the solution.

Table 1 Effect of additives on current efficiency during zinc electrodeposition

Additives/ mg dm^{-3}	Current efficiency/%	Cell voltage/V	Power consumption/kWht^{-1}
Blank	89.3	2.89	2,655
[BMIM]HSO$_4$			
1	90.5	2.78	2,520
2	91.6	2.84	2,543
5	92.7	2.84	2,513
10	91.8	2.87	2,564
50	87.8	2.90	2,709
Gelatine			
1	89.5	2.84	2,603
2	88.8	2.85	2,633
5	87.4	2.87	2,694
10	86.1	2.92	2,782
50	81.6	2.92	2,935
Combined[a]	91.8	2.85	2,547

[a] Combined addition of 5 mg dm^{-3} [BMIM]HSO$_4$ and 1 mg dm^{-3} gelatine

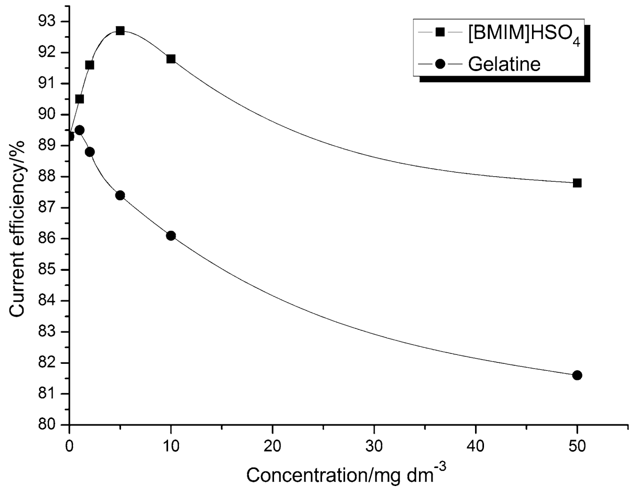

Fig. 1 Effect of additives on current efficiency during zinc electrowinning

3.2 Polarization studies

The effect of various additives alone and the combined effect on the electroreduction of Zn^{2+} ion on aluminum electrode was investigated cyclic voltammetrically (Figs. 2–4). The voltammograms were initiated at point 'A' (−0.70 V vs. SCE, Fig. 2), scanned in the negative direction and reversed at −1.30 V in the positive direction. No significant current is observed until the potential reaches point 'B', corresponding to the reduction of Zn^{2+} ion, then the current increased sharply to point 'C', where it was reversed. This resulted in a decrease in current which subsequently reached zero at the crossover potential, 'D' and the current then became anodic corresponding to the dissolution of the deposited zinc previously formed. The potential difference between the electroreduction potential of zinc ion at 'B' and the crossover potential at 'D' is a measure of nucleation overpotential (NOP) for zinc deposition on an aluminum substrate. It is clear that the addition of additives increased the 'NOP' value (Table 2) substantially, along with the reduction of cathodic process area, denoting an inhibition of the electrocrystallization. This is generally attributed to the surface coverage of the cathode

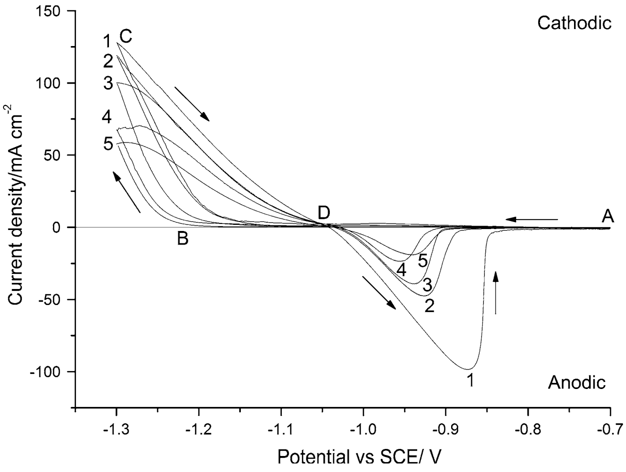

Fig. 2 Cyclic voltammograms of acidic zinc sulphate solutions in the presence of [BMIM]HSO$_4$. (1) Blank, (2) [BMIM]HSO$_4$—1 mg dm^{-3}, (3) [BMIM]HSO$_4$—2 mg dm^{-3}, (4) [BMIM]HSO$_4$—5 mg dm^{-3}, (5) [BMIM]HSO$_4$—10 mg dm^{-3}

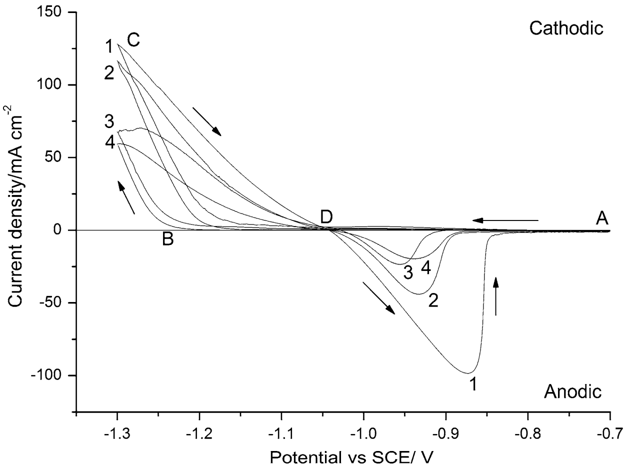

Fig. 4 Cyclic voltammograms of acidic zinc sulphate solutions in the presence of different additives. (1)Blank, (2) gelatine—1 mg dm^{-3}, (3) [BMIM]HSO$_4$—5 mg dm^{-3}, (4) [2] + [3]

by a strongly adsorbed additive layer. Such a layer increases the interfacial viscosity and decreases the mass transfer. At high additive concentration, with the enhancing of the blocking effect on the active sites, a higher driving force for zinc ion reduction is required [19]. For example, addition of 2 mg dm^{-3} of [BMIM]HSO$_4$ increases the NOP from 112 to 123 mV. At 5 mg dm^{-3} [BMIM]HSO$_4$ the NOP value becomes 131 mV. Gelatine is found to be a stronger polariser than [BMIM]HSO$_4$, by adding of 2 mg dm^{-3} increases the NOP from 112 to 127 mV, and further increases to 154 mV at 5 mg dm^{-3}.

The cathodic polarization curves for zinc eletrodeposition on aluminum electrode from acidic zinc sulphate solutions in the absence and in presence of additives were presented in Figs. 5–7. From the cathodic polarization curves for zinc deposition, Tafel slopes were determined and transfer coefficients were calculated using the following equations [18]:

$$\eta = a + b \log I$$

$$b = RT/\alpha nF$$

where η is the overpotential (V), b is the Tafel slope (mV decade^{-1}), α is the transfer coefficient and I the current density (Ma cm^{-2}). Exchange current densities, i_0, for zinc deposition was found by extrapolating the Tafel lines to zero overpotential. The values of b, α, and i_0 are given in Table 3 as functions of additive concentrations. It is found that the cathodic Tafel slope is varying from 120 to 135 mV per decade. Small changes in the Tafel slopes indicate that the charge transfer reaction is not controlled

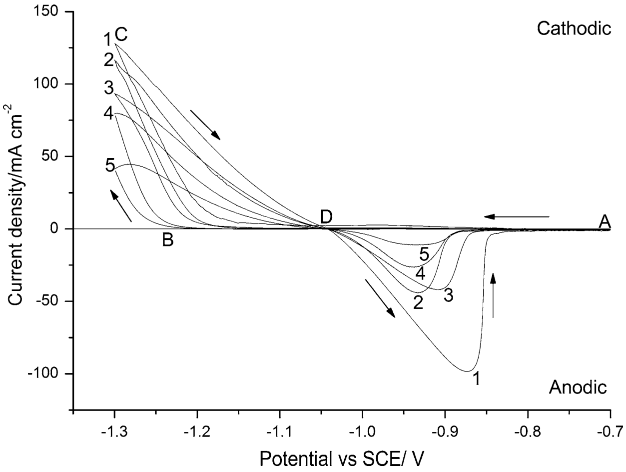

Fig. 3 Cyclic voltammograms of acidic zinc sulphate solutions in the presence of gelatine. (1) Blank, (2) gelatine—1 mg dm^{-3}, (3) gelatine—2 mg dm^{-3}, (4) gelatine—5 mg dm^{-3}, (5) gelatine—10 mg dm^{-3}

Table 2 Effect of additives on nucleation overpotential (NOP) during zinc electrodeposition from acidic sulphate solution

Additives/mg dm^{-3}		NOP/mV
[BMIM]HSO$_4$	Gelatine	
0	0	112
1	0	115
2	0	123
5	0	131
10	0	160
0	1	119
0	2	127
0	5	154
0	10	173
5	1	158

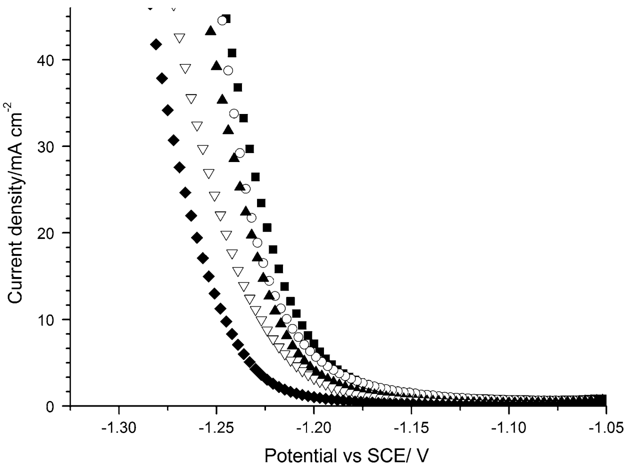

Fig. 5 Effect of [BMIM]HSO$_4$ on the cathodic polarization during zinc deposition on aluminum with different concentrations: (■) blank, (○) 1, (▲) 2, (▽) 5, (◆) 10 mg dm^{-3}

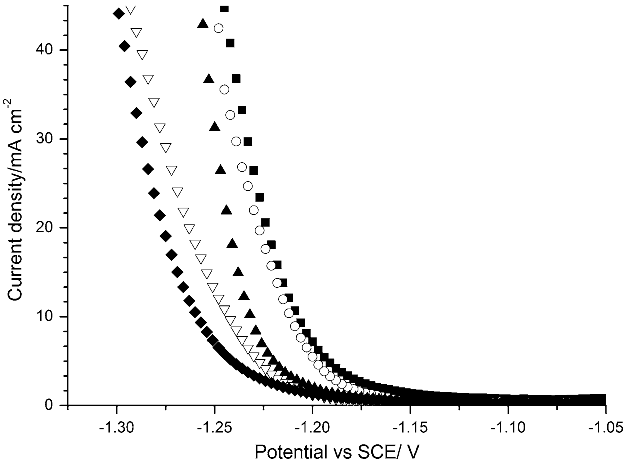

Fig. 6 Effect of gelatine on the cathodic polarization during zinc deposition on aluminum with different concentrations: (■) blank, (○) 1, (▲) 2, (▽) 5, (◆) 10 mg dm^{-3}

by the addition of [BMIM]HSO$_4$ or gelatine. The obtained results also show that the presence of additives have an inhibiting effect on the kinetics of the Zn^{2+} reduction process, indicate by the decrease of the exchange current density. The inhibition enhancing due to increasing of additive concentration could be related to the strong adsorption of additives on the cathodic electrode surface. This adsorption results the blocking of the active nucleation sites of the cathode surface.

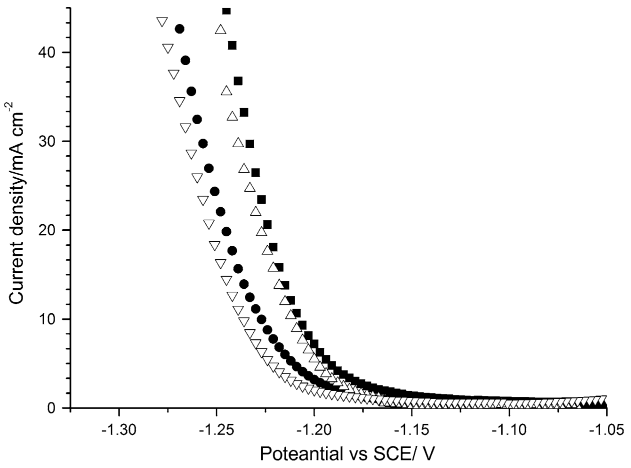

Fig. 7 Effect of different additives on the cathodic polarization during zinc deposition on aluminum. (■) blank, (●) [BMIM]HSO$_4$—5 mg dm^{-3}, (△) gelatine—1 mg dm^{-3}, (▽) [BMIM]HSO$_4$—5 mg dm^{-3}+gelatine—1 mg dm^{-3}

3.3 Effect of additives on deposit morphology and orientation

To understand the effect of the various additives on the electrodeposited zinc morphology and orientation, the zinc deposits were examined using scanning electron microscope and X-ray diffraction to determine the surface morphology and crystallographic orientations. Typical SEM photomicrographs are shown in Fig. 8a–d and the crystallographic orientations of zinc deposits in the absence and in presence of different additives are given in Table 4.

As it can be seen from Fig. 8b–d, the investigated additives significantly changed the morphology of the zinc deposits as compared with those obtained from solutions without additives (Fig. 8a). The zinc deposited from additive-free solution is bright but not smooth. The addition of [BMIM]HSO$_4$/gealtine improved the quality of deposits at low concentrations. Both additives are efficient as leveling agents. Moreover, simultaneous addition of the

Table 3 Effects of additives on the kinetic parameters during zinc electrodeposition from acidic sulphate solution

Additives/ mg dm^{-3}	Tafel slope/mV per decade	Transfer coefficient, α_c	Exchange current density, i_0/mA cm^{-2} ($\times 10^{-2}$)
Blank	120	0.49	6.5
[BMIM]HSO$_4$			
1	121	0.49	5.8
2	122	0.48	5.4
5	127	0.46	4.8
10	131	0.45	4.3
Gelatine			
1	135	0.44	4.7
2	121	0.49	4.5
5	126	0.47	4.4
10	120	0.49	4.2
Combined[a]	125	0.48	5.1

[a] Combined addition of 5 mg dm^{-3} [BMIM]HSO$_4$ and 1 mg dm^{-3} gelatine

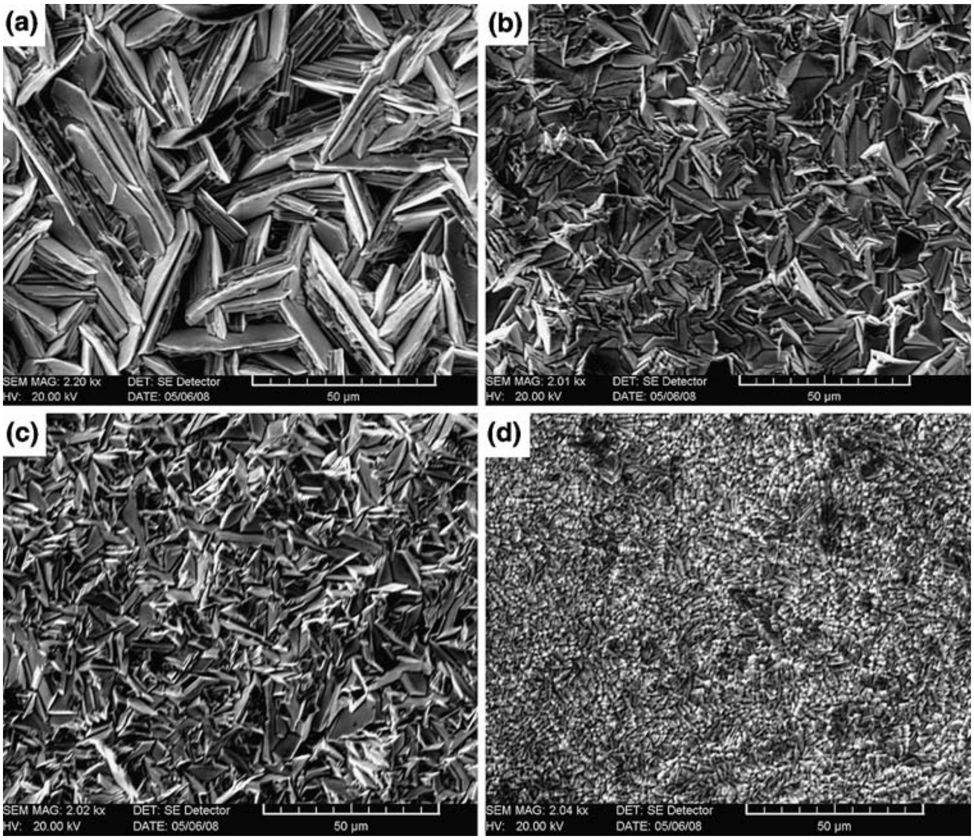

Fig. 8 Scanning electron micrographs of zinc deposits. **a** Blank, **b** [BMIM]HSO_4-5 mg dm^{-3}, **c** gelatine-1 mg dm^{-3}, **d** [BMIM]HSO_4-5 mg dm^{-3}+gelatine-1 mg dm^{-3}

Table 4 Crystallographic orientations of zinc deposits in the absence and in presence of different additives

Additives/mg dm^{-3}		Crystallographic orientations (*hkl*) and peak intensity ratio (I/I_{max})/%							
[BMIM]HSO_4	Gelatine	(002)	(100)	(101)	(102)	(103)	(110)	(112)	(201)
0	0	1	13	100	4	1	2	11	20
5	0	–	4	100	2	–	2	10	9
0	1	–	1	100	4	1	–	1	3
5	1	1	2	100	10	20	7	3	3

two additives leads to more leveled and fine-grained cathodic deposits, showing a synergetic effect between the two additives. This can be attributable to the coadsorption of the two additives on the cathodic electrode surface.

The analysis of the zinc deposits by X-ray diffraction showed the deposit obtained from addition-free solution consisted of hexagonal platelets of moderate size with (101) (201) (100) (112) crystal orientations (Fig. 8a). Addition of 5 mg dm^{-3} [BMIM]HSO_4 reduced the growth of basal (100) and pyramidal (201) planes along with a reduction in platelet size (Fig. 8b). Gelatine affects the preferred crystallographic orientations similar to [BMIM]HSO_4. The addition of 1 mg dm^{-3} gelatine markedly reduced the growth of (100) (112) (201) planes and decreased the platelet size (Fig. 8c) producing a smooth and compact deposit. Addition of 5 mg dm^{-3} [BMIM]HSO_4 to the solution containing 1 mg dm^{-3} gelatine changed the preferred crystallographic orientations from (101) (201) (100) (112) to (101) (103) (102) (110) with a further decrease in the size of the crystallites (Fig. 8d). In all cases, the grain refinement showed clearly that an inhibition of the electrocrystallization process took place. The action of [BMIM]HSO_4, gelatine and also their mixture is one of inhibition of the crystal growth process, so that a relative enhancement of the nucleation process is induced [37]. This results in a finer grained deposit.

4 Conclusions

The comparative study of the effect of [BMIM]HSO_4, gelatine and combined addition of the two additives above on zinc electrodeposition from acidic sulphate solutions has been investigated and the conclusions drawn from the results are summarized as follows:

(i) [BMIM]HSO_4 behaves similarly to gelatine and is a better levelling agent than gelatine. Thus the addition of [BMIM]HSO_4 increases current efficiency, reduces power consumption, and produces smooth and compact zinc deposits similar to that achieved with gelatine.

(ii) Although gelatine is a stronger polariser than [BMIM]HSO_4, it is not as effective as [BMIM]HSO_4 in increasing current efficiency and reducing power consumption.

(iii) [BMIM]HSO_4, gelatine and their mixture affect the cathodic polarization of zinc similarly. All are found to have an inhibiting effect on the kinetics of the Zn^{2+} reduction process.

(iv) The combined addition of [BMIM]HSO_4 and gelatine result in smoother, more leveled and fine-grained cathodic deposits compared to [BMIM]HSO_4 or gelatine.

(v) The presences of additives do not change the structure of the electrodeposited zinc but strong influence on the preferred crystallographic orientations of the crystal planes.

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