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Effect of Addition of Ethylene Glycol on Electrodeposition of Cobalt in 1-Ethyl-3-methylimidazolium Bromide-Cobalt Bromide Molten Salt

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Activities of the cobalt ionic species in the 1-ethyl-3-methylimidazolium bromide (EMIB)-$CoBr_2$-ethylene glycol (EG) baths were calculated by the computer simulation method fitting the measured and calculated rest potential of cobalt and the relationships between the calculated activities and the results of the actual cobalt electrodeposits were considered. Smooth and metallic coloured cobalt deposits with 100 % of cathodic current efficiencies even at high current densities of 200-300 Am^{-2} were obtained from baths in which the activities of $CoBr_4^{2-}$ were dominant compared with those of $CoBr_3^-$ and Br^-. This suggests that $CoBr_4^{2-}$ is the effective cobalt ionic species for cobalt electrodeposition. At compositions where the activities of $CoBr_3^-$ were relatively high, the dendritic deposits were obtained at the edge of the substrate. The reduction of $CoBr_3^-$ causes the dendritic deposits. The appropriate amount of ethylene glycol addition to EMIB-$CoBr_2$ bath promotes the formation of $CoBr_4^{2-}$ that forms the smooth cobalt deposits.

Keywords: Cobalt, Electrodeposition, $CoBr_2$, Cathodic current efficiency, Dendritic deposits.

INTRODUCTION

The electrodeposition of Co and Co-Mg alloy in the baths using 1-ethyl-3-methylimidazolium bromide (EMIB) have been studied [1-7]. In order to obtain Co-Mg alloy, the electrodeposition should be conducted in non-aqueous solution because magnesium can't be obtained from aqueous solution. For that purpose, the electrodeposition of cobalt has been studied in low temperature EMIB organic molten salt as a previous step to the study of Co-Mg alloy electrodeposition. In the previous works, the smooth and metallic coloured cobalt deposits were obtained with high cathodic current efficiencies even at high current densities at 393 K from the ethylene glycol (EG) added EMIB-$CoBr_2$ baths [6,7]. The effect of ethylene glycol addition is supposed as follows: ethylene glycol promotes the dissociation of EMIB to the EMI^+ and Br^-, then Br^- is coordinated with $CoBr_2$ and the activity of the cobalt ionic species such as $CoBr_3^-$ and/or $CoBr_4^{2-}$ that are effective species for cobalt electrodeposition increase. Investigation of the ionic species in the bath is important to understand the reduction behaviour of the ions and is of help to preparation of baths. The activities of the ionic species in a number of systems including molten salts and organic ionic liquids have been calculated by the computer simulation method [8-18]. In order to clarify the cobalt ionic species in the EMIB-$CoBr_2$-EG and EMIB-$CoBr_2$ baths, the activities of chemical species were calculated by the computer simulation method. In this paper, the effective cobalt ionic species for cobalt electrodeposition in EMIB-$CoBr_2$-EG baths and the effect of ethylene glycol addition were considered by comparing the results of the computer simulation and the actual cobalt electrodeposits.

EXPERIMENTAL

Preparation of baths: The baths used in this study were prepared from EMIB, $CoBr_2$ and ethylene glycol. Before use, EMIB was dried at 353 K under vacuum using a rotary oil pump for 259.2 ks and $CoBr_2$ was dried for 18 ks at 453 K in air. Ethylene glycol was dehydrated by the molecular sieves. 1-Ethyl-3-methylimidazolium bromide and $CoBr_2$ were weighed, heated to 393 K and dehydrated under vacuum for 86.4 ks. An appropriate amount of ethylene glycol was added to the EMIB-$CoBr_2$ bath and dehydrated under vacuum again to prepare the baths for the cobalt electrodeposition. The water content in this bath was under 10 ppm (measured by a moisture meter, CA-100, Mitsubishi Chemical Corp.). The preparations of baths were conducted in an argon gas filled glove box.

Measurement of the rest potential of cobalt electrode: The reference electrode used for the measurement of cobalt electrode potential was a cobalt wire immersed in a separate fritted glass tube containing the EMIB-$CoBr_2$-EG (45:10:45 mol %) bath. The cobalt plates (purity: 99.99 %, 10 mm × 10 mm, 0.2 mm thickness) were used as a cathode and an anode. The rest potential changes of the cobalt cathode with time in various compositions of the EMIB-$CoBr_2$-EG baths were recorded by HSV-100 (Hokuto Denko Co.). The rest potential of cobalt in the bath was adapted when the potential change with time was within ± 0.001 V.

Electrodeposition of cobalt: Cobalt was electrodeposited from EMIB-$CoBr_2$ baths with and without ethylene glycol using a copper cathode (purity: 99.99 %, 0.2 mm thickness) and a cobalt anode (purity: 99.99 %, 0.2 mm thickness). Electrodeposition was conducted under the constant current densities of 50-300 Am^{-2} at 393 K. The charge passed was 2.5 × 10^5 cm^{-2} of the cathode substrate. The cathodic current efficiency for the cobalt electrodeposition was calculated from the mass gain of the cathode. Cobalt electrodeposits were observed by the naked eye and classified into four types.

RESULTS AND DISCUSSION

Rest potential change of cobalt electrode: Fig. 1 shows the rest potential of cobalt as a function of (i) $CoBr_2$ content and (ii) $CoBr_2$/EMIB ratio measured in (a) EMIB-$CoBr_2$ baths, (b) EMIB-$CoBr_2$-EG (mole ratio of EMIB:EG was 70:30) baths and (c) EMIB-$CoBr_2$-EG (mole ratio of EMIB:EG was 50:50) baths at 393 K. The rest potentials of cobalt shift to the positive with $CoBr_2$ content, especially in the ethylene glycol added baths, they shift rapidly at around the $CoBr_2$/EMIB ratio of 0.5 as shown in Fig. 1(ii-b) and Fig. 1(ii-c). This suggests that the cobalt ionic species and their activities change drastically at that $CoBr_2$ content and ethylene glycol have some influences on the formation of cobalt ionic species. In the previous works, the activity of the cobalt ionic species such as $CoBr_3^-$ or $CoBr_4^{2-}$ that was effective for cobalt electrodeposition increase by the addition of ethylene glycol [6,7]. In order to know the properties of the cobalt ionic species, the rest potentials of cobalt in EMIB-$CoBr_2$ and EMIB-$CoBr_2$-EG baths were calculated theoretically by the computer simulation method to compare with the measured data shown in Fig. 1.

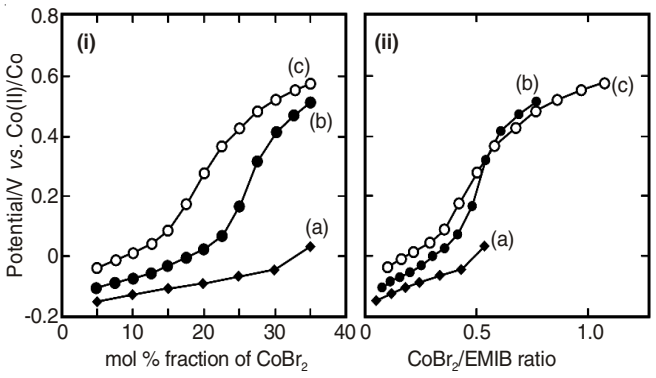

Fig. 1. Rest potential changes of cobalt electrode as a function of (i) $CoBr_2$ content and (ii) $CoBr_2$/EMIB ratio measured in (a) EMIB-$CoBr_2$ baths, (b) EMIB-$CoBr_2$-EG (EMIB:EG = 70:30 mol %) baths and (c) EMIB-$CoBr_2$-EG (EMIB:EG = 50:50 mol %) baths at 393 K

Activity of cobalt ionic species: It is assumed that cobalt ionic species exist as $CoBr_3^-$ and/or $CoBr_4^{2-}$ referring to the works in other bromide or chloride molten salt systems and the coordination of ethylene glycol species with cobalt species does not occur [14,19]. The following three chemical equilibria were postulated to calculate the activities of the species. The one is the dissociation reaction of EMIB to EMI^+ cation and Br^- anion.

$$EMIB = EMI^+ + Br^-, K_0 \quad (1)$$

The others are the formation of cobalt ionic species.

$$CoBr_2 + Br^- = CoBr_3^-, K_1 \quad (2)$$

$$CoBr_3^- + Br^- = CoBr_4^{2-}, K_2 \quad (3)$$

K_0, K_1 and K_2 represent the equilibrium constants of each reaction. To simplify the calculation, the total number of moles of EMIB, $CoBr_2$ and ethylene glycol before preparation of a bath is converted into unity and the number of moles of $CoBr_2$ is set to C_0. Numbers of moles of the chemicals before preparation of the bath are written as follows

$$n(CoBr_2)_{init} = C_0 \quad (4)$$

$$n(EMIB)_{init} = r(1-C_0) \quad (5)$$

$$n(EG)_{init} = (1-C_0)(1-r) \quad (6)$$

r is constant ratio of EMIB in the bath without $CoBr_2$ and defined as

$$r = n(EMIB)_{init}/\{n(EMIB)_{init} + n(EG)_{init}\} \quad (7)$$

After preparation of the bath, *x* moles of $CoBr_3^-$, y moles of $CoBr_4^{2-}$ and z moles of Br^- are formed by the reaction (2), (3) and (1), respectively. The number of moles of each chemical species in the bath can be described as follows:

$$n(CoBr_3^-) = x \quad (8)$$

$$n(CoBr_4^{2-}) = y \quad (9)$$

$$n(EMI^+) = z \quad (10)$$

$$n(Br^-) = z-x-2y \quad (11)$$

$$n(CoBr_2) = C_0-x-y \quad (12)$$

$$n(EMIB) = r(1-C_0)-z \quad (13)$$

$$n(EG) = (1-C_0)(1-r) \quad (14)$$

Thus, the total number of moles, n(total), is given as follows:

$$n(total) = 1-x-2y+z \quad (15)$$

Assuming that the activity is equal to the mole fraction, the activity of each chemical is given by dividing eqns. 8 to 14 by the eqn. 15 and the equilibrium constants of K_0, K_1 and K_2 are described as follows:

$$K_0 = a(EMI^+) \cdot a(Br^-)/a(EMIB) \quad (16)$$
$$= n(EM\ I^+) \cdot n(Br^-)/\{n(EMIB) \cdot n(total)\} \quad (16')$$

$$K_1 = a(CoBr_3^-)/\{a(Br^-) \cdot a(CoBr_2)\} \quad (17)$$
$$= n(CoBr_3^-) \cdot n(total)/\{n(Br^-) \cdot n(CoBr_2)\} \quad (17')$$

$$K_2 = a(CoBr_4^{2-})/\{a(Br^-) \cdot a(CoBr_3^-)\} \quad (18)$$
$$= n(CoBr_4^{2-}) \cdot n(total)/\{n(Br^-) \cdot n(CoBr_3^-)\} \quad (18')$$

The electrode reactions occurred at cobalt electrode in the EMIB-$CoBr_2$-EG and EMIB-$CoBr_2$ baths are considered to be the following reactions.

$$CoBr_3^- + 2e^- = Co + 3Br^- \quad (19)$$

$$CoBr_4^{2-} + 2e^- = Co + 4Br^- \quad (20)$$

The theoretical potential of cobalt electrode for eqn. 19 is given by the Nernst equation:

$$E_{19} = E^0_{19} + (RT/2F)\ln\{a(CoBr_3^-)/a(Br^-)^3\} \quad (21)$$

where E^0_{19} is the standard electrode potential for eqn. 19, R is the gas constant, T is temperature of the bath and F is the Faraday constant. For the reference electrode, which is a cobalt wire immersed in the EMIB-$CoBr_2$-EG (45:10:45 mol %) bath, the theoretical potential of the reference electrode, E_{ref}, is given by:

$$E_{ref} = E^0_{19} + (RT/2F)\ln\{a(CoBr_3^-)^{ref}/a(Br)_{ref}^3\} \quad (22)$$

Assuming that the rest potential of cobalt is equal to the cobalt electrode potential, the theoretical rest potential of cobalt is:

$$E = E_{19}\text{-}E_{ref}$$

$$= (RT/2F)\ln[\{a(CoBr_3^-)/a(Br)^3\}\cdot\{a(Br)_{ref}^3/a(CoBr_3^-)_{ref}\}] \quad (23)$$

The theoretical rest potential of cobalt derived from eqn. 20 in the same way is:

$$E = (RT/2F)\ln[\{a(CoBr_4^{2-})/a(Br)^4\}\cdot\{a(Br)_{ref}^4/a(CoBr_4^{2-})_{ref}\}] \quad (24)$$

Solving eqn. 18 for $a(CoBr_4^{2-})$ and $a(CoBr_4^{2-})_{ref}$ and substituting them into eqn. 24 gives eqn. 23. That is, the theoretical rest potentials of cobalt calculated from either eqns. 19 and 20 are the same.

Substituting appropriate vales for K_0, K_1 and K_2 gives x, y and z for the constant values of C_0 and r determined by the composition of the bath. Using a PC (OS: Linux, programming language: C^{++}), K_0, K_1 and K_2 were changed gradually and the theoretical rest potential of cobalt and the activities of chemicals in the bath were calculated until the difference between the measured and the calculated rest potential of cobalt was within 0.01 V.

The calculated potential of cobalt at 393 K in the EMIB-$CoBr_2$-EG baths (EMIB:EG = 70:30 mol %, r = 0.7) and in the EMIB-$CoBr_2$-EG baths (EMIB:EG = 50:50 mol %, r = 0.5) were well fitted with the measured potential at almost the same equilibrium constants of $K_0 = 2 \times 10^{-2}$, $K_1 = 4 \times 10^4$ and $K_2 = 6 \times 10^3$ as shown in Fig. 2.

The activities of the chemical species in these baths calculated using the equilibrium constants as described above are shown in Figs. 3 and 4. In Fig. 3, the dominant cobalt ionic species below the $CoBr_2$ mole fraction of 0.30 is $CoBr_4^{2-}$. The activity of $CoBr_4^{2-}$ reaches maximum at the $CoBr_2$ mole fraction of 0.25 and then the activity of $CoBr_3^-$ gradually increases. The same trend in the change of the activities of cobalt ionic species is observed in Fig. 4.

Relationship between the ionic species and cobalt electrodeposits: Fig. 5 shows the results of visual observation of the electrodeposits obtained from EMIB-$CoBr_2$-EG baths. These deposits were identified as cobalt by X-ray diffraction analyses. Cobalt electrodeposits were classified into four types;

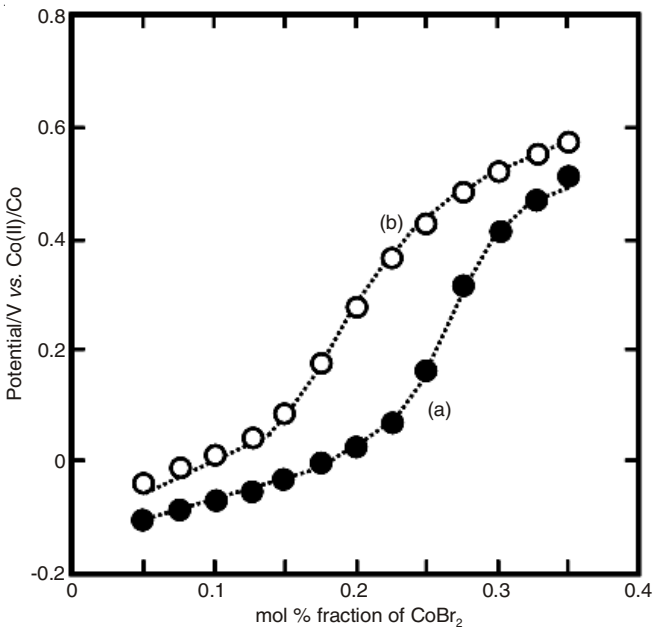

Fig. 2. Calculated (dashed lines) and measured (symbols) rest potential changes of cobalt electrode as a function of $CoBr_2$ mole fraction in (a) EMIB-$CoBr_2$-EG (EMIB:EG = 70:30mol %) baths and (b) EMIB $CoBr_2$-EG (EMIB:EG = 50:50 mol %) baths at 393 K

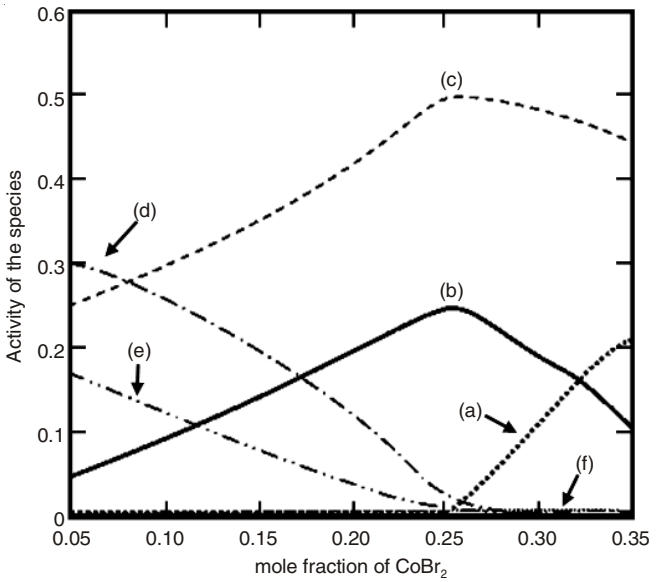

Fig. 3. Activities of chemical species in the EMIB-$CoBr_2$-EG (EMIB:EG = 70:30 mol %) bath. (a) $CoBr_3^-$, (b) $CoBr_4^{2-}$, (c) EMI^+, (d) EMIB, (e) Br^- and (f) $CoBr_2$

(i): Smooth metallic silver-coloured cobalt deposit keeping 100 % current efficiency even at 300 Am^2 (◎), (ii): Smooth metallic silver-coloured cobalt deposit keeping 100 % current efficiency at 200 Am^2 (○), (iii): Smooth metallic silver-coloured cobalt deposit with high current efficiency having dendrites at the edge (▲) and (iv): Smooth cobalt deposit having a grayish tinge with low current efficiency (●). Comparing Figs. 3-5, the following relationships between the cobalt ionic species and the cobalt electrodeposits are found. Smooth metallic silver-coloured cobalt deposits were obtained from the EMIB-$CoBr_2$-EG baths (EMIB:EG = 70:30 mol %, r = 0.7) containing 20~25 mol % $CoBr_2$ and from the EMIB-$CoBr_2$-EG baths (EMIB:EG = 50:50 mol %, r = 0.5) containing

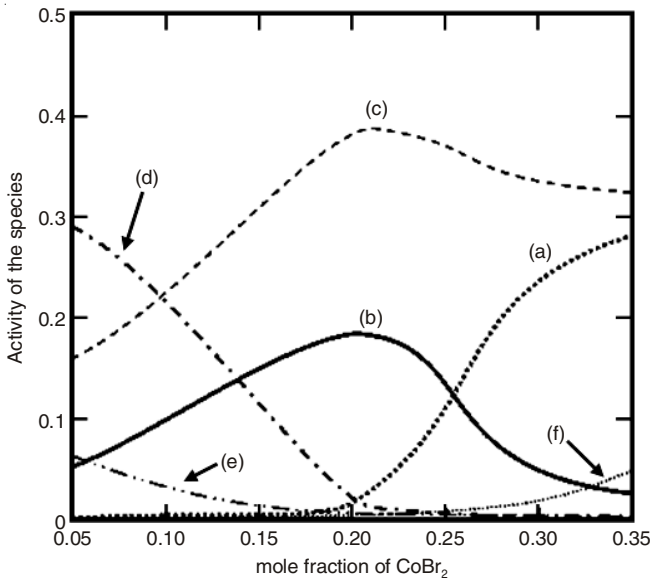

Fig. 4. Activities of chemical species in the EMIB-$CoBr_2$-EG bath (EMIB: EG = 50:50 mol %). (a) $CoBr_3^-$, (b) $CoBr_4^{2-}$, (c) EMI^+, (d) EMIB, (e) Br and (f) $CoBr_2$

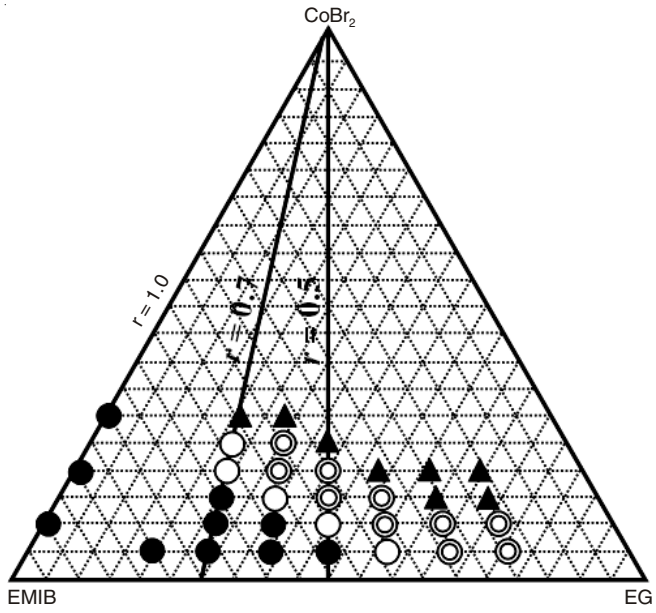

Fig. 5. Results of visual observation and cathodic current efficiency of electrodeposits. ◎: smooth metallic silver-coloured cobalt deposit with 100 % cathodic current efficiency until 300 Am^{-2}; ○: Smooth metallic silver-coloured cobalt deposit with 100 % cathodic current efficiency until 200 Am^{-2}; ▲: Smooth metallic silver-coloured cobalt deposit with high current efficiency having dendrites at the edge; ●: Smooth cobalt deposit having a grayish tinge with low current efficiency

10~25 mol % $CoBr_2$. These regions of $CoBr_2$ compositions coincide with the high $CoBr_4^{2-}$ activity regions in both baths. Therefore, this suggests that metallic silver-coloured Co deposits are formed by the reduction of $CoBr_4^{2-}$ as shown in eqn. 20. However, smooth gray deposits were obtained though the dominant cobalt ionic species was $CoBr_4^{2-}$ in the baths with low $CoBr_2$ content. The reasons for this are that the activities of $CoBr_4^{2-}$ in these $CoBr_2$ compositions are low and the unexpected cobalt ionic species such as $CoBr_6^{4-}$ and/or the multimeric cobalt species for which it's difficult to reduced to cobalt metal are formed because the activities of Br^- are relatively high in those compositions.

The activities of $CoBr_3^-$ increase from the $CoBr_2$ composition where the activities of $CoBr_4^{2-}$ reach maximum. The cobalt electrodeposits obtained from the bath containing $CoBr_3^-$ to some extent have tendency to have dendrites at the edge. This indicates that the reduction of $CoBr_3^-$ as shown in eqn. 19 causes the dendrite. Thus, smooth metallic silver-coloured deposits with high current density having dendrites at the edge as shown in Fig. 5 (▲) were formed by the reduction of $CoBr_4^{2-}$ and $CoBr_3^-$ simultaneously.

Effect of ethylene glycol: The same calculations about the cobalt ionic species in the non-ethylene glycol added baths (EMIB-$CoBr_2$ baths) were conducted. The activities of chemical species in the EMIB-$CoBr_2$ baths are shown in Fig. 6. The calculated potentials of cobalt in the EMIB-$CoBr_2$ bath were well fitted with the measured potentials at the equilibrium constants of $K_0 = 1 \times 10$, $K_1 = 6 \times 10^2$ and $K_2 = 7 \times 10^3$, which are different from the results for ethylene glycol added baths mentioned above. The reason for this is considered that the system about the ionic species in the EMIB-$CoBr_2$ baths is the quite different from that in the EMIB-$CoBr_2$-EG baths. However, in this study, the same analyses were conducted to guess the cobalt ionic species in the EMIB-$CoBr_2$ baths.

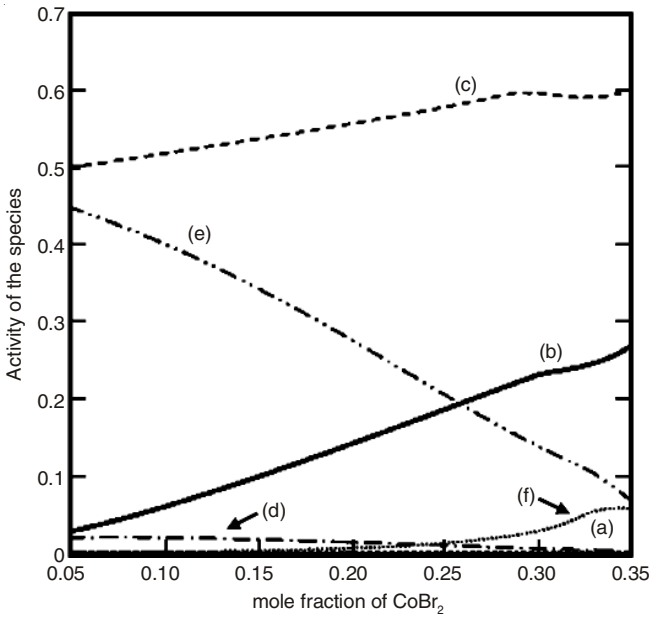

Fig. 6. Activities of chemical species in the EMIB-$CoBr_2$ bath. (a) $CoBr_3^-$, (b) $CoBr_4^{2-}$, (c) EMI^+, (d) EMIB, (e) Br and (f) $CoBr_2$

From Fig. 6, it is obvious that $CoBr_4^{2-}$ is the dominant cobalt ionic species in the EMIB-$CoBr_2$ baths. However, metallic silver-coloured cobalt deposit could not be obtained as shown in Fig. 5. This is due to the same reasons as mentioned before and it is recognized that smooth metallic silver-coloured cobalt deposits are not formed by the reduction of $CoBr_4^{2-}$ in the baths that include much of Br^-. Comparing Fig. 6 with Fig. 3 and 4, the decrease of Br^- is accelerated by the addition of ethylene glycol. Ethylene glycol promotes the coordination of Br^- to Co species and the formation of $CoBr_4^{2-}$ that is effective cobalt ionic species for cobalt electrodeposition and/or $CoBr_3^-$ that is undesirable for smooth cobalt depositions. It is found that the composition of the bath should be controlled to

the region where the activity of $CoBr_4^{2-}$ is high compared with that of $CoBr_3^-$ and Br^- in order to obtain the smooth metallic coloured cobalt deposits.

Conclusions

The activities of chemical species in the EMIB-$CoBr_2$-EG and EMIB-$CoBr_2$ baths were calculated by the computer simulation to consider the effective cobalt ionic species for cobalt electrodeposition and the effect of addition of ethylene glycol. The following conclusions were obtained:

• The effective cobalt ionic species for cobalt electrodeposition in the EMIB-$CoBr_2$-EG bath is $CoBr_4^{2-}$. A smooth metallic silver-coloured cobalt deposit is obtained from the bath in which the activity of $CoBr_4^{2-}$ is high compared with that of $CoBr_3^-$ and Br^-.

• The reduction of $CoBr_3^-$ causes the dendrites at the edge. Smooth metallic silver-coloured deposits with high current density having dendrites at the edge are formed by the reduction of $CoBr_4^{2-}$ and $CoBr_3^-$ simultaneously.

• The addition of ethylene glycol promotes the coordination of Br to Co species and the formation of $CoBr_4^{2-}$ and/or $CoBr_3^-$.

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