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ORIGINAL PAPER

Current efficiency and kinetics of cobalt electrodeposition in acid chloride solutions. Part II: the influence of chloride and sulphate concentrations

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Abstract The influence of cobalt chloride concentration, total chloride concentration and sulphate in the electrolyte on cobalt deposition were studied. The current efficiency increased and the overpotential for electrodeposition of cobalt decreased with increasing cobalt chloride concentration. Only minor changes were observed with addition of sodium chloride to the cobalt chloride solution. Sulphate electrolyte resulted in lower current efficiency and higher overpotential for electrodeposition when compared to a similar cobalt chloride electrolyte.

Keywords Cobalt · Current-efficiency · Electrodeposition · Overpotential

1 Introduction

The background and the motivation for the present work are outlined in the preceding publication [1]. Cobalt is known to form complexes with chloride and with water [2–4]; consequently it was of interest to investigate the influence of addition of sodium chloride to the cobalt chloride electrolyte. In order to adjust the cobalt activity the cobalt chloride concentration was varied. Since electrowinning of cobalt is being carried out in chloride as well as sulphate solutions [5], a comparison of the two processes is warranted. This was done by adding sulphate to the chloride solutions and by conducting electrolysis in pure sulphate solutions.

2 Experimental

The experimental details are described in part I of this work [1], and the standard conditions were the same. To adjust the electrolyte concentration either ultra pure water was added to lower the concentration, or the electrolyte was heated to 80 °C in an open container to increase the concentration by evaporation of water. The concentration was determined by weighing the electrolyte before and after evaporation. The cobalt sulphate electrolyte was produced in the laboratory by anodic dissolution of cobalt metal, supplied form Falconbridge, in sulphuric acid of p.a. quality (Typical compositions of similar metal grades are for example given by [5]). Sulphuric acid and sodium hydroxide were used to adjust the pH in the cobalt sulphate electrolyte.

3 Results and discussion

3.1 Influence of cobalt chloride concentration

The cobalt chloride concentration was varied at four levels, while the HCl(aq) concentration was kept constant at 0.035 M. Because the cobalt chloride concentration had an effect on the activity coefficient for H^+(aq), the pH in these experiments was not constant. The main reason for this is that the water activity decreases with increasing salt concentration. The reversible potentials in Table 1 were calculated from activity data given by Gmelin [6].

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Table 1 Tafel parameters for the deposition of cobalt at different cobalt chloride concentrations

$c_{\mathrm{CoCl_2}}$(aq)/M	c_{NaCl}(aq)/M	$E_{\mathrm{rev}}/V_{\mathrm{SHE}}$	b_c/V decade^{-1}	log(|i_0/A m^{-2}|)	1 – β
0.23	0.05	–0.319	–0.067 ± 0.01	–0.9 ± 0.5	0.5 ± 0.1
0.46	0.09	–0.300	–0.066 ± 0.002	–0.8 ± 0.1	0.50 ± 0.02
0.92	0.19	–0.288	–0.067 ± 0.004	–0.6 ± 0.2	0.49 ± 0.03
1.84	0.38	–0.272	–0.066 ± 0.004	–0.4 ± 0.2	0.50 ± 0.03

From Table 1 it can be seen that the Tafel gradients were independent of the cobalt concentration. The table also shows that the exchange current density increased with increasing cobalt concentration. A correlation of the exchange current density with the activity of the reacting species and the value of (1 – β) is expressed by Eq. 1.

$$i_0 = -nFk_0 a_O^{\beta} a_R^{1-\beta} \tag{1}$$

In Eq. 1 a_o and a_R are the activities of an oxidised species and a reduced species respectively. From Eq. 1 it can be seen that a log-log plot of i_0 versus the cobalt chloride activity should give a straight line with a slope of (β). In Fig. 1 the logarithm of the exchange current density in Table 1 is plotted versus the logarithm of the cobalt chloride activity. The data for the logarithm of the activities with the corresponding cobalt chloride concentrations used in Fig. 1 can be found in Table 2.

The log-log plot of i_0 versus $a_{\mathrm{CoCl_2}}$(aq) in Fig. 1 yields a straight line. The slope of the regression (β) line is 0.45 ± 0.16, at the confidence level 95%. This is in agreement with the other calculated values for (1 – β) in Table 1.

In Table 2 the logarithm of the current densities at –0.400 V_{SHE} and –0.500 V_{SHE} for deposition of cobalt from the Tafel parameters given in Table 1 are calculated. The logarithm of the cobalt chloride activity is calculated from the cobalt chloride concentrations and the activity coefficients given in Gmelin [6]. The activity coefficients were assumed to be independent of temperature and the total ionic strength of the electrolyte.

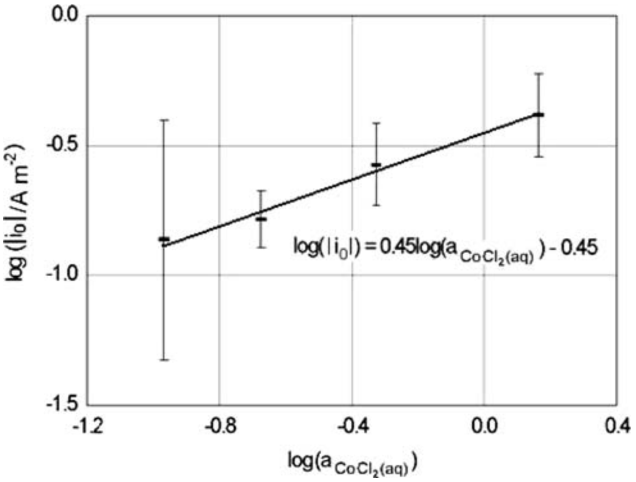

Fig. 1 Logarithm of the exchange current density for cobalt deposition versus the logarithm of the activity of cobalt chloride. The data points are given in Table 1

The expression for the reaction order in Eq. 2 is taken from [7].

$$\left(\frac{\partial \log(i)}{\partial \log(a_A)}\right)_{a_b,\ldots,a_N,E} = z_A \tag{2}$$

From Eq. 2 it can be seen that a plot of the logarithm of the current density versus the logarithm of the activity should give a line with the slope being equal to the reaction order. Plots of the logarithm of the current densities at –0.400 V_{SHE} and –0.500 V_{SHE} as a function of the logarithm of the cobalt chloride activity are shown in Fig. 2; the data in the figure are taken from Table 2.

Plots of the logarithm of the current density for cobalt deposition at two potentials versus the logarithm of the activity of cobalt chloride gave straight lines. The formulae for the regression lines are given in the figure. Statistical calculations gave the slopes of 0.96 ± 0.1 at –0.400 V_{SHE} and 1.07 ± 0.2 at –0.500 V_{SHE}, indicating that the reaction for deposition of cobalt was first order with respect to $a_{\mathrm{CoCl_2}}$(aq).

The current efficiency for cobalt deposition was also determined in the experiments where the cobalt chloride concentration was varied. Figure 3 shows plots of the current efficiency versus the current density for the four levels of cobalt chloride concentration. Increasing cobalt concentration has a positive influence on the current efficiency. The main reason for this effect is the fact that the exchange current density for electrodeposition of cobalt increases with increasing cobalt concentration in the electrolyte.

3.2 Influence of cobalt concentration at constant chloride concentration

Cobalt chloride complexes and equilibria in chloride solutions were studied by Zeltermann et al. [2], Bjerrum et al. [3] and Belousov et al. [4].

Table 2 Calculated log ($|i_{Co}|$) values at two potentials for different cobalt chloride concentrations

c_{CoCl_2}(aq)/M	log(a_{CoCl_2}(aq))	log($|i$/A m$^{-2}|$) at –0.400 V_{SHE}	log($|i$/A m$^{-2}|$) at –0.500 V_{SHE}
0.23	–0.97	0.5 ± 0.2	1.8 ± 0.2
0.46	–0.68	0.72 ± 0.06	2.23 ± 0.03
0.92	–0.33	1.09 ± 0.07	2.56 ± 0.07
1.84	0.16	1.55 ± 0.06	3.07 ± 0.06

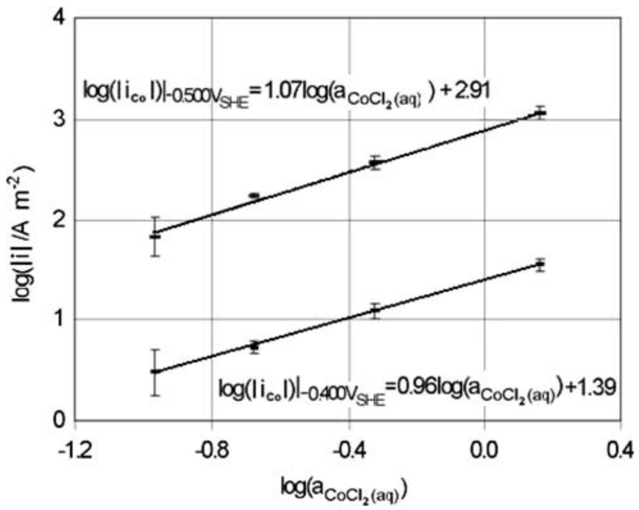

Fig. 2 Plots of log ($|i_{Co}|$) calculated from the Tafel parameters in Table 1 at –0.400 V_{SHE} and at –0.500 V_{SHE} versus log (a_{CoCl_2}(aq)). The data points are given in Table 2

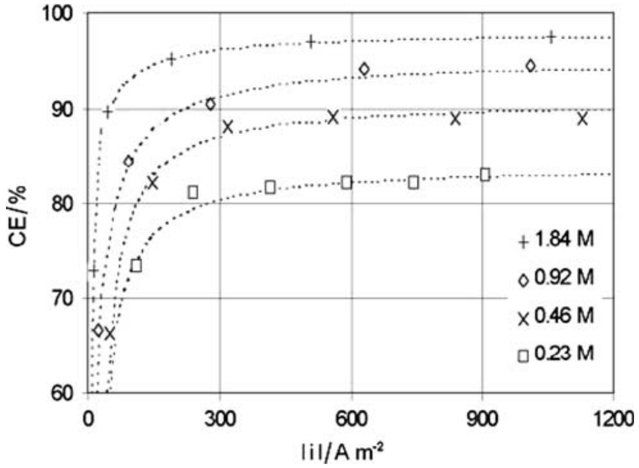

Fig. 3 Current efficiency for cobalt deposition versus current density at different cobalt chloride concentrations

The aim of the present work was to see if the cobalt deposition was dependent on the chloride concentration. The concentration of Cl^-(aq) was adjusted with NaCl to 4 M, and the H^+(aq) concentration was adjusted with HCl(aq) to 0.035 M. The pH in the electrolyte became approximately 0.9 at 60 °C in all the experiments; the calculated Tafel parameters are given in Table 3.

The Tafel slopes were almost constant with varying cobalt concentration, at constant chloride concentration. Comparison of the Tafel slopes in Tables 1 and 3 shows that these were probably independent of the chloride concentration. The current densities at –0.400 V_{SHE} and –0.500 V_{SHE} both increased with increasing cobalt concentration. To find the reaction order for cobalt deposition with respect to the cobalt activity, a plot was made of the logarithm of the current density for deposition of cobalt at –0.400 V_{SHE} and –0.500 V_{SHE} in Table 3, versus the logarithm of cobalt activity. This plot is shown in Fig. 4.

The activities in Fig. 4 where taken from [6], neglecting the effects of temperature and NaCl(aq) concentration. The reaction order became 0.8 ± 0.5 at –0.500 V_{SHE} and 0.9 ± 0.4 at –0.400 V_{SHE}. This result was only slightly lower than the reaction order calculated from the experiments in Sect. 3.1, where the cobalt chloride concentration was varied. This may indicate that cobalt deposition was not influenced by the chloride concentration. However, no definite conclusion could be made, because of the noise level in the experiments. According to Bates et al. [8] an increase in ionic strength has a tendency to increase the activity of other ions. If this effect were taken into consideration in the calculation of the activity of $CoCl_2$ (aq) the lines in Fig. 4 would be steeper.

Plots of the current efficiency for cobalt deposition versus current density for the measurements where the cobalt concentration was varied, and the chloride concentration was kept constant at 4 M Cl^-(aq), are shown in Fig. 5, which shows that an increase in cobalt concentration has a marked positive influence on the current efficiency. Comparison with Fig. 3 shows that for current densities above about 700 A m^{-2}, addition of NaCl had only a minor effect on current efficiency. At 0.23 M Co^{2+}(aq) the addition of NaCl had a negative effect on the current efficiency at low current densities. Figures 5 and 3 also indicate that addition of NaCl at 0.46 M Co^{2+}(aq) had only a minor effect on the current efficiency. At 0.92 M Co^{2+}(aq) the addition of NaCl had a positive effect on current efficiency at low current densities. Several effects may have caused the trends shown (change in potential gradients, change in the concentrations of cobalt chloride complexes and adsorption). Since these parameters

Table 3 Tafel parameters and logarithm of current density at two potentials for deposition of cobalt at 4 M chloride concentration

$c_{Co^{2+}}$(aq)/M	b^C/V decade^{-1}	log(|i_0/A m^{-2}|)	log(|i/A m^{-2}|) at –0.400 V_{SHE}	log(|i/A m^{-2}|) at –0.500 V_{SHE}
0.23	–0.06 ± 0.02	–1.0 ± 1.0	0.5 ± 0.5	2.2 ± 0.3
0.46	–0.062 ± 0.006	–0.7 ± 0.3	0.9 ± 0.1	2.5 ± 0.1
0.92	–0.060 ± 0.007	–0.7 ± 0.3	1.2 ± 0.1	2.8 ± 0.2
1.84	–0.066 ± 0.004	–0.4 ± 0.2	1.6 ± 0.1	3.1 ± 0.1

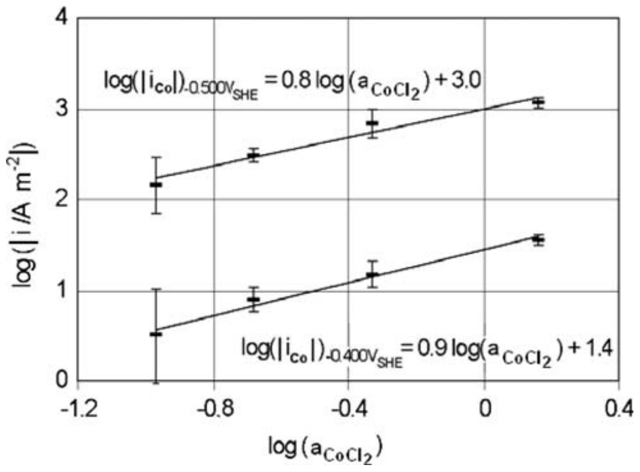

Fig. 4 Plot of log(i_{Co}) versus log(a_{CoCl_2}(aq)) calculated from the Tafel parameters in Table 3 at –0.400 V_{SHE} and –0.500 V_{SHE}. The data points are given in Table 3

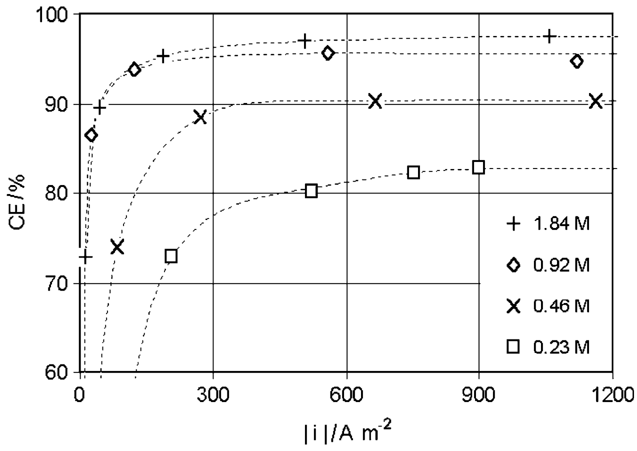

Fig. 5 Plots of current efficiency for cobalt deposition versus current density at different cobalt concentrations and constant chloride concentration (4 M)

were not controlled, a further discussion of the results in Fig. 5 is not warranted.

3.3 Influence of sulphate addition

The experiments described so far were carried out in pure chloride electrolytes. It is known that cobalt sulphate solutions are being used for cobalt electrowinning, and for comparison it was interesting to carry out some experiments in sulphate and sulphate/chloride electrolyte. In these experiments the sulphate and chloride concentrations in the electrolyte were varied. Three different electrolytes with cobalt concentration 0.92 M were used. The measured pH values in the electrolytes at 60 °C are given in Table 5. The rest of the experimental parameters are given in [1].

The reversible potentials for cobalt deposition were calculated from the activity data given in [6] using the Nernst equation and the same activity coefficient was assumed for cobalt in the all-chloride electrolyte and in the chloride/sulphate electrolyte. The calculated Tafel parameters for cobalt deposition in these experiments are given in Table 4, which shows that the kinetics for the deposition of cobalt from the chloride and chloride/sulphate electrolytes were similar. The deposition from the all-sulphate bath differs from the other two, and there was a larger estimated error for the Tafel line measured in the sulphate electrolyte. From the same data as the results in Table 4, the Tafel parameters for hydrogen evolution were calculated, and these are given in Table 5. The reversible potentials given in Table 5 were calculated from the pH values at 60 °C. From the last column in Table 5 where the current at –0.500 V_{SHE} was calculated, it can be seen that the current for hydrogen evolution tended to increase with increasing sulphate concentration.

The Tafel lines for cobalt deposition in Table 4 and for hydrogen evolution in Table 5 for the all-chloride and for the all-sulphate electrolytes are shown in Fig. 6. The Tafel plot for cobalt deposition in the all sulphate electrolyte was not a straight line, but tended to bend downwards. Therefore, the Tafel coefficients calculated from the sulphate experiments was not very informative. It can also be seen that the potential was lower for deposition of cobalt from sulphate electrolyte relative to the chloride electrolyte. The activities given by Gmelin [9] for cobalt chloride are higher than the corresponding activities for cobalt sulphate. This difference in the reversible potential was probably the main reason for the difference in the partial current densities for cobalt deposition from chloride and sulphate electrolytes at low overpotentials.

Table 4 Calculated kinetic parameters for deposition of cobalt from an all-chloride, a mixed chloride/sulphate and an all-sulphate electrolyte, the cobalt concentration being 0.92 M

Electrolyte	c_{Cl^-} (aq)/M	$c_{SO_4^{2-}}$ (aq)/M	E_{rev}/V_{SHE}	b^C/V decade^{-1}	log(|i_0/A m^{-2}|)	log(|i/A m^{-2}|) at –0.500 V_{SHE}
Chloride	2.05	0	–0.288	–0.066 ± 0.007	–0.5 ± 0.3	2.69 ± 0.07
Sulph./chlo.	1.62	0.21	–0.288	–0.067 ± 0.003	–0.5 ± 0.1	2.64 ± 0.05
Sulphate	0	1.03	–0.319	–0.07 ± 0.03	–0.4 ± 1.0	2.3 ± 0.3

Table 5 Calculated kinetic parameters for hydrogen evolution from an all-chloride, a mixed chloride/sulphate and an all-sulphate electrolyte, the cobalt concentration being 0.92 M

Electrolyte	pH	E_{rev}/V_{SHE}	b^C/V decade^{-1}	log(|i_0/A m^{-2}|)	log(|i/A m^{-2}|) at –0.500 V_{SHE}
Chloride	1.58	–0.104	–0.23 ± 0.04	–0.5 ± 0.3	1.29 ± 0.03
Sulph./chlo.	1.39	–0.092	–0.15 ± 0.04	–1.0 ± 0.7	1.6 ± 0.1
Sulphate	1.48	–0.098	–0.16 ± 0.04	–0.8 ± 0.6	1.8 ± 0.1

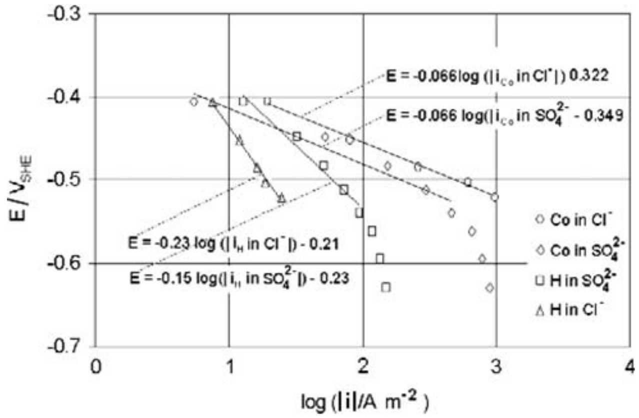

Fig. 6 Tafel plots for deposition of cobalt and evolution of hydrogen in chloride and sulphate electrolytes (see Tables 4 and 5)

The partial current density for hydrogen evolution given in Fig. 6 was higher in sulphate electrolyte compared to chloride electrolyte. The reason for this can be the equilibrium: $HSO_4^-(aq) \leftrightarrow SO_4^{2-}(aq) + H^+(aq)$ in the sulphate solution, which tends to increase the concentration of protons close to the electrode surface. This was also suggested by Zech and Landolt [10] in the case of Ni–Fe plating in sulphate electrolyte. Plots of the current efficiency versus the current density for the three sulphate and chloride solutions are shown in Fig. 7. The current efficiency for cobalt decreases with increasing sulphate concentration. In sulphate electrolyte at a given potential the partial current density for electrodeposition of cobalt was lower and the partial current density for hydrogen evolution was higher compared to deposition from chloride solutions; this explains the lower current efficiency in sulphate electrolytes.

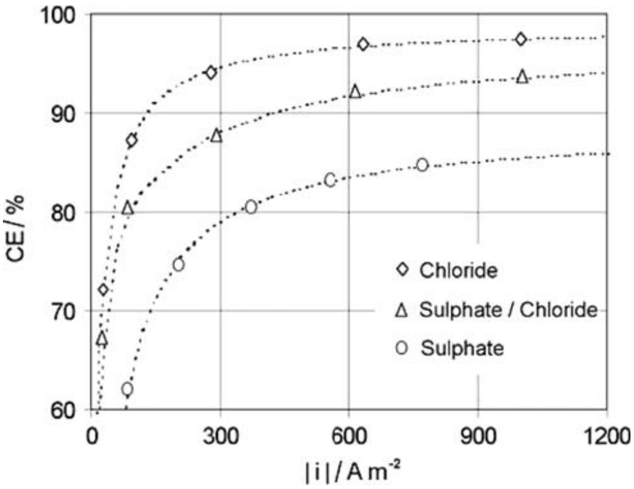

Fig. 7 Plots of current efficiency for cobalt deposition versus current density in all-chloride, chloride/sulphate and all-sulphate solutions

3.3.1 *Influence on the Total Current Density by Addition of NaCl to Sulphate Electrolyte*

In Sect. 3.1 the reaction order for cobalt deposition with respect to $CoCl_2$(aq) was shown to be close to one. In Sect. 3.2 the influence of addition of NaCl to chloride electrolytes was investigated. The reaction order with respect to $CoCl_2$(aq) was close to one, indicating that the reaction mechanism for cobalt deposition was independent of chloride concentration. However, the estimated error was high and an unambiguous conclusion could not be drawn. Hence, another attempt was made to investigate the influence of chloride concentration on cobalt deposition.

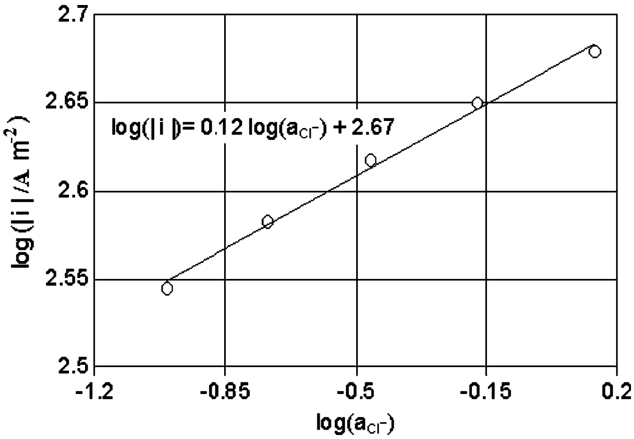

Fig. 8 Plot of log(*i*) versus log(a_{Cl^-}) at –0.500 V_{SHE}, and the calculated regression line

The initial electrolyte was 0.92 M cobalt sulphate, and pH was 1.48 at 60 °C. The experiment was carried out at 60 °C. During the experiments NaCl was added, the potential was kept at –0.500 V_{SHE}, and the current was measured point by point. The activity of chloride was calculated from $a_{NaCl(aq)}$ data given by Robinson and Stokes [11, p. 477]. The chloride activity was assumed to be equal to the sodium chloride activity; temperature and cobalt sulphate concentration were not taken into account. The results are given in Fig. 8, which shows that the total current density at –0.500 V_{SHE} increased with the addition of sodium chloride. The main reason for the increase in current density was probably the increased activity of Co^{2+}(aq), caused by the addition of sodium chloride. This indicates that the true reaction order with respect to chloride was close to zero, and Cl^-(aq) probably does not participate in the cobalt deposition reaction. The current efficiency for cobalt deposition was probably above 80% for all the measured points in Fig. 8, and changes in the current density for hydrogen evolution should not influence the slope of the line significantly.

4 Conclusion

Current efficiencies for cobalt deposition increased with current density and cobalt chloride concentration, and the reaction order with respect to Co^{2+}(aq) was close to unity. The reaction order with respect to Cl^-(aq) was close to zero. In sulphate electrolyte the partial current for cobalt deposition was lower, and the partial current for hydrogen evolution was higher compared to the corresponding chloride electrolytes, leading to a lower current efficiency for cobalt deposition from sulphate solutions.

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References

1. Kongstein OE, Haarberg GM, Thonstad J, J Appl Electrochem, doi: 10.1007/s10800-007-9299-z
2. Zeltermann H, Matwiyoff NA, Morgan LO (1968) Phys Chem 72(1):121
3. Bjerrum J, Halonin AS, Skibsted LH (1975) Acta Chem Scand A 29(3):326
4. Belousov EA, Bocharov VV, Mironov VE (1972) Russ Inorg Chem 17(12):1717
5. Kerfoot DGE, Weir DR (1988) In: Tyroler GP, Landolt CA (eds) Extractive metallurgy of nickel, cobalt. The Metallurgical Society, Warrendale PA pp 241–267
6. Meyer RJ (ed) (1932) Handbuch der Anorganische Chemie, Co, Teil A. Verlag Chemie GmbH, Berlin, achte völlige neu bearbeitete Auflag
7. O'M Bockris J, Khan SUM (1993) Surface electrochemistry, a molecular level approach. Plenum Press, New York
8. Bates G, Staples BR, Robinson RA (1970) Anal Chem 42(8):867
9. Meyer RJ, Pietsch EHE (eds) (1961) Handbuch der anorganische Chemie, Kobalt Teil A. Verlag Chemie GmbH., Weinheim/Bergstrasse, achte völlige neu bearbeitete Auflag
10. Zech N, Landolt D (2000) Electrochim. Acta 45:3461
11. Robinson A, Stokes RH (1955) Electrolyte solutions. Butterworths Scientific Publications, London p 88