

## Cobalt Electrochemistry in Aqueous Chloride Solutions: Study of the Cobalt Oxidation

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**Abstract:** The electrochemical oxidation of cobalt and the cobalt electrode open circuit potential have been studied in the complexing aqueous cobalt chloride solutions, when the pH of the solution, the  $\text{CoCl}_2$  concentration and the temperature were changed on a large scale. The open circuit potential of an immobile cobalt disk electrode did not obey NERNST's law. It was 0.17 to 0.2 V more positive than the  $\text{Co}/\text{Co(II)}$  equilibrium potential and close to the hydrogen electrode equilibrium potential; it increased linearly with  $\log[\text{CoCl}_2]/M$  and decreased with pH. The hydrogen evolution kinetics was rather slow and controlled by convective diffusion when the potential was set at a more negative potential than  $-1 \text{ V/SCE}$ .  $\text{CoCl}_2$  additions did not affect this kinetics significantly for  $\text{pH} = 3$ , whereas they slowed it down for  $\text{pH} \leq 3$ . The kinetics of the cobalt dissolution was controlled by the slow transfer of the  $\text{Co(II)}$  sp. to the solution. It was accelerated by  $\text{CoCl}_2$  or  $\text{NaCl}$  additions to the electrolyte, which increased the free  $\text{Cl}^-$  sp. concentration. The dissolution of cobalt in complex aqueous chloride solutions was assumed to result either in the formation of  $\text{Co(H}_2\text{O)}_6^{2+}$  or of  $\text{CoCl}^+$  sp. at the electrode surface, according to either of the two mechanisms:  $\text{Co} + 6 \text{H}_2\text{O} \Rightarrow \text{Co(H}_2\text{O)}_6^{2+} + 2 \text{e}^-$ ,  $\text{Co} + \text{Cl}^- \Rightarrow \text{CoCl}^+ + 2 \text{e}^-$ . The effects of either high  $\text{CoCl}_2$  and  $\text{NaCl}$  concentrations or of the most anodic overpotentials were linked to the evolution of conductivity and viscosity of the electrolyte.

**Key words:** Cobalt chloride, cobalt o. c. potential, cobalt oxidation,  $\text{Co(II)}$  complex sp., mechanism

### INTRODUCTION

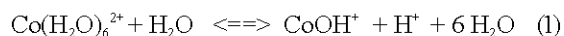
Cobalt is a strategic metal, only used on a small scale, nevertheless the 2005 world production of refined cobalt was about 55 000 tons<sup>[1]</sup>.

Nowadays, cobalt is mainly employed to make quick stainless steel and super alloys and recently in the lithium-ion batteries used in cellular phones. Moreover it is always employed on a rather large scale for the production of permanent magnets and of cobalt powders used as catalysts, or as binder agents in the preparation of sintered refractory carbides and diamond tools.

Cobalt can be electro-won, either from chloride or sulphate aqueous solutions<sup>[2-6]</sup>, whereas the cobalt electrochemistry and electrocrystallization have been studied also in other aqueous solutions<sup>[6-22]</sup>.

From literature data<sup>[23]</sup> the cobalt electrode o. c. potential in aqueous non complexing solutions is a mixed potential, due to the simultaneous occurrence of hydrogen evolution and cobalt oxidation. Scoyer *et al.*<sup>[7,8]</sup> showed that the o. c. potential of a cobalt electrode in  $\text{CoCl}_2$  aqueous solution is governed by the  $\text{H}_2/\text{H}^+$  couple, whereas Popov *et al.*<sup>[12]</sup> observed that the o. c. potential of a cobalt electrode, dipped in a deaerated aqueous  $\text{NaOH}$  solution, initially free of cobalt ions, corresponds to the  $\text{Co}/\text{HCoO}_2$ -couple.

According to Heusler<sup>[6]</sup>, the  $\text{Co}/\text{Co(II)}$  electronic exchange in a non complexing  $\text{Co}(\text{ClO}_4)_2$  aqueous solution ( $\text{HClO}_4$  being the supporting electrolyte) involves the following two-step mechanism:





where (s) are adsorption sites on the cobalt surface and  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  the main Co(II) stable sp. in the solution. He assumed that the active sites are formed in two steps involving the fast adsorption of  $\text{OH}^-$  ions on the anodic side and the adsorption of  $\text{CoOH}^+$  ions on the cathodic side. The following equation was suggested for the stationary polarisation curves of the cobalt electrode:

$$I = k_+ a_{(\text{s}^+)} a_{(\text{OH}^-)} \exp(2\alpha \text{FE}/RT) - k_- a_{(\text{s}^-)} a_{(\text{OH}^-)} a_{(\text{Co}^{2+})} \exp(-2(1-\alpha)\text{FE}/RT) \quad (3)$$

where  $a_{(\text{s}^+)}$  and  $a_{(\text{s}^-)}$  are the surface activities of the adsorption sites on the cobalt electrode surface in the stationary state.

Popov *et al.*<sup>[13]</sup> proposed a dissolution-precipitation mechanism for the anodic oxidation of cobalt in NaOH aqueous solution, involving  $\text{CoOH}_{\text{ads}}$  and  $\text{Co}(\text{OH})_{2,\text{ads}}$  as intermediate adsorbed sp..

This study deals with the study of the cobalt o. c. potential and of the anodic oxidation of the cobalt electrode in complexing aqueous chloride solutions.

The chemical equilibrium between the two soluble stable aquo and chloro Co(II) sp. and the solubility of the corresponding compounds, have been discussed. The o. c. potential of an immobile, or rotating, cobalt disk electrode was measured. The effects of pH, temperature,  $\text{CoCl}_2$  concentration and of the rotation speed of the cobalt electrode have been analysed in detail.

Hydrogen evolution kinetics onto a cobalt rotating disk electrode has then been characterised in NaCl or NaCl +  $\text{CoCl}_2$  aqueous solutions.

In a third part, the kinetics of the anodic oxidation of cobalt has been studied in a complexing aqueous chloride solution. The effects of pH, temperature, NaCl and  $\text{CoCl}_2$  concentrations have been analysed and a mechanism has been postulated for the cobalt oxidation process.

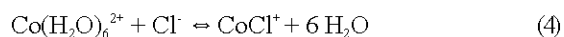
**Experimental arrangement and procedure:** A temperature-controlled cell and a three-electrode arrangement was used. The working electrode was a cobalt ("JOHNSON MATTHEY products", 99.99% purity) rotating disk embedded in a Teflon tube. A platinum rod was used as the counter electrode; the reference electrode was a saturated calomel electrode. The electrolyte was a 0.0001 M to 1.1 M cobalt dichloride aqueous solution, with sodium chloride as the supporting electrolyte. The pH value was varied from 1 to 6 and the experiments were carried out at temperatures ranging from 15 to 60°C.

The cobalt disk electrodes were polished with abrasive papers (grade 600 and 1200), then with 6 and 1

micrometer diamond pastes. Finally, the electrodes were washed for 10 min with acetone under an ultrasonic field, rinsed with deionised water, then washed for 5 min with ethanol under an ultrasonic field and finally rinsed with deionised water just before the experiment. The electrolyte was deoxygenated with a fast stream of argon. Argon was passed over the electrolyte during experiments. The electrochemical studies were carried out using either a potentiostat-galvanostat ("EEG PAR 273") or a potentiostat ("TACUSSEL PRT 20-10") coupled with a signal generator ("TACUSSEL PIL 01").

The o. c. potential of the cobalt disk electrode was measured, either when the disk electrode was rotated or not, by using a high impedance voltmeter. The hydrogen evolution and the cobalt dissolution were studied via steady or quasi steady state polarisation curves obtained on the cobalt rotating disk electrode. For the study of the anodic cobalt oxidation, the linear sweep voltammetry method was preferred to steady state measurements, in order to minimise the electrode polarisation time and consequently the corrosion of the electrode surface. The selected sweep rate of 50 mV/s was assumed to allow a quasi steady state since the forward and direct scans could be considered as identical.

**Equilibrium concentrations of the  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and  $\text{CoCl}^+$  sp., solubility of the  $\text{Co}(\text{OH})_2$  and  $\text{CoCl}_2$  compounds in complexing aqueous chloride solutions:** According to literature data<sup>[23-25]</sup>, the  $\text{CoCl}^+$  and  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  sp. are the only stable Co(II) sp. in complexing aqueous chloride solutions. They balance each other according the Eq.



The variation of the stability constant of the  $\text{CoCl}^+$  sp.  $k_c$ , according to the ionic strength I of the media, was computed at 25 °C from the experimental data reported in literature<sup>[26-28]</sup>:

$$k_c = -0.1709 I + 1.0634 \quad (5)$$

with a correlation coefficient of 0.99.

This relation was then used to calculate  $k_c$  and the bulk concentration of the  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{CoCl}^+$  and  $\text{Cl}^-$  sp.. The results for the solutions involved in the cobalt anodic oxidation study are summarized below:

- in 0.7 M NaCl solutions at pH=3, when the  $\text{CoCl}_2$  concentration was varied between 0.1 M and 1.1 M, the free  $\text{Cl}^-$  sp. concentration increased from 0.86 M to 2.38 M, whereas each of the  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and  $\text{CoCl}^+$  sp. concentrations increased and the ratio of the  $\text{CoCl}^+$  sp. concentration to the  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  one remained close to unity ( it was only varied from 0.75 to 0.90);

- in 0.1 M  $\text{CoCl}_2$  solutions at  $\text{pH}=3$ , when the  $\text{NaCl}$  sp. concentration was changed from 0.2 M to 2.7 M, the  $\text{CoCl}^+$  to  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  sp. concentration ratio increased from 0.37 to 1.56, the total  $\text{Co[II]}$  sp. concentration remaining 0.1 M, whereas the free  $\text{Cl}^-$  sp. concentration increased from 0.37 M to 2.84 M;
- in 0.7 M  $\text{NaCl}$  - 0.76 M  $\text{CoCl}_2$  solutions, with  $\text{pH}$  values varying from 6 to 1, the  $\text{Cl}^-$   $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and  $\text{CoCl}^+$  sp. concentration did not vary significantly.

According to the acidity of the solution and to the concentration of the  $\text{Co(II)}$  and  $\text{Cl}^-$  sp., the precipitation of  $\text{CoCl}_2$  and  $\text{Co}(\text{OH})_2$  compounds occur. From literature data<sup>[29]</sup>, the apparent solubility product of  $\text{Co}(\text{OH})_2$  is  $k_{s,\text{Co}(\text{OH})_2} = 5.9 \cdot 10^{-15}$  at  $25^\circ\text{C}$ , whereas the apparent solubility of  $\text{CoCl}_2$  is 0.3599 g per g of solution (which corresponds to  $k_{sp,\text{CoCl}_2} = 325$ ).

## RESULTS AND DISCUSSION

### The o. c. potential of a cobalt electrode

**Case of an immobile cobalt electrode:** Figure 1 (curve 1) presents a series of experimental cobalt electrode o. c. potentials in  $\text{NaCl-CoCl}_2$  aqueous solutions at  $\text{pH} = 2.75$  when the  $\text{CoCl}_2$  concentration was changed within the 0.0001-0.1 M range. The experimental curve fitted with the Eq:

$$E_{i=0/\text{sce}}/\text{V} = -0.359 + 0.018 \log[\text{CoCl}_2]/\text{M} \quad (6)$$

The theoretical curve corresponding to NERNST's law for the  $\text{Co/Co}(\text{H}_2\text{O})_6^{2+}$  couple is also reported on Fig. 1 (curve 2). One can see that the slopes of the two curves are different and that the experimental o. c. potential is 0.17 to 0.2 V more positive than the NERNST  $\text{Co/Co(II)}$  equilibrium potential.

The cobalt o. c. potential variation with the  $\text{CoCl}_2$  concentration will not be related to the evolution of the ratio of the two  $\text{Co[II]}$  sp. since, from data of §3, it could be considered as close to one. So, it can be assumed to be a mixed potential, in keeping with POURBAIX's diagram of cobalt<sup>[24]</sup>, due to the simultaneous hydrogen evolution and cobalt oxidation.

The variation of the o. c. potential with  $\text{pH}$  is shown on Fig. 2.

### Two preliminary remarks can be made:

- Firstly, when  $\text{pH} = 6$  in the bulk, the  $\text{pH}$  near the electrode surface is increased due to hydrogen evolution and the formation  $\text{pH}$  of  $\text{Co}(\text{OH})_2$  may be locally reached.

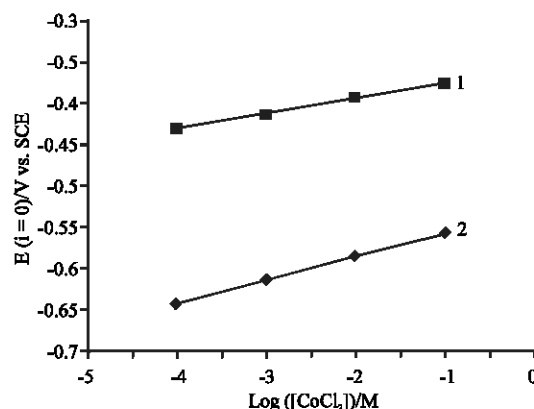


Fig. 1: Evolution of the o. c. potential of a stationary cobalt electrode with the  $\text{CoCl}_2$  concentration, Temperature:  $17^\circ\text{C}$ ;  $\text{pH} = 2.75$ ; ( $\text{NaCl}$ ) : 0.97 M. 1: experimental curve; 2: theoretical NERNST's law corresponding to the  $\text{Co/Co}(\text{H}_2\text{O})_6^{2+}$  couple

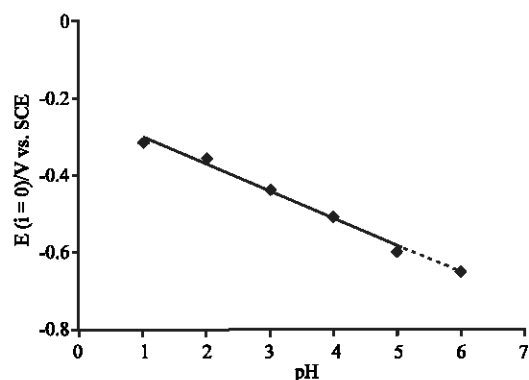


Fig. 2: Evolution of the o. c. potential of a stationary cobalt electrode with  $\text{pH}$ . Temperature:  $25^\circ\text{C}$ ; ( $\text{CoCl}_2$ ) = 0.01 M; ( $\text{NaCl}$ ) : 0.97 M

- Secondly, one can see from Fig. 2, that when  $\text{pH}$  increases up to 6, the cobalt o. c. potential reaches that of  $\text{Co/Co(II)}$  NERNST potential and can become more negative if the  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  sp. concentration calculated from the data from § 3 is considered.

Finally, if only the data corresponding to  $\text{pH} = 5$  are considered, the experimental curve can be described by the equation:

$$E_{i=0/\text{sce}}/\text{V} = -0.233 - 0.071 \text{pH} \quad (7)$$

which is very similar to that of the hydrogen electrode.

These results are consistent with those obtained previously in aqueous non complexing media by Scoyer *et al.*<sup>[7,8]</sup>.

**Case of a rotating disk cobalt electrode:** The variations of the o. c. potential of a cobalt RDE with the angular rotation speed were measured at 25°C in a 0.97 M NaCl-0.01 M CoCl<sub>2</sub> aqueous solution with pH values of 2, 4 and 6. It was observed that the cobalt o. c. potential increased with  $\omega$  and decreased with pH.

These observations confirm that the cobalt electrode o. c. potential is a mixed potential, due to the simultaneous hydrogen evolution and cobalt oxidation.

**Study of hydrogen evolution on a cobalt rotating disc electrode:** A series of experimental stationary polarisation curves obtained at pH = 1.9 are reported on Fig. 3. The proton reduction wave starts from E = -0.6 V/SCE, whereas the NERNST H<sub>2</sub>/H<sup>+</sup> equilibrium potential is equal to -0.36 V/SCE. The proton reduction is slow and limited by diffusion only at very negative potentials and can be considered as a quasi-reversible reaction.

A well known procedure<sup>[30]</sup>, involving the study of the dependence of  $i$  on  $\omega$ , makes it possible to determine kinetics data from the mixed region of the I(E) curve. Moreover, for cathodic overpotentials  $\eta_c < -2.3RT/2(1-\alpha)nF$ , it is not necessary to consider both the forward and backward reactions and the equation  $i(\omega)$  simplifies to:

$$1/i = 1/i_{act,H_2/H^+} + 1/i_{\infty,H^+} \quad (8)$$

Thus, taking into account the expressions of  $i_{act,H_2/H^+}$ , the activation current density related to the H<sub>2</sub>/H<sup>+</sup> couple and  $i_{\infty,H^+}$ , the convective diffusion current density limit of H<sup>+</sup>:

$$i_{act,H_2/H^+} = i_0 \exp(-(1-\alpha_{H^+})F\eta/RT) \quad (9)$$

$$i_{\infty,H^+} = 0.62nF[H^+]_0 D_{H^+}^{2/3} \nu^{-1/6} \omega^{1/2}, \quad (10)$$

Equation 8 becomes:

$$1/i = 1/i_0 \exp(-(1-\alpha_{H^+})F\eta/RT) + 1.61 \nu^{1/6} / nF(H^+)_0 D_{H^+}^{2/3} \omega^{1/2} \quad (11)$$

Plots of  $1/i$  versus  $f(1/\nu)$  reported on Fig. 4 were drawn for several values of the potential selected in the range -0.85 to -1.01 V/ECS. These plots are linear and reasonably parallel, in keeping with Eq. 11. They intercept the  $1/i$  axis at negative values which correspond to the activation current density. The corresponding ( $i$ ,  $\eta$ ) couples of values reported on Table 1 are used to obtain the TAFEL plot related to the H<sub>2</sub>/H<sup>+</sup> exchange.

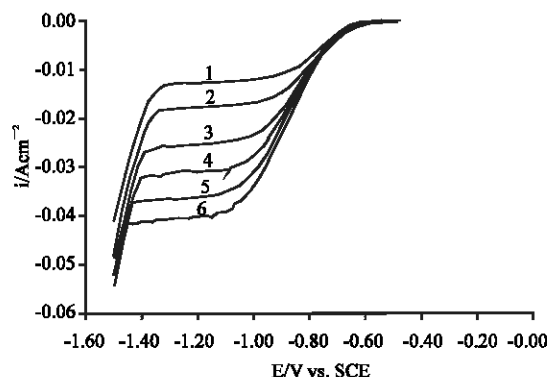


Fig. 3: The steady polarisation curves related to the hydrogen evolution on a rotating cobalt disk electrode, for various electrode rotation speeds. Temperature: 17.5 °C; electrolyte: (NaCl) : 1 M, pH = 1.9. 1: 500 rpm; 2: 1000 rpm; 3: 2000 rpm; 4: 3000 rpm; 5: 4000 rpm; 6: 5000 rpm

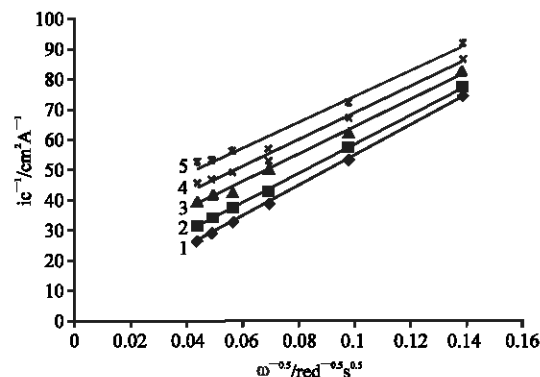


Fig. 4:  $i_c^{-1} (A^{-1} cm^2)$  vs  $\omega^{-0.5} (rad^{-0.5} s^{0.5})$  curves related to the hydrogen evolution on a rotating cobalt disk electrode, for various cobalt electrode potentials. 1: -1.01 V/SCE; 2: -.948 V/SCE; 3: -.9 V/SCE; 4: -.875 V/SCE; 5: -.85V/SCE; 6: -.8V/SCE Data obtained from Fig. 3

The equilibrium exchange current density obtained is  $i_{0,H^+/H_2} = 4.2 \cdot 10^{-5} A.cm^{-2}$ , the cathodic transfer coefficient computed from the slope is 0.33. The kinetics of the reduction of the proton on a cobalt electrode can be described by a classical BUTLER-VOLMER equation, using these values.

**Effect of the addition of CoCl<sub>2</sub> into the electrolyte on the proton reduction kinetics:** Polarisation curves of a cobalt RDE in aqueous NaCl solution, before and after CoCl<sub>2</sub> additions, were recorded at various pH values between zero and six.

The addition of CoCl<sub>2</sub>, at a concentration lower than 0.01 M, slowed down the kinetics of hydrogen evolution for pH = 3, but did not alter the kinetics of hydrogen evolution when  $3 < pH < 6$ .

Table 1: A series of ( $i$ ,  $\eta$ ) values related to the  $H_2/H^+$  exchange (data from Fig. 4)

$\eta(V)$	-0.650	-0.588	-0.540	-0.514	-0.494
$i_c(A/cm^2)$	0.256	0.098	0.054	0.041	0.032

Table 2: Experimental parameters for the study of the cobalt anodic oxidation

	Fixed parameters	Varied parameters	Results
Set n°1	pH=3, 0.7M NaCl, 0.76M $CoCl_2$	22.5°C < T < 62°C	See Fig. 5,6
Set n°2	pH=3, 0.7M NaCl, 22.5°C	0 < [ $CoCl_2$ ] < 1.1M	See Fig. 7,8
Set n°3	pH=3, 0.76M $CoCl_2$ , 22.5°C	0.2 < [NaCl] < 2.7M	See Fig. 9
Set n°4	0.7M NaCl, 0.76M $CoCl_2$ , 22.5°C	1 < pH < 6	Without Fig.

But when the  $CoCl_2$  concentration was higher than 0.01 M, the experiments became unreliable in the whole pH domain investigated, due to the modification of the surface resulting from cobalt dendrites growth.

**Study of the cobalt anodic oxidation:** Direct and reverse anodic transients were obtained on a cobalt disk electrode, in a  $CoCl_2$ -NaCl aqueous solution; each of the four parameters, temperature, pH,  $CoCl_2$  and NaCl concentration were successively varied, whereas the three others were kept constant.

The values of the experimental parameters and the results are summarised on Table 2.

**Analysis of experimental results:** One can see that for all the experiments, the current density increases versus the electrode potential but the shape of the  $I(E)$  curves is altered in the more positive potentials range.

**Influence of temperature:** The cobalt oxidation rate increases with temperature Fig. 5 within the whole range of temperature investigated.

Since oxidation of cobalt is the unique reaction when the electrode potential is more positive than the  $H_2/H^+$  equilibrium potential, a TAFEL representation can be used to analyse the cobalt oxidation mechanism.

As an example, if one considers the polarisation curve obtained at 22.5°C Fig. 5, curve 1, a TAFEL representation is possible for potentials up to 0.15 V more positive than the  $H_2/H^+$  equilibrium potential (dashed line A for  $E = -0.425$  V/ECS). This result allows us to suppose that an electronic transfer step controlled the kinetics of the cobalt anodic oxidation, as was suggested earlier by Heusler<sup>[6]</sup> and Qui<sup>[16]</sup>. The corresponding curve, reported on Fig. 6, shows a good linear variation of the potential,  $E$  versus  $\log i$ , up to -0.15 V/ECS, yielding the value  $dE/d(\log i) = 0.106$  V/decade for the TAFEL slope. The exchange current density can be obtained through the extrapolation of the TAFEL curve to the  $Co/Co(H_2O)_6^{2+}$

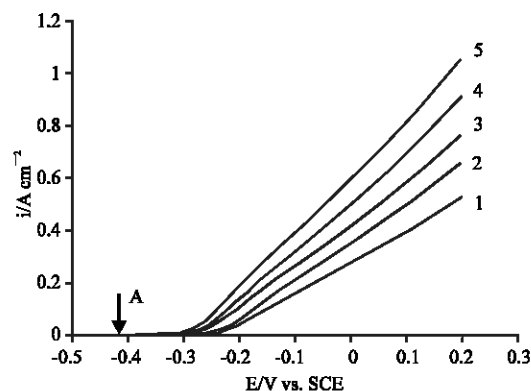


Fig. 5: Quasi steady state voltammetric direct and reverse anodic polarisation curves obtained at a cobalt disk electrode at various temperatures. ( $CoCl_2$ ) = 0.76 M; (NaCl) : 0.7 M; pH = 3; A ( $E = E_{th}$ ,  $i = 0$ ); 1: 22.5°C; 2: 32°C; 3: 42°C; 4: 52°C; 5: 62°C

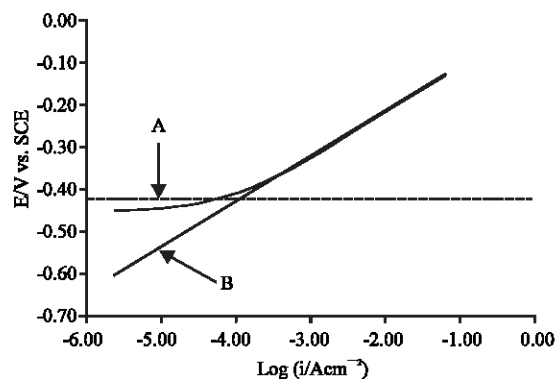


Fig. 6: Logarithmic analysis of curve 1, Fig. 5. ( $CoCl_2$ ) : 0.76 M; (NaCl) : 0.7 M; pH = 3; A ( $E = E_{th}$ ,  $i = 0$ ); B ( $E = -0.54$  V/SCE,  $i = i_0$ )

NERNST potential. This potential, can be estimated ( $E_{th, Co/Co(H_2O)_6^{2+}} \approx -0.54$  V/SCE, point B) by using the  $Co(H_2O)_6^{2+}$  sp. bulk concentration ( $\approx 0.38$  M) resulting from the data § 3. The equilibrium exchange current density determined by this method is  $10^{-5}$  A/cm<sup>2</sup>.

From these results, it can be concluded that the cobalt oxidation is a slow process described by the Eq.

$$i_{ox} = i_0 \exp[(2\alpha F(E_i - E_{th, Co2+/Co})/(RT)] \quad (12)$$

**Influence of  $CoCl_2$  concentration:** On Fig. 7, it can be observed that, as  $CoCl_2$  is added, cobalt oxidation occurs at an increasingly positive potential and also that the initial metal dissolution kinetics gets faster. A crossing of the curves and a difference from the Tafel linear dependence occur as the potential becomes more and more positive.

The fact the cobalt oxidation starts at a more and more positive potential can be attributed to the increase of the Co/Co[II] equilibrium potential with CoCl<sub>2</sub> concentration and consequently to the increasingly positive cobalt o.c. potential.

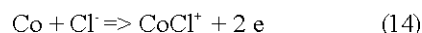
When the electrode potential increases up to +0.2 V/ECS and when CoCl<sub>2</sub> concentration is lower than 0.76 M Fig. 7, curves 1-4, the anodic current level increases with CoCl<sub>2</sub> concentration. This could be linked to the growing conductivity of the electrolyte in this range of CoCl<sub>2</sub> concentration. But, if CoCl<sub>2</sub> concentrations are higher than 0.76 M Fig. 7, curves 5-6, the anodic current starts to decrease when more CoCl<sub>2</sub> is added, the viscosity of the electrolyte increases and affects the mass transport, which could provide an explanation. The formation of a CoCl<sub>2</sub> layer on the cobalt electrode surface could also have accounted for these results but this has not been proved.

TAFEL plots, corresponding to curves 1 and 5 on Fig. 7, are reported on Fig. 8, since they better illustrate the phenomena observed when the cobalt electrode potential is made to increase from the cobalt o.c. potential. A linear part can be seen at the foot of the curve Fig. 8, curve 1 which is assumed to correspond to the slow transfer of the Co[II] ions from the metal to the electrolyte. The increase of the initial metal dissolution kinetics with the CoCl<sub>2</sub> concentration results in the moving of the linear part of the curve towards a second one in the more positive potentials region Fig. 8, curve 5. The curves cross each other as the potential becomes more positive.

A change in the mechanism of the cobalt dissolution, can be assumed to be connected to the increase of the Cl<sup>-</sup> sp. concentration (§ 3). In this hypothesis, the reaction:



takes place at the electrode surface for the lowest Cl<sup>-</sup> sp. concentration Fig. 8, curve 1, whereas for the highest Cl<sup>-</sup> sp. concentration Fig. 8, curve 5 the cobalt dissolution occurs through reaction (14):



**Influence of sodium chloride:** The general shape of the cobalt logarithmic anodic polarisation curves does not change when sodium chloride is added to the electrolyte Fig. 9. As the sodium chloride added increases, the linear part of the curves is extended to more positive potentials and a difference from TAFEL linear plots arise for the highest current densities.

Once again, when the electrode potential increases up to +0.2 V/ECS, the anodic current increases as the NaCl

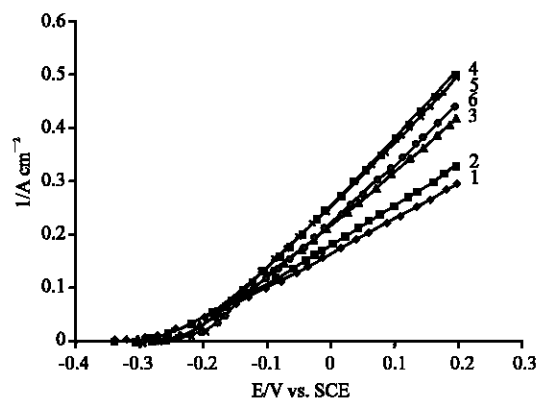


Fig. 7: Quasi steady state voltammetric anodic polarisation curves obtained at a cobalt disk electrode for different CoCl<sub>2</sub> concentrations. Temperature: 22.5 °C; (NaCl) : 0.7 M; pH = 3. 1: 0 M; 2: 0.1M; 3: 0.43M; and4: 0.76M; and5: = 1M; and6: 1.1M

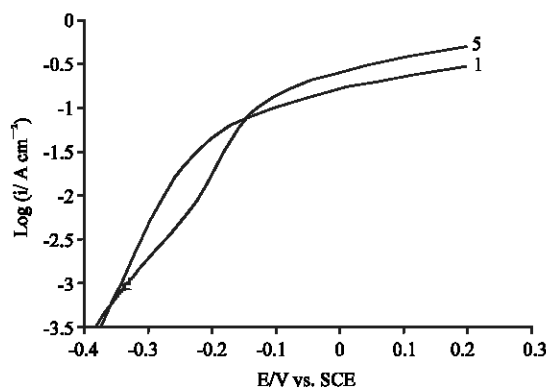


Fig. 8: Logarithmic analysis of the quasi steady state voltammetric anodic polarisation curves obtained at a cobalt disk electrode for two different CoCl<sub>2</sub> concentrations. Temperature: 22.5 °C; (NaCl) : 0.7 M; pH = 3; and 1: 0 M; and and5: = 1M

concentration added becomes higher, since the conductivity of the electrolyte increases.

It seems likely that the mechanism of the cobalt oxidation does not change in the NaCl concentration range investigated; the oxidation process occurs according to Eq. 13.

**Influence of pH:** No significant influence of the pH of the solution on the cobalt anodic oxidation kinetics was noticed when the pH was varied within the 6 to 1 range. It could only be observed that the cobalt anodic polarisation curves shifted towards more anodic potentials when the pH was changed from 6 to 1, which is similar to the corresponding variation of the cobalt

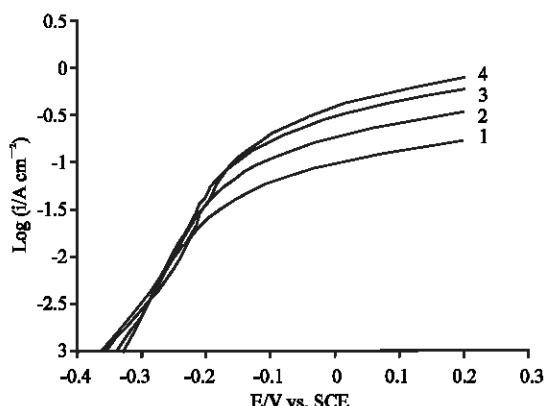


Fig. 9: Logarithmic analysis of the quasi steady state voltammetric direct anodic polarisation curves obtained at a cobalt disk electrode for different NaCl concentrations. Temperature : 22.5 °C; (CoCl<sub>2</sub>) : 0.76 M; pH = 3. 1: 0.2M; 2: 0.7M; 3: 1.7M; 4: 2.7M

electrode o. c. potential. This result is not very surprising since the data of § 3 show that none of the Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, CoCl<sup>+</sup> and Cl<sup>-</sup> sp. concentration varies when the pH changes from 1 to 6.

**Discussion of the cobalt oxidation mechanism:** The kinetics of the cobalt dissolution process was shown to be controlled by the slow transfer of the Co(II) sp. from the electrode to the solution.

The shift of the anodic polarisation curves towards more positive potentials, with the increase of the CoCl<sub>2</sub> concentration or with the decrease of the pH, is assumed to be related to the shift both of the Co/Co(II) equilibrium and of the o. c. cobalt electrode potential.

The increase of the cobalt anodic oxidation kinetics with CoCl<sub>2</sub> or NaCl additions is presumably linked to the free Cl<sup>-</sup> sp. concentration increase: cobalt is assumed to be transferred to the solution through the formation of Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> for the lowest Cl<sup>-</sup> sp. concentration or through the formation of CoCl<sup>+</sup> sp. for the highest Cl<sup>-</sup> sp. concentration.

In the more positive potentials explored, the cobalt oxidation is favoured by the increase of the conductivity of the electrolyte with the CoCl<sub>2</sub> and NaCl concentration sp., but it slows down when the viscosity increases at high CoCl<sub>2</sub> concentration.

## CONCLUSION

The Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and CoCl<sup>+</sup> sp. are the only Co(II) sp. stable in the CoCl<sub>2</sub>, NaCl aqueous complexing solutions.

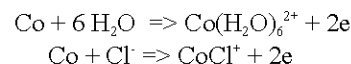
The relative stability of the two Co(II) sp. is not very sensitive to the CoCl<sub>2</sub> or NaCl sp. concentrations, or to the pH of the electrolyte. The Cl<sup>-</sup> sp. concentration increases in keeping with the CoCl<sub>2</sub> or NaCl sp. concentration of the electrolyte.

The cobalt electrode o. c. potential, was shown to be a mixed potential in these solutions, in keeping with POURBAIX's diagram of cobalt and with the results obtained by Scoyer and et al.<sup>[7,8]</sup> in non complexing aqueous solutions. The variation of the o. c. potential of a cobalt rotating disk electrode with the angular rotating disk rate showed the major role of hydrogen evolution.

The analysis of the stationary polarisation curves related to hydrogen evolution on a cobalt rotating disk electrode showed that the proton reduction was under mixed transfer and diffusion control. The presence of CoCl<sub>2</sub> slowed down the hydrogen evolution kinetics in the more acidic solutions.

The analysis of the cobalt quasi stationary anodic cobalt polarisation curves obtained at a cobalt disk electrode showed that the Co/Co(II) exchange was rather slow, the exchange current density measured in the CoCl<sub>2</sub> 0.76 M, NaCl 0.7 M solution, at pH = 3 and temperature = 22.5°C, was equal to 10<sup>-5</sup> A/cm<sup>2</sup>.

The cobalt dissolution occurred through one of the two mechanisms below, depending on the Cl<sup>-</sup> sp. concentration:



Cobalt could be assumed to be transferred to the solution through the formation of Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> or CoCl<sup>+</sup> sp., according to Cl<sup>-</sup> sp. concentration. The dissolution of the cobalt as Co(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> was favoured from a thermodynamical point of view, whereas the rate of formation of the CoCl<sup>+</sup> sp. was kinetically enhanced.

The cobalt anodic oxidation kinetics was found to be limited by the ionic transport process in the most concentrated CoCl<sub>2</sub> or NaCl solutions and for the highest anodic potentials. The cobalt oxidation was favoured by the increase of the conductivity of the electrolyte with the CoCl<sub>2</sub> and NaCl concentration sp., but it slowed down when the viscosity increased for high CoCl<sub>2</sub> concentrations.

## REFERENCES

1. Van. Der Bossche, P., 2006. Cobalt news, 1.
2. Fujimori, M., 1982. Chloride Electrometallurgy Symposium, Metallurgical Society AIME, Warrendale, Pa, pp: 155.

3. Mackinnon, D.J., 1983. Hydrometallurgical Research Development Plant Processes Metallurgical Society AIME, Warrendale, Pa, pp: 659.
4. Stenshold, E.O., 1986. Nickel Metallurgy Annual Conference 25th, Montreal, pp: 1-442.
5. Agnew, R. and P. Garritsen, 1988. Extractive metallurgy of nickel and cobalt, Metallurgical society AIME, Warrendale, Pa, pp: 555.
6. Heusler, K.E., 1967. Ber. Bunsenges, pp: 71-620.
7. Scoyer, J. and R. Winand, 1977. Surface Technology pp: 5-294.
8. Scoyer, J., 1977. Thèse de l'Université Libre de Bruxelles, Belgique.
9. Das, S.C. and J. Subbaiah, 1984. Hydrometallurgy, pp: 12-317.
10. Das, S.C. and J. Subbaiah, 1987. J. Appl. Electrochem. pp: 17-675.
11. Jiang, X., P.M. May and J.M. Ritchie, 1987. Electrochim. Acta, pp: 32-1035.
12. Popov, B., Z. Koneska, J. Ivshin and D.M. Drazic, 1989. J. Serg. Chim. Soc., pp: 54-431.
13. Popov, B., Z. Koneska, J. Ivshin and D.M. Drazic, 1989. J. Serg. Chim. Soc., pp: 54-443.
14. Stupnisek-Lisac, E. and H. Takenouti, 1989. J. Electroanal. Chem., pp: 259-147.
15. Jiang, Y. and Z. Chen, 1990. J. Electrochem. Soc., pp: 137-3374.
16. Cui, C.Q., S.P. Jiang and A.C.C. Chen, 1992. J. Electrochem. Soc., pp: 139-60.
17. Paunovic, M., T. Nguyen, R. Mukherjee, C. Sambucetti and L.T. Romankiw, J. Electrochem. Soc., pp: 142-1495.
18. Mitchell, J.A., W.R. Pitner, C.L. Hussey and G.R. Stafford, J. Electrochem. Soc., pp: 143-3448.
19. Sasaki, K.Y. and J.B. Talbot, 1998. J. Electrochem. Soc., pp: 145-981.
20. Chen, P. and I.W. Sun, 2001. Electrochimica Acta, pp: 46-1169.
21. Pradham, N., P. Singh, B.C. Tripathy and S.C. Das, 2002. Mineral Enginee., pp: 14-775.
22. Floate, S., M. Hyde and R.G. Compton, 2002. J. Electroanal. Chem., pp: 523-49.
23. Millazzo, G. and S. Carolis, 1978. Tables of standard Electrode Potentials, Interscience Pub., John Wiley and Sons Ltd.
24. Pourbaix, M., 1963. Atlas d'équilibres électrochimiques, Ed. GauthierVilars et Cie, Paris.
25. Klíxbull Jorgensen, C.H.R., 1963. Inorganic complexes, Academic Press, London and New York.
26. Javet, P.A., P. Lerch and E. Plattner, 1992. Introduction à la chimie pour ingénieur, Presses polytechniques et universitaires romandes, Lausanne, Suisse.
27. Philipps, C.S.G. and R.J.P. Williams, 1971. Chimie minerale Tome 2 Métaux, Dunod, Paris.
28. Kotrly, S. and L. Sucha, 1985. Handbook of chemical equilibria in analytical chemistry, Ellis Horwood Ltd, England.
29. Handbook of Chemistry and Physics, 77th Ed, DAVID R. LIDE Editor-in-chief (1996-1997).
30. Pletcher, D., R. Greffe, R. Peat and L.M. Peter, 1985. J. Robinson, Instrumental Methods in Electrochemistry, Ed. Ellis Horwood Ltd, England.