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The Behaviour of Cobalt in Concentrated Nitric Acid Solutions

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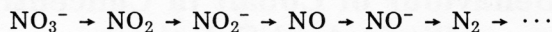
In our previous investigation it has been established that cobalt, unlike iron or nickel, does not passivate in concentrated or even fuming nitric acid. The dissolution of cobalt in this aggressive medium is, however, significantly reduced by the formation of a hydrated nitrate salt layer adhering tightly to the metal surface. On the basis of the open-circuit corrosion potential measurements of cobalt electrode, in a wide range of nitric acid concentrations, and polarization curves, obtained in 11 mol dm⁻³ nitric acid using a regulating device with negative output resistance, along with electrode impedance results, it was proved that the hydration number of nitrate salt plays the crucial role in the electrochemical behaviour of cobalt in concentrated nitric acid solutions. The importance of the free water released through a decrease in the hydration number was clearly observed.

INTRODUCTION

Iron, nickel and cobalt form the so-called ferrous group metals. It is well known that iron passivates spontaneously in moderately concentrated nitric acid (*ca.* 7 M). We have demonstrated that the reduction reaction of nitrate is not only catalyzed by nitrous ions but also by ferrous ions through the formation of ferro-nitroso complexes.^{1,2}

During the anodic dissolution of iron, ferrous ion is oxidized into ferric ion by the action of nitrate ion. Thus, there is a close coupling of anodic and cathodic processes. Both processes favour the passivation of iron, constituting a highly intricate auto-

catalytic reaction chain. For nickel electrodes, since the bivalent nickel is stable in acidic media, there is no intricate coupling of the anodic and cathodic process.^{3,4} Hence, the spontaneous passivation of nickel occurs at higher concentrations of nitric acid (*ca.* 10 M) than in the case of iron, although nickel is considered to be an easy metal to passivate. Furthermore, for both iron and nickel electrodes, the reduction reaction of nitrate was found to take place at a significant rate only at the active electrode surface:



In other words, in the presence of a passive film, the cathodic process is considerably hindered. This results in a coupling of the anodic and cathodic processes displaying an N-shaped polarization curve.³

In contrast to the passivation of cobalt in neutral and basic solutions^{5,6} the anodic passivation of cobalt in acid solutions is far more difficult than that of iron and nickel.⁷

It was found that in fuming nitric acid, the surface of cobalt becomes covered with a compact nitrate salt layer. Comparison between the open-circuit corrosion potential of a cobalt electrode with the nitric acid concentration and the state diagram of $\text{Co}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system clearly shows a change in the hydration number of the cobalt-nitrate salt formed near the electrode surface. The state diagram⁸ indicates that, for concentrations below 12 M, the precipitate salt is hexahydrate. Between 12 M and 19 M, the salt is tetrahydrate. Beyond this concentration, the bihydrate salt is stable. It has been suggested in our earlier work that this salt layer protects the metal from rapid dissolution.⁹⁻¹¹

The aim of this work is to provide further experimental data to elucidate the behaviour of cobalt in concentrated nitric acid solutions.

EXPERIMENTAL

Electrolytes ranging in concentrations from 1 M to 24 M were prepared from 65% or 100% analytical grade chemicals and doubly ion-exchanged water. The solutions were at room temperature (*ca.* 20 °C). No gas bubbling was performed.

The electrode was a cylindrical cobalt rod (Johnson-Matthey), 5 mm in diameter. Only a cross-section of the rod was allowed to come into contact with the electrolyte, forming a disk electrode with a 0.2 cm² surface area. The remaining rod surface was covered with a thermal-fitting polyethylene sheath.

Preliminary investigations have shown that the electrochemical behaviour of cobalt in 11 M and 19 M nitric acid is dependent upon the orientation of the electrode surface and rotation (or stirring). A peculiar feature in the polarization curve was obtained only when the electrode was stationary, without stirring, and its surface facing up. All measurements were performed under these conditions.

A home-made potentiostat was coupled with a frequency response analyzer (SOLARTRON 1250) for impedance measurements. Impedance measurements were controlled using a personal computer (SORD M68) through GP-IB bus. A circuit for the negative resistance converter was made in our laboratory.¹² As seen in Figure 1, this circuit was inserted between the working electrode and the earth of the potentiostat circuit. The value of the negative resistance (*r*) can be adjusted to yield polarization curves over the widest possible current-voltage range.

The potential was measured with a calomel reference electrode and expressed in the hydrogen scale by adding 0.25 V to the measured value. No correction for ohmic drop was made.

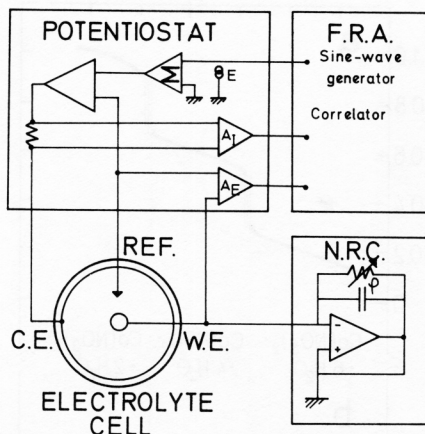


Figure 1. Schematic diagram of the experimental setup. (F. R. A. Frequency Response Analyser, N. R. C. Negative Resistance Converter, A_1A_E Current and voltage differential amplifier).

Furthermore, the liquid junction potential between the working solution and the concentrated KCl was ignored.

RESULTS AND DISCUSSION

The open-circuit corrosion potential (E_{corr}) of a cobalt electrode in a wide range of nitric acid concentrations (1 M – 24 M) was measured. Figure 2 summarizes the results of open circuit potential measurements¹¹ and the solubility diagram of $\text{Co}(\text{NO}_3)_2$ depending on the concentration of nitric acid.⁸ According to the E_{corr} -concentration diagram, the potential value can be divided into three domains. At transition ranges, a steep potential change of about 0.3 V in width can be seen. At these threshold concentrations, potential oscillation between two corresponding values often occurs and is illustrated in Figure 2a by a few vertical lines. The hydration number of the cobalt nitrate salt in the $\text{Co}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ system changes also at about 11 M and 19 M nitric acid solution (Figure 2b). These two concentrations are essentially coincident with the threshold concentration observed for the corrosion potential of the cobalt electrode.

Figure 3 depicts the polarization curve obtained in 14 M HNO_3 by the potentiodynamic method. The voltage sweep rate was 5 mV/s. The open-circuit corrosion potential is close to 0.6 V, corresponding to that of the medium concentration range (12 M – 18 M) given in Figure 2a. The polarization curve did not exhibit the passivation phenomenon characterized by a current decrease with increasing potential. The electrode surface is covered by a nitrate cobalt salt layer. The limiting dissolution current is determined by the solubility of the cobalt salt. The limiting current density is ca. 0.12 A/cm². This current density is markedly dependent on the acid concentration: the higher the acid concentration, the lower the limiting current. But, the polarization curve showed a feature similar to that in Figure 3 at all acid concentrations except for two narrow concentration ranges, as described below.

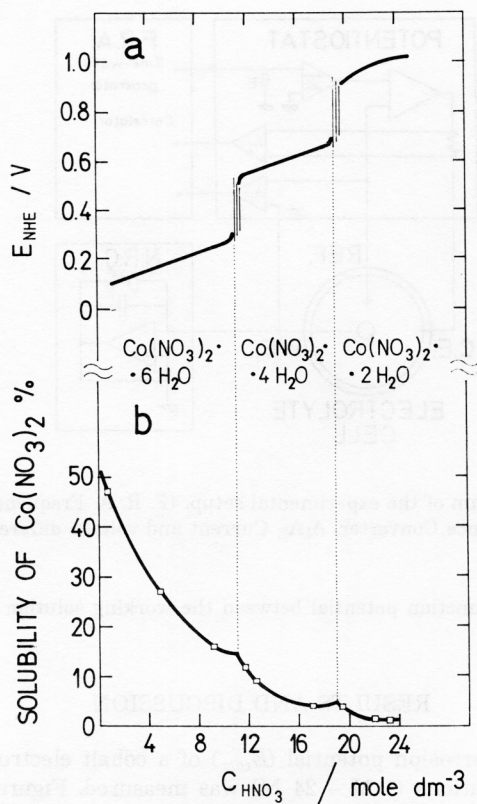


Figure 2. a) Open-circuit corrosion potential of cobalt with respect to the nitric acid concentration.¹¹ b) Diagram of the solubility of $\text{Co}(\text{NO}_3)_2$ in nitric acid at 20 °C, according to Schumpelt.⁸

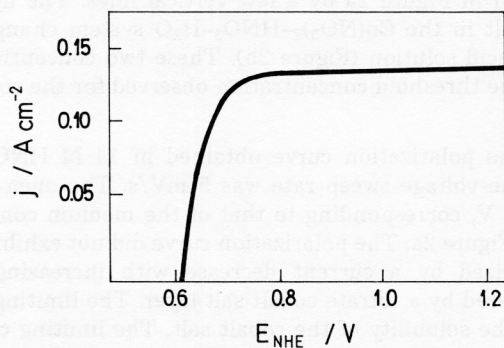


Figure 3. Potentiodynamic anodic polarization curve of Co in 14 M HNO_3 . ($dE/dt = 5 \text{ mV/s}$).

The polarization curves had a very different shape near the concentrations at which steep potential changes were observed, *i.e.* 11 M and 19 M. Figure 4a indicates the steady-state polarization curve obtained under potentiostat control in 11 M HNO₃ solution. The open-circuit corrosion potential, marked A, corresponds to that of the low concentration range (*ca.* 8 M) (Figure 2a). The polarization curve exhibits two steep current changes, marked by arrows at 0.45 V and 0.35 V describing a hysteresis cycle. This potential range corresponds to the oscillation range of the open-circuit potential of cobalt in 11 M nitric acid (Figure 2a). At approximately 0.53 V (point E) the overall current is zero. This potential corresponds to the open-circuit potential observed for the medium concentration range (*ca.* 13 M).

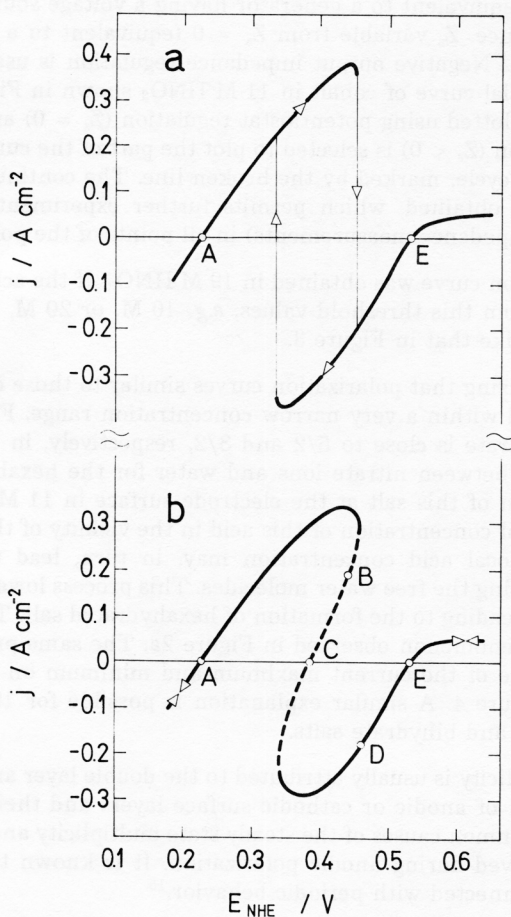


Figure 4. a) Potentiostatic polarization curve of cobalt obtained in 11 M HNO₃. b) Polarization curve of cobalt in 11 M HNO₃ obtained with a negative resistance regulation device.

In general, oscillations seem to be related to phenomena that appear when a system is far from its equilibrium state. The hysteresis loop obtained is often characteristic of a multi-steady-state system. It is noteworthy that the states characterized by the branch marked by arrows in Figure 4a are inaccessible in that case. The system states cannot be determined unambiguously by varying either the current that flows through the system or the potential difference developed across it. This can, of course, make it very difficult to determine the properties of the process under investigation. As a matter of fact, only the accessible and stable states can be studied experimentally.

The problem now is how to reach experimentally the state to be studied and how to control it. This is done using an external constraint, a device of negative output impedance regulation. This device permits the unstable domains to be investigated, using positive feedback. It is equivalent to a generator having a voltage source, E_s , in series with an output impedance, Z_s , variable from $Z_s = 0$ (equivalent to a potentiostat) to some negative value.^{13,14} Negative output impedance regulation is used to obtain the plot of a current-potential curve of cobalt in 11 M HNO_3 shown in Figure 4b. Part of the curve (full-line) is plotted using potentiostat regulation ($Z_s = 0$) and negative output impedance regulation ($Z_s < 0$) is selected to plot the part of the curve in the potential range of hysteresis cycle, marked by the broken line. The continuous and reversible characteristics are obtained, which permits further experimental investigation (like electrochemical impedance measurements) in all points of the polarization curve.

A similar polarization curve was obtained in 19 M HNO_3 . If the acid concentration differs slightly more from this threshold values, *e.g.* 10 M, or 20 M, the polarization curve shows a feature like that in Figure 3.

It is worth emphasizing that polarization curves similar to those displayed in Figure 4 are only observed within a very narrow concentration range. Furthermore, the mole ratio of water/nitrate is close to 5/2 and 3/2, respectively, in 11 M and 19 M HNO_3 . The mole ratio between nitrate ions and water for the hexahydrate is three. Hence, the precipitation of this salt at the electrode surface in 11 M HNO_3 solution should increase the local concentration of this acid in the vicinity of the electrode surface. This change of local acid concentration may, in turn, lead to formation of tetrahydrate salt, releasing the free water molecules. This process lowers the local concentration of the acid, leading to the formation of hexahydrated salt. This explains the potential oscillation phenomenon observed in Figure 2a. The same process is responsible for the appearance of the current maximum and minimum on the polarization curve, as shown in Figure 4. A similar explanation is possible for 19 M HNO_3 with the formation of tetra- and bihydrate salts.

Steady state multiplicity is usually attributed to the double layer and electrode surface origins. Formation of anodic or cathodic surface layers and their destruction or change are the most common causes of the steady state multiplicity and also the source of the hysteresis observed during anodic polarization. It is known that steady state multiplicity is often connected with periodic behavior.¹⁵

The free water molecules in the vicinity of the electrode surface play a determining role in the electrochemical behaviour of the cobalt electrode in a concentrated nitric acid. As suggested in previous papers,⁹⁻¹¹ the free water is involved in the reduction reaction of nitrate. The current maximum and minimum observed in Figure 5 are linked to the change of local free water concentration.

Figure 5 shows impedance diagrams obtained at various polarization points, marked A to D in Figure 4b. Diagram A shows common features of the corroding electrode. From the high frequency capacitive loop, the parallel capacitance equal to 150 mF/cm^2 and resistance equal to 1 ohm cm are obtained. The capacitance can be attributed to the double layer and the resistance to the charge transfer layer. The small resistance value may indicate that a rapid corrosion process takes place at the interface. A corrosion rate equal to 20 mA cm^{-2} can be calculated.

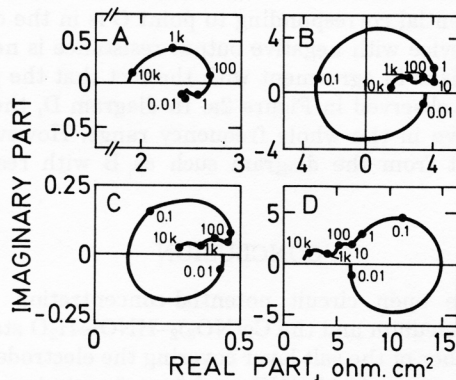


Figure 5. Impedance diagrams of Co in 11 M HNO_3 . (A to D corresponds to the points marked in Figure 4b by the same letters. Parameters are frequency in Hz).

Diagrams B and C are similar in shape. The capacitive loop observed in the high frequency range ($f > 1 \text{ KHz}$) indicates capacitance close to 100 mF/cm^2 , which may be attributable to the double layer capacitance parallel to the charge transfer resistance. Another capacitive loop is centered near 100 Hz . It is remarkable that this capacitance loop occurs also in diagram D at the same frequency. The potential change is 0.2 V after ohmic correction for the drop. The origin of this time constant is likely to be due to the surface relaxation of a species implied in the autocatalytic reactions.¹⁶ For lower frequencies, the impedance returns to a positive value through a large inductive loop, thus describing a large circle around the origin of the diagram. A similar diagram form was observed during the transpassive dissolution of nickel.¹⁵ This feature was explained by a reaction scheme including an autocatalytic process.

If electrolyte resistances, *i.e.* high frequency limits of the impedance at different polarization points, are compared, resistance is seen to be particularly low in diagram C. Therefore, the change in the electrolyte resistance indicates modification in the electrolyte composition in the immediate vicinity of the cobalt electrode. Since the solution is highly concentrated near the electrode surface because of hydrated salt formation, the decrease in the electrolyte resistance corresponds well to the release of free-water due to the change in the hydration number.

Regarding diagrams B and C, it can also be noted that the low frequency limit of the impedance (polarization resistance) is greater than the electrolyte resistance, *i.e.*, the polarization curve corrected for the ohmic drop might show a positive slope at

points B and C. In other words, the polarization curve shows an overhanging shape, exhibiting a multiplicity of steady states at this potential range. Such a feature is again to be related to an auto-catalytic reaction in the electrode process involved.¹²

The interfacial states at points A and D are stable in current regulation. Since the open-circuit conditions correspond to the current regulation at zero overall current, both situations can be observed. By contrast, the states at points B and C are unstable. An interesting feature can be noted in diagram B, since this diagram is stable under potential regulations.¹² The problem is how to approach this polarization point bound by unstable ranges on both sides. Point C is neither stable at the potential nor at the current regulation. Potential corresponding to point C is in the oscillation range (Figure 2a). A regulating device with negative output resistance is necessary to yield such dynamic behaviour. This is in agreement with the fact that the potential corresponding to point C was not observed in Figure 2a. In diagram D, the real part of the impedance remains positive in the whole frequency range. However, this shape is not fundamentally different from the diagram such as B with respect to the reaction mechanism.¹⁷

CONCLUSION

Comparison of the open circuit potential-concentration curve of the cobalt electrode in nitric acid medium and the $\text{Co}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ state diagram indicated that the hydration number of the salt layer covering the electrode surface changes suddenly from six to four at about 11 M HNO_3 and from four to two at about 19 M HNO_3 . The polarization curve showed a peculiar feature at these threshold concentrations: it displayed a current maximum and minimum with a rapid rate of cathodic process. Our earlier work linked this process to an autocatalytic reaction of nitrate reduction.

The impedance measurements along different polarization points showed that electrolyte resistance is abnormally small in the transition range. This phenomenon was attributed to the changes in free water concentration in the vicinity of the electrode surface due to a change in the salt hydration numbers.

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SAŽETAK

Ponašanje kobalta u koncentriranoj dušičnoj kiselini

E. Stupnišek-Lisac i H. Takenouti

Iako se, za razliku od željeza i nikla, kobalt ne pasivira u koncentriranoj, čak ni u dimećoj dušičnoj kiselini, njegovo je otapanje znatno usporeno stvaranjem sloja hidratizirane nitratne soli koja čvrsto prianja na metalnu površinu.

Na osnovi mjerenja potencijala kobalta pri otvorenom krugu u širokom području koncentracija nitratne kiseline, polarizacijskih krivulja u dušičnoj kiselini (11 mol dm^{-3}) dobivenih upotrebom uređaja s negativnim unutarnjim otporom zajedno s rezultatima elektrodne impedancije pokazano je da hidratacijski broj nitratne soli igra odlučujuću ulogu u elektrokemijskom ponašanju kobaltne elektrode u koncentriranim otopinama dušične kiseline. Jasno je utvrđena i važnost otpuštene slobodne vode.