

Effects of Magnetic Field on Open-Circuit Potential of the Ni | HNO₃ + NaCl System

Jiaojiao Qi, Xiaoping Wang, Yu shao, Liang Li*, Chao Wang*

Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Department of Chemistry, Jiangsu Normal University, Xuzhou 221116, P.R.China

*E-mail: lil@jsnu.edu.cn, wangc@jsnu.edu.cn

Received: 28 December 2020 / Accepted: 10 February 2021 / Published: 31 March 2021

The effects of the magnetic field on the open-circuit potential (OCP) of the Ni | HNO₃ + Cl⁻ system were studied by using the electrochemical method, the surface analysis, and the nonconvective electrode. Although OCP was always shifted positively when the magnetic field was applied in the direction parallel (B_{//}) or perpendicular (B_⊥) to the electrode surface, the reasons were quite different. With the application of B_{//}, the anodic shift of OCP was attributed to the positive shift of the cathodic overpotential (η_c) because the Lorentz force (F_L) was too low to affect the anodic reaction. However, with the application of B_⊥, it was attributed to the positive shift of the anodic overpotential (η_a) because the field gradient force ($F_{\nabla B}$) affects η_c slightly.

Keywords: Nickel; open-circuit potential; corrosion; magnetic field

1. INTRODUCTION

Since the metallic materials are often used in natural conditions, the effects of the magnetic field (MF) on the open-circuit potential (OCP), which has been studied since the 1880s [1], has potential industrial applications. Waskaas [2] reported that OCP of iron was shifted positively by the static MF in a paramagnetic iron (III) chloride solution. Lu *et al.* [3] also reported that the positive shift in the neutral or acidic solutions under the remembering effect of MF and that it was shifted more significantly by MF in the acidic solution than in the neutral solution. However, Sueptitz *et al.* [4] found that OCP was shifted either positively or negatively in low concentrated sulfuric acid solutions with a low or high magnetic flux density gradient. They proposed that the Lorentz force (F_L) enhanced the hydrogen ion reduction and led to the positive shift. However, the negative shift was caused by the action of the field gradient force ($F_{\nabla B}$) that attracted iron ions to regions of high magnetic flux density and decreased the reduction rate of the hydrogen ions. Dass *et al.* [1] also found that OCPs of the ferromagnetic electrodes moved in

opposite directions when MF was applied in the direction either parallel or perpendicular to the surface of the electrode. They proposed that OCP was changed by MF because it modified the surface concentrations of paramagnetic participants in the corrosion process of the ferromagnetic electrode by species in solution.

When the electrode surfaces were oriented parallel to MF, OCP of Ni was shifted positively in CH_3CN solution containing $0.5 \text{ mol dm}^{-3} \text{ LiClO}_4$ and 6 mmol dm^{-3} of the redox couple $[\text{Co}(\text{bipy})_3]^{3+/2+}$ [1]. However, when the surfaces were perpendicular to MF, different results were observed under various magnetic flux densities [2,5]. At MF of 600 mT, no effect was observed in $1.0 \text{ mol dm}^{-3} \text{ NiCl}_2$ solution [2]. When MF increased to 800 mT, OCP was shifted negatively in $1.0 \text{ mol dm}^{-3} \text{ NiCl}_2$ or $1.0 \text{ mol dm}^{-3} \text{ NiSO}_4$ solution [5].

Nickel, as one of the most important structure materials, is often used in the environment under the external MF. We [6] studied the effects of MF on the anodic dissolution of nickel, and found that the MF effects were different in the different regions. Recently, we studied the effects of MF on the anodic dissolution of Ni | $\text{H}_3\text{PO}_4 + \text{KSCN}$ system, and found that MF promoted intergranular corrosion [7]. However, there are few papers about the effects MF on OCP of nickel. Therefore, it is necessary to study the effects of MF on OCP of Ni. In this study, we studied the effects of MF on OCP of the Ni | $\text{HNO}_3 + \text{Cl}^-$ system by the perturbing method [8].

2. EXPERIMENTAL

The electrochemical cell contained a three-electrode system. The working electrodes ($d = 2.0$ mm, Johnson Matthey Company) were made from a Ni (99.98%), Co (99.995%), or Cu (99.999%) rod, respectively, and sealed by a thin layer of epoxy resin in a glass tube, leaving only the end of the rod to be exposed to the solution. The electrodes were carefully polished with emery papers to form a mirror-like surface and then washed with double distilled water in an ultrasonic bath before each experiment. The counter electrode and reference electrode were the large-sheet platinum and the saturated calomel electrode (SCE) respectively. The IR drop was minimized with the application of a Luggin capillary between the working electrode and the reference electrode. All the potentials were reported with respect to SCE.

The solutions used in this study were prepared with reagents of analytical grade and double distilled water. The voltammetry experiments were performed using a CHI604B electrochemical station at room temperature (25 ± 2 °C).

An electromagnetic field was used in the experiment. The electrochemical cell was centered carefully between the two electromagnets prior to each experiment. Fig. 1 shows the sketch maps of the orientation of the magnetic field (B), working electrode (WE) surface, and current (i). In this study, the uniform MF was applied in the direction either parallel (Fig.1a, $B_{//}$) or perpendicular (Fig.1b, B_{\perp}) to the surface of the electrode.

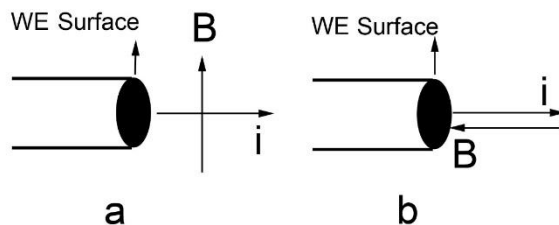


Figure 1. The sketch maps of the orientation of the magnetic field (B), working electrode (WE) surface, and current (i), and the magnetic field applied in the direction parallel (Fig.1a, $B_{//}$) or perpendicular (Fig.1b, B_{\perp}) to the electrode surface.

3. RESULTS AND DISCUSSIONS

3.1 Effects of MF on OCP of the Ni | $\text{HNO}_3 + \text{Cl}^-$ system

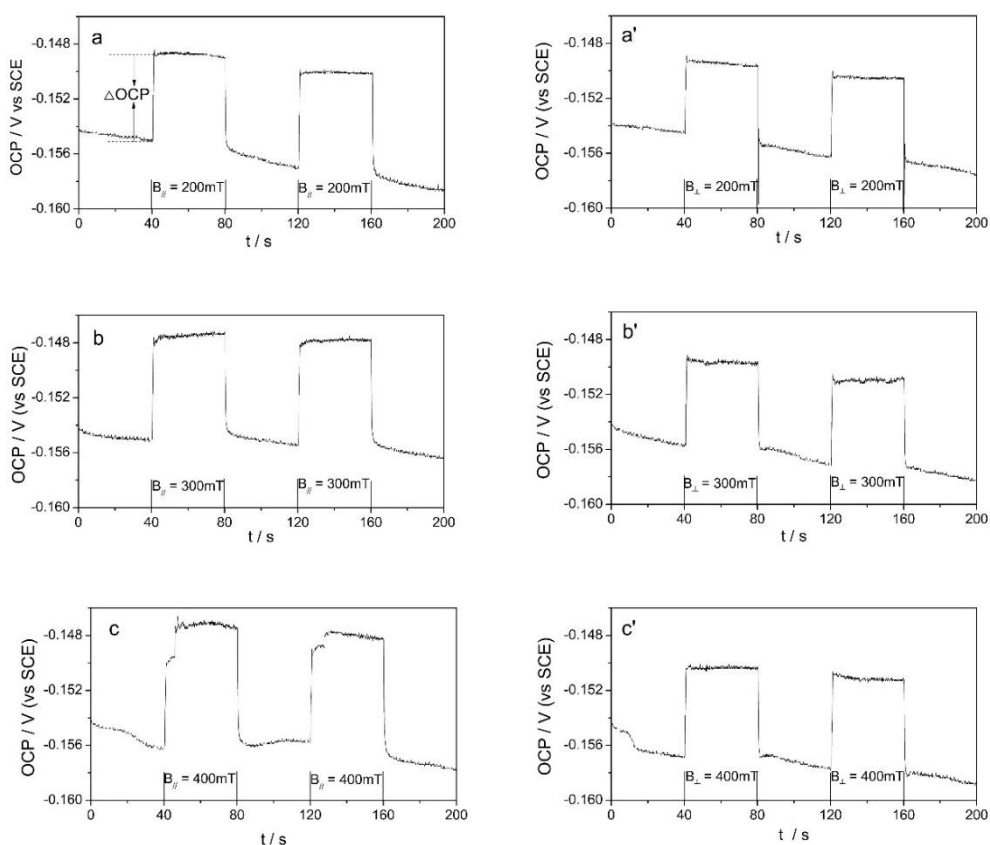


Figure 2. Effects of $B_{//}$ (a-c) and B_{\perp} (a'-c') on OCPs of the Ni electrodes in 0.50 mol dm⁻³ HNO₃ + 5.0 mmol dm⁻³ NaCl solution.

Fig. 2 shows the effects of $B_{//}$ and B_{\perp} on OCP of Ni in 0.50 mol dm⁻³ HNO₃ + 5.0 mmol dm⁻³ NaCl solution. For each experiment, MF was respectively applied for 40–80 s and 120–160 s. As shown in Fig. 2, when the magnetic flux density was increased from 200 (Figs. 2a and a') to 300 (Figs. 2b and b') and 400 mT (Figs. 2c and c'), respectively, OCP was shifted positively after the application of either

$B_{//}$ or B_{\perp} . Under all the conditions, OCP was restored to its original value after MF was removed, proving that the effect was only caused by MF. Table 1 lists the effects of MF on ($\Delta\text{OCP}=\text{OCP}$ (with MF)– OCP (without MF)) corresponding to Fig. 2. As shown in Fig. 2a, OCP (without MF) is the potential formed just before the application of MF, while OCP (with MF) is the potential formed just after the application of MF. As listed in Table 1, at the same magnetic flux density, ΔOCP with the application of $B_{//}$ was higher than that of B_{\perp} , indicating that the effect of $B_{//}$ was more obvious; as the magnetic flux density increased, ΔOCP increased with the application of $B_{//}$ or B_{\perp} .

Table 1. Effects of MF on ΔOCP for Ni | $0.50 \text{ mol dm}^{-3} \text{ HNO}_3 + 5.0 \text{ mmol dm}^{-3} \text{ NaCl}$ system. $\Delta\text{OCP} = \text{OCP}$ (with MF)– OCP (without MF)

B / mT	200	300	400
ΔOCP / mV ($B_{//}$)	6.3	7.4	9.0
ΔOCP / mV (B_{\perp})	5.3	6.1	6.6

3.2 Surface morphology

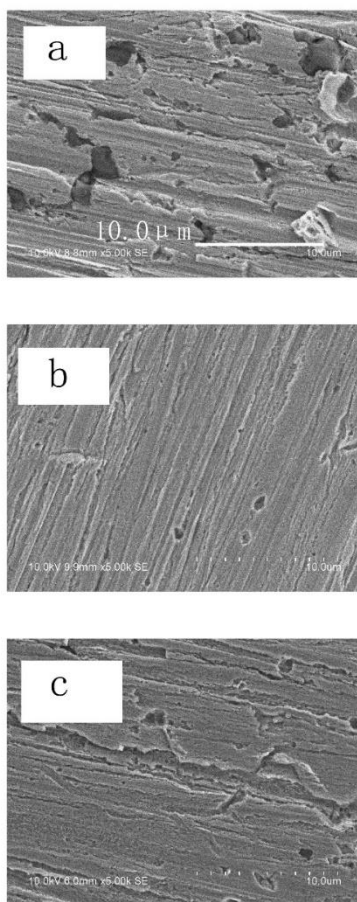


Figure 3. Surface morphology of the Ni electrodes without (a) and with MF (b: $B_{//}$, c: B_{\perp}) in $0.50 \text{ mol dm}^{-3} \text{ HNO}_3 + 5.0 \text{ mmol dm}^{-3} \text{ NaCl}$ solution at OCP for 600 s.

Fig. 3 shows the surface morphology of the Ni electrodes without (a) or with the application of MF (b: B//, c: B⊥) in 0.50 mol dm⁻³ HNO₃ + 5.0 mmol dm⁻³ NaCl at OCP for 600 s. Without the application of MF (Fig. 3a), the surface was rough, indicating that the electrode was obviously corroded. However, the electrode surfaces were relatively smooth after the application of MF (Figs. 3b and 3c), indicating that the electrodes were less corroded after the application of MF than that without the application of MF (Fig. 3a).

3.3 Discussion

During an electrochemical reaction with the applied MF, the force (F_{mag}) includes [9–11] the Lorentz force (F_L), field gradient force (also known as the Kelvin force or magnetophoretic force) ($F_{\nabla B}$) [12], and paramagnetic concentration gradient force ($F_{\nabla C}$). Weier *et al.* [13] reported that the effect of $F_{\nabla C}$ on the mass transport processes at room temperature was not obvious. Therefore, the effect was mainly induced by F_L and/or $F_{\nabla B}$ [14–16].

Because the working electrode is made of the metallic material (Ni), OCP is also called the corrosion potential or mixed potential. In this study, we assume that the current (I_a) and overpotential (η_a) of the anodic reaction are positive and those (I_c and η_c) of the cathodic reaction are negative. At OCP, the rate of the anodic reaction is equal to that of the cathodic reaction, then:

$$I = I_a + I_c = 0 \quad (1)$$

$$\text{OCP} = E_a + \eta_a = E_c + \eta_c \quad (2)$$

E_a and E_c are the equilibrium potentials of the anodic and cathodic reactions respectively.

According to equation (2), it is known:

$$2 \times \text{OCP} = (E_a + E_c) + (\eta_a + \eta_c) \\ \text{OCP} = \frac{E_a + E_c}{2} + \frac{\eta_a + \eta_c}{2} \quad (3)$$

$$\text{If, } \frac{E_a + E_c}{2} = \overline{E_e} \text{ and } \frac{\eta_a + \eta_c}{2} = \overline{\eta_e} \quad (4)$$

Then:

$$\text{OCP} = \overline{E_e} + \overline{\eta_e} \quad (5)$$

Since the effects of MF on the anodic dissolution of the Ni | HNO₃ + Cl⁻ system were caused by enhancing or reducing the rate of the mass-transfer step by MF [17], MF may only affect the concentration polarization of the electrochemical reactions. Thus MF may not affect the equilibrium potentials (E_a and E_c), and the effects of MF on OCP may be only attributed to the change of $\overline{\eta_e}$.

According to equations (3), (4), and (5):

$$\Delta \text{OCP} = \frac{\Delta \eta_a + \Delta \eta_c}{2} = \Delta \overline{\eta_e} \quad (6)$$

$$\Delta \text{OCP} = \text{OCP}(\text{with MF}) - \text{OCP}(\text{without MF})$$

$$\Delta \eta_a = \eta_a(\text{with MF}) - \eta_a(\text{without MF})$$

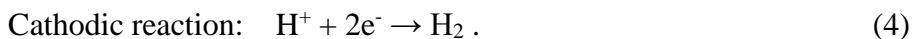
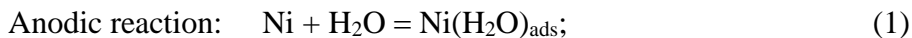
$$\Delta \eta_c = \eta_c(\text{with MF}) - \eta_c(\text{without MF})$$

$$\Delta \overline{\eta_e} = \overline{\eta_e}(\text{with MF}) - \overline{\eta_e}(\text{without MF})$$

If the rate of the mass-transfer step is decreased by MF, the concentration polarization of both the anodic and cathodic reactions is enhanced by MF, thus $\eta_a(\text{with MF})$ is more positive than $\eta_a(\text{without MF})$.

MF), then $\Delta\eta_a > 0$; however, η_c (with MF) is more negative than η_c (without MF), then $\Delta\eta_c < 0$. On the contrary, if the rate of the mass-transfer step is increased by MF, $\Delta\eta_a < 0$ but $\Delta\eta_c > 0$.

Since OCP depends on both the anodic and cathodic reactions affected by MF [18], the reactions of Ni | HNO₃ + NaCl system should be considered. At OCP, the possible anodic [8] and cathodic reactions are as follows:



3.3.1 Effects of $B_{//}$ on OCP

After the application of $B_{//}$, the effects were mainly induced by F_L . An anodic shift in OCP may be explained as follows:

(1) The mass transport process was enhanced by F_L , and it seems that the anodic polarization was reduced as mentioned above. However, some of the intermediate ions, such as NiClH^+ , may diffuse away from the electrode surface. Because the intermediate ions can inhibit the formation of the oxide film [18], the oxide film is easily formed to enhance the anodic polarization with the application of $B_{//}$.

(2) Because of the concentration polarization of H^+ and Coulomb repulsion of the anodic products (Ni^{2+}) for H^+ , pH at the interface was higher than that in the bulk solution before the application of MF. However, after the application of $B_{//}$, the induced convection decreased pH at the interface and drove the cathodic products (H_2) to quickly diffuse away from the electrode surface, thus reducing the concentration polarization of the cathodic reaction by F_L [3,14].

Because the anodic current was low at the low potential in the active region of the Ni | HNO₃ + Cl⁻ system, F_L was too low to affect the anodic dissolution [18]. It is reasonable to deduce that F_L affects η_a slightly at OCP, $\Delta\eta_a \approx 0$, thus the positive shift of OCP should be attributed to shifting η_c ($\Delta\eta_c > 0$) positively by F_L according to equation (6).

3.3.2 Effects of B_{\perp} on OCP

Although MF applied in this experiment was uniform, $F_{\nabla B}$ was still induced because of the ferromagnetic property of Ni. With the application of B_{\perp} , the effects were mainly induced by $F_{\nabla B}$, thus attracting the paramagnetic species (Ni^{2+}) to the electrode surface but driving the diamagnetic species (H_2) away from the surface [19]. The anodic polarization was enhanced and the cathodic one was reduced, thus both η_a and η_c shifted positively ($\Delta\eta_c > 0$ and $\Delta\eta_a > 0$), as a result, OCP shifts positively according to equation (6). However, the force acting on the diamagnetic species can be neglected because the absolute value of their molar susceptibility (χ_m) is ~ 4 orders of magnitude lower than that for the paramagnetic species [4]. That is to say, $\Delta\eta_c \approx 0$, the positive shift caused by $F_{\nabla B}$ may be mainly attributed to the positive shift of η_a . It is also verified that the anodic dissolution of the electrochemical system is always inhibited by $F_{\nabla B}$ [18].

3.3.3 Effects of the mass transport process on OCP

Due to the effects of both $B_{//}$ and B_{\perp} , OCPs were affected directly by the mass transport process. For example, OCP may vary with the rate of the mass transport process. To verify this hypothesis, the mass transport process was either enhanced by stirring or inhibited with a nonconvective electrode [20].

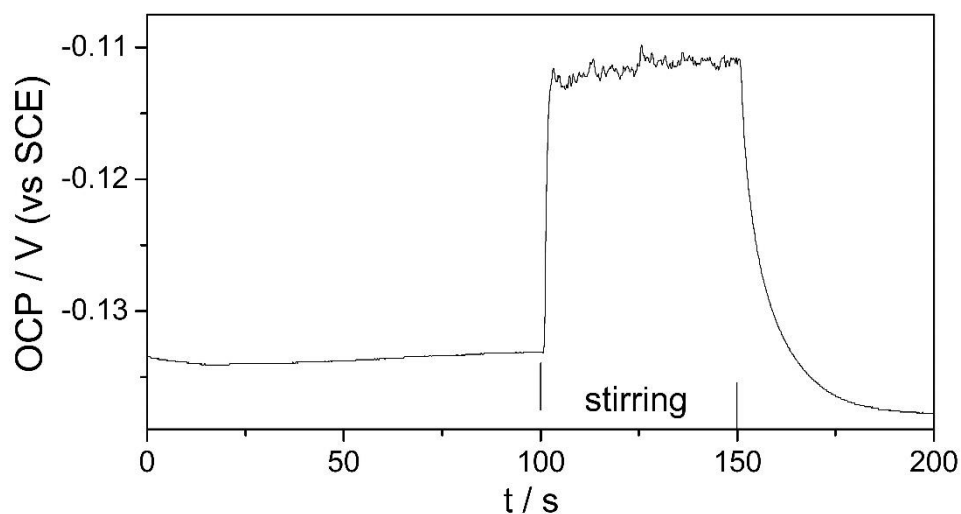


Figure 4. Effects of a stirring on OCP of the Ni electrode in $0.50 \text{ mol dm}^{-3} \text{ HNO}_3 + 5.0 \text{ mmol dm}^{-3} \text{ NaCl}$ solution.

As shown in Fig. 4, OCP was shifted positively after stirring and tended to restore to its original value when the stirring stopped. In contrast, when a nonconvective electrode [20] was used to decrease the rate of the mass transport process, as shown in Fig. 5, OCP shifted negatively with the increase of the distance from the electrode surface to the bulk solution (L) [21]. The effect of $B_{//}$ was the same as that with the stirring, indicating that it was caused by the enhancement of the mass-transport processes. Although it was proposed that the mass transport processes of the anodic products (Ni^{2+}) decreased with the application of B_{\perp} , the effect of B_{\perp} was quite different from that with the nonconvective electrode.

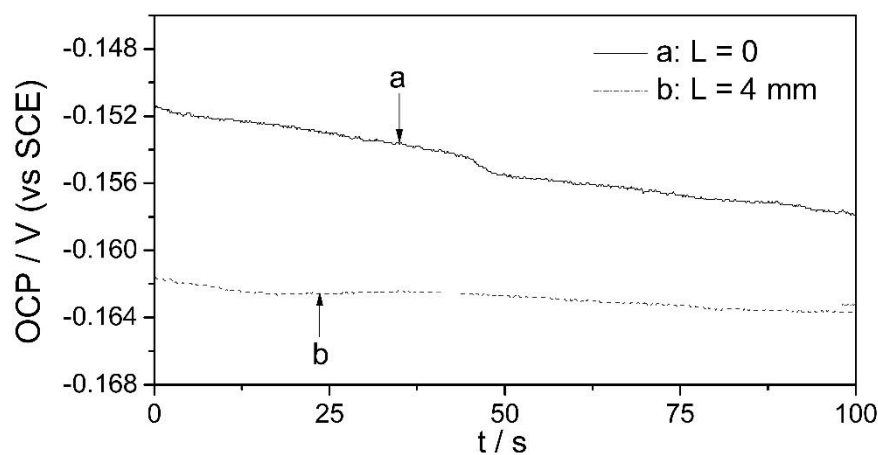


Figure 5. Effects of L on OCP of the nonconvective Ni electrode in $0.50 \text{ mol dm}^{-3} \text{ HNO}_3 + 5.0 \text{ mmol dm}^{-3} \text{ NaCl}$ solution. a: $L=0 \text{ mm}$, b: $L=4 \text{ mm}$, L : the distance from the surface of the electrode to the bulk solution.

The reason can be explained as follows: with the application of the nonconvective electrode, the rates of the mass transport processes of both the anodic and cathodic products decrease. Because the anodic products (Ni^{2+}) are accumulated at the interface to repel H^+ , pH increases. As a result, the cathodic polarization is enhanced more significantly than the anodic polarization, that is to say, $|\Delta\eta_c'| > |\Delta\eta_a'|$ ($\Delta\eta_c' = \eta_c(L=4\text{mm}) - \eta_c(L=0)$, $\Delta\eta_a' = \eta_a(L=4\text{mm}) - \eta_a(L=0)$). Because $\Delta\eta_c' < 0$ but $\Delta\eta_a' > 0$, thus OCP shifts negatively when the nonconvective electrode is used. However, as mentioned above, with the application of B_{\perp} , the anodic was enhanced but the cathodic polarization was affected slightly by $F_{\nabla B}$ ($\Delta\eta_c \approx 0$ but $\Delta\eta_a > 0$), thus OCP shifted positively.

This can also be used to explain the results in Table 1. With the increase in the magnetic flux density, both F_L and $F_{\nabla B}$ increase. Therefore, ΔOCP also increases. These results were verified [5]. However, at the same density, ΔOCP with the application of B_{\parallel} was higher than that with the application of B_{\perp} because of the following reasons:

- (1) The absolute value of F_L might be higher than that of $F_{\nabla B}$ because the uniform MF was applied in this study;
- (2) The natural convection was enhanced by F_L but inhibited by $F_{\nabla B}$;
- (3) $\Delta\bar{\eta}_e$ caused by F_L is higher than that by $F_{\nabla B}$.

In other word, the effects caused by F_L were more obvious than those by $F_{\nabla B}$.

Besides the mass transport processes, the effects of MF on OCP may also be related to the magnetic property of electrodes.

3.3.4 The magnetic property of electrode

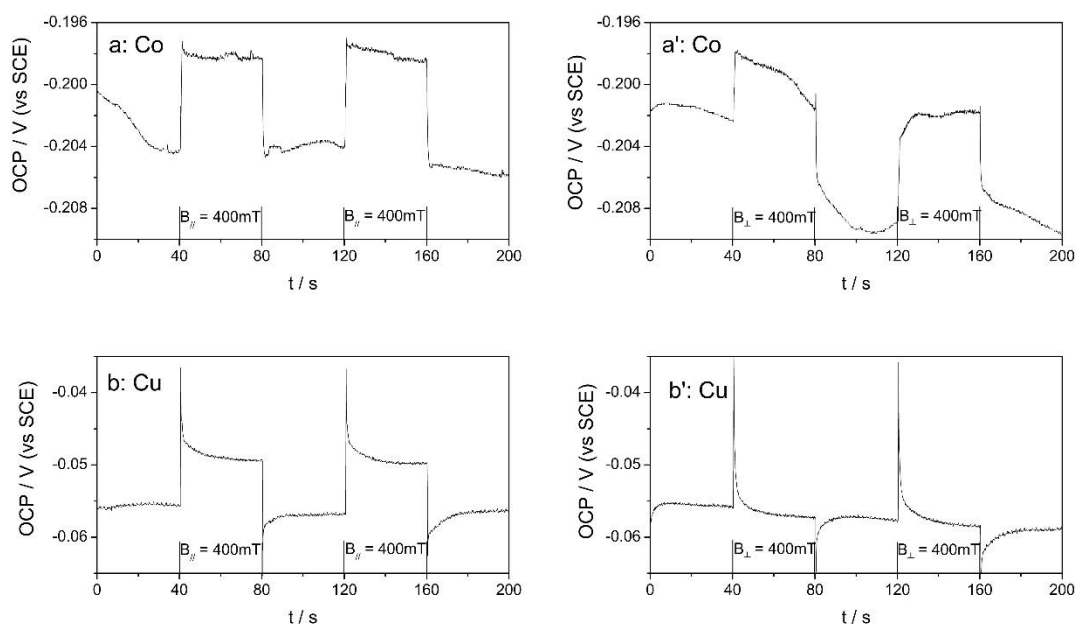


Figure 6. Effects of B_{\parallel} (a, b) and B_{\perp} (a', b') on OCPs of the Co (a, a') and Cu (b, b') electrodes in $0.50 \text{ mol dm}^{-3} \text{HNO}_3 + 5.0 \text{ mol dm}^{-3} \text{NaCl}$ solution.

To verify whether the MF effects were related to the magnetic property of the electrode or not, we studied the effects of MF on OCP of both ferromagnetic (Co) and non-ferromagnetic (Cu) electrodes in $0.50 \text{ mol dm}^{-3} \text{ HNO}_3 + 5.0 \text{ mmol dm}^{-3} \text{ NaCl}$ solution. As shown in Fig. 6, with the application of $B_{//}$, OCP was always shifted positively irrespective of ferromagnetic (Co, Fig. 6a) or non-ferromagnetic (Cu, Fig. 6b) electrodes. With the application of B_{\perp} , OCP was also shifted positively for the ferromagnetic electrode (Co, Fig. 6a'), but it was changed slightly for the non-ferromagnetic electrode (Cu, Fig. 6b). At each condition, OCP was restored to its original value before the application of MF.

In this solution, the effect of $B_{//}$ on OCP did not depend on the property of the anodic material, thus it is reasonable to deduce that the positive shift of OCP is attributed to reducing the cathodic polarization ($\Delta\eta_c > 0$) by $B_{//}$. However, the B_{\perp} effect may depend on the property of the electrode. With the application of B_{\perp} , the ferromagnetic electrodes (Co, Fig. 6a'; Ni, Fig. 2a'-c') are easily magnetized [22]. Therefore, $F_{\nabla B}$ is induced to pull paramagnetic species (Ni^{2+} and Co^{2+}) to the electrode surface and enhance the anodic polarization ($\Delta\eta_a > 0$), thus OCP is shifted positively. However, the non-ferromagnetic electrode (Cu, Fig. 6b') cannot be magnetized with the application of B_{\perp} . Therefore, it affects OCP slightly.

4. CONCLUSIONS

(1) The effects of MF on OCP were attributed to enhancing or reducing the anodic and cathodic polarization, thus η_c and η_a were affected by MF.

(2) Although OCPs of the Ni electrode in $0.50 \text{ mol dm}^{-3} \text{ HNO}_3 + 5.0 \text{ mmol dm}^{-3} \text{ NaCl}$ solution were shifted positively after the application of both $B_{//}$ and B_{\perp} , the reasons are quite different. The anodic shift in OCP can be mainly attributed to reducing the cathodic polarization ($\Delta\eta_c > 0$) by F_L ; however, the anodic shift in OCP is mainly caused by enhancing the anodic polarization ($\Delta\eta_a > 0$) by $F_{\nabla B}$.

(3) Because the non-ferromagnetic electrode could not be magnetized with the application of B_{\perp} , the effect of B_{\perp} was related to the ferromagnetic property of the electrode. However, the effect of $B_{//}$, the same as that of the stirring, was caused by reducing the concentration polarization of the cathodic reaction, thus it is not related to the ferromagnetic property.

ACKNOWLEDGEMENT

This research was supported by the National Natural Science Foundation of China (Nos. 21972059) and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX20_2264).

Reference

1. A. Dass, J. A. Counsil, X. Gao, N. Leventis, *J. Phys. Chem. B*, 109 (2005) 11065.
2. M. Waskaas, *Acta Chem. Scand.*, 50 (1996) 516.
3. Z. P. Lu, Y. Wu, *Corros. Sci.*, 50 (2008) 510.
4. R. Sueptitz, K. Tschulik, M. Uhlemann, A. Gebert, L. Schultz, *Electrochim. Acta*, 55 (2010) 5200.

5. M. Waskaas, Y. I. Kharkats, *J. Phys. Chem. B*, 103 (1999) 4876.
6. L. Li, W. Wang, C. Wang, S. Chen, *Electrochem. Commun.*, 11 (2009) 2109.
7. M. Zhang, B. Yuan, Q. Wu, Y. Zhu, L. Li, C. Wang, *Int. J. Electrochem. Sci.*, 13 (2018) 739.
8. S. Liu, Y. Shao, C. Yan, B. Yuan, L. Li, C. Wang, *Corros. Sci.* 169 (2020) 108614.
9. N. Leventis, X. Gao, *Anal. Chem.*, 73 (2001) 3981.
10. N. Leventis, X. Gao, *J. Am. Chem. Soc.*, 124 (2002) 1079.
11. N. Leventis, A. Dass, *J. Am. Chem. Soc.*, 127 (2005) 4988.
12. L. M.A. Monzon, J.M.D. Coey, *Electrochem. Commun.*, 42 (2014) 42.
13. T. Weier, K. Eckert, S. Mühlenhoff, C. Cierpka, A. Bund, M. Uhlemann, *Electrochem. Commun.*, 9 (2007) 2479.
14. F.M.F. Rhen, G. Hinds, J.M.D. Coey, *Electrochem. Commun.*, 6 (2004) 413.
15. O. Lioubashevski, E. Katz, I. Willner, *J. Phys. Chem. C*, 111 (2007) 6024.
16. S.R. Ragsdale, K.M. Grant, H.S. White, *J. Am. Chem. Soc.*, 120 (1998) 13461.
17. X. Wang, J. Zhao, Y. Hu, L. Li, C. Wang, *Electrochim. Acta*, 117 (2014) 113.
18. L. M.A. Monzon, J.M.D. Coey, *Electrochem. Commun.*, 42 (2014) 38.
19. A. Ručinskienė, G. Bikulčius, L. Gudavičiūtė, E. Juzeliūnas, *Electrochem. Commun.*, 4 (2002) 86.
20. O. Devos, O. Aaboubi, J.P. Chopart, A. Olivier, C. Gabrielli, B. Tribollet, *J. Phys. Chem. A*, 104 (2000) 1544.
21. M. Zeng, C. Wang, L. Li, *Electrochem. Commun.*, 11 (2009) 1888.
22. R. Sueptitz, J. Koza, M. Uhlemann, A. Gebert, L. Schultz, *Electrochim. Acta*, 54 (2009) 2229.