CHEMISTRY

The effect of halide ions on nickel corrosion in perchloric acid solutions

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Abstract. A comparative study of the effect of halide anions on the corrosion of mechanically and chemically polished nickel in perchloric acid solutions was carried out. Perchloric acid was chosen for the reference as perchlorate anion is one of the least adsorbed anions on nickel and this property allows examining adsorption of halogenide anions down to very low concentrations. It was established that in 0.1 M perchloric acid so low concentration of halogenides as 1×10^{-5} M has significant influence on nickel corrosion. Adsorption of halide ions depends remarkably on the energetic properties of the nickel surface. This effect was the most pronounced in the case of chloride ions, which essentially accelerated the corrosion of mechanically polished electrodes but had only a weak effect on chemically polished electrodes.

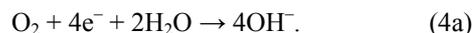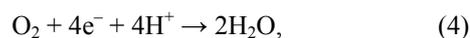**Key words:** nickel, corrosion, perchloric acid, halide ions, voltammetry.

INTRODUCTION

The corrosion of nickel in aqueous electrolytes has been the subject of numerous studies, motivated by the high technological importance of nickel and Ni-containing alloys, such as stainless steels and brasses, as well as by fundamental questions concerning the understanding of the mechanisms of metal corrosion. Nickel is malleable, resists corrosion, and maintains its mechanical and physical characteristics under extreme temperatures.

Most corrosion phenomena are of electrochemical nature. They imply two or more electrode reactions: the oxidation of a metal (anodic partial reaction) and the reduction of an oxidizing agent (cathodic partial reaction). For example, the corrosion of nickel in an acid environment proceeds according to the overall reaction 1:

$$Ni + 2H^+ \rightarrow Ni^{2+} + H_2. \tag{1}$$
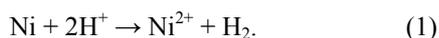
This reaction includes the anodic partial reaction 2 and the cathodic partial reaction 3. In the presence of air the reduction of molecular oxygen takes place (reaction 4 in acidic and reaction 4a in neutral and alkaline solutions) and the corrosion potential shifts into a more

positive direction. In this work we avoided presence of oxygen in the solutions.

$$Ni \rightarrow Ni^{2+} + 2e^-, \tag{2}$$

$$2H^+ + 2e^- \rightarrow H_2, \tag{3}$$

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O, \tag{4}$$

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-. \tag{4a}$$

The corrosion potential always lies between the equilibrium potentials of the respective anodic and cathodic partial reactions. Its exact value is determined by the kinetics of the partial reactions [1–11]. It is a simplified approach and the real corrosion process is much more complicated. One of the most important phenomena is the formation of passive compounds on the surface of the electrode. These compounds, NiO and/or Ni(OH)$_2$, form a relatively compact layer and so decrease the rate of corrosion.

Postlethwaite and Freese [12] studied the effect of halide ions on the anodic behaviour of pure nickel in H$_2$SO$_4$ solutions and observed that all the halides accelerate the dissolution in active state and can break down the passive oxide layer so that the metal becomes severely pitted. Rehim et al. [13] examined the effect of halide ions of the mechanically polished nickel anode in

0.1 M, 0.75 M, and 1 M H_2SO_4 solutions. They found that the anodic potential excursion is a complex phenomenon. The curves of the active region can display one or two anodic current peaks. They supposed that the first peak is due to the anodic oxidation of nickel (to give the complex $NiOH^+$ on the electrode surface). The second peak may be due to the direct formation of NiO from the metal through the pores in the film. The presence of halides in lower concentrations has an inhibiting action on the anodic dissolution. The adsorbed anions can prevent any reaction of the metal atoms with H_2O dipoles or OH^- ions by displacing the latter and covering the metal surface. The inhibitive action of the anions decreases in the sequence $I^- > Br^- > Cl^-$.

Burstein and Wright [14] studied the kinetics of the anodic dissolution of nickel in acidic bromide and iodide solutions using a potentiostatic sweep technique. They found that the rate of dissolution is almost unaffected by the halide at low concentrations due to the presence of a prepassive film. At higher halide concentrations the prepassive film was removed and active dissolution occurred. Said and coworkers [15] used electrochemical techniques to study the effect of halides on the corrosion of nickel in 1 M sulphuric acid medium. After one hour of immersion they noted an acceleration of the nickel corrosion process when KCl and KBr had been added to the electrolyte. Potassium iodide exhibited an inhibition of the anodic Ni corrosion process. They concluded that KI addition decreases the material corrosion rate without changing the alteration mechanism.

Real et al. [16] examined the influence of the concentration of chloride ion on the active dissolution and passivation of polycrystalline nickel rotating disk electrodes in sulphuric–potassium sulphate solutions at pH 2.6 and 25 °C. The voltammetric data suggest that the passive layer results from a complex reaction involving the electrodissolution of the base metal and the formation and partial chemical dissolution of the anodic layer. The influence of chloride ions under different hydrodynamic conditions was discussed taking into account the competitive adsorption involving chloride ions and species containing oxygen at the initial stages of the reaction yielding soluble products, and the appearance of $Ni(OH)_2$ as a new phase. Stirring the solution favours the electrodissolution reaction by increasing the transport rate of Cl^- and H^+ ions to the electrode surface, and simultaneously decreasing the thickness of the $Ni(OH)_2$ layer.

The mechanism of active dissolution of nickel remains highly controversial. It seems that there is no agreement so far even on the actual shape of the current–voltage profiles. Two-peak or single-peak curves are reported depending on the potential sweeping rate, the prepolarization conditions, the structural properties of the metal, etc. This erratic behaviour is tentatively ascribed to either the remains of stable natural oxides on the metal surface or strong interaction with hydrogen [1,17,18].

Allergy to nickel is a phenomenon that has assumed growing importance in recent years, largely because of the introduction of cheap fancy jewellery in which the underlying metal layer consists of nickel. About 8% of the population is estimated to be allergic to nickel. In fact the allergy is not caused by nickel itself but by the nickel salts that are formed under the effect of perspiration in contact with the piece of jewellery or watch. This phenomenon is always accompanied by the corrosion of the object. The degree of allergy varies. Some people develop dermatitis (eczema) from even a brief contact with nickel-containing items, while in others it breaks out only after many years of skin contact with nickel. Sometimes it is due to contact with metal items containing nickel, but often there is no obvious reason for it. It has been suggested that in some persons dyshidrotic hand dermatitis is due to nickel in the diet [19–21]. This essentially increases the importance of the examination of the corrosion of nickel in various environments.

The anodic dissolution of nickel is a typical heterogeneous reaction proceeding on the metal–solution interface at a rate that depends on the surface concentration of reactants and the existence of free sites on the surface. The adsorption of reactants, including the intermediate of the reaction atomic hydrogen, is of great importance in the determination of the kinetic relationship of the reaction [4,11]. The surface of nickel in acidic solutions is primarily covered by adsorbed water molecules and to a smaller extent by hydrogen ions.

The aim of this study is to examine the effect of halide ions on nickel in perchloric acid medium. The most detailed examinations of corrosion of nickel have been carried out in sulphuric acid. It is established that SO_4^{2-} ions also are able to adsorb on the nickel surface [22–24]. As perchlorate anion does not adsorb on the nickel surface there is no significant competition between various anions for better adsorption places. This allows examining the influence of the halide anions on the corrosion of nickel at lower concentrations. It appears that no detailed studies of the corrosion of chemically polished nickel are available in the literature. A comparative study of the effect of halide anions on the corrosion of the mechanically and chemically polished nickel was carried out in the study reported here.

EXPERIMENTAL

The working electrode was made of nickel rods (99.99% purity), its exposed area was from 0.5 to 1.3 cm^2 depending on the experiment. Before use the electrodes were polished (1) with emery paper (of 2000 grade) or (2) after mechanical polishing chemically (solution of

concentrated acids: 33% HNO_3, 33% CH_3COOH, 33% $CH_3COOOCCH_3$, and 1% HCl). When the mechanical polishing method was used the electrodes were degreased with concentrated KOH and then rinsed with MilliQ water. Experiments were performed in 0.1 M $HClO_4$ solution. Three salts – KCl, KBr, and KI – were used to introduce the halide ions in solutions. All the chemicals were of analytical grade and all the solutions were prepared using MilliQ water. The experiments were carried out at room temperature ($23°\pm2°C$).

In order to study the corrosion of nickel a classical three-electrode cell was used with an Ag/AgCl electrode as reference and a graphite stick as the counter electrode. The working electrode was immersed into the acid solution. The solution was deaerated with argon (99.999%), which constantly ran except during the registration. There was prepolarization during one hour at the potential of -0.3 V (all the potentials are given in the hydrogen scale). This potential is sufficiently high for the reduction of oxides on the surface of nickel electrodes [22,23]. After the prepolarization, a polarization was performed at the potential of -0.15 V for 5 min in order to reduce the amount of molecular hydrogen in the solution and so to decrease the current caused by the ionization of dissolved hydrogen during the measurement of CV curves. All the experiments started with the registration of the voltammograms of nickel in perchloric acid. After that the necessary amounts of halide salt were added. Pontentiodynamic polarization experiments were conducted using a potentiostat/galvanostat 263A (PAR EG&G, USA). The cyclic voltammograms were obtained by a single sweep of the potential from -0.15 V to $+0.65$ V and the reversing of the sweep at the same scan rate to -0.30 V. High positive potentials were avoided during the experiments because intensive pitting corrosion appeared in some solutions at high potentials. The scan rates were varied: 10, 50, 100, and 300 mV s^{-1}. Generally, three different concentrations of halides were introduced to the acid solution: 1×10^{-5}, 1×10^{-4}, and 1×10^{-3} M, in some cases also 1×10^{-6}, 5×10^{-5} M.

RESULTS AND DISCUSSION

The full voltammograms of mechanically and chemically polished nickel in the half logarithmic scale are presented in Fig. 1. The voltammograms reveal differences in the behaviour of the mechanically and chemically polished electrodes. The remarkable influence of the oxidation of the surface of an electrode on the corrosion potential is also well seen. It is interesting to note that the rate of hydrogen evolution also changed and the shifts of reversible polarization curves are different for mechanically and chemically polished electrodes OB. In the present work we examine in some detail mainly the corrosion area.
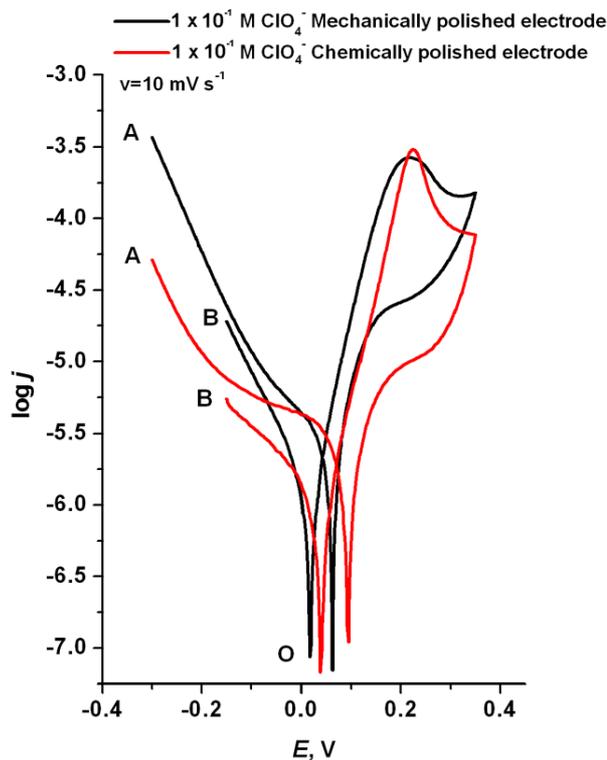

Fig. 1. Full voltammograms of mechanically and chemically polished nickel in 0.1 M $HClO_4$ in the half logarithmic scale. B, the starting point of measurements ($E = -0.15$ V); O, the open circuit (corrosion) potential; A, end of the program ($E = -0.30$ V). The curves AO and BO describe the cathodic evolution of hydrogen and the curves lying at more positive potentials than point O represent corrosion (oxidation and dissolution) of the Ni electrode.

The anodic voltammograms of mechanically and chemically polished nickel in 0.1 M $HClO_4$ are presented in Figs 2 and 3, respectively, at scan rates ranging from 10 to 300 mV s^{-1}. The single sweep started from the potential -0.15 V and proceeded to $+0.65$ V; the sweep was reversed at the same scan rate to -0.30 V. Such program was chosen to avoid possible complications connected with the influence of the ionization of molecular hydrogen on the form of the polarization curve. Nickel exhibits an active–passive transition peak at the anodic potentials [13]. The curve of the active region displays anodic oxidation of nickel to give mainly the complex $NiOH_{ads}$ on the electrode surface (reaction 5). This one-electron reaction is proposed in the literature as the rate-determining reaction of the active dissolution of nickel. The second step is oxidation of this complex to $NiOH^+$ (reaction 6). As a result of this reaction a stable oxidation step for nickel atom (Ni^{2+}) is achieved and the following processes are chemical reactions. There are at least two possibilities: $NiOH^+$ joins a proton and transfers to Ni^{2+} cation (reaction 7) or loses a proton and forms NiO (reaction 8) [25].
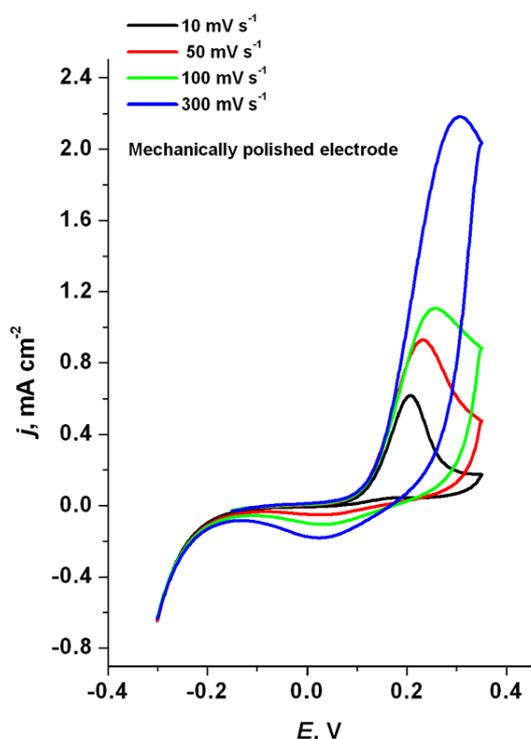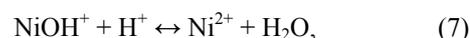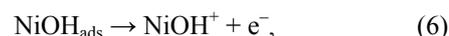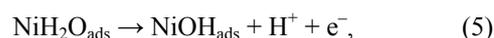
Fig. 2. Potentiodynamic anodic polarization characteristics of a mechanically polished nickel electrode in 0.1 M HClO$_4$ at various scan rates.
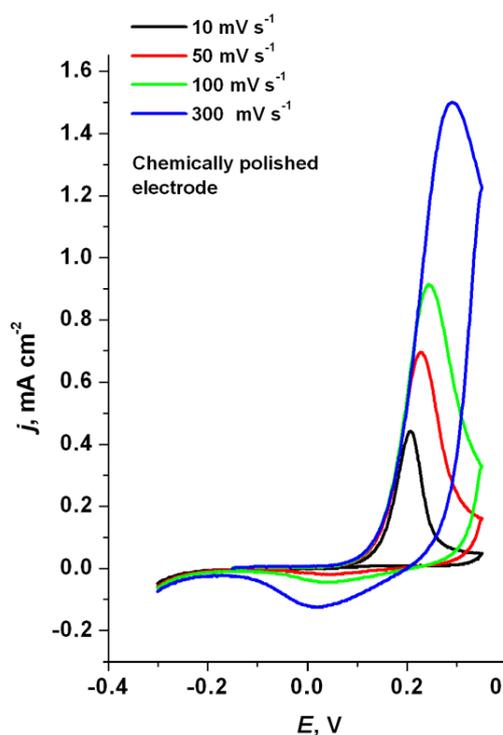
Fig. 3. Potentiodynamic anodic polarization characteristics of a chemically polished nickel electrode in 0.1 M HClO$_4$ at various scan rates.

The formation of NiO is very important for the following behaviour of nickel in acidic solutions as it is the main compound that blocks dissolution of nickel and causes the prepassivation of the metal. Intensive formation of NiO decelerates the increase of the current with rising potential, which causes the formation of maximum on voltammograms and the following essential decrease of the current. By increasing the scan rate it is possible to examine the polarization curves in a broader area of current densities.

$$NiH_2O_{ads} \rightarrow NiOH_{ads} + H^+ + e^-, \qquad (5)$$

$$NiOH_{ads} \rightarrow NiOH^+ + e^-, \qquad (6)$$

$$NiOH^+ + H^+ \leftrightarrow Ni^{2+} + H_2O, \qquad (7)$$

$$NiOH^+ \rightarrow NiO + H^+. \qquad (8)$$

Integration of the different parts of voltammograms gives useful information about the distribution of the consumed charge between various electrochemical processes taking place during voltammetric measurements. For instance, the value of the charge consumed during the increase of the current from zero to the potential maximum on the CV curve Q_2 characterizes the active dissolution of Ni before prepassivation and the value of reduction charge Q_3 carries information about the amount of the reduced form of oxide-type compounds formed on the surface of Ni during the consumption of the charge Q_1 and reduced in this potential interval and time. The results of such measurements are presented in Tables 1 and 2. These data show clearly that chemically polished electrodes have energetically more uniform

Table 1. The values of charge Q (mC cm^{-2}) at scan rates v (mV s^{-1}) for mechanically polished electrode: Q_1 – oxidized form, Q_2 – half-oxidized form, Q_3 – reduced form; the concentration of the halide ions is 1×10^{-5} M

| Anion	Charge	Scan rate v			
		10	50	100	300
ClO$_4$	Q_1	11.39	2.93	1.87	1.13
	Q_2	5.02	1.62	0.86	0.51
	Q_3	3.35	1.05	0.54	0.29
Cl$^-$	Q_1	48.14	19.88	14.29	9.31
	Q_2	25.69	9.89	6.76	3.75
	Q_3	1.61	0.28	0.10	0.05
Br$^-$	Q_1	25.13	11.40	6.55	5.30
	Q_2	12.57	5.55	3.24	2.58
	Q_3	2.40	0.79	0.60	0.36
I$^-$	Q_1	9.28	7.78	6.60	–
	Q_2	3.76	3.33	3.09	–
	Q_3	2.27	1.52	0.86	–

– Not measured.

Table 2. The values of charge Q (mC cm^{-2}) at different scan rates v (mV s^{-1}) for chemically polished electrode: Q_1 – oxidized form, Q_2 – half-oxidized form, Q_3 – reduced form; the concentration of the halide ions is 1×10^{-5} M

| Anion	Charge	Scan rate v			
		10	50	100	300
ClO$_4$	Q_1	4.30	1.19	0.93	0.86
	Q_2	1.83	0.76	0.58	0.41
	Q_3	0.28	0.14	0.12	0.10
Cl$^-$	Q_1	3.77	1.15	0.89	0.54
	Q_2	1.27	0.58	0.36	0.23
	Q_3	0.65	0.24	0.20	0.16
Br$^-$	Q_1	5.01	2.77	2.02	1.82
	Q_2	1.94	1.56	1.05	0.79
	Q_3	3.03	0.75	0.61	0.47
I$^-$	Q_1	8.82	4.59	1.31	–
	Q_2	2.16	1.45	0.47	–
	Q_3	1.03	0.37	0.10	–

– Not measured.

and stable surfaces and the rate of corrosion in 0.1 M HClO$_4$ solution is less pronounced. Thus, all charge values of the mechanically polished nickel electrode are larger than those of the chemically polished nickel electrode because of the different surface roughness.

The effect Cl$^-$, Br$^-$, and I$^-$ ions on the anodic behaviour of nickel in perchloric acid solution was examined in the concentration interval of anions from 10^{-5} to 10^{-3} M. Figures 4 and 5 show typical voltammograms of mechanically and chemically polished nickel electrodes in 0.1 M HClO$_4$ solution devoid of and containing addition of Cl$^-$, Br$^-$, and I$^-$. The scan rate was 10 mV s^{-1}. Inspection of the data obtained reveals that Br$^-$ and I$^-$ ions shifted the active–passive transition to more positive potential values. The inhibitive action of these halide ions could be ascribed to their chemical adsorption on the surface of nickel. The adsorbed anions can prevent any reaction of the metal atoms with H$_2$O dipoles or OH$^-$ ions by displacing the latter and covering the metal surface. The influence of Cl$^-$ ions is essentially different. These ions shift the active–passive transition a little to more positive potential values and nickel starts dissolving. The Cl$^-$ ions themselves are more hydrated than Br$^-$ and I$^-$ ions. This leads to weaker adsorption ability. Thus, the inhibitive action of these ions decreases in the sequence I$^-$ > Br$^-$ > Cl$^-$. It is in good agreement with the influence of halide anions on the hydrogen evolution in acid solutions [22,26]. The following mechanism is proposed for the direct halide adsorption onto the metal surface (reaction 9) and oxidation of Ni in the
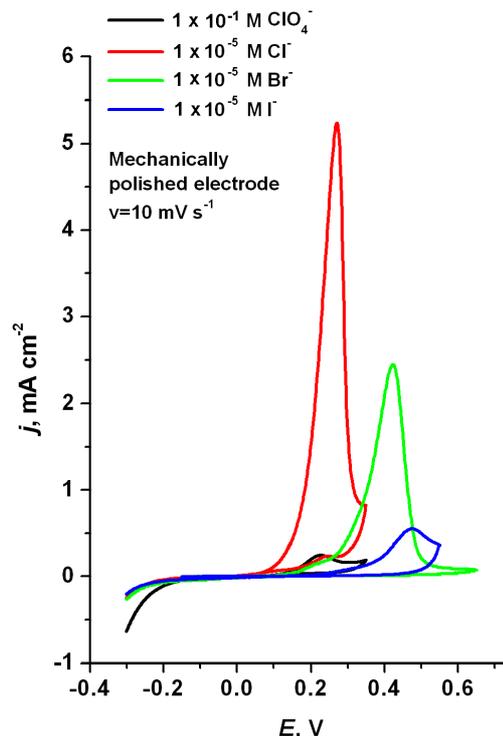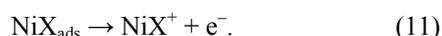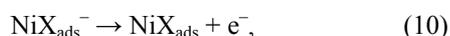

Fig. 4. Potentiodynamic anodic polarization characteristics of a mechanically polished nickel electrode in 0.1 M HClO$_4$ and the effects of halides (Cl$^-$, Br$^-$, I$^-$).
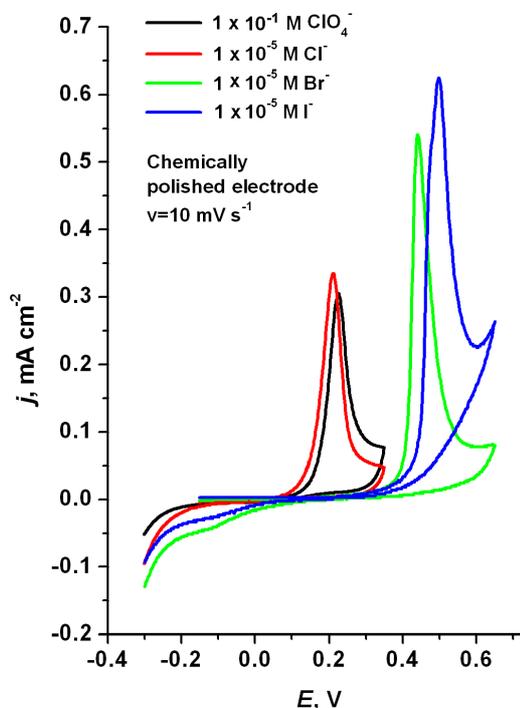
Fig. 5. Potentiodynamic anodic polarization characteristics of a chemically polished nickel electrode in 0.1 M HClO$_4$ and the effects of halides (Cl$^-$, Br$^-$, I$^-$).

presence of X_{ads}^- anions (reactions 10 and 11) [14]. The X^- stands for the halide anion.

$$NiH_2O_{ads} + X^- \rightarrow NiX_{ads}^- + H_2O, \qquad (9)$$

$$NiX_{ads}^- \rightarrow NiX_{ads} + e^-, \qquad (10)$$

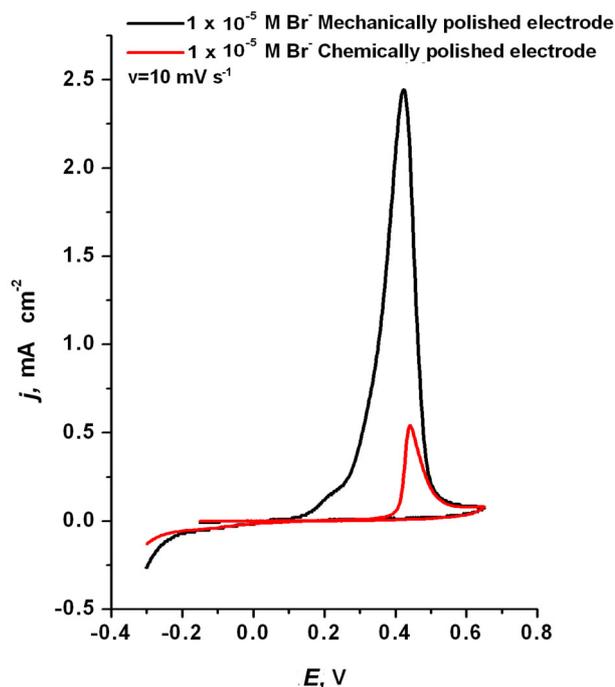$$NiX_{ads} \rightarrow NiX^+ + e^-. \qquad (11)$$

Comparison of Figs 4 and 5 shows clearly that the influence of halide anions on the corrosion of Ni is strongly dependent on the preparation of electrodes: the halide effects on the mechanically polished electrode are more intensive than on the chemically polished electrode. Figures 6 and 7 demonstrate the differences between Cl⁻ and Br⁻ effects on mechanically and chemically polished nickel electrodes in 0.1 M HClO₄ solution. When the electrode was polished chemically, most of the active sites of the surface dissolved. Therefore the effects of halide ions were lesser than on the mechanically polished nickel where it is easier for the halide ions to adsorb due to the active sites on the nickel surface.

Figure 8 shows the effect of 1×10^{-5} M Br⁻ ions at different scan rates on a chemically polished electrode. The values of charge determined by integration of CV curves are presented in Tables 1 and 2.

Increasing the concentration of halide anions generally shifts the active–passive transition to more positive potentials. Such shifts for a chemically polished nickel electrode can be seen in Figs 9–11. At the same
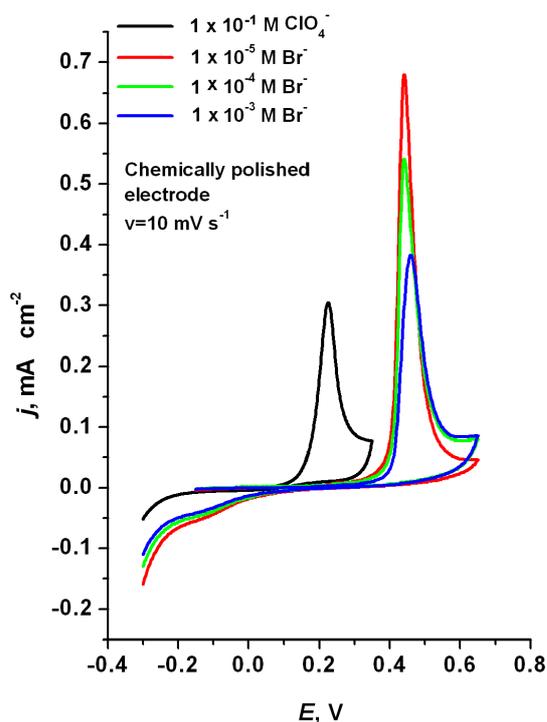

Fig. 7. The difference between the Br⁻ ion effects on the mechanically and chemically polished nickel electrode in 0.1 M HClO₄ solution.
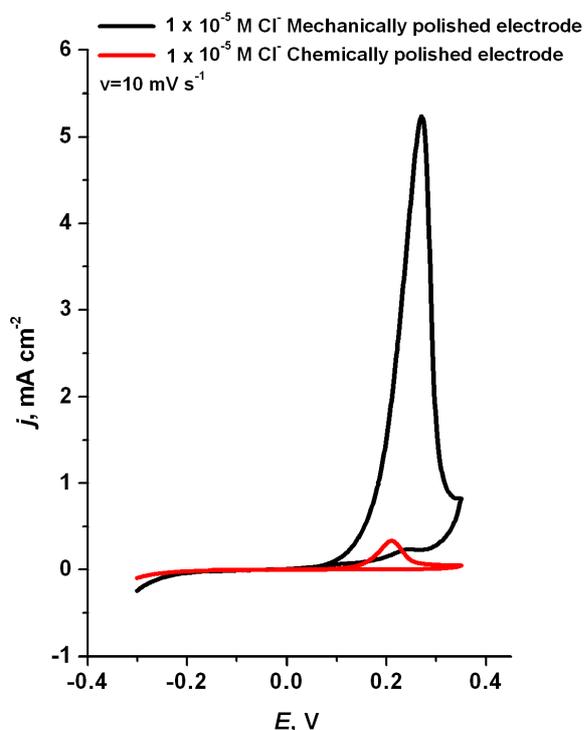
Fig. 6. The difference between the Cl⁻ ion effects on the mechanically and chemically polished nickel electrode in 0.1 M HClO₄ solution.
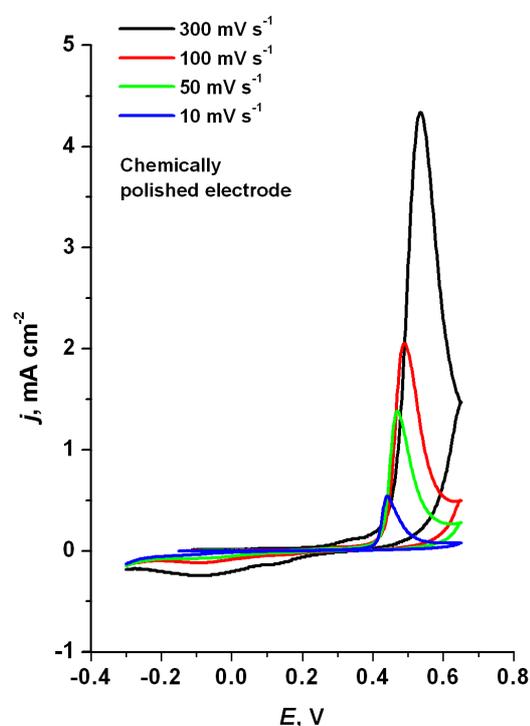
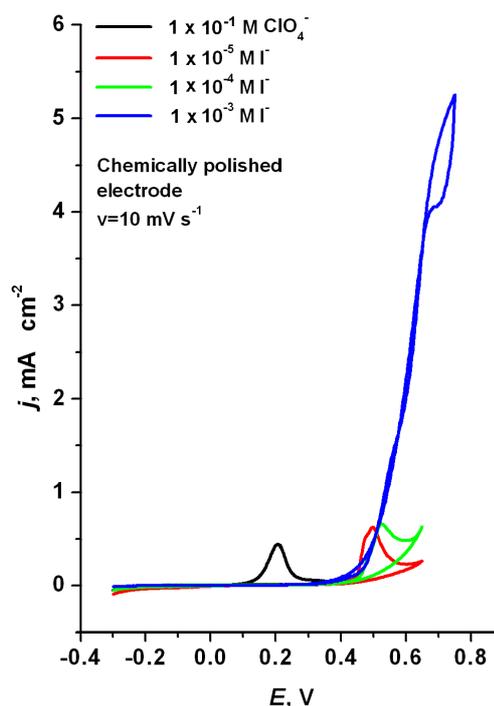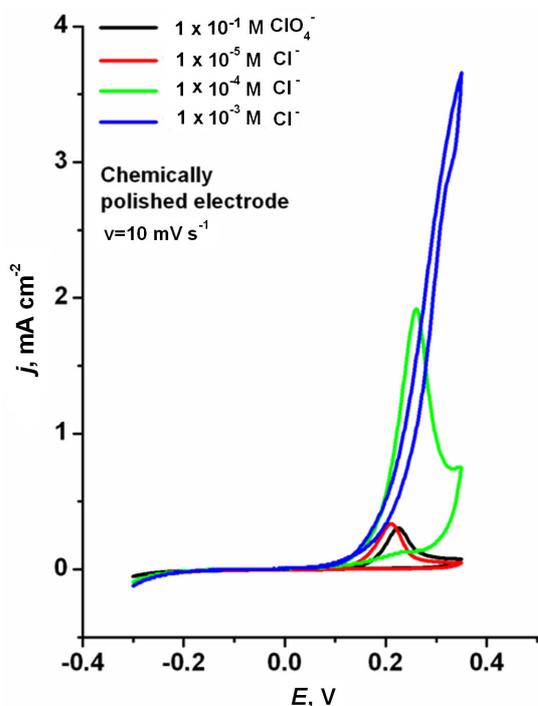**Fig. 8.** The effect of 1×10^{-5} M Br⁻ ions at different scan rates on chemically polished Ni electrode.

Fig. 9. Potentiodynamic anodic polarization characteristics of a chemically polished nickel electrode in 0.1 M HClO₄ and the effects of the halide Br⁻ at various concentrations.

Fig. 11. Potentiodynamic anodic polarization characteristics of a chemically polished nickel electrode in 0.1 M HClO₄ and the effects of the halide I⁻ at various concentrations.

Fig. 10. Potentiodynamic anodic polarization characteristics of a chemically polished nickel electrode in 0.1 M HClO₄ and the effects of the halide Cl⁻ at various concentrations.

time the corrosion blocking effect at these relatively high positive potentials decreases especially in the case of I⁻ anions (see Fig. 11). It is connected with very intensive pitting corrosion: some very large and deep pits appeared on the electrode surface. In order to preserve the quality of the electrodes the scans were generally stopped before reaching the maximum current densities.

CONCLUSIONS

Comparison of the voltammograms and the corresponding charges reflecting active corrosion and prepassivation of nickel showed clearly that the corrosion of the electrodes with mechanically polished surface was much more intensive than that of chemically polished electrodes. One conclusion is that relatively weakly adsorbed chloride anions cannot block the corrosion; on the contrary, they accelerate the corrosion of Ni probably by stimulating the formation of pits. Bromide anions shifted only the maximum potential by 205–215 mV into the positive potential direction but did not depress the rate of corrosion. Iodide anions of low concentration had the largest blocking effect – the maximum shift was 340–400 mV, but at higher concentrations a remarkable acceleration of corrosion of Ni took place with the formation of pits. A general con-

clusion is that the adsorption of halide anions in the acid solutions with weakly adsorbed acid anions, such as ClO_4^-, is pronounced even at very low concentrations, resulting in a variable corrosion rate of nickel.

ACKNOWLEDGEMENT

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Halogeniidioonide mõju nikli korrosioonile perkloorhappelahuses

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Käesolevas töös uuriti halogeniidioonide mõju nikli korrosioonile. Elektrokeemilisi omadusi uuriti voltamperomeetriliselt.

Katsed viidi läbi 0,1 M perkloorhappelahuses (HClO$_4$). Katse käigus uuriti erinevate halogeniidioonide mõju nikli korrosioonile. Tööelektroodi poleeriti mehaaniliselt liivapaberiga. Sellele järgnes kas puhastamine kontsentreeritud naatriumhüdroksiidilahusega või keemiline poleerimine vastavalt eksperimendi ülesehitusele. Esmalt tehti voltamperomeetrilised mõõtmised puhtas perkloorhappelahuses. Tsüklilised voltamperomeetrilised mõõtmised toimusid režiimis hoidmisega (potentsiaalil −0,15 V hoiti 5 minutit). Skaneeritavaks potentsiaalide vahemikuks oli −0,15 kuni +0,65 V ja tagasitulek kuni −0,30 V. Varieeriti ka skaneerimiskiirust: 10, 50, 100 ja 300 mV/s. Seejärel lisati vastavad kontsentratsioonid halogeniidioone.

Perkloorhape valiti fooniks sellepärast, et perkloraatanioon on üks nõrgemini adsorbeeruvaid anioone nikli pinnal. See omadus võimaldas uurida halogeniidioonide mõju väga madalatel kontsentratsioonidel. Uurimise tulemusena leiti, et 0,1 M perkloorhappes on võimalik uurida kuni $1 \cdot 10^{-5}$ M halogeniidi kontsentratsioonini ja halogeniididel on märkimisväärne efekt nikli korrosioonile. Halogeniidioonide adsorptsioon sõltub nikli pinna energeetilistest omadustest. Eriti märgatav on see kloriidioonide puhul, mis kiirendavad korrosiooni väga tugevasti mehaaniliselt poleeritud elektroodi korral, kuid keemiliselt poleeritud elektroodi puhul on efekt oluliselt väiksem. Tuvastati, et Br$^-$ ja I$^-$ ioonid nihutavad aktiivse lahustumise ja eelpassiivsesse olekusse ülemineku rohkem positiivsematele potentsiaaliväärtustele. Neid halogeniidioonide inhibeerivaid omadusi saab selgitada ioonide keemilise adsorptsiooniga nikli pinnal. Adsorbeerunud anioonid takistavad metalli aatomite reaktsiooni veega või OH$^-$ ioonidega, vahetades viimastega koha ja adsorbeerudes ise metalli pinnal. Teisalt, kloriidioonid nihutavad aktiivse/passiivse ülemineku isegi veidi negatiivsematele väärtustele ja intensiivistavad nikli lahustumist. See on selgitatav kloriidioonide nõrga adsorbeerumisvõimega ja pitingute teket stimuleeriva toimega. Halogeniidioonide inhibeerimisvõime väheneb reas I$^-$ > Br$^-$ > Cl$^-$. Halogeniidioonide efektid on mehaaniliselt poleeritud elektroodil suuremad kui keemiliselt poleeritud elektroodil. Kui elektroodi poleeritakse keemiliselt, siis enamik aktiivsetest kohtadest metalli pinnal lahustatakse ära. Seetõttu on ka halogeniidioonide adsorptsioon raskendatud ja efektid nõrgemad.