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Short communication

Stability of perchlorate ions in acid medium: Interaction with nickel and copper metals

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1. Introduction

Perchloric acid is often used as supporting electrolyte in electrochemical studies with various electrodes. Among these investigations reports concerning dissolution, deposition and corrosion of metals can also be found. For instance, in a recent communication corrosion and corrosion inhibition of nickel was studied in $HClO_4$ solutions using the EQCM technique [1]. Similarly, several studies were carried out with copper electrodes [2].

In such studies it is tacitly assumed that ClO_4^- ions are stable under the actual experimental conditions, that is, no reduction of these ions takes place. However, evidence for the occurrence of the reduction process has been reported for Rh [3–7], Pt [8–11], WC [12], Al [13], Ti [14], Ir [15], Ru [16], Re [17], Tc [18] and Sn [19] electrodes. A survey of the literature can be found in recent reviews [20, 21]. These observations prompt us to take into consideration the possibility of the occurrence of the reduction process at any electrode used in an aqueous acid medium containing perchlorate ions.

In accordance with this approach, for instance, the problem of whether the corrosion of nickel in the presence of perchloric acid is accompanied by the reduction of ClO_4^- ions should be considered as a self-evident question. In addition, it is known that nickel has certain catalytic activity in some reduction processes owing to the adsorption of hydrogen on its surface (similarly to Pt, Pd and Rh) thus the expectation concerning the ClO_4^- reduction at potentials where the dissolution of Ni and evolution of H_2 take place (i.e., in the course of the corrosion of nickel in acid media) can be considered as a well-founded assumption.

A closer examination of the literature shows that the problem of the reduction of perchlorate ions was the subject of a study by Fedotov and Bogdanshkina more than twenty years ago [22]. They concluded that, in the course of experiments carried out over several days, a very slow reduction of ClO_4^- to Cl^- ions takes place at ambient temperature. Considering the possible role of Cl^- ions in the corrosion processes, even if they are present in a very low concentration, confirmation of the observations reported in [22] is of great importance.

To our knowledge no similar results have been reported for copper, while the reduction of chlorate was observed in the course of its anodic dissolution [23].

The questions raised above can be answered easily by a very simple analysis of the solution phase in contact with the corresponding metal phase under open circuit conditions. The only task is to show that the products of perchlorate reduction appear in the solution phase. As almost in all cases where the reduction of perchlorate ions was observed Cl^- ion was the main reduction product, the analysis could be restricted to this species.

On the basis of the above considerations the intention of the present short communication is to show that the spontaneous corrosion of nickel and copper metal in the presence of perchloric acid is accompanied by the reduction of perchlorate ions leading to the formation of chloride ions.

2. Experimental details

The formation of Cl^- ions was followed either by chloride selective electrode (Radelkis OP-Cl-O711P, detection limit: 1×10^{-5} mol dm^{-3} Cl^-) or by potentiometric titration using a silver chloride electrode (detection limit: 2×10^{-5} mol dm^{-3} Cl^-). As the Cl^- selective electrode works in the pH range from 3 to 10 before the determination of the Cl^- concentration the sample taken out of the system was neutralized by addition of NaOH. The calibration of the electrode was carried out by addition of Cl^- ions to a neutral supporting electrolyte obtained by the neutralization of the acid solution used in the experiment. This procedure enabled us to neglect the role of Cl^- ions present in $HClO_4$ and NaOH used for the neutralization. Analytical grade (99.99%) metal powders and chemicals were used.

3. Results and discussion

3.1. *Nickel*

To compare our results with those reported in [21] a given amount of nickel powder was sprinkled into a given amount of perchloric acid solution (25 ml 3 mol dm^{-3} $HClO_4$) at ambient temperature and the change in the concentration of Cl^- ions was followed over three days.

Results are shown in Figure 1. In accordance with the observation reported in [21] a slow continuous increase in the Cl^- concentration is observed. This process is coupled with the dissolution of Ni and evolution of H_2. Thus the reduction of ClO_4^- ions in the course of the dissolution of Ni is clearly demonstrated.

Both the dissolution rate of Ni and the reduction of ClO_4^- should depend on the acid concentration and temperature. As at the present stage of our study no detailed and systematic kinetic investigation was attempted only some experiments as to the concentration and temperature dependence were carried out. These results are summarized in Table 1. A given amount of Ni powder was dissolved in an excess of perchloric acid.

From the data of Table 1, the molar ratio of Cl^- ions formed to nickel dissolved is independent of $HClO_4$ concentration. The influence of temperature is not strong as a temperature change of 25 °C results in less than a doubling in the value of B/A.

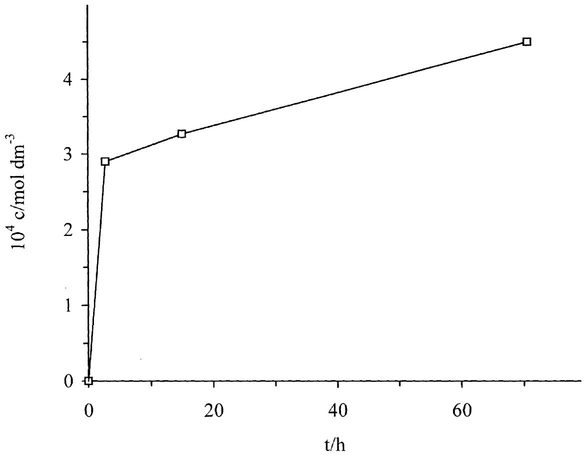

Fig. 1. Changes in the Cl^- concentration in the solution phase in the presence of 1 g Ni powder + 25 ml 3 mol dm^{-3} $HClO_4$ at ambient temperature without stirring.

Table 1. Interaction of $HClO_4$ with nickel

Temperature /°C	c_{HClO_4} /mol dm^{-3}	*A* Amount of dissolved Ni /10^{-2} mol	*B* c_{Cl^-} formed /10^{-5} mol	*B*/*A* /10^{-3}
25	3	3.57	7.5	2.1
40	3	3.9	12	3.07
50	3	3.9	13.5	3.46
25	1	1.26	2.6	2
40	1	1.27	4.3	3.38
50	1	1.27	4.9	3.85

Considering the equation

$$4\,Ni + 8H^+ + ClO_4^- = 4\,Ni^{2+} + 4\,H_2O + Cl^- \qquad (1)$$

the formation of one mole Cl^- should be accompanied by the oxidation of 4 mol of nickel; thus at 50 °C the efficiency of the reduction process referred to the total amount of dissolved Ni is about 1.5% and at 20 °C is not far from 1%.

Although the data obtained do not allow far reaching conclusions to be drawn it can be stated, the owing to the high adsorbability of Cl^- ions the possible role of Cl^- ions formed at Ni electrodes in $HClO_4$ solutions cannot be neglected in the interpretation of phenomena observed in such systems.

In the above we have assumed that no significant amount of Cl^- containing intermediates of Reaction 1 accumulate in the solution phase. This assumption can be supported if it can be demonstrated that the rate of interaction of ClO_3^- ions with Ni is significantly higher than that of ClO_4^- under comparable conditions.

Data presented in Table 2 provides an unambiguous proof of the occurrence of the following overall process:

$$3\,Ni + ClO_3^- + 6\,H^+ \rightarrow 3\,Ni^{2+} + Cl^- + 3\,H_2O \qquad (2)$$

This has a very high rate when compared with Reaction 1. This means that we may assume that Reaction 3 is the rate-determining process in the reduction of perchlorate ions:

$$ClO_4^- + 2\,H^+ + Ni \rightarrow Ni^{2+} + ClO_3^- + 2\,H_2O \qquad (3)$$

3.2. *Copper*

In contrast to nickel, due to the standard potentials of the Cu^{2+}/Cu and Cu^{2+}/Cu systems, no hydrogen evolution can occur at the copper/aqueous $HClO_4$ solution interface under open circuit condition. Thus the spontaneous dissolution of copper in $HClO_4$ solution should be ascribed either to reactions with dissolved oxygen or to the reduction of the anion.

As in the case of nickel the formation of Cl^- ions would be unambiguous proof of the reduction of ClO_4^-

Table 2. Reduction of ClO_3^- ions by Ni
Amount of Ni 6×10^{-3} mol, temperature 25 °C, volume 50 cm^3.

Electrolyte /mol dm^{-3}	c_{NaClO_3} /mol dm^{-3}	Contact time /min	c_{Cl^-} /mol dm^{-3}
$HClO_4$			
1	0	60	$<10^{-5}$
1	5×10^{-2}	60	1.5×10^{-2}
1	5×10^{-1}	15	3.9×10^{-2}
H_2SO_4			
0.5	5×10^{-2}	60	1.24×10^{-2}
0.5	5×10^{-1}	15	3.9×10^{-2}

Table 3. Interaction of copper with ClO_4^- and ClO_3^- ions
6×10^{-3} mol Cu; $v = 50$ ml.

Electrolyte /mol dm^{-3}	c_{NaClO_3} /mol dm^{-3}	Temperature /°C	Contact time /min	c_{Cl^-} /mol dm^{-3}
$HClO_4$				
1	0	25	30	$<10^{-5}$
1	5×10^{-1}	25	30	2.1×10^{-2}
H_2SO_4				
0.5	5×10^{-1}	25	30	1.5×10^{-2}
$HClO_4$				
1	0	25	10^4	1.8×10^{-4}
3	0	25	10^4	3.7×10^{-4}
3	0	40	360	4.8×10^{-4}
5	0	40	360	5.6×10^{-4}
1	0	80	360	4.1×10^{-4}

ions. Table 3 summarizes the results of experiments carried out with copper powder. The dissolution rate of copper at low temperature ($\leqslant 25$ °C) is very low; however, it increases with increasing temperature. (Compare the contact time and chloride concentration data in Table 3 for 1 mol dm^{-3} $HClO_4$ at 25 and 80 °C.) Similarly to Ni, ClO_3^- ions react readily with Cu even at low temperatures.

4. Conclusions

The simple experimental procedures described provide unambiguous evidence concerning the spontaneous reduction of ClO_4^- ions at Ni and Cu/electrolyte interfaces in acid medium.

Although at low temperatures ($t \leqslant 25$ °C) the rate of the reduction processes is low their possible role in the interpretation of the behaviour of the interfaces cannot be neglected completely as is often the case. Considering the well known high adsorbability of Cl^- ions and the role ascribed them in corrosion processes, their formation even in very low concentrations may influence most of the processes occurring at Ni and Cu surfaces in the presence of $HClO_4$.

On the other hand, it is evident that at higher temperatures ($\geqslant 30$ °C) and in the presence of concentrated ClO_4^- solutions (>1 mol dm^{-3}), the processes leading to the formation of Cl^- ions may play a very important role.

A rough comparison of the interaction of ClO_3^- and ClO_4^- ions with Ni and Cu suggests that the perchlorate → chlorate transformation should be the rate determining step in the overall reduction of ClO_4^- ions. An interesting aside from this comparison might be that, in contrast to the assumption made in [23], the reduction of ClO_3^- ions at Cu does not require anodic polarization for the production of Cu^+ species reacting with ClO_3^-.

The high dissolution rate of copper in the presence of ClO_3^- ions should involve a direct first reaction step of ClO_3^- ions with the copper surface.

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