SHORT COMMUNICATION

Conversion of hypochlorite at a hydrogen gas-diffusion anode

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1. Introduction

Several mechanisms for the chemical conversion of hypochlorite (this term includes $HClO + ClO^-$) to chlorate have been proposed [1]. The reaction order with respect to $HClO$ and that to ClO^- are functions of the pH of the solution. The rate-determining step for the chlorate formation may depend on the pH of the solution [1]. Up to now the chemical conversion of hypochlorite has been studied only for solutions with $pH \geq 6$. Experiments at much lower pHs are very difficult to carry out because of the instability of $HClO$.

From the equilibrium constants for the hydrolysis of chlorine and the dissociation reaction of hypochlorous acid, it follows that in solutions with $pH < 2$ under equilibrium conditions the active chlorine (this term is used to include chlorine molecules, hypochlorous acid molecules and hypochlorite ions) is almost completely present as chlorine molecules [2].

To study the conversion of hypochlorite into chlorate in a strongly acidic solution and without simultaneous formation of oxygen, the chemical chlorate formation and the conversion of hypochlorite at a gas-diffusion anode in a weakly alkaline solution containing NaCl and NaClO were determined. During electrolyses H^+-ions are produced on the gas-diffusion anode by oxidation of hydrogen molecules and the solution layer adjacent to this anode will be very acidic.

2. Experimental details

Experiments were carried out in a membrane cell using a gas-diffusion electrode (GDE) with a geometric surface area of $4\,cm^2$ (E-TEK, Inc., Fuel cell grade on Toray Paper, Pt-loading $0.50\,mg\,cm^{-2}$) as the working electrode and a Pt-sheet with a geometric surface area of $6.8\,cm^2$ as the counter electrode. The electrolyses cell was described in [3]. The other part of the experimental setup was the same as described in [4].

During the electrolyses a mixture of hydrogen and nitrogen gases with a volumetric ratio of $1:8$, or pure nitrogen gas, was passed over the hydrophobic side of the GDE. A solution containing $0.5\,M$ NaCl and initially $0.02-0.09\,M$ NaClO was pumped along the hydrophilic side of the GDE. The linear rate of the solution flow in the working-electrode compartment was varied. The pH of the anolyte was kept at an almost constant value, viz. 9.5, by addition of NaOH solution. The temperature of the anolyte and catholyte was kept at 298 K.

The electrolyses were carried out potentiostatically. A saturated calomel electrode was used for a reference electrode. All potentials given are referred to the saturated calomel electrode. Sampling of NaCl–NaClO solution was carried out after each hour of electrolyses. Hypochlorite and chlorate concentrations were determined as described in [4].

3. Results and discussion

Preliminary experiments showed that the activity of the GDE for the oxidation of hydrogen can be very different. It was found that the anodic current density i_A can vary significantly for a GDE in a hypochlorite solution, at a potential of about $1.00\,V$ and with the hydrogen/nitrogen mixture as the gas feed. A GDE is considered as an active GDE if under the electrolyses conditions mentioned i_A is about $0.5\,kA\,m^{-2}$. For an inactive GDE $i_A \leq 0.01\,kA\,m^{-2}$. An active GDE had become inactive after storage for about 15 h in the hypochlorite solution used. The activity of the electrode was restored by cathodic polarization at potentials lower than about $-0.5\,V$ for a short period, viz. few minutes. The inactivity of a GDE may be caused by an oxide or oxygen layer present on its platinum particles. Useless otherwise stated, an active GDE was used to study the hypochlorite conversion.

Various electrolyses were carried out with an active GDE for a period of 3–5 h. During the electrolyses no detectable quantity of chlorate was found, the hypochlorite concentration in the anolyte decreased practically linearly with time of electrolysis and practically no hypochlorite diffused through the membrane into the catholyte. Separate experiments were carried out to investigate the stability of hypochlorite in a $0.5\,M$ NaCl + $0.03\,M$ NaClO solution at pH 9 and $25°\,C$. Practically no chlorate was formed and no hypochlorite was converted for a period of 15 h.

It can be concluded that the decrease in the hypochlorite concentration during the electrolyses is completely caused by reduction of hypochlorite to chloride at the hydrogen GDE, on which H^+ ions are also produced by oxidation of hydrogen molecules.

The rate constant of the hypochlorite conversion k_{hy} is given by

$$k_{hy} = (A_e c_{hy} V_a)^{-1} \frac{dc_{hy}}{dt} \quad (1)$$

where A_e is the GDE geometric surface area, c_{hy} the concentration of hypochlorite in the anolyte, and V_a the volume of anolyte.

Since the decrease in c_{hy} is relatively, about 20%, dc_{hy}/dt is practically constant, and the change in V_a by sampling is small, the rate constant k_{hy} is approximated by

$$(A_e, C_{hy,av}, V_{a,av})^{-1} h_{hy} \qquad (2)$$

where h_{hy} is the absolute slope of the linear $c_{hy}-t$ curve and the subscript 'av' indicates the average value during the electrolyses.

For an active hydrogen GDE in the hypochlorite solutions used the anodic current density at $1.10\,V$ was practically equal to that at $1.00\,V$, viz. $0.50\,kA\,m^{-2}$, the rate constant of hypochlorite conversion, k_{hy}, is also practically the same for both potentials and k_{hy} are 5.0×10^{-5} and $7.5 \times 10^{-5}\,m\,s^{-1}$ for, respectively, $v_s = 0.0095$ and $0.075\,ms^{-1}$, where v_s is the linear velocity of the anolyte flow in the electrolyses cell.

Owing to the order of magnitude of k_{hy} and the dependence of k_{hy} on v_s, it is likely that the hypochlorite conversion at the hydrogen GDE at $E = 1.00$ and $1.10\,V$ is determined mainly by the mass transfer of hypochlorite to the GDE, so that $k_{hy} = k_{hy,d}$ where the subscript 'd' indicates the diffusion limitation. After the replacement of the hydrogen/nitrogen by a nitrogen gas flow, the anode current density of the GDE at $E = 1.00\,V$ decreased quickly from 0.50 to $0.01\,kA\,m^{-2}$.

The results mentioned above indicate a very large effect of the hydrogen oxidation on the hypochlorite conversion. Hydrogen ions are produced by oxidation of hydrogen gas and react with ClO^- ions to $HClO$ molecules in a solution layer adjacent to the GDE.

The net anodic current density i_A on an active hydrogen GDE in a hypochlorite solution and at $E = 1.00$ and $1.10\,V$ was about $0.50\,kA\,m^{-2}$. Since hypochlorite is reduced to chloride with a current density $i_{c,hy}$, the current density for the oxidation of hydrogen $i_{a,H} = i_A + i_{c,hy}$.

In the following it is given the pH of the solution on the surface of the active hydrogen GDE at $E = 1.00\,V$, $v_s = 0.0074\,ms^{-1}$ and in a solution with hypochlorite concentration of $25\,mol\,m^{-3}$. From the hypochlorite conversion coefficient it follows that in this case $i_{a,hy} = 0.375\,kA\,m^{-2}$, $i_{a,H} = 0.875\,kA\,m^{-2}$ and the rate of the mass transfer for hypochlorite is $1.87 \times 10^{-3}\,mol\,s^{-1}\,m^{-2}$. From $i_{a,H} = 0.875\,kA\,m^{-2}$ it follows that the rate of H^+ formation is $8.75 \times 10^{-3}\,mol\,s^{-1}\,m^{-2}$.

In the solution layer adjacent to the GDE H^+ reacts with ClO^- according to

$$H^+ + ClO^- \rightarrow HClO \qquad (a)$$

and hypochloric acid is reduced according to

$$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad (b)$$
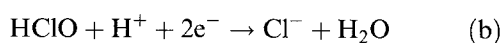
and a part of H^+ formed, viz. $5.0 \times 10^{-3}\,mol\,s^{-1}\,m^{-2}$, diffuses from the electrode surface into the bulk of electrolyte where H^+ reacts with ClO^- to produce $HClO$. During the experiments the pH of the bulk solution is kept constant by addition of NaOH solution.

Taking into account the ratio between the diffusion coefficients for H^+ and ClO^-, about 6.2 in dilute solutions at 298 K, and since the mass transfer coefficient is proportional to $D^{2/3}$, where D is the diffusion coefficient, it follows that the mass transfer coefficient for H^+ is $k_{H^+,d} = (D_{H^+}/D_{ClO^-})^{2/3} k_{hy,d}$, being $3.4 k_{hy,d}$. From $k_{hy,d} = 7.5 \times 10^{-5}\,m\,s^{-1}$ it follows that $k_{H^+,d} = 25.5 \times 10^{-5}\,m\,s^{-1}$. From this parameter and the rate of mass transfer for H^+, $5.01 \times 10^{-3}\,mol\,s^{-1}\,m^{-2}$, it follows that the pH of the solution on the electrode surface is approximately 1.29.

This means that the solution layer adjacent to the active hydrogen GDE at $E = 1.00\,V$ is strongly acidic and that near the electrode surface hypochlorite is practically completely present as hypochlorous acid, since ionic reactions are very fast. The standard electrode potential for the electrochemical reduction of $HClO$, namely

$$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad (c)$$
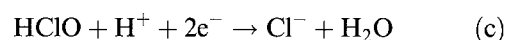
is $1.26\,V$ vs SCE [5]. This standard electrode potential supports the experimental results on the reduction of hypochlorous acid to chloride. Flis and Vorob'ev [6] have proposed that hypochlorous acid is reduced indirectly to chloride where chlorine is an intermediary.

In solutions at $pH \leq 2$ the equilibrium of the reaction

$$HClO + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O \qquad (d)$$
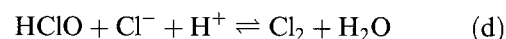
lies practically completely on the chlorine side of the reaction [2]. Despite this fact, it is possible that the reduction of $HClO$ takes place directly according to (b), for kinetic reasons.

The rate of the reduction of hypochlorite on the hydrogen GDE at $E = 1.00$ and $1.10\,V$ is determined by mass transfer of hypochlorite.

If a large part of the $HClO$ formed is converted into chlorine, the rate of reduction of hypochlorite to chloride is clearly smaller than that corresponding to the rate of mass transfer of hypochlorite, since chlorine diffuses to and from the electrode surface of the GDE. Moreover, the rates of the hypochlorite conversion at 1.00 and $1.10\,V$ are practically equal. These potentials are, respectively, below and just above the equilibrium electrode potential for the reaction $2Cl^- \rightleftharpoons Cl_2 + 2e^-$ assuming a chlorine pressure of 1 atm and a chloride concentration of $0.5\,M$. Consequently, it is more likely that hypochlorous acid is reduced directly to chloride.

Formation of chlorate does not take place under these conditions. This may be due to the fast reduction of hypochlorous acid to chloride. Unfortunately, the method used is not useful for study of chemical chlorate formation in strongly acidic solution.

References

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