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Anodic chlorate formation on platinized titanium

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The mechanism of anodic chlorate formation on platinized titanium was studied under well-controlled forced-convection conditions identical to those of previous experiments with graphite. Experimental results obtained in 4 M NaCl and in 0·05 M NaCl were compared to those predicted by mass transfer models describing anodic chlorate formation on graphite. In concentrated NaCl solution anodic chlorate formation rates for both electrode materials are smaller than expected for a diffusion controlled process. In dilute NaCl the ratio between measured rates and those predicted for diffusion control is shifted to higher values in qualitative agreement with predictions. Quantitative differences observed between the two electrode materials were attributed to the fact that hypochlorite oxidation on platinized titanium did not proceed at limiting current because of the slowness of the heterogeneous oxidation reaction.

Introduction

Platinized titanium anodes are of technological interest in chlorate electrolysis [1, 2] because of their corrosion resistivity which allows for cells to be operated at higher temperatures than with graphite anodes. In chlorate electrolysis this is of particular importance since the rate of chemical chlorate formation by disproportionation of hypochlorite (Equation 1) increases faster with temperature than that of the anodic loss reaction (Equation 2) which is generally believed to be mass transfer controlled under technical electrolysis conditions [4–9].

$$OCl^- + 2HOCl \rightarrow ClO_3^- + 2H^+ + 2Cl^- \qquad (1)$$

$$6\ OCl^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3/2\ O_2 + 6e \qquad (2)$$

The maximum current efficiency in a chlorate cell when all chlorate is formed according to Equation (2) is 66·7%, while it is 100% when all chlorate is formed according to Equation (1). The rate of anodic chlorate formation (Equation 2) has been studied previously by the authors on graphite electrodes [8, 9] under conditions where reaction (1) was negligible. It was found that observed rates in dilute NaCl solution (<0·1 mol/liter) differed from those in concentrated NaCl solutions (>1 mol/liter). However, the rate of anodic chlorate formation was governed by mass transfer and local chemical equilibrium conditions near the anode in both cases and hypochlorite was oxidized anodically under limiting current conditions. One may expect that as long as hypochlorite oxidation proceeds at limiting current, the rate of anodic chlorate formation is independent of the electrode material. During constant current electrolysis of NaCl solutions the hypochlorite concentration which builds up in the bulk electrolyte in cells containing anodes of different material ought therefore to be the same. However, it was noted by Foerster many years ago [3] that more hypochlorite built up in the bulk electrolyte during chlorate electrolysis with platinized platinum anodes than with blank platinum anodes. The conditions of the experiments were not well enough defined to allow for definite conclusions, but the results indicate that, aside from mass transfer and homogeneous reaction equilibria, the influence of heterogeneous kinetic factors and hence the anode material may not be negligible.

In view of this it was considered of practical and theoretical interest to perform a study under well-defined experimental conditions which would allow for direct comparison of anodic chlorate formation rates on graphite and on platinized titanium anodes.

Experimental method

The experimental apparatus used has been described before [8]. It consisted of an electrochemical flow channel cell through which the electrolyte was recirculated continuously. The design of the apparatus allowed for reproducible control of mass transfer conditions at the anode. Temperature and pH were maintained automatically during experiments. A platinized titanium* anode 5 cm wide and 20 cm long was positioned flush with the flow channel wall. A diaphragm was inserted between the anode and the cathode. Some experiments were performed under addition of 0·1% bichromate to the electrolyte, and the cathode was positioned in the place of the diaphragm. No significant difference in results obtained with the two types of experiments was observed. During experiments, sodium chloride solutions were subjected to electrolysis at constant current for prolonged periods of time, typically 30–50 h. Temperature and pH were such that no chemical chlorate formation occurred, i.e., all chlorate was formed by reaction (Equation 2). Concentrations of hypochlorite and chlorate were determined periodically using a potentiometric titration method which has been described elsewhere [8]. During electrolysis of dilute NaCl solutions, chloride concentration was determined simultaneously and adjusted if necessary by adding HCl to the cell electrolyte and neutralizing with NaOH. The anode potential was measured versus a saturated calomel electrode using a backside capillary. The history of a typical experiment is given in Fig. 1. During electrolysis of a neutral NaCl solution, hypochlorite builds up in the bulk at first but gradually more chlorate is formed. A steady state is reached after several hours when the hypochlorite concentration in the bulk and the rate of anodic chlorate formation become constant. The anodic chlorate formation rate is determined from the slope of the chlorate concentration versus time curve. Experimental chlorate formation rate and hypochlorite concentration at steady state may then be compared to those predicted by theoretical models.

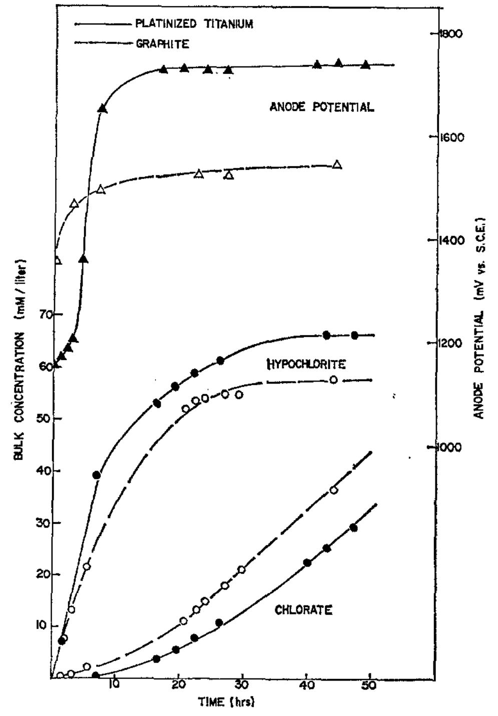

Fig. 1. History of constant current experiments on graphite (experiment 4 in [9]) and on platinized titanium anodes (experiment 1, Table 1) in 4 M NaCl.

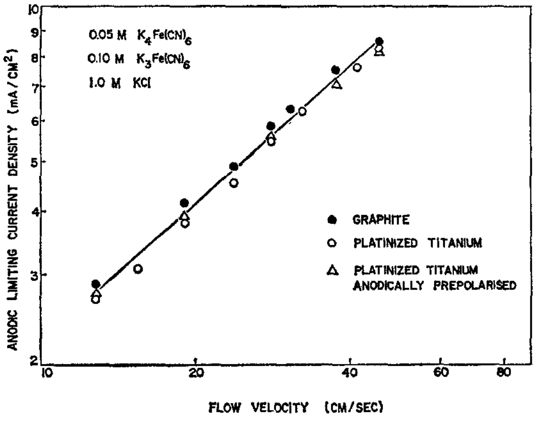

Fig. 2. Limiting currents for ferrocyanide oxidation on graphite and platinized titanium electrodes in flow channel cell. Electrode distance 9 mm.

Mass transfer characteristics of the present

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* Electroplated by Heraeus AG, Hanau, Germany.

apparatus and their experimental determination by limiting current measurements for the reduction of ferricyanide have been described in an earlier publication [8]. In the present study additional comparative measurements were performed in order to check whether the use of the platinized platinum electrode altered mass transfer conditions in the experimental system. Such might, for example, result from incomplete coverage of the titanium electrode with platinum or from surface roughness effects. Limiting currents for the oxidation of ferrocyanide to ferricyanide were determined at different flow rates on both graphite and platinized titanium.

A freshly prepared solution of 0·050 mol/liter potassium ferrocyanide, 0·100 mol/liter potassium ferricyanide and 1·00 moles/liter potassium chloride were used in these experiments. The measurements of oxidation rather than reduction currents were preferred here in view of the later use of the platinized titanium electrode as anode rather than cathode. Limiting currents measured on graphite were 3–10% higher than those on platinized platinum (Figure 2). It was concluded that within the experimental accuracy of the later chlorate experiments, this difference was negligible. Prolonged anodic polarization of the platinized titanium anode did not alter the measured limiting currents. Mass transfer conditions in this study were therefore assumed to be identical to those of the previous studies [8, 9].

Constant current experiments

Results of constant current experiments for the electrolysis of NaCl solutions of different concentrations at different flow rates and pH are summarized in Table 1. A current density of 5 mA/cm^2 was employed in all experiments. The choice of current density was given on one hand by the desire to keep the experimental time as short as possible by applying a large current density. On the other hand, current density had to be low to keep the stirring effect of anodically evolved oxygen smaller than that due to the external flow rate. Experimental results given in Table 1 were evaluated in terms of previously developed mass transfer models as shown in Table 2. The experimental hypochlorite flux at the anode j_e was calculated according to Equation (3) from measured chlorate formation rates assuming that all chlorate was formed by reaction (2).

$$j_e = 3\left(\frac{\text{electrolyte volume}}{\text{anode area}}\right)\left(\frac{dC_{\text{ClO}_3}}{dt}\right) \text{mol/cm}^2\ \text{s}| \tag{3}$$

The hypochlorite flux, j_d, corresponding to a simple diffusion controlled process, was obtained from Equation (4).

$$j_d = D\frac{C_0}{\delta} \tag{4}$$

C_0 is the total bulk concentration of hypochlorite ion and hypochlorous acid. The diffusion layer thickness δ was obtained from calibration measurements with ferricyanide [8]. The diffusion coefficient D was assumed to be 10^{-5} cm^2/s in order to facilitate comparison of the present data with those reported previously. The value 10^{-5} had originally been assumed for the lack of experimental data. In the meantime, Chao [10] reported experimental values of hypochlorite diffusion coefficients obtained by a chronopotentiometric method. At 10°C the given experimental values are $0{\cdot}9\times10^{-5}$ and $0{\cdot}8\times10^{-5}$ for HOCl and OCl$^-$, respectively. The assumed value of 10^{-5} is therefore very close to the real value determined by experiment. Using the value $0{\cdot}8\times10^{-5}$ cm^2/s, the ratio j_e/j_d in Table 2 (and in [8] and [9]) would be larger by a factor 1·25.

The flux j_h was calculated for dilute chloride solutions from Equation (5) [8].

$$j_h = \frac{i\phi_1}{2F}\left(\frac{1}{a\delta}-1\right) - D\frac{C_0}{\delta} - \frac{i\phi_1}{2Fa\delta}e^{-a\delta} \tag{5}$$

ϕ_1 is the current efficiency for chloride oxidation to chlorine and its numerical value is equal to the value of the current efficiency for chlorate formation. The reciprocal thickness of the reaction layer is a, given by $a = \sqrt{(k/D_{\text{Cl}})}$ (k = rate constant for chlorine hydrolysis, D_{Cl} = diffusion coefficient of chlorine). j_h is the hypochlorite flux predicted by a model considering chlorine hydrolysis proceeding in the immediate vicinity of the anode [8].

Experiments 1 to 4 of Table 2 were performed in 4 M NaCl solution. According to a previously

Table 1. Constant current electrolysis of NaCl solutions

No.	Cl^- (mol/liter)	T_c (°C)	*pH*	u (cm/s)	E_a (mV versus SCE)	*Gap width* (mm)	c_{st} (mM/liter)	v_{ClO_3} (mol/cm² s)	τ_{ClO_3}
1	4·0	7	9	13	1745	9D	66·5	5·27	61·0
2	4·0	6·5	9	13	1670	9DV	64·5	4·51	52·2
3	4·0	−0·2	9–10	46	1810	9DB	64–70	4·24	49·0
4	4·0	7	9	158	1730	2·25D	16·5	2·44	28·3
5	0·06	7	9	13	1975	9D	13·0	2·09	24·2
6	0·05	0·6	9·3	46	2050	9D	10	2·88	33·3
7	0·05	7	9–10	46	1990	9D	5–6	1·31	15·2
8	0·08	7	9–10	46	1995	9DV	(14)	(4·93)	(57·1)
9	0·05	7	2·2	46	1990–2010	9D	6	2·34	27·0

Cl^- = average value of chloride concentration in steady state; T_c = average cell temperature; u = linear flow velocity; E_a = steady-state anode potential; gap width = distance between anode and diaphragm; c_{st} = measured total steady-state concentration of hypochlorous acid and hypochlorite ion; v_{ClO_3} = chlorate formation rate in the steady state; τ_{ClO_3} = current efficiency of chlorate formation (6F per mol ClO_3 = 100%); D = diaphragm, B = potassium bichromate added, V = experiment started with excess hypochlorite present.

Table 2. Comparison between experimental and calculated hypochlorite flux

No.	$c_0 \times 10^6$	$\delta \times 10^2$	$j_e \times 10^9$	$j_d \times 10^9$	j_e/j_d	j_e/j_h
1	66·5	2·1	15·81	31·7	0·50	—
2	64·5	2·1	13·53	30·7	0·44	—
3	64–70	1·0	12·72	70·0	0·18	—
4	16·5	0·36	7·32	45·8	0·16	—
5	13·0	1·8	6·27	7·22	0·87	0·65
6	10	0·67	8·64	14·9	0·58	0·42
7	5–6	0·67	3·93	8·95	0·44	0·33
8	(14)	0·67	(14·8)	20·9	0·71	0·46
9	3·9	0·67	7·02	5·82	1·2	0·63

δ = Average thickness of diffusion layer, calculated from limiting current measurements for ferricyanide reduction (cm).

c_0 = Concentration of hypochlorite and hypochlorous acid in the steady state. c_0 is related to the total concentration of chlorine, hypochlorous acid, and hypochlorite, c_{st}, by

$$c_0 = \frac{K_1\, c_{st}}{(Cl^-)\,(H^+)+K_1} \times 10^{-3}\ (\text{mol/cm}^3)$$

where K_1 is the equilibrium constant of the chlorine hydrolysis

$$K_1 = \frac{(HOCl)\,(Cl^-)\,(H^+)}{(Cl_2)}\ [\text{mol}^2/\text{liter}^2].$$

j_e = Experimental hypochlorite flux at the anode (Equation 3) (mol/cm² s).

j_d = Hypochlorite flux at anode calculated for a diffusion controlled process according to Equation (4) (mol/cm² s).

j_h = Hypochlorite flux at anode calculated by taking into consideration the chlorine hydrolysis within the diffusion layer (Equation 5) (mol/cm² s).

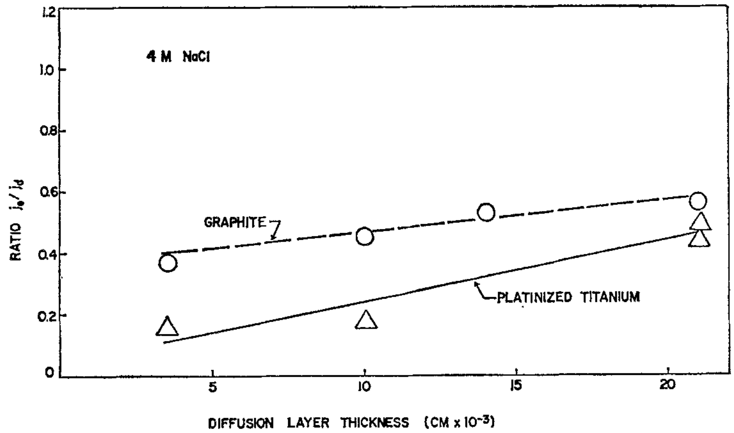

Fig. 3. Ratio j_e/j_d as function of diffusion layer thickness in 4 M NaCl. ○ Average values for graphite (Table 2, [9]); △ Values for platinized titanium (experiments 1–4, Table 2).

developed model, mass transfer controlled chlorate formation rates smaller than predicted for a simple diffusion process are to be expected in concentrated NaCl solutions where the hydrolysis equilibrium in the diffusion layer lies much more on the chlorine side than in dilute solutions. Under these conditions the hydrolysis of dissolved chlorine can proceed in the vicinity of the anode only if the H^+ ions generated* in reaction (2) and in the hydrolysis process are neutralized by ClO^- ions (or alkali) diffusing from the bulk towards the interface. The initial hypochlorite buildup observed during NaCl electrolysis can then be explained by the necessity to reach a bulk concentration of ClO^- high enough to ensure a rate of diffusion sufficient to buffer the diffusion layer. Owing to this buffering, only part of the hypochlorite reaches the anode and is oxidized there, i.e., the rate of chlorate formation is smaller than would correspond to the diffusion of the hypochlorite toward the interface. The ratios j_e/j_d in Table 2 (experiments 1 to 4) are indeed smaller than unity in qualitative agreement with the above model developed to describe experimental results obtained on graphite anodes.

On the other hand, the ratios j_e/j_d of experiments 1 to 4 show a definite trend toward decreasing values as the flow rate is increased. A somewhat similar trend has been observed with graphite, but it was much less pronounced in that case as evidenced by Fig. 3. In addition, absolute values of j_e/j_d observed with platinized titanium are smaller than could be reconciled with the described simple mass transfer model even when considering that presented j_e/j_d ratios involve considerable experimental uncertainties. This suggests that with platinized titanium anodes other factors may have to be taken into account at high flow rates.

The behavior in dilute NaCl solutions (experiments 5–9) also shows significant differences compared to the behavior observed previously with graphite electrodes. In dilute NaCl, anodic chlorate formation rates higher than those predicted for a diffusion controlled process are to be expected because in this case equilibrium conditions are such that chlorine hydrolysis may proceed within the anodic diffusion layer without any buffering. Since hypochlorite is generated in the immediate vicinity of the anode, less bulk hypochlorite is necessary in dilute NaCl solutions to maintain a

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* If one considers the overall process of technical chlorate electrolysis, the acid generated at the anode is, of course, in the end, neutralized by the alkali produced at the cathode. But the concentration of the OH^- ions in the bulk is very small and their rate of diffusion toward the anode is negligible. The OH^- ions thus act indirectly by neutralizing the HClO in the bulk solution. The ClO^- thereby formed diffuses back to the anode and buffers the diffusion layer, provided the bulk concentration of ClO^- is high enough to ensure a sufficient rate of diffusion. In contrast to OCl^- the HClO generated in the diffusion layer is not readily oxidized at the anode [9] and therefore it diffuses towards the interior and the cycle is thus closed: the hydrogen is transported away from the anode not as H^+ ion but as HClO, on the 'back' of the hypochlorite.

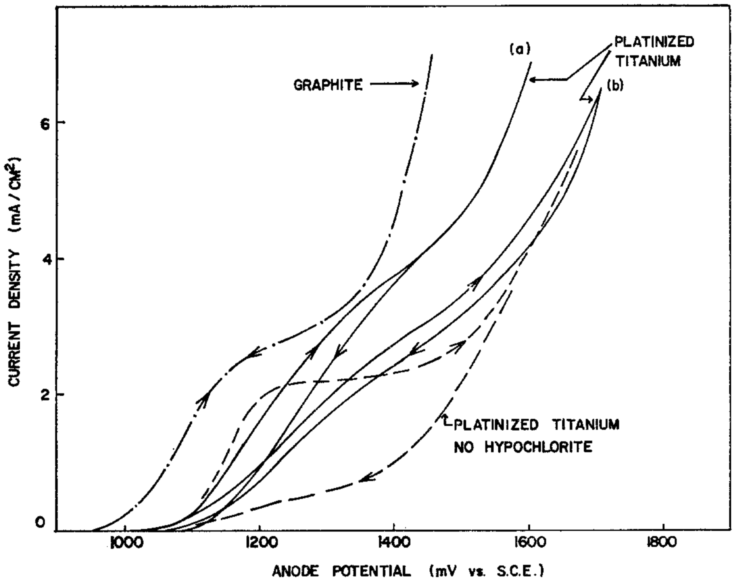

Fig. 4. Quasi steady-state current voltage curves for the oxidation of hypochlorite on graphite and platinized titanium anodes. Solution: 4 M NaCl+ 0·038 M NaClO; pH 10. (a) Platinized titanium, no pretreatment; (b) platinized titanium, pretreated by immersion in chromic acid. Flow rate: 29 cm/s.

given anodic chlorate formation rate. The results of Table 2 show that indeed less bulk hypochlorite was built up in the experiments 5–9 performed in dilute NaCl solutions compared to the experiments 1–4. The quantitative agreement with the hydrolysis model is poor, however, as evidenced by the small values of the j_e/j_h ratios of Table 2. Considerably more hypochlorite was built up in the bulk in the present dilute NaCl experiments with platinized titanium anodes than previously with graphite. In contrast to observations with graphite anodes where ratios of j_e/j_d for dilute NaCl solutions were much larger than unity [8], the corresponding ratios computed from the present data with platinized titanium anodes (Table 2) are close to unity or even smaller. Since the equilibrium conditions in the immediate vicinity of the anode have to be independent of anode material, factors related to the heterogeneous surface reactions have to account for the higher hypochlorite buildup found with platinized titanium anodes.

Potentiostatic experiments

The above results suggest that mass transfer models describing the rate of anodic chlorate formation may not describe adequately the behavior under present experimental conditions. The models are based on the assumption that either hypochlorite or hypochlorous acid react under limiting current conditions at the potentials prevailing during electrolysis [5–9]. To test the validity of this assumption in the case of platinized titanium anodes, anodic current potential measurements were performed using the same apparatus as in the constant current experiments. A potentiostat (Tacussel, PRT 2000) was used as power supply. Electrolyte solutions containing hypochlorite were prepared by bubbling chlorine gas through a chloride solution and neutralizing with NaOH. Obtained results of current-voltage measurements differed considerably from previous measurements on graphite electrodes [9] (Fig. 4). On graphite, well-reproducible hypochlorite oxidation curves with a limiting current plateau proportional to the bulk hypochlorite concentration and dependent on convection rate had been observed at pH > 8·5. On platinized titanium, reproducibility of comparable experiments was extremely poor. Measured currents at a preset potential depended heavily on the previous history of the anode and slow variations with time occurred. Only a few experiments were therefore performed. Results indicate that hypochlorite oxidation proceeds less smoothly on platinized titanium than on graphite. Fig. 4 illustrates the behavior qualitatively. Anodic current flow sets in at potentials approximately 100 mV more positive than previously on graphite, i.e., the anode reaction proceeds under higher activation overvoltage. This is in agreement with the results of Rius and Llopis who found a much higher overvoltage for the oxidation of hypochlorite on Pt–Ir than on graphite anodes [23]. The value of the current plateau (Fig. 4) depends heavily on electrode pretreatment and therefore it does not represent a mass transfer limited current. It is further noted that the second rise in current corresponding to chloride oxidation occurs at different potentials depending on electrode pretreatment. This is again in marked contrast to previous results on graphite anodes. Fig. 4 also shows that, in pure 4 M NaCl solutions on platinized titanium anodes, current-voltage curves of similar shape can be obtained even in the absence of hypochlorite. The current plateaus observed on platinized titanium anodes are, therefore, not due solely to hypochlorite oxidation. Cathodic pretreatment of the platinized titanium electrode resulted in the complete suppression of the plateau as illustrated in Fig. 5 because chloride oxidation now proceeded at much lower overpotentials than on an anodically pretreated electrode.

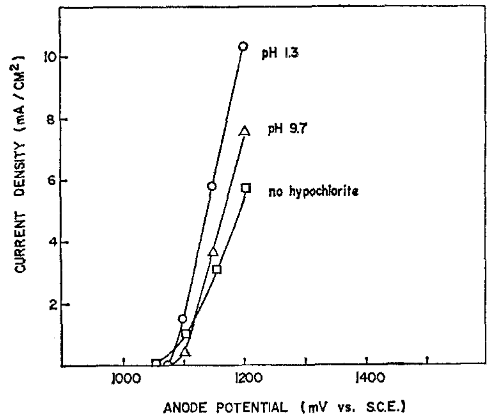

Fig .5. Quasi steady-state current potential measurements on cathodically prepolarized platinized titanium anodes. Solution: ○ 4 M NaCl + 0·010 M NaOCl, pH 1·3; △ 4 M NaCl + 0·013 M NaOCl, pH 9·7; □ 4 M NaCl, pH 9·5. Flow rate: 29 cm/s.

Discussion

It is well known that chloride oxidation on platinum may be strongly inhibited under certain conditions [11–15] because of oxidation of the platinum surface as was first recognized by Pfleiderer [11]. Recently Littauer and Shreir [13] and Bittles and Littauer [14] investigated the anodic behavior of platinum in chloride solutions by potentiostatic current-voltage measurements and concluded that at a potential of 1·4 V (versus NHE) anodic inhibition occurred independently of pH or chloride concentration. This resulted in current plateaus covering a potential range of several hundred millivolts. The value of the plateau current increased with increasing chloride concentration in the solution and with decreasing pH. Tafel parameters for chloride oxidation differed in the current density regions above or below the plateau current. Results of the present study suggest that platinized titanium in chloride shows a similar anodic behavior. Unfortunately, due to the above-mentioned irreproducibilities, no kinetic data for hypochlorite oxidation are available, but the results of Figs 4 and 5 suggest that at a cathodically prepolarized platinized titanium anode, chloride ion may be oxidized more readily than hypochlorite. It is likely, although no definite proof is available at present, that on an oxidized platinized titanium surface, chloride as well as hypochlorite oxidation may proceed in the region of the apparent current plateau. The data of Table 1 indicate that anode potentials during the present constant current electrolysis experiments corresponded to the oxidized state of the platinum surface. One might then explain the relatively lower j_e/j_d values found with platinized titanium compared to graphite by postulating that the kinetics of the anodic hypochlorite oxidation reaction on the oxidized platinum surface is considerably slower than on graphite, while the difference in the Cl^- oxidation kinetics between the two electrode materials is less pronounced. Oxidation of hypochlorite on platinized titanium therefore does not always proceed at the limiting current,

Table 3. Anodic chlorate formation at smooth platinum and platinized platinum after Foerster and Muller [16, 17]. Electrolyte: 4·8 M *NaCl; Temperature 13°C; no external stirring*

Experiment	*Anode*	*i*	c_{OCl}	ϕ_{O_2}	$v_{gas} \times 10^2$	$\delta \times 10^3$	$j_d \times 10_7$	$j_e \times 10_7$	j_e/j_d
1	smooth	17	0·34	33·3	2·06	10·4	2·04	0·587	0·29
2	plat.	17	0·61	31	1·92	10·8	3·53	0·608	0·17
3	smooth	170	0·68	30–33	19·5	3·40	1·25	6·03	0·48
4	plat.	170	0·89	34·5	21·3	3·24	1·72	5·77	0·34

i = current density (mA/cm^2), c_{OCl} = steady-state hypochlorite concentration (gram hypochlorite oxygen per 100 cm^3 solution), ϕ_{O_2} = fraction of total current used for oxygen evolution (steady state); v_{gas} = gas evolution rate (ml/min cm^2) calculated from $v_{gas} = \phi_{O_2}$ (RT/P4F)60; δ = calculated diffusion layer thickness (cm), j_d = diffusion hypochlorite flux (mol/cm^2 s), j_e = experimental hypochlorite flux calculated from oxygen evolution rate:

$$j_e = \frac{i\,(1-\phi_{O_2})}{2F}, \text{ (mol/cm}^2\text{ s).}$$

but a finite hypochlorite concentration at the surface is required to sustain observed anodic chlorate formation rates. This view is consistent with the observation that the ratios j_e/j_d of experiments 1 to 4 (Table 2) are smallest at high convection rates because, upon increasing the mass transfer rate, hypochlorite oxidation is expected to become more and more kinetics controlled.

In the context of the present discussion it is of interest to analyze early chlorate electrolysis experiments by Foerster and Muller [16, 17] which already suggest that the hypochlorite buildup may depend on the anode material and that the rate of anodic chlorate formation, therefore, may not be solely mass transfer controlled. Pertinent experimental data obtained during electrolysis of non-stirred concentrated NaCl solutions on vertical blank platinum and platinized platinum sheet electrodes are given in Table 3. Values for j_d were calculated by estimating the diffusion layer thickness according to a relation given by Ibl and Venzcel [18] for vertical smooth electrodes with hydrogen evolution (Equation 6).

$$\delta \approx 1{\cdot}5\times 10^{-3}\, v_{gas}{}^{-0.5} \qquad (6)$$

δ is the diffusion layer thickness in cm, v_{gas} is the oxygen evolution rate in ml/cm^2 min. The same relation has been applied previously to the estimation of mass transfer rates in chlorate electrolysis by Beck [6] and by Hammar and Wranglen [5]. Since no chlorate formation rates were measured in the experiments by Foerster and Muller, j_e in Table 3 was estimated from the rate of oxygen evolution assuming reaction (2) to be the only source of oxygen. The calculation yields ratios j_e/j_d smaller than unity consistent with the discussed models.*

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* Beck [6] from a similar analysis of experimental data obtained by Foerster on stationary platinum wire gauze electrodes [19] came to different conclusions. Because Equation (6) was derived from experiments on platinum sheet rather than wire gauze electrodes and because local electrolysis conditions on a wire gauze electrode are not well defined (as already observed by Foerster), the present analysis (Table 3) appears more pertinent than that given in reference [6].

Recent measurements of Janssen and Hoogland [22] and by Ibl and Venzcel [21] indicate that mass transfer coefficients for gas evolving electrodes also depend on the chemical nature of the evolved gas. Substantially higher mass transfer coefficients were found on oxygen than on hydrogen evolving electrodes. The anodic mass transfer coefficient measurements contain a considerable uncertainty factor, however. Therefore, to provide a direct comparison with Beck's analysis the data of Table 3 were evaluated based on mass transfer coefficients for hydrogen evolution (Equation 6). It is interesting to note that if the analysis were based on mass transfer coefficients for oxygen evolving electrodes, even lower values for the ratio j_e/j_d than given in Table 3 would be obtained. In fact, the mentioned mass transfer data for oxygen evolving electrodes might also lead to a reinterpretation of Hammar and Wranglen's hypochlorite oxidation data [5] cited by Beck [6]. According to Beck, the mass transfer coefficient k_L for hypochlorite oxidation on stationary oxygen evolving graphite electrodes is larger than or equal to k_L for ferricyanide reduction on hydrogen evolving electrodes. In terms of the j_e/j_d ratios used here, this would indicate a j_e/j_d ratio larger or equal to one. However, k_L values for oxygen evolving electrodes under the conditions of interest are 1·5 to 3 times higher than k_L values for hydrogen evolving electrodes [21]. In addition, when comparing mass transfer coefficients of different species at gas evolving electrodes, a correction taking into account the dependency of k_L on the diffusion

The ratio j_c/j_d for platinized platinum electrodes is consistently smaller than that for smooth platinum. Since platinized platinum is likely to have a higher surface roughness, i.e., larger surface area, one would expect just the opposite trend in the case that mass transfer alone is rate-limiting. It was noted by Foerster and Muller [16, 17] that on platinized platinum, chloride oxidation proceeded more readily than on smooth platinum. In addition to mass transfer, the heterogeneous reaction rate, therefore, played a role in governing anodic chlorate formation in these experiments. This also follows from the different time dependence of hypochlorite buildup and chlorate formation rate for the two electrode materials. It was observed by Foerster and Muller [17] that on platinized platinum no chlorate at all was formed at the beginning of electrolysis, but after some time a rapid increase in anodic chlorate formation set in. On platinum anodes, on the other hand, chlorate formation set in immediately and increased steadily with increasing bulk hypochlorite concentration.

A somewhat similar difference in behavior was observed here between platinized titanium and graphite anodes (Fig. 1). The potential-time behavior of Fig. 1 indicates that the onset of chlorate production on platinized titanium coincided with a sharp rise in anode potential which is probably due to oxidation of the platinized titanium surface and which leads to a change in the kinetic parameters for chloride oxidation.

Conclusions

The rate of anodic chlorate formation on platinized titanium anodes is only partly governed by mass transfer and chemical equilibrium conditions within the anodic diffusion layer. While on graphite, under chlorate electrolysis conditions, hypochlorite is oxidized at limiting current; it appears that on platinized titanium electrodes the hypochlorite oxidation reaction proceeds more sluggishly. The relative rate of chloride and hypochlorite oxidation at these electrodes depends strongly on the oxidation state of the electrode surface. For example, on a cathodically pretreated surface, chloride oxidation rather than hypochlorite oxidation appears to be the favored reaction. Because of heterogeneous kinetic limitations, more hypochlorite builds up in the bulk electrolyte during chlorate electrolysis with platinized titanium anodes than with graphite anodes. The effect is most noticeable in dilute NaCl solutions or at high external convection rates. The behavior leads to some interesting consequences with respect to the design of technical chlorate cells.

It was recently shown by Beck [6] that when hypochlorite mass transfer is the rate-limiting step in anodic chlorate formation, it is advantageous to operate chlorate cells in connection with an external reactor volume. High electrolyte convection rates are then employed between the electrodes. The present results suggest that, with platinized titanium anodes, even better current efficiencies ought to be obtained than predicted by Beck's model because hypochlorite is not oxidized at limiting current. Furthermore, it is probable that if one succeeds in maintaining the active state of the platinized titanium anode, the rate of anodic hypochlorite oxidation may be further reduced. Such might perhaps be possible by applying periodic short cathodic pulses or by suitably alloying the platinum deposit [20]. The active surface state is also favored by low local pH at the anode and by high chloride concentration. Anode potential measurements performed during the constant current experiments of the present study indicated that, as long as the platinized titanium anode was in its active state, lower potentials than on graphite prevailed, as illustrated by the initial potential values given in Fig. 1. After prolonged electrolysis, on the other hand, measured anode potentials on platinized platinum were some 200 mV higher than on graphite.

The present study illustrates the complexity of

coefficient has to be made. According to a model developed by Ibl and Venzcel [18], k_L is proportional to $\sqrt{D}$. The diffusion coefficient D for ferricions (used in k_L measurements on hydrogen evolving electrodes) is 2 times smaller, and that of cerium ions (used in k_L measurements on oxygen evolving electrodes) is approximately 3 times smaller than that of hypochlorite in Hammar and Wranglen's study. Therefore the actual k_L values for hypochlorite oxidation in that study may well have been 2 to 4 times smaller than estimated by Beck. The ratios j_c/j_d corresponding to those experiments might therefore be smaller rather than larger than one, in qualitative agreement with data on graphite obtained by the present authors under forced convection conditions [9].

heterogeneous and homogeneous kinetic factors affecting the rate of anodic chlorate formation on platinized titanium anodes. It appears that models based on limiting current oxidation of hypochlorite can describe the behavior of chlorate cells containing platinized titanium electrodes only approximately. The development of more sophisticated models is impeded, however, by the lack of data describing the kinetics of the anodic oxidation reactions which strongly depend on the oxidation state of the platinized titanium surface.

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