

The efficiency of chlorine evolution in dilute brines on ruthenium dioxide electrodes

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The efficiency of chlorine evolution from dilute brines (0.5–0.1M) was studied on RuO₂ and IrO₂ coated Ti anodes at 20°C and 70°C. Efficiencies are generally much higher than on graphite electrodes. However at low current densities at 70°C the efficiency on RuO₂ is considerably lower than on IrO₂.

1. Introduction

Recently titanium electrodes coated with the oxides of the platinum metals, especially mixtures based on RuO₂, have been introduced into the chlor-alkali industry on a considerable scale. As yet few studies have been published on the behaviour of such electrodes [1–3], and these deal principally with their behaviour in strong brines. However, the use of such electrodes may be even more important in dilute brines as the current efficiencies in Cl₂ are much higher than on graphite electrodes [4, 6]. Various data are to be found on the performance of Pt [4, 5], and Pt/Ir [6] alloy electrodes under these conditions but there are as yet no data relevant to RuO₂ coatings. We have, therefore, determined the current efficiency of chlorine evolution on the latter in brines from 1 mol dm⁻³ to 0.1 mol dm⁻³ and at temperatures of 20°C and 70°C, under conditions relevant to chlorine production; that is to say at a pH of about 2 when the electrolyte is saturated with chlorine. In general the differences between the behaviour of RuO₂ and Pt/Ir or IrO₂ are most apparent at low current densities, in dilute brines and at high temperatures.

One of the difficulties in assessing some of the previous work [4] is that the average current efficiency has been determined in an electrolyte where both the pH and concentration changed

considerably during the course of a run. From such data it is difficult to extract more than general trends. In order to avoid this problem in the present work the electrolyte was caused to flow through the cell at such a rate as to keep concentration changes in the electrolyte to 5–10%. This also minimized chlorate build-up.

When dilute brines are electrolysed the following anodic and homogeneous reactions may occur.

- (1) $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ (anode)
- (2) $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{Cl}^- + \text{H}^+$
- (3) $\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^-$
- (4) $6\text{OCl}^- + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 6\text{H}^+ + 3/2 \text{O}_2 + 6\text{e}^-$ (anode)
- (5) $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 1/2 \text{O}_2 + 2\text{e}^-$ (anode)
- (6) $\text{ClO}_3^- + \text{H}_2\text{O} \rightarrow \text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^-$ (anode)
- (7) $\text{OCl}^- + 2\text{HOCl} \rightarrow \text{ClO}_3^- + 2\text{Cl}^- + 2\text{H}^+$

Reaction (1) is the primary process. Reactions (2)–(4) lead to the production of chlorate by an anodic process. It may be seen that this sequence is favoured by low [Cl⁻] and [H⁺]. The stoichiometry of reaction (4) seems to depend on the pH [7, 8] but the above reaction applies in acid and neutral solutions. Reaction (4) can proceed faster than the rate of diffusion of bulk HOCl to the electrode as reactions (2) and (3) are fast and proceed in the diffusion layer [7]. Reaction (5) was found to be negligible on Pt[5] by analyses of

$[\text{ClO}_3^-]$ and O_2 in a region where reaction (7) was insignificant (below about 50°C in acid solution). Moreover in the case of RuO_2 , although the overvoltages for oxygen evolution are low [2] they are still considerably higher than those for chlorine evolution [3], which would again suggest that reaction (5) may be neglected. It may be seen that the amounts of oxygen produced in reactions (4) and (5) are equivalent and thus it is possible to determine the chlorine current efficiency even without a knowledge of the current distribution between these two reactions when reaction (6) is neglected. Reaction (6) seems to occur exclusively at low temperatures under the general conditions of this study (below 10°C) [5] and has not been considered. Thus the current efficiency in this study has been determined by oxygen analysis.

2. Experimental

The apparatus used is shown in Fig. 1. The brines were made from GPR grade NaCl and distilled water. They were initially purged with nitrogen to remove dissolved oxygen and then saturated with chlorine in (A). It was found that chlorine by itself did not remove dissolved oxygen from the brine in a reasonable length of time (a few hours). In brines of concentration less than 1.0 mol dm^{-3} the actual $[\text{Cl}^-]$ is increased by the chloride ions from the dissociation of the chlorine (reaction (2) above). This was taken into account in determining $[\text{Cl}^-]$. The ionic

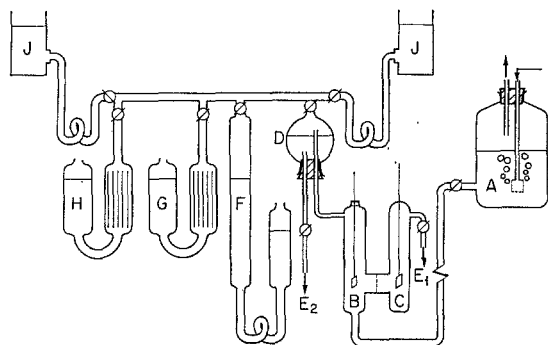


Fig. 1. Diagram of the apparatus used: A, brine reservoir with chlorine purge; B, anode compartment; C, cathode compartment; D, gas-liquid separator; E_1 , E_2 , brine to waste; F, gas burette; G, chlorine absorption vessel; H, oxygen absorption vessel; J, water reservoirs.

strength was kept constant at 1 mol dm^{-3} by the addition of NaClO_4 . During the course of a run the brine flowed from (A) into the anode compartment (B). A small flow through the cathode compartment (C) prevented cathodic products back-diffusing into the anode compartment. The brine and the anode gases then flowed into (D) and thence to waste. The gas was periodically aspirated into (F) and the Cl_2 was absorbed in concentrated KOH. At the end of a run when between 3 and 10 cm^3 of gas had been collected in (F) the oxygen was then absorbed in alkaline pyrogallol. There was usually a residual amount of nitrogen in the gas of the order of 10% of the total which arose from the further purging of the brine by the chlorine evolved. At 70°C the proportion was somewhat higher. Some of the work in 0.1 mol dm^{-3} brine was done on a rotating electrode (Fig. 2), to determine the possible effect diffusion limitation by Cl^- ions. Problems were experienced in the design of a gas-tight rotating electrode as the gas is drawn to the centre by the rotation and the lower PTFE bearing needs to be a good fit. The use of glass-filled PTFE would have been advantageous as far as bearing life was concerned. In retrospect it might have been preferable to have designed an electrode with a gas space above the electrolyte [9] and to have arranged to purge this with Cl_2 at the beginning and end of each run.

Electrodes were prepared as in [3]. Current was supplied from a Farnell (C2) constant current source. Overpotential measurements were made in a separate system [3].

3. Results and Discussion

It may be seen from Fig. 3 that the current efficiency for chlorine evolution in 1 mol dm^{-3} brine is constant within experimental error at about 97%. A run in 5 mol dm^{-3} brine showed that the efficiency was greater than 99%, no appreciable oxygen was collected during a run of 2 hr at a current of 200 mA ($CD = 10 \text{ kA m}^{-2}$). In 0.4 mol dm^{-3} brine the efficiency is constant at 92% up to about 15 kA m^{-2} . This decrease in efficiency is related to the increase in $[\text{OCl}^-]$ as $[\text{Cl}^-]$ decreased (reactions (2) and (3)). This will favour reaction (4). Above 15 kA m^{-2} the current efficiency starts to fall off. This decrease takes

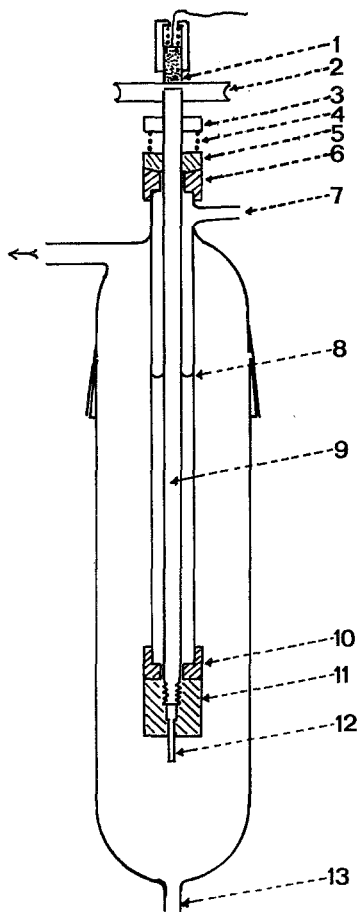


Fig. 2. Diagram of the rotating disc apparatus: 1, carbon brush; 2, drive pulley; 3, collar fixed to shaft; 4, spring; 5, teflon bearing, sliding fit on shaft; 6, teflon bearing, fixed to glass stem (8); 7, gas inlet to balance hydrostatic head of electrolyte; 8, glass stem; 9, titanium shaft; 10, teflon bearing fixed to glass stem; 11, teflon bearing screwed to the shaft end; 12, electrode cylinder, secured to shaft by (11); 13, brine inlet;

place at a lower current density than might be expected for diffusion limitation by Cl^- when this is considered (see below). However, at these current densities it is probable that the surface concentration of Cl^- is beginning to decrease significantly, favouring reaction (4) once again.

Initial results on a stationary electrode in $0.13 \text{ mol dm}^{-3} \text{ Cl}^-$ are shown in Fig. 3. Results at current densities above 15 kA m^{-2} were not obtained as corrosion destroyed the electrode. This may have been due to insufficient flow of electrolyte through the cell leading to depletion of Cl^- in the bulk electrolyte.

On a rotating disc at speeds of 500 and 5000

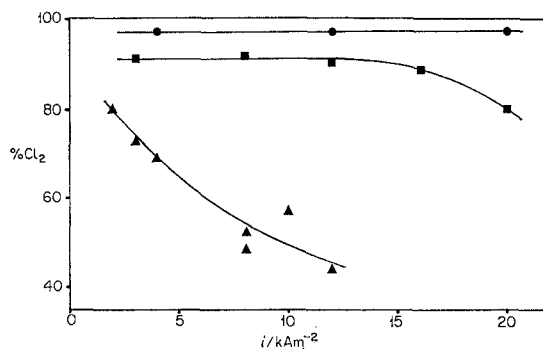


Fig. 3. Current efficiency for Cl_2 evolution at 20°C , on a stationary electrode. \bullet , $[\text{Cl}^-] = 1.0 \text{ mol dm}^{-3}$; \blacksquare , $[\text{Cl}^-] = 0.4 \text{ mol dm}^{-3}$; \blacktriangle , $[\text{Cl}^-] = 0.13 \text{ mol dm}^{-3}$

rpm, the results are shown in Fig. 4 where the chlorine current is plotted against the total current. It is seen that the higher rotation speed increases the chlorine efficiency. These results suggest that diffusion limitation of Cl^- is almost certainly occurring; however, it is to be noted that reaction (4) leads to the production of Cl^- ions in the diffusion layer, which complicates the diffusion conditions. If this is neglected and the equation due to $|b|$ and Venzel [10] for mass transfer to a stationary electrode on which gas is being liberated is assumed to apply, i.e.

$$K = \frac{D V^{\frac{1}{2}}}{1.5 \times 10^{-3}}$$

where K = mass transfer coefficient.

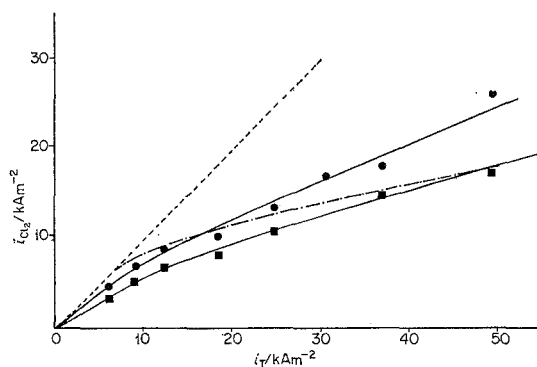


Fig. 4. Graph of the chlorine current, i_{Cl_2} , plotted against the total current i , on a rotating electrode in $0.1 \text{ mol dm}^{-3} \text{ NaCl}$ ($[\text{Cl}^-] = 0.13$) at 20°C . ----- shows 100% efficiency, - · - · - shows the relationship calculated from (10). \blacksquare 500 rpm, and \bullet 5000 rpm.

D = Diffusion coefficient for Cl^- ($\text{cm}^2 \text{s}^{-1}$).

V = Volume of gas evolved ($\text{cm}^3 \text{min}^{-1} \text{cm}^{-2}$)

Then we have:

$$i_{\text{lim}} = \frac{2FDV^{\frac{1}{2}}c_b}{1.5 \times 10^{-3}}$$

where c_b is the bulk concentration of Cl^- (mol cm^{-3}). The limiting current can be calculated from this equation if the difference in the gas volume when this is an oxygen/chlorine mixture rather than pure chlorine (the differences arising from the fact that $n = 2$ for Cl_2 and $n = 4$ for O_2), is neglected. This is reasonable since the volume is raised to the power of $\frac{1}{2}$, and this offsets the effect of the difference. Such a calculation gives the curve plotted on Fig. 4. When a comparison is made between the effective diffusion layer thickness on an electrode evolving gas at a current density $> 10 \text{ kA m}^{-2}$ and that on a slowly rotating electrode (500 rpm), it is found that the stirring effect of gas evolution outweighs that of rotation. This explains why the chlorine current (Fig. 4) is not increased by a factor of *ca.* $3 \times$ (i.e. $\sqrt{[\omega_2/\omega_1]}$) on increasing the rotation speed from 500 to 5000 rpm, and why the results on a stationary electrode are almost the same as those on an electrode rotating at 500 rpm.

At current densities below 8 kA m^{-2} , Ibl and Venzel's equation shows that diffusion of Cl^- will not be limiting. However in this region a lowering of the surface $[\text{Cl}^-]$ will effect the kinetics as argued above for $[\text{Cl}^-] = 0.4 \text{ mol dm}^{-3}$ favouring O_2 evolution. At high current densities the agreement between the results at 500 rpm and the limiting current predicted by Ibl and Venzel is as good as can be expected in view of the approximations made.

Fig. 5 shows the rather different picture when the current efficiencies are measured at 70°C . The most notable feature of these results is the fact that the current efficiency tends to zero at low current densities. This is due to reaction (4) being favoured at low current densities especially at high temperatures. On open circuit a considerable evolution of oxygen occurs on the electrode, and this results from the coupled simultaneous reaction of chlorine reduction, i.e.

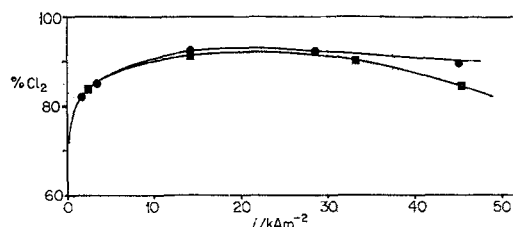
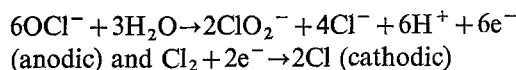


Fig. 5. Current efficiency for Cl_2 evolution at 70°C on a stationary electrode. ●, $[\text{Cl}^-] = 1.0 \text{ mol dm}^{-3}$ [Cl⁻] = 0.5 mol dm^{-3}



In 0.5 mol dm^{-3} NaCl on open circuit, the rate of oxygen evolution is the equivalent of about 40 A m^{-2} , which is probably the diffusion limiting current of Cl_2 to the electrode, as the oxygen current increases very rapidly on going from open circuit to low anodic current densities where Cl_2 evolution takes place. The fact that chlorine reduction is occurring on RuO_2 electrodes on open circuit is confirmed by the fact that they do not take up the Cl_2/Cl^- reversible potential in dilute brines as do Pt and Pt/Ir electrodes [11, 12] but show considerable deviations (i.e. in 0.1 mol dm^{-3} brine at 20°C the rest potential of a RuO_2 electrode is -23 mV with respect to Cl_2/Cl^- on Pt). Deviations are also measurable in strong brines at high temperatures (i.e. in 5 mol dm^{-3} NaCl at 80°C the rest potential is -7 mV). A confirmation of the basic assumption that this is due to the oxidation of hypochlorite rather than of water was obtained by leaving RuO_2 powder in contact with chlorine water for 24 hr at 20°C . Analysis of the resultant solution confirmed the presence of chlorate whereas it was not appreciable in a control solution.

In comparison with RuO_2 , an electrode coated with IrO_2 in 0.5 mol dm^{-3} NaCl showed a current efficiency of 90% over the current density range $3\text{--}15 \text{ kA m}^{-2}$. This would suggest that for work in dilute brines, electrodes based on Pt/Ir or IrO_2 would be preferable to those based on RuO_2 from the point of view of current efficiency.

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