SHORT COMMUNICATION

The influence of some fluoroanions on the anodic oxidation of chlorate ion to perchlorate ion at a lead dioxide electrode

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1. Introduction

Perchloric acid and a variety of perchlorate salts, the applications of which are well documented [1], are produced from sodium perchlorate. Among the various methods known, the electrochemical process is the only economic route for manufacture of this chemical [2]. The process involves the electrolysis of an aqueous solution of sodium chlorate, in which the oxidation of chlorate ion takes place at the anode producing the perchlorate ion.

$$ClO_3^- + H_2O \longrightarrow ClO_4^- + 2H^+ + 2e^- \quad (1)$$
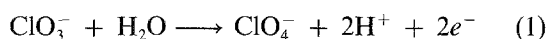
Simultaneously, oxidation of water, producing oxygen gas (Reaction 2), also takes place at the same potentials required for Reaction 1.

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad (2)$$
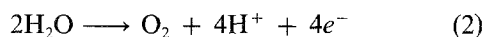
As a result the current efficiency for Reaction 1 is usually less than unity.

In order to enhance the current efficiency for the anodic oxidation of chlorate ion, one method described in the literature involves the addition of foreign ions to the electrolyte. Sodium fluoride, sodium dichromate and potassium persulphate were reported as additives [3–7], sodium fluoride being more commonly employed at a concentration of 2gl^{-1} in sodium chlorate electrolyte. Though there was increased current efficiency, up to 70% when fluoride was present in the electrolyte, a current efficiency approaching unity was not achieved. In an attempt to approach the theoretical current efficiency, we have used fluoroanions including fluoride, as additives. In this paper, we report results concerning the effect of fluoroanions on the kinetics of oxidation of chlorate ion to perchlorate ion at a lead dioxide coated titanium anode.

2. Experimental details

Smooth β-PbO$_2$ coated titanium anodes were prepared electrochemically from an electrolyte containing lead nitrate and copper nitrate under the conditions reported earlier [8]. The thickness of the β-PbO$_2$ layer was 2 mm and the area of the electrode was 8 cm^2.

The following laboratory grade fluorosalts were used: 1. sodium fluoride (NaF); 2. sodium tetrafluoroborate (NaBF$_4$); 3. sodium hexafluorophosphate (NaPF$_6$); 4. sodium hexafluoro silicate (Na$_2$SiF$_6$) 5.

sodium hexafluorotitanate (Na$_2$TiF$_6$); and 6. sodium hexafluoro aluminate (Na$_3$AlF$_6$). Commercial grade sodium chlorate was subjected to repeated recrystallization to ensure the absence of chloride and sodium perchlorate was free from chloride and chlorate. Stock solutions of NaClO$_3$ (6.5 M) and NaClO$_4$ (sat.) were prepared and suitably diluted according to the requirement. Experiments were carried out in NaClO$_3$ (6.5 M), NaClO$_3$ (3.5 M) and also in NaClO$_3$ (1 M) containing NaClO$_4$ (6 M) electrolytes with and without the fluorocompounds. The fluorocompounds (5gl^{-1}) were added to 0.6 l samples of the electrolyte. Some of the compounds (NaF, Na$_3$AlF$_6$ and Na$_2$TiF$_6$), which did not dissolve in the electrolyte readily, were allowed to remain in the electrolyte under continuous stirring for about 48 h before the experiments were carried out with the filtrate. In order to reduce the time of stirring ultrasonic agitation for a shorter time was attempted, which also gave the same results. The concentrations of these compounds (viz., NaF, Na$_3$AlF$_6$ and Na$_2$TiF$_6$) in the electrolytes were not estimated experimentally.

The instantaneous current efficiency measurements at different anode current densities and steady-state galvanostatic polarization measurements were carried out in electrolytes of volume 0.61 (pH 6.5) using a β-PbO$_2$ anode of 8 cm^2 area at a cell temperature of $60 \pm 2 \degree$C. The instantaneous current efficiency measurements were made by a gas analysis technique, the experimental details of which were reported earlier [9]. The polarization measurements were made in a stirred electrolyte with a calomel electrode saturated with sodium chloride (SSCE) as the reference electrode and stainless steel sheet as the counter electrode.

3. Results and discussion

The current efficiency results, obtained as a function of the anode current density in NaClO$_3$ (3.5 M) and NaClO$_3$(1 M) + NaClO$_4$(6 M) electrolyte solutions with and without the additives, are shown in Figs 1 and 2. The current efficiency for perchlorate formation increases significantly when the electrolyte solutions contain NaF and Na$_3$AlF$_6$, whereas it decreases drastically in the presence of NaBF$_4$ and NaPF$_6$. The current efficiency in electrolytes containg Na$_2$TiF$_6$ and Na$_2$SiF$_6$ is nearly the same as that in the additive free electrolyte.

Several continuous electrolyses were carried out in electrolytes with and without NaF and Na$_3$AlF$_6$. The cumulative current efficiency values for anodic oxida-
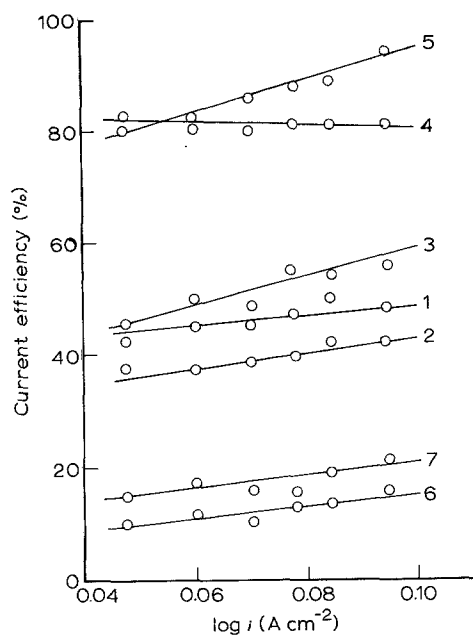
Fig. 1. Current efficiency as a function of current density (i) for anodic oxidation of chlorate ion to perchlorate ion in (1) NaClO$_3$ (3.5 M) containing no additive, (2) Na$_2$SiF$_6$, (3) Na$_2$TiF$_6$, (4) Na$_3$AlF$_6$, (5) NaF, (6) NaPF$_6$, and (7) NaBF$_4$ at pH 6.5 and temperature 60 $\pm$ 2° C.

Fig. 2. Same as Fig. 1 except that now the electrolyte is NaClO$_3$ (1 M) + NaClO$_4$ (6 M) instead of NaClO$_3$ (3.5 M) in Fig. 1.

tion of chlorate to perchlorate are given in Table 1. The increase in cumulative current efficiency due to the presence of NaF or Na$_3$AlF$_6$ is more than 20%. Further, the gain in current efficiency was uniform throughout the course of the reaction (Fig. 3).

A possible explanation for the fluoroanion influence on the kinetics of oxidation of chlorate ion may include the shifting of the overpotential of either the chlorate oxidation or oxygen evolution or both, and changes in the surface properties of the lead dioxide anode. However, the reproducible results obtained, when an anode used in the electrolyte containing NaBF$_4$ (a retardant) was subsequently used in the electrolyte containing NaF (a catalyst) and on repetition of this sequence, confirmed that the surface of the anode was not affected during electrolyses.

It is known [6] that NaF increases the overpotential of the oxygen evolution reaction in NaClO$_4$ at platinum and PbO$_2$ electrodes. From these studies, however, the shift in overpotential of the oxygen evolution reaction in relation to that of the chlorate oxidation cannot be estimated, as the latter reaction is absent in NaClO$_4$ electrolyte. In order to understand this, steady-state galvanostatic polarization measurements were made in a mixed electrolyte of NaClO$_3$ (1 M) and
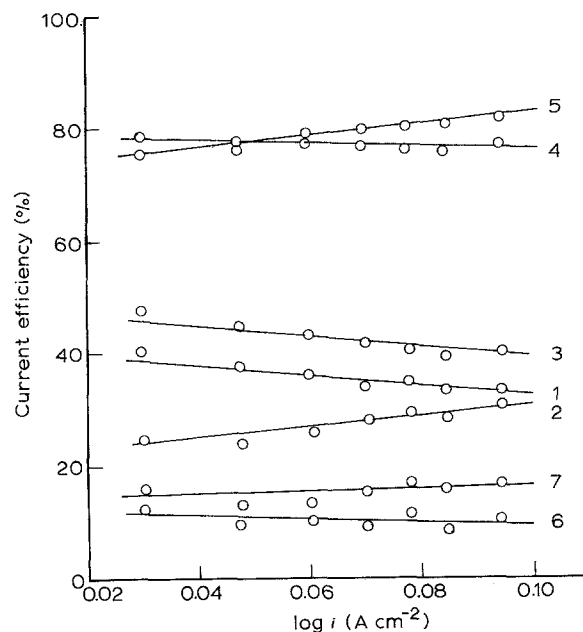
NaClO$_4$(6 M) with and without fluoroanions and the results are presented in Fig. 4. It may be seen that, at practical current densities, the electrode potential is higher by about 200 mV in electrolytes containing the retarding fluorocompounds (viz., NaBF$_4$ and NaPF$_6$) than in solutions containing the catalytic fluorocompounds (viz., NaF and Na$_3$AlF$_6$). As the polarization curves in Fig. 4 are composite in nature corresponding to both the chlorate oxidation and oxygen evolution reactions, partial polarization curves were derived from these using the current efficiency curves in Fig. 2. Thus, the current density corresponding to the chlorate oxidation reaction (i_1) and to the oxygen evolution reaction (i_2) were calculated from the anode current density (i) and the polarization curves are replotted with the electrode potential versus i_1 and i_2 separately. The partial polarization curves for two different electrolytes are shown in Fig. 5. It may be seen that, with respect to the potential of oxygen evolution, the potential of chlorate oxidation is lower in the electrolyte containing Na$_3$AlF$_6$ (a catalyst) but higher in the electrolyte containing NaPF$_6$ (a retardant) at all current densities. At a current density of 0.1 A cm^{-2}, for example, the potentials in Na$_3$AlF$_6$ and NaPF$_6$ containing electrolytes, respectively, are 1.98 V and 2.52 V relative to SSCE for the chlorate oxidation, and 2.20 V and 2.12 V relative to SSCE for

Table 1. Cumulative current efficiency data for perchlorate formation at a β-lead dioxide coated titanium anode at a current-density 0.5 A cm^{-2}. The cell current was 4A, the electrolyte volume 0.6 l, pH 6.5 and temperature 60 $\pm$ 2° C

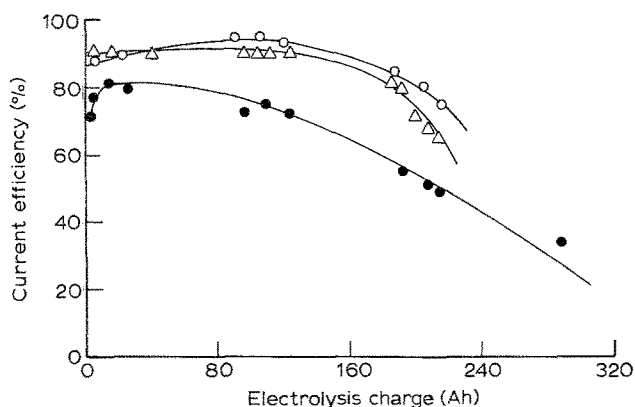| Electrolyte	NaClO$_3$ concentration (g l^{-1})		Electrolysis time (h)	Cumulative current efficiency (%)
	Initial	Final		
NaClO$_3$	690	110	72.0	61
NaClO$_3$ + NaF	690	80	52.5	88
NaClO$_3$ + Na$_3$AlF$_6$	690	90	53.5	85

Fig. 3. Current efficiency during continuous electrolysis as a function of the charge in $NaClO_3$ containing no additive (●), NaF (O) and Na_3AlF_6 (△). The concentrations and other details are as given in Table 1.

oxygen evolution as shown in Fig. 5. That is, the potentials of Reaction 2 are very close (2.12–2.20 V), whereas the potentials of Reaction 1 are separated (1.98–2.52 V). The fluoroanions, therefore, seem to influence the kinetics of chlorate oxidation as a result of their effect on the overpotential of this reaction more than the overpotential of the oxygen evolution reaction.

4. Conclusions

The present studies reveal that both NaF and Na_3AlF_6 catalyze the anodic oxidation of chlorate ion to perchlorate ion at a β-PbO_2 coated titanium electrode. Na_2SiF_6 and Na_2TiF_6 do not affect the reaction. However, $NaBF_4$ and $NaPF_6$ retard the reaction. It is demonstrated that the fluorocompounds influence the overpotential of the chlorate oxidation reaction more than that of oxygen evolution, thus resulting in either electrocatalysis or retardation of the reaction.
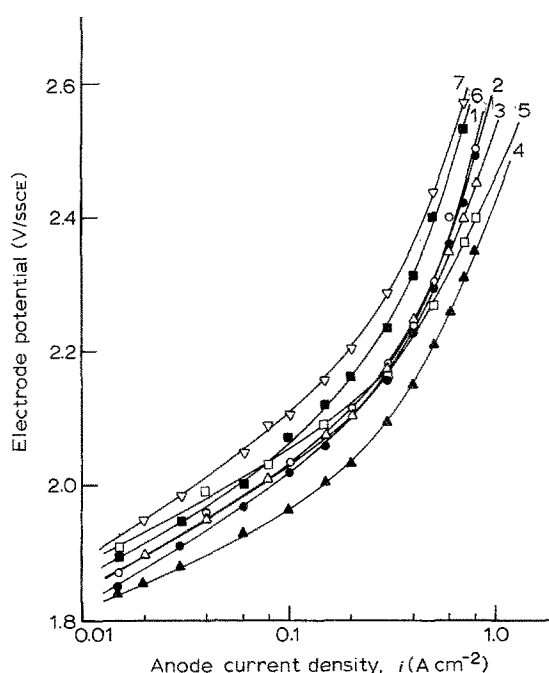

Fig. 4. Steady-state galvanostatic polarization curves as measured at a β-PbO_2 coated titanium anode in $NaClO_3$ (1 M) + $NaClO_4$ (6 M) electrolyte containing (1) no addditive (O), (2) Na_2SiF_6 (●), (3) Na_2TiF_6 (△). (4) Na_3AlF_6 (▲), (5) NaF (□), (6) $NaBF_4$ (■) and (7) $NaPF_6$ (▽) at pH 6.5 and temperature 60 ± 2° C.

Acknowledgement

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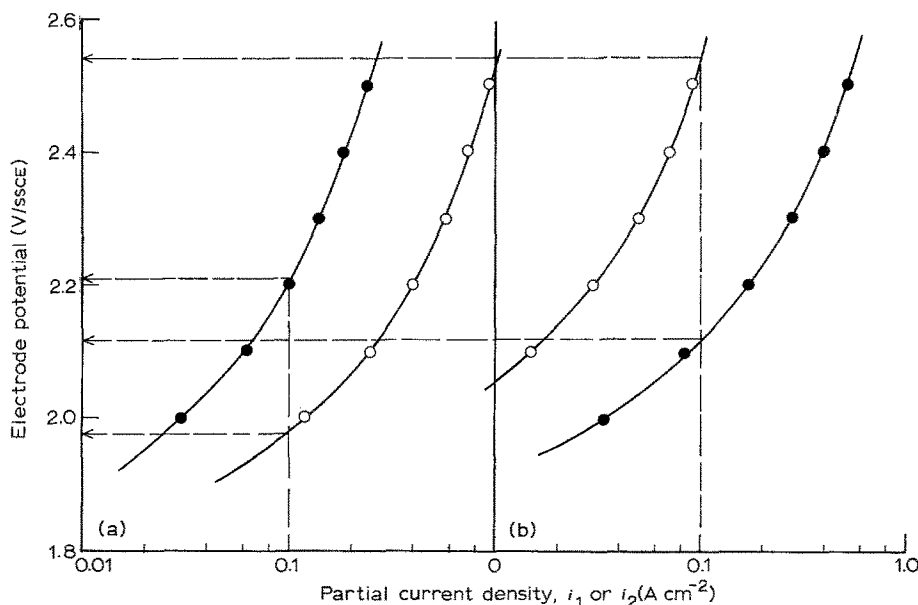[1]   J. C. Schumacher, 'Perchlorates', Reinhold, New York (1960) p. 71.

Fig. 5. Partial polarization curves for anodic oxidation of chlorate ion to perchlorate ion (O) and oxygen evolution reaction (●) in $NaClO_3$ (1 M) + $NaClO_4$ (6 M) electrolyte containing Na_3AlF_6 (a) and $NaPF_6$ (b). These curves are derived making use of the data in Figs 2 and 4. i_1 and i_2 refer to the partial current densities of chlorate ion oxidation and oxygen evolution reaction respectively. The arrows correspond to the potentials of the reactions at 0.1 A cm^{-2} partial current density.

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[9] *Idem, ibid.* **17** (1987) 33.