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The influences of the electrolyte and the physical conditions on ozone production by the electrolysis of water

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The electrosynthesis of ozone at ambient temperature can be achieved using anodes (preferably PbO_2) in aqueous, buffered electrolytes (neutral to slightly acidic media). Traces of highly adsorbing anions raise the oxygen overpotential and the O_3 yield, whilst anions with a high charge/radius ratio as well as certain transition metal ions have detrimental effects. Ozone is evolved at high electrode potentials despite corrosion of the (PbO_2, Pt or Au) anode. The same is true in general, when competing electrooxidations occur (e.g. with ClO_3^-). At fixed temperature and current density the O_3 yield at a PbO_2 anode decreases when the pressure is raised from 1 to 10 atm.

1. Introduction

The generation of ozone by the electrolysis of water is a known process [1]. It has not been introduced technologically, however, presumably due to the necessity of using noble metal anodes (which also show considerable corrosion) either at low temperatures or in strongly acidic media. We recently described the generation of ozone at ambient temperatures using low cost PbO_2/Ti anodes [2] and at pH values of about 7 [3]. A recent report giving astonishingly high ozone yields (of more than 50% current efficiency) obtained using e.g. hexafluorophosphoric acid [4] has prompted us to publish our systematic investigations on different electrolyte systems for ozone production. It had the objective of the eventual application of non-poisonous, low cost materials. Therefore, for example, neither platinum anodes nor the highly poisonous HPF_6 were considered. Additionally, most of the electrolyte systems studied in published work deal either with (obviously) short time experiments or with conditions such as very low temperatures (down to − 56° C) [5] or extremely high current densities (up to 81 A cm^{-2}) [6, 7] thus neglecting excessive anode corrosion, etc.

2. Experimental details

2.1. *Apparatus, chemicals and analyses*

The following electrochemical cells were used [3].

Cell type	*Anolyte volume (cm^3)*	*Initial charge (C)*	*Symbol*
Divided	900	–	DC1
Divided + intermediate chamber	320	2200	DC2
Divided + intermediate chamber	20	150	DC3
Undivided	200	1200	UC1
Undivided	1000	2800	UC2

The *Initial charge* refers to the minimum charge necessary to saturate the anolyte and the dead volume with ozone before gas analysis. The cell current was in the range of 0.7 to 2 A, and the temperature was usually *ca.* 20° C. DC2 had two sintered glass frits (G3) to separate the anolyte and catholyte compartments. The intermediate chamber was filled with an electrolyte similar to the anolyte. Due to the high conductivity of the electrolytes and the large frits fairly high current

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densities and total currents could be achieved without excessive Joule heating. A high pressure H-type cell was made of stainless steel and lined with Teflon. The generated gas could be collected at regular intervals through a Teflon valve with a titanium needle, so that the pressure fluctuations in the cell were kept low.

The lead dioxide anodes on titanium substrate (PbO_2/Ti) were prepared as described by Wabner [8]. The geometrical surface area of the electrodes varied from 2 to 45 cm^2. The electrodes were planar, and depending on the cell used either both plane surfaces were in contact with the electrolyte or one of them was covered with a Teflon sheet and a fairly uniform current density was ensured.

The analyses of gaseous O_3 and $S_2O_8^{2-}$ in aqueous solution were respectively made iodometrically and cerimetrically [9, 10]. Perchlorate produced from a $NaClO_3$ solution was estimated qualitatively by precipitation of the potassium salt and quantitatively from the consumption of $NaClO_3$ [11].

The reagents were chemically pure for synthesis and of analytical grade for analytical and electrochemical purposes. These were supplied by Merck except for $NaBrO_3$ and $NaBF_4$, supplied pure by Riedl-de Haen; Ti as Contimet 35 supplied by TEW; surfactant FC 98 from 3M; KF, puriss. from Roth; $Na_2Sn(OH)_4$, 43–44% from Riedl-de Haen; $NaIO_4$, puriss. from Fluka; and 65% HPF_6 from Ega.

Ohmic drop (IR) corrected polarization curves of the PbO_2/Ti anodes were recorded relative to a SCE electrode. The signal was recorded through a high input impedance preamplifier (Knick, Type 73 W). The IR drop was determined by measuring the potential change at the beginning of a fast current pulse (10 μs). The capacitances at the Ti/PbO_2 and PbO_2/electrolyte interphases were of the order of several μF so that they by-passed the pulse current in the first μs without a noticeable potential drop across them. The potential drop at the Ti/PbO_2 interphase [12] was measured outside the electrolyte at the corresponding current by substituting the auxiliary and reference electrodes with gold contacts on the PbO_2 electrode [13].

2.2. *Experimental results*

2.2.1. Variation of the electrolyte. The influence of anions and cations on the O_3 yield was tested with a series of aqueous acid and salt solutions, with the results given in Table 1. In several cases the pH of the anolyte near the anode surface was determined (± 0.3 units) showing that the non-buffered solutions rapidly become acidic near the PbO_2 electrode.

Results from alkaline baths (KOH) are shown in Table 2 as well as data obtained with several buffers at different pH values with and without the addition of small quantities of foreign anions. Small amounts of $Na_2Sn(OH)_4$ or OsO_4 in a phosphate buffer (of pH *ca.* 7) did not affect the O_3 yield at a fixed current density (c.d.). The perfluorinated surfactant FC 98 is oxidized in a phosphate medium at pH7 and 200 mA cm^{-2} and the O_3/O_2 yield drops to 1% v/v.

Electrolysis of water in the presence of ClO_3^-, BrO_3^- or IO_3^- has been carried out with the initial pH values being neutral or acidic. O_3 yields do not respond to additions of $HClO_4$. The results are shown in Table 3. In most of the electrolytes studied the current yield for ($O_3 + O_2$) exceeds 95%.

2.2.2. Reactions competing with the electrolysis of water. Potapova *et al.* [14] correlated the O_3 and O_2 production and the competing persulphate synthesis on Pt with the anode potential. Persulphate electrosynthesis at our β-PbO_2 electrodes is not the predominant process, as can be seen from the following results:

Reactants (mol dm⁻³)	*Products with current efficiences (c.e.)*			*Current (A)*	*Time of electrolysis (min)*	*c.d. (mA cm⁻²)*	*Temperature*	*Type of cell*
2.0 H_2SO_4	$S_2O_8^{2-}$ c.e. 4.5%	O_3^* c.e. –	O_2^* c.e. –	2	300	200	7°	DC1
1.75 H_2SO_4 0.4 HF	$S_2O_8^{2-}$ c.e. 8.8%	O_3 c.e. –	O_2 c.e. *ca.* 90%	2	300	200	7°	DC1

* The main product was O_2. Small, time dependent amounts of O_3 (Table 1) are also produced [3].

Table 1. Electrolysis of water for ozone production in acids and salts

Electrolyte	*Aqueous concentration ($mol\ dm^{-3}$)*	*Cell current (A)*	*Current density ($mA\ cm^{-2}$)*	*Charge consumed (C)*	*O_3 gaseous concentration (v/v%)*	*$O_3 + O_2$ current efficiency*	*Temperaure (° C)*	*Cell*	*Initial pH*	*Anode pH*
$HClO_4$	0.5	2.0	200	3600	4.1	98 ± 5%	18	UC1	0.3	–
				8400	5.5					
$HClO_4$	4.0	2.0	200	5400	3.8	97 ± 5%	19	UC1	– 0.6	–
H_2SO_4	0.25	2.0	200	3600	3.0	96 ± 5%	24	UC1	0.3	–
H_2SO_4	0.8	2.1	210	4200	3.1	103 ± 5%	20	DC2	– 0.2	–
H_3PO_4	0.6	2.0	200	3600	3.5	97 ± 6%	31	UC1	*ca.* 1.3	–
				7200	3.6		29			
				13 000	4.3		25			
H_2SeO_4	0.25	0.5^a	60	2000	0.4	–	23	DC2	0.3	–
		0.8	100	3200	0.6	–				
HPF_6	*ca.* 11%	2.0	200	5600	1.7^b	98 ± 5%	19	DC2	< 1.0	–
$HClO_4$	0.5	1.0	100	4500	2.3	–	16	DC2	0.2	–
H_2SeO_4	0.06	2.0	200	2500	4.2	–	19			
H_2SeO_3	0.25	2.0	250	7200	0.5	much less than 100%	21	DC2	–	–
				21 500	1.2					
				86 000	2.0					
$NaClO_4$	0.5	2.0	200	4200	5.0	99 ± 5%	22	DC2	6.7	–
				7200	5.4					
$NaIO_4$	0.38	1.4	200	3400	4.6	95 ± 7%	22	DC2	6.0	–
				11 300	5.6				–	0.8
$NaNO_3$	0.5	1.6	210	2900	3.3	–	24	UC2	7.0	–
				9000	0.4	–				
$NaNO_3$	0.5	1.5	200	5700	4.0	97 ± 5%	23	DC2	–	–
				13 000	5.1	–				
KNO_3	0.5	1.5	200	5800	4.2	–	22	DC2	7.0	–
				12 500	5.2	–				
KF	0.5	1.5	200	5400	1.4	98 ± 5%	31	DC2	7.0	–
				19 000	1.2	–	28		–	0.3

Table 1. (Continued)

Electrolyte	*Aqueous concentration (mol dm^{-3})*	*Cell current (A)*	*Current density (mA cm^{-2})*	*Charge consumed (C)*	*O_3 gaseous concentration (v/v%)*	*O_3 + O_2 current efficiency*	*Temperaure (° C)*	*Cell*	*Initial pH*	*Anode pH*
$NaBF_4$	1.0	2.0	200	3600	4.6	98 ± 5%	21	UC1	–	–
NH_4PF_6	1.0	1.7	170	5100 8200	6.6 6.5	99 ± 5%	19	DC2	5.0	1.0
K_2SO_4	0.5	2.0	170	3600 9000	3.9 3.8	98 ± 5%	26	UC1	7.0	–
Cs_2SO_4	0.5	2.0	200	3600	4.3	–	25	UC1	–	–
$Al_2(SO_4)_3$	0.6	1.4	200	2600 6700	3.0 2.5	– –	21 26	UC2	–	2.0
$KMnO_4$	0.45	1.6	200	5300	0.75	–	22	DC2	–	–

[a] At higher currents a very high potential was developed in our cell (after 10 min) and the current fell to the value noted here. Higher current flow could be effected only in the form of galvanostatic pulses.

[b] A considerable anode corrosion has been noticed as well as attack of our glass cell. Attempts to use 65% HPF_6 in our glass cell failed due to immediate dissolution of our glass frits.

Table 2. Water electrolysis for O_3 production in alkaline and buffered solutions

Electrolyte	*Concentration ($mol\,dm^{-3}$)*	*Current (A)*	*Current density ($mA\,cm^{-2}$)*	*Charge consumed (C)*	*O_3% (v/v%)*	*$O_3 + O_2$ current efficiency*	*Temperature (° C)*	*Cell*	*Initial pH*	*Anode pH*
KOH	5	2.0	200	8600	0.0	–	18	UC2	–	–
KOH	1	2.0	200	4800	0.0	96 ± 5%	23	DC2	–	–
$NaBO_2$	2	1.4	200	4200	2.3	–	20	UC2	*ca.* 12	–
$NaHPO_4$ $NaBO_2$	0.43 2	1.4	200	6700 37 000	2.3 3.8	–	20	UC2	*ca.* 11.5	–
$NaVO_3$ NaOH	1 0.38	1.4	200	3400	2.4	–	22	UC2	*ca.* 10	–
KOH K_2HPO_4	0.2 0.6	1.5	200	5200	3.6	95 ± 5%	22	UC2	12.2	*ca.* 2.0
KOH As_2O_5	1.3 0.37	1.4	200	5500	5.8	–	23	UC2	*ca.* 7.5	
K_2HPO_4 KH_2PO_4	0.52 0.22	1.4	200	5500	6.2	101 ± 5%	22	UC2	*ca.* 7.0	–
Water glass (65% SiO_2, 18% Na_2O) NaH_2PO_4 Na_2HPO_4	 21 $g\,l^{-1}$ 0.22 0.47	1.4	200	5900	5.0	–	20	UC2	*ca.* 7.0	–
NaH_2PO_4 Na_2HPO_4	0.22 0.52	2.0	200	7200 1400	4.6 5.5	98 ± 5%	22	UC1	*ca.* 7.0	–
$NH_4H_2PO_4$ $(NH_4)_2HPO_4$	0.23 0.5	2.0 2.0	200 200	3800 115 000	5.1 5.2	97 ± 5%	22	UC2	*ca.* 7.0	–
K_2SO_4 K_2HPO_4 KOH	0.33 0.40 0.20	1.0	100	7200	6.1	–	21	UC2	7.8	–
K_2HPO_4 KH_2PO_4 KF	0.52 0.22 0.0025	1.0	100	2000	7.8	98 ± 5%	23	UC1	*ca.* 7.0	–
K_2HPO_4 KH_2PO_4 $NaPF_6$	0.52 0.22 0.046	2.0	200	3600 7200	7.65 7.2	–	25	UC1	–	–

Table 3. O_3 electrosynthesis in the presence of ClO_3^-, BrO_3^- and IO_3^-

Electrolyte	*Aqueous concentration ($mol\,dm^{-3}$)*	*Cell current (A)*	*Current density ($mA\,cm^{-2}$)*	*Charge consumed (C)*	*O_3 gaseous concentration (v/v%)*	*$O_3 + O_2$ current efficiency*	*Temperature (° C)*	*Initial pH*	*Anode pH*
$NaClO_3$	0.5	2.0	200	3600	5.9	100 ± 7%	25	DC2	6.5 0.8
$NaBrO_3$	0.5	1.3	200	2700	2.9	–	23	DC2	6.5 –
$NaIO_3$	0.5	1.4	200	4200 15 000	0.6 1.9	much less than 100%	22	DC2	6.5 –
$HClO_4$ $NaClO_3$	0.5 3.5	2.05	200	4800	6.6	25 ± 7%	22	CD2	0.3 –
$HClO_4$ $NaBrO_3$	0.5 0.5	2.05	200	4800	2.2	96 ± 5%	18	DC2	0.3 –
$HClO_4$ $NaIO_3$	0.5 0.24	2.05	200	7200	0.5	74 ± 5%	18	DC2	0.3 –
NaH_2PO_4 Na_2HPO_4 $NaClO_3$	0.18 0.36 0.20	2.0	200	3000 8500	6.5 5.2	–	25	UC1	7.0 –
$(NH_4)_2HPO_4$ $(NH_4)H_2PO_4$ $NaBrO_3$	0.68 0.26 0.30	2.0	200	4500	3.2	101 ± 5%	21	DC2	*ca.* 7.0

A reaction which may suppress the electrolysis of water is the oxidation of ClO_3^- to ClO_4^-. In DC3 a 1.5 mol dm^{-3} $NaClO_3$ solution gave the following c.e. after 150 min.: $NaClO_4$ 15%, O_3 4% and O_2 *ca.* 80%. In this cell type convectional mass transport is difficult and very low pH values result in the vicinity of the electrode surface. This presumably causes a drop in the O_3 yield and the observed electrode corrosion. Moreover, freshly prepared 5 mol dm^{-3} solutions of $NaClO_3$ are not readily oxidized to $NaClO_4$ with $O_2 + O_3$ being mainly produced. If, however, the electrolyte is given time to partially disproportionate (e.g. by heating briefly) O_2/O_3 evolution is reduced and a very high ClO_4^- yield is obtained, depending on the electrode history. Therefore ClO_4^- might be synthesized directly from chlorates or predominately via an intermediate. The results of the corresponding oxidation of IO_3^- are also given in Table 3.

The phosphate electrolyte (of pH *ca.* 7) was recrystallized after electrolysis and Debye–Scherrer measurements were made to check for new products. Within the (low) sensitivity of the method none were detected. By 'energy dispersion analysis' a layer of unknown composition was detected on the PbO_2 surface. It contains Pb, O, P and K and might be a mixture of recrystallized PbO_2 and a phosphate salt†.

E vs log *i*-plots for water electrolysis with ozone evolution at β-PbO_2 electrodes in acidic electrolytes (Fig. 1) and in four phosphate buffers in the pH range 5.0–7.2 (Fig. 2) have been obtained. Only a few points were recorded to avoid errors arising from the shift of the potential with time under galvanostatic conditions. The slopes in all cases were *ca.* 125 mV $decade^{-1}$ and $(\partial E/\partial pH)_i = 75 \pm 5$ mV $(pH\ unit)^{-1}$. The values at pH 5.0 result from an electrode with a different prehistory when deviation from the expected potential may occur. Similar *E* vs pH relations have also been observed by Hivarinen in a more acidic region in H_2SO_4 [16]. Much lower (dE/dpH) ratios are reported with Pt electrodes [17].

In the buffered solutions, the slopes of the *E* vs log *i* curves may change at higher c.d. where diffusion polarization progressively becomes more important especially at lower pH values, where the concentration ratio $[H_2PO_4^-]/[HPO_4^{2-}]$ is much

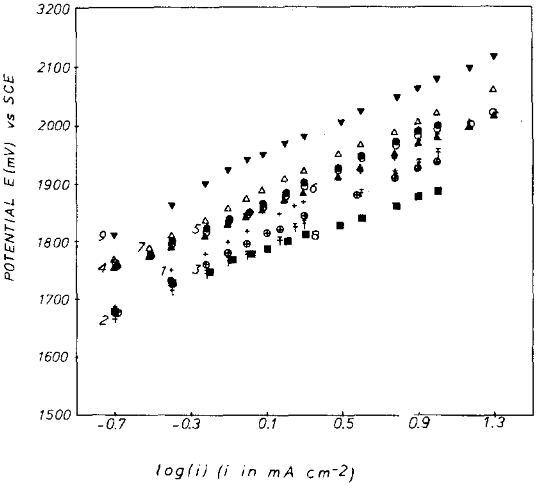

Fig. 1. Galvanostatic polarization curves in acidic media: 1. + 0.25 mol dm^{-3} H_2SO_4, 2. ∓ 0.25 mol dm^{-3} H_2SO_4 with older electrode, 3. ⊕ 0.25 mol dm^{-3} H_2SO_4 after 14 h prepolarization, 4. ▲ 0.5 mol dm^{-3} $HClO_4$, 5. ● 0.5 mol dm^{-3} $HClO_4$ + 0.43 mol dm^{-3} $NaClO_3$, 6. ○ 0.5 mol dm^{-3} HNO_3, 7. △ 0.5 mol dm^{-3} $HClO_4$ + *ca.* 0.001 mol dm^{-3} H_2SeO_4, 8. ■ 0.5 mol dm^{-3} $HClO_4$ + 0.26 mol dm^{-3} $NaIO_3$, 9. ▼ 0.5 mol dm^{-3} $HClO_4$ + 0.5 mol dm^{-3} $NaBrO_3$. Curves 5–9 were recorded in a separated cell.

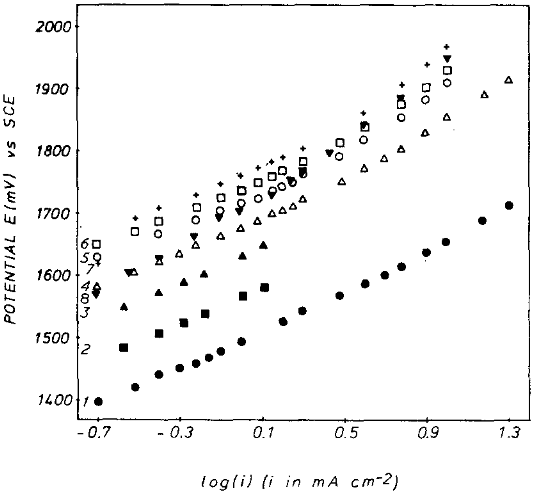

Fig. 2. Galvanostatic polarization curves in phosphate buffered electrolytes, with and without KF additions. 1. ● phosphate of pH 7.2, 2. ■ phosphate of pH 6.5, 3. ▲ phosphate of pH 5.6, 4. △ phosphate of pH 5.0, 5. ○ phosphate of pH 5.0 + 2 mmol dm^{-3} KF, 6. □ phosphate of pH 5.0 + 15 mmol dm^{-3} KF, 7. + phosphate of pH 5.0 + 100 mmol dm^{-3} KF, 8. ▼ phosphate of pH 5.0 + 101 mmol dm^{-3} KF after strong prepolarization.

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† Details given by Thanos [15].

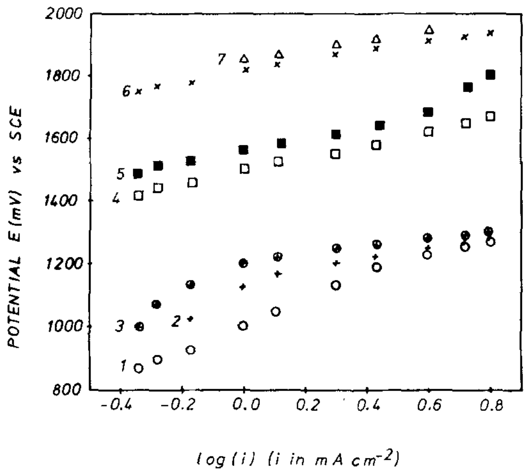

Fig. 3. Salt effect on the galvanostatic polarization curves in alkaline, neutral and acid electrolytes. 1. 0.1 mol dm^{-3} NaOH recorded after 7 min prepolarization at 100 mA cm^{-2}, 2. 0.1 mol dm^{-3} NaOH after 37 min at 100 mA cm^{-2}, 3. after recording of curve 2 $NaClO_4$ is added while $i = 2$ mA cm^{-2}, and the curve is recorded after 5 min, 4. 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaH_2PO_4, pH = 6.6 after 5 min prepolarization (100 m A cm^{-2}), 6. 0.1 mol dm^{-3} $HClO_4$ after 25 min prepolarization at 100 mA cm^{-2}. The same procedure as for curve 3 was followed for 5 and 7, after addition of $NaClO_4$ to solutions corresponding to 4 and 6.

greater than unity. We verified this effect by checking the potential changes at constant pH and c.d. and varying the total salt concentration.

Fig. 3 shows polarization curves in 0.1 mol dm^{-3} NaOH or (0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} NaH_2PO_4) or 0.1 mol dm^{-3} $HClO_4$, respectively, before and after addition of $NaClO_4$ (equivalent to 1 mol dm^{-3}) to check the nature of the salt effect. The ratio of the changes of overpotential and salt concentration at constant current and pH is negative for charge transfer from H_2O, and positive for charge transfer from OH^-. In our case the positive effect in the whole pH range indicates the predominant effect of adsorption of ClO_4^-, unless we assume that OH^- ions in water are discharged even in acidic media, which seems improbable.

2.2.3. Addition of F^-. After adding to the solution corresponding to curve 4 of Fig. 2, solutions of 2.5, 15 and 101 mol dm^3 KF, the potential shifts to higher values (curves 5, 6 or 7, respectively of Fig. 2). After each addition of KF and before recording the galvanostatic curves, the anodes were prepolarized for 5 min (at 100 mA cm^{-2}). Curve 7 changes to curve 8 when the electrode is polarized anodically for a further 2 h at 1 A cm^{-2} and a change in the electrode texture was observed by SEM [13]. The relative effect of KF on the electrode potential is stronger at smaller KF concentrations, probably due to the high adsorbing ability of the F^- ion.

As we reported earlier [3] small additions of KF (1–2.5 mol dm^{-3}) resulted in an increase of the O_3 yield. Further addition of F^- caused a decrease of the O_3 c.e. in contrast to the findings of Foller and Tobias [4].

2.2.4. Variation of physical parameters. At a higher pressure (10 bar), using a pulsed current or irradiating the anode, the O_3 yield changed only slightly. In fact it always decreased. These results can be explained by assuming increased O_3 decomposition, a decrease in the number of gas bubbles covering the electrode and mechanical damaging of the PbO_2 surface at higher pressure. They are, however, also compatible with the postulate of a short-lived, activated species at the PbO_2 surface. If the electrode surface does not change with temperature (concomitant corrosion, etc.) then at lower temperatures there is an increase in the oxygen overpotential even after taking into account the temperature dependence of the SCE potential and the temperature variation of the free energy of formation for the following reaction [18, 27].

$$2H_2 + O_2 = 2H_2O \qquad (1)$$

An increase of the O_3 yield is observed with β-PbO_2 electrodes (in 0.5 mol dm^{-3} $HClO_4$) on changing from 20 to 5° C as long as the electrodes are not used at the maximum c.d. before electrode modification sets in. In such a case the O_3 yield does not change or even decreases with temperature [3]. Such a temperature effect is found also on Pt, where Bowden [19] observed an activation energy of *ca.* 78.2 kJ mol^{-1} at $E = 1.23$ V (NHE) for O_2 evolution, hence the higher O_3 yields on Pt at lower temperatures as noted before. It must be also noted that at 2–5° C at Au and at 5 A cm^{-2} quantities of O_3 comparable to those at Pt are obtained despite the high corrosion of Au and contrary to previous results [20], where only traces of O_3 were found at Au. This supports the idea that O_3 may be evolved even at quite different anodes and with widely different electrolytes if only a high enough O_2 overpotential is achieved.

The long known fact that high current densities influence the O_3 yields in strongly acidic systems [21] was checked for the electrolyte systems studied here. The data of Tables 1–3 are to be correlated with the E vs log i lines of Fig. 1. In order to obtain reproducible data a 7 min pre-polarization of the electrode at 100 mA cm^{-2} was found necessary, similar to previous observations [22, 28].

The lines of Fig. 1 were recorded only up to 30 mA cm^{-2}, since at higher c.d. values the potential was not stable due to the formation of gas bubbles. However, in the case of 0.5 mol dm^{-3} $HClO_4$ potentials recorded up to 200 mA cm^{-2} fit well on the E vs log i slope extrapolated from lower current densities. The slopes of most of the lines are around 125 mV decade^{-1} in the c.d. range 0.3–10 mA cm^{-2}. Deviations are observed for an already used β-PbO_2 electrode in H_2SO_4. However, the surface of this electrode (as checked by SEM) differed markedly from that of a freshly prepared anode, which again in H_2SO_4 has a E vs log i slope near 125 mV decade^{-1}. In phosphate buffer E vs log i slopes differ from those measured by other workers in different electrolytes with c.d. values of 7–25 mA cm^{-2} [23]. As noted previously positive potential deviations occur at these c.d. values due to diffusion. Table 4 shows that in a phosphate buffer a small increase in the O_3 yield is observed with time at several c.d. values, which might be caused by the observed change in electrode texture. At still higher c.d. values than those used in our work, a gradual and rapid surface modification of the anode prevents reproducible results.

Table 4. Concentration of ozone in the anodic gas as a function of the current density in a buffer electrolyte (Phosphate: 0.52 mol dm^{-3} K_2HPO_4, 0.22 mol dm^{-3} KH_2PO_4) cell: UC1, T = 21 ± 2° C

Current density (mA cm^{-2})	*Charge consumed (C)*	*Cell current (A)*	O_3 *(v/v%)*
17	1700	0.7	3.2
17	3300	0.7	4.0
17	5800	0.7	4.1
17[a]	5300	0.7	4.7
17[a]	7700	0.7	4.8
31	2100	1.4	4.5
31	3900	1.4	5.2
31	8300	1.4	5.9
31	26 000	1.4	5.7
58	1800	0.7	5.2
58	3300	0.7	5.7
58	6300	0.7	5.5
140	2700	1.4	6.7
140	8200	1.4	6.2
140	11 000	1.4	6.5
475	2200	0.95	6.4
475	4230	0.95	6.5
600	2300	1.2	6.4

[a] Results with an electrode which was used in a phosphate buffer (310 mA cm^{-2}) in the past for *ca.* 8 h.

2.2.5. Electrode poisoning. In concentrated acids or with electrolytes containing titanium ions from the anode material, corrosion and recrystallization at the β-PbO_2 anodes occur. The 'modified' PbO_2 surface usually has a higher surface area and lower oxygen overpotential, so that the O_3 yield drastically decreases after a short time of operation [13].

2.2.6. PFT–NMR carried out on wetted β-PbO_2 powder. The PFT–NMR showed a *ca.* 500 Hz wide proton resonance slightly shifted in a paramagnetic direction. After reaction in a O_2 stream for 2 h the signal is nearly constant in intensity but more than 5000 Hz wide. Reaction in a O_3 stream leads to signal weakening and further widening of the proton peak occurs. Action of H_2 on the PbO_2 powder leaves the NMR spectra unaltered.

3. Discussion and conclusion

Very similar ratios of $[O_3]/[O_2]$ in the gas phase have been obtained with fairly different electrolytes, at least for short-time electrolyses. Hence, a specific chemical participation of the electrolyte is probably not necessary for O_3 synthesis. Of course, the presence of a reactive species may change the reaction path. The participation of SO_4^{2-} in O_3-generation on Pt has been proposed [24]. On the other hand for the low-temperature O_3 synthesis, Gerovich *et al.* [25] showed by isotope exchange techniques (in concentrated $HClO_4$) that after steps common to O_2 and O_3 generation the third O in O_3 originates from a water molecule reacting with a higher oxygenated species of platinum. Such a scheme would comply with our observation that during the synthesis of ClO_4^- from ClO_3^- the O_2 and O_3 yields are lowered to almost the same extent while the anode potential does not change much if large amounts of ClO_3^- are present in a ClO_4^- electrolyte (Fig. 2). We are currently checking whether the exchange reaction observed on Pt electrodes occurs on β-PbO_2 also using an ^{18}O-tracer.

In conclusion, the features of the electrolytes used for O_3-synthesis in this study are as follows.

(a) Within the studied concentration range of weakly acidic or neutral electrolytes, the O_3-concentration in the gas phase is higher than using more concentrated acids. Foller and Tobias [4] report experimental data contrary to our systematic observations. It is of interest in this connexion that in H_3PO_4 at PbO_2 electrodes [7] the highest O_3 yields were obtained with H_3PO_4 concentrations of less than 70% where anode disintegration occurs. We find that in highly concentrated acids the β-PbO_2 surface is attacked on prolonged electrolysis and the O_2 overpotential is decreased.

(b) In weakly acidic media, anions with higher charge or smaller radius lead to a smaller O_3 yield with time, e.g. better yields are observed in the presence of IO_4^-, ClO_4^-, $H_2PO_4^-$ and NO_3^- than in the presence of SO_4^{2-}, SeO_4^{2-} or F^-. Correlations with species containing transition metals are difficult (e.g. MnO_4^-, VO_3^- or VO_2^+ in acidic medium). It is well known that Co^{2+} decreases the O_2 overpotential at PbO_2 [16]. Such cations cause a suppression of O_3 evolution.

(c) Small amounts of KF have a positive effect on the O_3 synthesis. At high concentrations of F^-, however, an increased attack on the PbO_2 is observed. This could explain our earlier observations [3] as well as the results of Foller and Tobias [4] in which a higher O_3 yield was not obtained by excessive additions of F^- to the electrolyte.

(d) Larger cations seem to cause slight improvements of O_3 yields. However, no obvious preference may be made between Na^+, K^+, NH_4^+ or Cs^+.

(e) In alkaline medium with anolytes containing BO_2^-, HPO_4^{2-}, OH^- or silicate the O_3 yields are very low, probably due to the low stability of O_3 in alkaline media [3].

(f) In phosphate and arsenate buffers (pH 7.5–5) the O_3 yields were highest and remained high for extended periods of electrode operation. With a phthalate buffer (not listed in Tables 1–3) the anions are oxidized and the O_3 yield drops down to zero.

(g) Addition of some oxidizable anions (e.g. SeO_3^{2-}, BrO_3^- or IO_3^-) caused a decrease in O_3 yield, which was not observed with ClO_3^-. Although ozone is known to be liberated from periodic acid [29], the presence of IO_3^- radically decreased the O_3 yield. From Fig. 1 it may be seen that depolarization of PbO_2 observed during the oxidation of IO_3^- may cause a great decrease in the O_3 yield. This explains why the O_3/O_2 ratio is relatively constant despite the competition from the ClO_3^- oxidation, since there no depolarization of the electrode is observed. With BrO_3^- the electrode potential is high but the O_3-yield slightly decreased, which was shown not to be due to a homogeneous reaction of ozone in the electrolyte.

We may conclude that in such an electrolyte the hindered step in ozone synthesis follows an activated electrochemical step which leads to an intermediate precursor of the O_3-molecules and may interact with BrO_3^-. Modifying the proposal for metals [26] and applying it to metal oxides, the E vs log i slope suggests the rate determining step to be either the discharge of H_2O or the recombination of surface adsorbed $OH^{\cdot}$ radicals. The first alternative seems to be favourable, but the mechanism must be amended to account for the pH dependence of the yields. The affinity of PbO_2 for oxygen and probably for oxygenated species follows from the NMR data reported before.

A formal description would include the assumption of an adsorbed OH^- or H_2O in a H^+-rich surface. A discharge of such a species would result in activated intermediates yielding O_2 and O_3 after additional discharge of a water molecule.

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