

The electrochemistry of Magnéli phase titanium oxide ceramic electrodes

Part II: Ozone generation at Ebonex and Ebonex/lead dioxide anodes

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Uncoated Ebonex is not a suitable anode material for the generation of ozone. By contrast, Ebonex electroplated with PbO₂ can be highly stable in the forcing conditions essential to the formation of ozone and gives current yields comparable to lead dioxide on other substrates in both acid and neutral electrolytes.

1. Introduction

Ozone is now perceived to be an important chemical for the future with applications in the purification and sterilization of water, paper bleaching, synthesis etc. This is reflected in a number of papers describing studies of electrolytic ozone generation [1–9]. Indeed, these investigations have led to significant technological advances; the Membrel cell technology based on a solid polymer electrolyte (Nafion®) and a lead dioxide anode is commercially available [10–13] while a liquid electrolyte cell with a vitreous carbon anode, air cathode and concentrated fluoroboric acid electrolyte has been operated on a pilot scale [14, 15].

It is now generally agreed that a high current efficiency for ozone is favoured: (a) by the use of a concentrated acidic electrolyte [1, 4, 14, 15] (although ozone can also be produced in somewhat lower yields in some neutral media such as phosphate buffers [2, 6]); (b) by media with added fluoride or based on fluoride containing anions [2, 4, 9, 14, 15] (adsorption of anions is considered to be a key factor determining the yield of ozone [3, 9]); (c) by a high current density [1, 2, 4] since ozone is only formed at more positive potentials than oxygen evolution (where anode stability becomes a critical consideration); (d) by a high oxygen overpotential anode [4, 9] to minimize the co-evolution of oxygen – PbO₂ [1–13] and vitreous carbon [14, 15] are recommended materials; and (e) by cooling of the anode/electrolyte interface and some workers have proposed the use of very low temperatures [3, 4, 14, 15].

Ebonex®* is a conducting ceramic material mainly

composed of the Magnéli phase titanium oxides, Ti₄O₇ and Ti₅O₉ [16–19]. It has been reported to have several properties which led us to believe that it should be investigated as an anode for ozone formation. It has a high oxygen overpotential [20], it is stable in fluoride containing media [21, 22] and is an excellent substrate for lead dioxide [22, 23]; other aspects of the electrochemistry of Ebonex® are discussed in two other recent papers [24, 25]. Hence, in this paper, ozone formation at both bare and PbO₂ coated electrodes is considered.

2. Experimental details

Ebonex® and PbO₂/Ebonex® electrodes were supplied as sheets by Ebonex Technologies Inc. The lead dioxide was electroplated onto the Ebonex® and its thickness was estimated to be 200 μm by scanning electron microscopy. For potential sweep experiments, an Ebonex® disc electrode, area 0.07 cm² was constructed and cleaned as described in [25]. The vitreous carbon electrode was a disc, area 0.07 cm², sealed in glass and was polished before use with 0.3 μm and 0.05 μm alumina powder. The Ebonex®/PbO₂ electrode, area 0.7 cm², was cut in the shape of a spade from a sheet using a diamond tipped saw. In order to provide electrical contact, a copper wire was attached to the electrode using silver loaded epoxy cement (RS Components 552–652). The spade electrode was then sealed into a glass tube using an epoxy resin (A24–100, Philip

* Ebonex® is a registered trademark.

Harris Scientific) and the back and sides of the electrode were insulated using a coating of Lacomit (G371, Agar Aids). Teflon tape was wrapped around the stem of the spade and the epoxy resin to prevent exposure to the electrolyte.

All voltammetry was carried out in a three electrode, two compartment cell. The counter electrode was a platinum ring and the saturated calomel electrode was mounted in a separate compartment connected to the working electrode via a Luggin capillary. Voltammograms were recorded using a Hi-Tek Instruments potentiostat (model DT 2101) and function generator (model PPR1) with a Gould (model 60000) X-Y recorder. The electrochemical cell was cooled in an ice bath.

For the constant current electrolyses, a vitreous carbon rod electrode, area 1.23 cm^2 , was used. The Ebonex[®] and $\text{PbO}_2/\text{Ebonex}^{\text{®}}$ spade electrodes were constructed as described above. Nearly all of the experiments were carried out in an undivided H-type cell. A platinum gauze was used as a counter electrode. During the electrolyses, nitrogen gas was passed through both sides of the cell and the gas off take from the anode was bubbled through a phosphate buffered solution of 1.0 M KI, pH 5.8. The iodine formed from the oxidation of iodide with ozone was determined, after acidification (10 ml of 6 M H_2SO_4) of the phosphate buffer solution, by titration with sodium thiosulphate (0.01 M). Starch solution was used as an indicator. A Dreschel bottle was also connected to the catholyte side of the cell in order to balance the pressures within the cell. The electrolyte was cooled by immersing the cell in an ice/acetone or ice/salt bath. The electrolyses were run for one to four hours depending on the selected current density. The constant current source was the potentiostat which had been converted to a galvanostat by the insertion of a resistor between the working and reference inputs. The cell voltage was monitored using a Fluke Digital Multimeter (model 8050A).

All solutions were prepared from triply distilled water and high quality chemicals.

3. Results

3.1. Potential sweep experiments

Current-potential responses were recorded using potential sweep procedures over the potential range where ozone formation was to be expected for anodes of vitreous carbon, Ebonex[®] and Ebonex[®] electroplated with a layer of lead dioxide. In general, the curves were almost featureless showing only an anodic current which increased up to the positive limit; Fig. 1 shows a typical set of curves recorded when the electrolyte is 7.7 M (48 wt %) HBF_4 . Clearly, there are no features which could be interpreted in terms of a change in product from oxygen to ozone. The potentials required for the passage of 0.15 A cm^{-2}

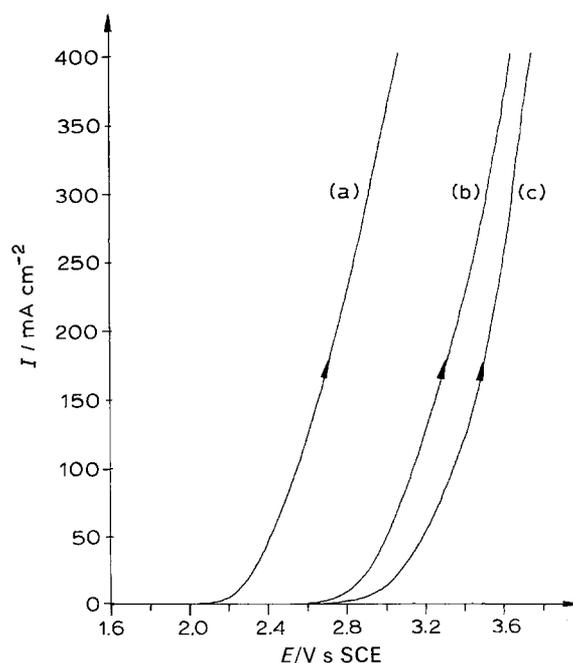


Fig. 1. Current-potential curves recorded in 7.7 M fluoroboric acid at 273 K. The electrodes were (a) Ebonex[®]/lead dioxide (b) Ebonex[®] (c) vitreous carbon. Potential scan rate: 50 mV s^{-1} .

are:

| | |
|-----------------------------------|--------------|
| vitreous carbon | + 3.46 V/SCE |
| Ebonex [®] | + 3.26 V/SCE |
| Ebonex [®] /lead dioxide | + 2.66 V/SCE |

3.2. Electrolyses

Foller and Goodwin [14, 15] have reported excellent yields of ozone using cells with a vitreous carbon anode, temperatures in the range 263–273 K and 48 wt % HBF_4 as the electrolyte. Hence, this was selected as the medium for the initial experiments and an electrolysis using these conditions and a current density of 0.4 A cm^{-2} led to the formation of ozone with a current efficiency of 39%, very similar to that reported by Foller and Goodwin [14, 15]. It was also confirmed that the vitreous carbon anode showed no sign of corrosion, at least on the hours timescale.

When the vitreous carbon anode was replaced by a bare Ebonex[®] anode, however, the results degraded catastrophically. Over a series of experiments where several electrolysis parameters were varied (for example: current density $0.003\text{--}0.40 \text{ A cm}^{-2}$, porosity of the Ebonex[®] 0–25%, HBF_4 concentration 1.4–7.7 M), the current efficiencies for ozone formation were always in the range 0 to 0.6%. Moreover, in many experiments the Ebonex[®] was severely corroded; in some cases, a passivating white film was formed on the surface while in others, the Ebonex[®] flaked or led to a white precipitate in the anode compartment. In the worst case, the Ebonex[®] lost all its conducting and ceramic properties and was converted to a flexible, white paste. The corrosion was worst at high current densities in the strong acid media. On the other hand, at low current densities where the formation of ozone was considered unlikely, $< 30 \text{ mA cm}^{-2}$, the Ebonex[®]

Table 1. Current efficiencies for ozone and electrode stability during electrolyses in aqueous fluoroboric acid. Electrolyte temperature 270 ± 5 K.

| [HBF ₄]/M | I/ A cm ⁻² | Current Eff./% | Evidence for PbO ₂ corrosion |
|-----------------------|--------------------------|----------------|---|
| 7.7 | 0.8 | 15.5 | Electrolyte discoloured. Brown deposit in cell. Metal deposit on cathode. |
| | 0.4 | 14.6 | Electrolyte discoloured. Brown deposit in cell. |
| | 0.2 | 9.8 | Electrolyte discoloured. Brown deposit in cell. |
| | 0.05 | 10.1 | None |
| | 0.025 | 8.3 | None |
| | 0.005 | 0 | None |
| 6.0 | 0.4 | 7.5 | None |
| 3.5 | 0.4 | 7.5 | None |
| 1.4 | 0.4 | 7.7 | None |
| | 0.2 | 8.1 | None |
| | 0.05 | 6.9 | None |
| | 0.025 | 4.1 | None |
| | 0.005 | 0 | None |
| 0.1 | 0.4 | 7.6 | None |
| 0.05 | 0.4 | 7.1 | None |

appeared to be stable [21, 22]. A few electrolyses were also carried out with an aqueous phosphate buffer as the electrolyte and although the Ebonex[®] was stable to corrosion, no significant ozone formation occurred.

In view of these disappointing results, it was decided to investigate the performance of Ebonex[®] coated with lead dioxide. It will be seen that the results improve significantly and it should be stressed immediately that there was never evidence for corrosion of the Ebonex[®] substrate. The reason can be seen in Fig. 1; the potential of the PbO₂ surface is always markedly lower than the bare Ebonex[®] when current is passing. Table 1 reports the current efficiencies for ozone formation and comments on the stability of the lead dioxide during a series of electrolyses carried out with a PbO₂/Ebonex[®] anode in fluoroboric acid. The variables were the concentration of acid and the current density. It can be seen that the maximum current efficiency for ozone is about 15%, a value which compares well with that reported by Foller and Tobias [4]. Regrettably, however, the highest current efficiencies are observed at high current density and acid concentration where the lead dioxide is least stable. Slow corrosion is indicated by a yellow discolouration which probably results from colloidal PbO₂ particles in the electrolyte. Rather faster corrosion leads to the deposition of PbO₂ in the base of the cell and obvious loss of material from the anode surface during extended electrolyses. In extreme conditions, a lead metal deposit was observed on the cathode and this may be further evidence that a soluble lead species is formed in concentrated HBF₄ [5]. It is, on the other hand, not difficult to define conditions where the lead dioxide appears to be completely stable and the yield of ozone is 7–10%; this can be achieved either by lowering the current density or the fluoroboric acid concentration.

Electrolyses were also carried out in neutral media

Table 2. Current efficiencies for ozone during electrolyses in neutral aqueous media. Electrolyses carried out at room temperature. The pH of the phosphate buffers were 7.4

| Electrolyte | I/ A cm ⁻² | Current efficiency/ % |
|--|--------------------------|--------------------------|
| 1 M Na ₂ SO ₄ | 0.4 | 5.1 |
| 0.52 M K ₂ HPO ₄ 0.22 M KH ₂ PO ₄ | 0.4 | 5.5 |
| 0.52 M K ₂ HPO ₄ 0.22 M KH ₂ PO ₄ 2.5 mM NaF | 0.4 | 11.7 |
| 70 mM K ₂ HPO ₄ | 0.4 | 6.9 |
| 30 mM KH ₂ PO ₄ | 0.6 | 7.1 |
| 70 mM K ₂ HPO ₄ | 0.4 | 10.5 |
| 30 mM KH ₂ PO ₄ | 0.1 | 9.5 |
| 2.5 mM NaF | 0.025 | 5.7 |
| 7 mM K ₂ HPO ₄ | 0.1 | 5.9 |
| 3 mM KH ₂ PO ₄ 2.5 mM NaF | 0.025 | 3.9 |

and the results are reported in Table 2. In these media there is no evidence for corrosion of either the lead dioxide coating or the Ebonex substrate and the electrodes can certainly be used for several electrolyses without any loss in performance. The current efficiencies are comparable to those reported by Wabner *et al.* [2, 6] for PbO₂ on titanium. Of particular interest were the experiments with low concentrations of phosphate buffer; it remains possible to obtain a current efficiency > 10% in the 0.1 M buffer and some ozone is formed even when the current density is as low as 25 mA cm⁻². The advantage of fluoride ion in the electrolyte is also confirmed [2, 6].

4. Discussion

The current efficiencies at PbO₂ are always low compared to those at vitreous carbon and the energy consumption of a cell with a PbO₂ anode is likely to be much too high to consider the technology for the preparation of ozone on a large scale. There are, however, other applications of ozone where the current efficiency and energy consumption are likely not to be critical. An example would be the (continuous) sterilization of a closed volume of water where, in some cases, a low concentration of phosphate buffer (and perhaps fluoride ion) would not be deleterious. As might be expected, the current efficiencies for ozone generation at PbO₂/Ebonex[®] are similar to PbO₂ on other substrates. On the other hand, we believe that the lifetime of the Ebonex[®] substrate anodes will be much longer than those with a titanium substrate, especially in media containing fluoride or fluorinated anions; titanium is known to corrode in fluoride containing media, while Ebonex[®] has proved stable in such solutions during extended trials [21–23]. Hence, we plan further, long term tests of PbO₂/Ebonex[®] anodes for ozone generation in appropriate media and cell configurations.

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