The Influence of High Concentrations of Fluoride on the Electrosynthesis of Peroxodisulfates at β-PbO₂ Anodes

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Dedicated to Prof. Dr. H. P. Fritz on the occasion of his 60th birthday
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Peroxodisulfate, Lead-dioxide Anodes, Fluoride, Electrolysis, High Current Efficiencies

During electrolysis with β-PbO₂ anodes in acidic sulfate electrolytes high current efficiencies of peroxodisulfate are obtained (60–70%) when high amounts of fluoride (1 Mol·L⁻¹ to 3 Mol·L⁻¹) are added to the electrolyte. This reaction is examined by means of current efficiency of peroxodisulfate, rate of ozone formation, polarization curves, and impedance measurements. The reason for the high current efficiencies is the formation of fluorosulfonic acid in the electrolyte and its reaction with the OH-radical (from the discharge of H₂O) to form HSO₄⁻ radicals.

1. Introduction

In a search for a substitute for the expensive anode material platinum for the electrochemical production of peroxodisulfates, β-PbO₂ has been investigated by several authors [e.g. 1–4]. The highest current efficiencies (60–70%) have been achieved by Sugino [3] as well as by Dzhafarov and Bajramov [4] in acidic solutions of ammonium sulfate by adding high amounts of fluoride (up to 3 Mol·L⁻¹). However, these authors report neither about anode gases nor about the mechanism of S₂O₈²⁻ formation.

During our work on the electrochemical formation of pero xo compounds [5, 17] – among others with β-PbO₂ anodes – these questions have been examined and clarified.

2. Experimental

2.1. Electrodes

Titanium expanded metal and platinum wire (⌀ 1 mm) were pretreated and a layer of β-PbO₂ was electrochemically deposited (acidic Pb(NO₃)₂-bath, as described in [6–8]).

Fig. 1. Apparatus for galvanostatic electrolysis. For better survey only the circle of the anolyte solution is shown (it’s the same for catolyte solution). Arrows indicate the direction of electrolyte flow.

2.2. Electrolysis

Electrolysis experiments were carried out in a flow cell of filter press construction [9] (T = 25–32 °C, Vₐ = 350 ml, Fₐ = 100 cm²). Cathode and anode compartments were separated by a cation exchange membrane (Nafion 497). Anolyte and catolyte solutions were circulated through a reflux condenser (for control of temperature) back to the cell (Fig. 1.).

Abbreviations: C_D = double layer capacity; F_A = anode surface; R₀ = transfer resistance; Rₐ = electrolyte resistance; R_p = polarization resistance; R_re = reaction resistance (R_p – R₀); V_A = anolyte volume.

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2.3. Electrochemical examination methods

In a Metrohm measuring cell (Nr. 6.1415.22X) a working electrode made of platinum wire covered with a $\beta$-PbO$_2$ layer ($F_A = 0.5 \text{ cm}^2$) was used. The counter electrode was made of platinum ($F = 25 \text{ cm}^2$). The potential was measured against Hg/Hg$_2$SO$_4$/K$_2$SO$_4$ (sat.).

For measuring the galvanostatic polarization curves a galvanostat/potentiostat (Solartron ECI 1286) was used, controlled by a Turbo-Pascal program of J. Ober [10]. Potential values were controlled to be stationary to $<0.1\%$. For conditioning the electrode, a constant current density of 400 mA·cm$^{-2}$ was applied for 15 min. After a waiting period of 30–45 min (at $I = 1–3$ nA) the measurement was started.

Impedance spectra ($1-100,000 \text{ Hz}$) were recorded with the same apparatus and with a frequency analyzer Solartron 1174, controlled by a Turbo-Pascal program [10] (measuring conditions: criteria of equilibrium 0.1%, ten-fold integration, 10 measuring points every decade).

2.4. Electrolytes

Electrolyte solutions were prepared from 1.5 M H$_2$SO$_4$ and 2.3 M (NH$_4$)$_2$SO$_4$ (further called “GE”) with several additions of NaF (0–2 M), NaF (2 M) and HF (1 M) were added to the basic 3 molar fluoride electrolyte solution. Solutions for electrolysis were made from purified chemicals, solutions for analysis and electrode kinetic measurements were made from reagent grade chemicals.

2.5. Analysis

The yield of (NH$_4$)$_2$S$_2$O$_8$ was determined manganometrically. 1 l reduction solution contained:

- 77 g (NH$_4$)$_2$Fe(SO$_4$)$_6$ 6 H$_2$O
- 100 ml H$_2$SO$_4$ (conc.)
- 100 ml H$_3$PO$_4$ (conc.).

Titration solution: 0.02 M KMnO$_4$.

Sample solution: $0–4$ ml electrolyte sample (depending on S$_2$O$_8^{2-}$-concentration) + 5 ml reduction solution + 10 ml H$_2$O (deion.).

2.6. Current efficiency

For each electrolyte sample the total Faradaic current efficiency was determined.

3. Results

The current efficiency of S$_2$O$_8^{2-}$ increases with increasing fluoride concentration of the electrolyte (Fig. 2).

The increase is a maximum between 1 to 2 mol/l fluoride added to the sulfate electrolyte. More fluoride gives only very little further increase in current efficiency.

Also the shape of the curves changes. Up to a fluoride concentration of 1 M the current efficiency decreases with electrolysis time. With 2 mol/l fluoride added, it is constant over 1.5 h, and it increases slightly during electrolysis with 3 M F$^-$. To prove that no chemical reaction between the anode material and the electrolyte causes an “increase” in current efficiency, the experiment with 3 M F$^-$ was carried out without current flow. No peroxodisulfate could be detected.

The rate of ozone formation passes through a maximum when the fluoride concentration is increased (Fig. 3.).
Fig. 3. Amount of ozone in the anode gas during electrolysis with $\beta$-PbO$_2$ anodes in GE with different fluoride concentrations, $i = 100$ mA·cm$^{-2}$:
1. GE
2. GE + 0.5 M F$^-$
3. GE + 1 M F$^-$
4. GE + 2 M F$^-$
5. GE + 3 M F$^-$

Ozone formation increases up to a fluoride concentration of 0.5 M. With more fluoride in the electrolyte it decreases. During electrolysis in the 3 molar fluoride solution no more ozone can be detected.

Anode corrosion is strongest in 0.5 molar and 1 molar fluoride solution.

The equilibrium potential of $\beta$-PbO$_2$ drops from +1.590 mV (in GE) to +1.430 mV (in GE + 3 M F$^-$).

The anode potential during electrolysis shows a strong increase up to GE + 1 M F$^-$. At higher fluoride concentrations only a slight increase can be observed.

This behaviour is reflected in the polarisation curves (Fig. 4).

The polarisation curves have been corrected for the electrolyte resistance determined by impedance measurements (see below). Two ranges are to be distinguished:

At current densities above 200 mA·cm$^{-2}$:
Besides the formation of $\text{SO}_4^{2-}$ and gas evolution the corrosion of the PbO$_2$ anode is a factor of importance [5].

At current densities below 200 mA·cm$^{-2}$:
This is the range in which the electrolyses have been carried out (at 100 mA·cm$^{-2}$) and distinct differences are achieved with different electrolytes.

The results of electrolysis experiments in GE, GE + 0.5 M F$^-$ and GE + 1 M F$^-$ are similar. By adding fluoride the potential is raised by about 50 mV (curves 2 + 3 in fig. 4.). Between 100 and 150 mA·cm$^{-2}$ potential oscillations occur. After oscillation the curve continues with the higher of the two limiting potentials of oscillation. The results are totally different in GE + 3 M F$^-$. No sharp rise of the potential appears. The potential value is higher right from the start of the curve (about 150 mV) than in the other electrolytes. The polarisation curves in GE + 2 M F$^-$ (not shown in Fig. 4.) is nearly the same as in GE + 3 M F$^-$. All potential values of PbO$_2$ are much lower than those of Pt in GE [5, 17].

For further examination of the electrode reactions impedance measurements were carried out over a frequency range of 100,000 to 1 Hz. To show the differences between GE + 1 M F$^-$ and GE + 3 M F$^-$, the values of polarisation resistance ($R_{pol}$), charge-transfer resistance ($R_D$) and double-layer capacitance ($C_D$) are collected in Table 1 for the measurements from 50 to 200 mA·cm$^{-2}$. Electrolytic resistance ($R_\text{el}$), $R_D$ and $C_D$ have been determined by extrapolation [11] according to the method of Wabner and Schmittinger [12, 13].

Low fluoride concentrations (max. 1 M) cause a slight increase of $R_{pol}$ and $R_D$. Higher fluoride con-
centrations cause a decrease of these values. The turning point lies between 1 M and 2 M fluoride solutions. This is analogous at $i = 50 \text{ mA cm}^{-2}$: $C_D$ first decreases and then increases with increasing fluoride concentration. At higher current densities $C_D$ is constantly increasing with fluoride concentration. It is surprising to see that $C_D$ is about ten times higher in GE + 3 M F$^-$ than in GE + 1 M F$^-$.

4. Discussion

The greatest differences in electrode behaviour are seen when the electrolyte is changed from GE + 1 M F$^-$ to GE + 2 M F$^-$ (increase of current efficiency, potential, and $C_D$, decrease of $R_{pol}$ and $R_D$ as well as the absence of ozone formation and anode corrosion).

To understand this, the changes in composition of the anolyte must be considered. In an aqueous solution of sulfuric acid and hydrofluoric acid fluorosulfonic acid may form at room temperature [14], as shown in equation (1) and adapted to the pH in GE in equation (1a):

$$
\text{H}_2\text{SO}_4 + \text{HF} \rightarrow \text{HSO}_3^- + \text{H}_2\text{O} \quad (1)
$$

$$
\text{HSO}_4^- + \text{HF} \rightarrow \text{FSO}_3^- + \text{H}_2\text{O} \quad (1a)
$$

Fluorosulfonic acid may react with oxidizing agents [15]. Therefore in the electrolyte and at the anode surface the following reactions must be considered:

$$
2 \text{FSO}_3^- + \text{H}_2\text{O}_2 \rightarrow 2 \text{F}^- + \text{H}_2\text{S}_2\text{O}_8 \quad (2)
$$

$$
\text{FSO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{F}^- + \text{H}_2\text{S}_2\text{O}_8 \quad (3)
$$

$$
\text{FSO}_3^- + \cdot \text{OH} \rightarrow \text{F}^- + \text{HSO}_4^- \quad (4)
$$

$$
\text{resp. } 2 \text{FSO}_3^- + 2 \cdot \text{OH} \rightarrow 2 \text{F}^- + \text{H}_2\text{S}_2\text{O}_8 \quad (4a)
$$

The reaction with (possibly) formed ozone does not occur. The reaction of FSO$_3^-$ with PbO$_2$ to form S$_2$O$_8^{2-}$ and PbF$_2$ also does not take place, as shown by the result of the experiment without current flow. H$_2$O$_2$ and H$_2$SO$_4$ are products of the hydrolysis of the peroxydisulfate. Peroxydisulfate therefore can be formed either by direct discharge and followed by dimerization (equation 5)

$$
2 \text{HSO}_4^- \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2 \text{e}^- \quad (5)
$$
or by reaction of FSO$_3^-$ with OH-radical (equations 4 and 4a). Assuming that this reaction (equation 4) becomes the main anode reaction when the fluoride concentration in GE exceeds 1 M, the results can be explained in the following way:

1. Evolution of ozone (accompanied by anode corrosion [9]) does not take place, because OH-radicals do not react with O$_2$, but with the more active FSO$_3^-$. This is even more likely because of the high salt concentration in GE + 3 M F$^-$. In this electrolyte a great part of the water is bound in hydration of the sulfate and fluoride ions and is not available for O$_2$ and O$_3$ evolution.

The mechanism of O$_3$ formation proposed by Wabner and Grambow [16] is taken as a basis for these considerations:

$$
\cdot \text{OH} + \text{O}_2 \rightarrow \text{HO}_3^- \quad (6)
$$

$$
\text{HO}_3^- \rightarrow \text{HO}_3^+ + \text{e}^- \quad (7)
$$

$$
\text{HO}_3^+ \rightarrow \text{O}_3 + \text{H}^+ \quad (8)
$$

2. There are also other reasons for the high current efficiency in GE + 3 M F$^-$. Reaction (1) as...
well as (1a) are equilibrium reactions. By discharge of H₂O and “recycling” of HF (scheme 1.) the equilibrium is pushed to the right-hand side. High concentrations of FSO₃ and -OH promote the formation of peroxodisulfate.

\[
\begin{align*}
\text{HSO}_4^- + HF &\rightarrow \text{FSO}_3^- + \text{H}_2\text{O} - \text{H}^+ \\
\text{FSO}_3^- + \text{H}_2\text{O} &\rightarrow \text{H}^+ - \text{e}^- + \cdot\text{OH} \\
\text{HSO}_4^- + \text{F}^- &\rightarrow \cdot\text{OH} \\
\text{H}_2\text{SO}_4 &\rightarrow 2\text{H}^+ + \text{SO}_4^{2-}
\end{align*}
\]

Scheme 1. Survey of the reactions in GE + 3 M F⁻ during formation of peroxodisulfate.

If – as supposed in [5, 17] – the desorption of S₂O₅²⁻ from the PbO₂-surface is hindered in GE, this is not important in GE + 3 M F⁻. Fluorosulfonic acid is totally dissociated even in strong acidic media. The high acidic strength favours the protonation of S₂O₅²⁻ to form H₂S₂O₈, which is more easily desorbed from the surface.

3. The high current efficiency corresponds to a high reaction rate, which itself explains the strong increase of C_D. The total polarization capacitance is equivalent to the electrochemically active anode surface, which depends on the geometry of the anode as well as on the rate of adsorption, reaction, and desorption of the reactants involved.

4. The low value of R_D in GE + 3 M F⁻ is easily understood if the results of impedance measurements in 0.5 M H₂SO₄ are compared to those in GE + 3 M F⁻ (Table 2.).

In 0.5 M H₂SO₄ more gas (O₂ and O₃) is evolved (less S₂O₅²⁻ formed) than in GE with PbO₂ anodes. That means that R_D of the discharge of H₂O and -OH is much lower than R_D of the discharge of HSO₄⁻. The high rate of O₂ evolution is seen from the high value of C_D. The low R_D and high C_D values in GE + 3 M F⁻ therefore are another hint for the participation of an electron transfer reaction in O₂ evolution and for the (nearly complete) absence of HSO₄⁻ discharge.

5. The different course of the polarisation curve in GE + 3 M F⁻ points to other reaction mechanisms at the anode than in GE. There is no oscillation of the potential in GE + 3 M F⁻ (which the other electrolytes show between S₂O₅²⁻-formation and O₃ evolution). Right from the start the curve shows a potential corresponding to the potential of O₂/O₃-evolution (for the other electrolytes). This result agrees with the interpretation of the impedance measurements.

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