

Electrochemical removal of dissolved oxygen from water

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A new electrochemical method of oxygen removal has been developed in which oxygen-rich water flows through the three-dimensional cathode of an electrochemical cell. The cathode removes the dissolved oxygen from the water and the anode releases it as gas into the air. By this technique oxygen levels lower than $3 \mu\text{g}$ oxygen per kilogram of water can be reached (starting level: oxygen-saturated water, $8000 \mu\text{g kg}^{-1}$). This result is better than that obtained by physical methods and is equal to those obtained by chemical methods. Compared with conventional methods, the advantages of the electrochemical method are high efficiency, low energy consumption and avoidance of the use of toxic deoxygenation chemicals.

1. Introduction

Oxygen is the most common corrosive agent. In oxygen-containing neutral or mildly alkaline solutions the reduction of oxygen to hydroxyl ions is a very typical cathodic corrosion reaction:



Oxygen dissolved in water causes corrosion in technical systems, such as steam boilers, domestic heating systems and recirculating industrial cooling systems. Therefore, in many cases, oxygen has to be removed from water as completely as possible. The concentration of oxygen is also minimized in many processes in the chemical industry in order to prevent undesirable oxidation reactions.

Present methods of oxygen removal are physical or chemical deoxygenation. In physical deoxygenation water vapour is typically brought into contact with the water. This causes mass transfer of the oxygen from the water into the gas phase. With the physical deoxygenation method quite low levels of oxygen, about $10 \mu\text{g kg}^{-1}$, can be reached.

When eliminating residual amounts of oxygen, chemical deoxygenation is used. This is based on chemicals reacting with oxygen. Chemical deoxygenation permits oxygen levels lower than $5 \mu\text{g kg}^{-1}$ to be reached. The most common chemicals used are hydrazine and sodium sulphite.

The main disadvantage of the physical method is the high capital cost, especially in applications where water vapour is not available. In addition, in applications where cold water is needed, a great deal of energy is lost when heating and cooling the water. The drawback with the chemical method is that it presents an occupational and environmental risk. A non-toxic, economical and efficient, deoxygenating agent has not yet been found. In many heating systems oxygen is not removed at all due to the lack of a suitable technique [1, 2].

During the previous twenty years there has been

research on electrochemical oxygen removal, but almost no scientific publications. Some patent applications have been made, although no efficient methods have been found [1, 3, 4].

This work reports the development of a new electrochemical deoxygenating method. The invention is based on the oxygen-rich water flowing through the three-dimensional cathode of an electrochemical cell. When contacting the cathode, the oxygen molecules are reduced to water molecules and hydroxyl ions which are removed from the system by the anode reaction.

2. Experimental details

2.1. Apparatus

A laboratory scale flow cell was made of acrylic plastic. It was divided into one cathode and two anode compartments by membranes so that the water only flowed through the cathode compartment (Fig. 1).

The cathode was a 100 cm^3 packed-bed electrode, consisting of graphite, nickel or copper. Current was fed to the cathode bed through eight current feeders.

The anodes were two 70 cm^2 titanium sheets, plated with iridium-based oxide (Permascand). They were placed in two separate anode compartments at a distance of 0.6 cm from the cathode.

Nafion[®]-417 cation exchange membranes (DuPont) were used to separate cathode and anode compartments. These were permeable to cations, but almost impermeable to anions and nonpolar species.

The oxygen-saturated water, the catholyte, was prepared by stirring distilled water in an open vessel. To increase the conductivity, 0.05 mol dm^{-3} Na_2SO_4 was added. The water was at room temperature, 20–25 °C. This same solution was also used as the anolyte.

The oxygen-saturated catholyte flowed from a container through a pump and the first oxygen analyzer (Orion 1808) into the cell (Fig. 2). From the cell, the deoxygenated water flowed through the second

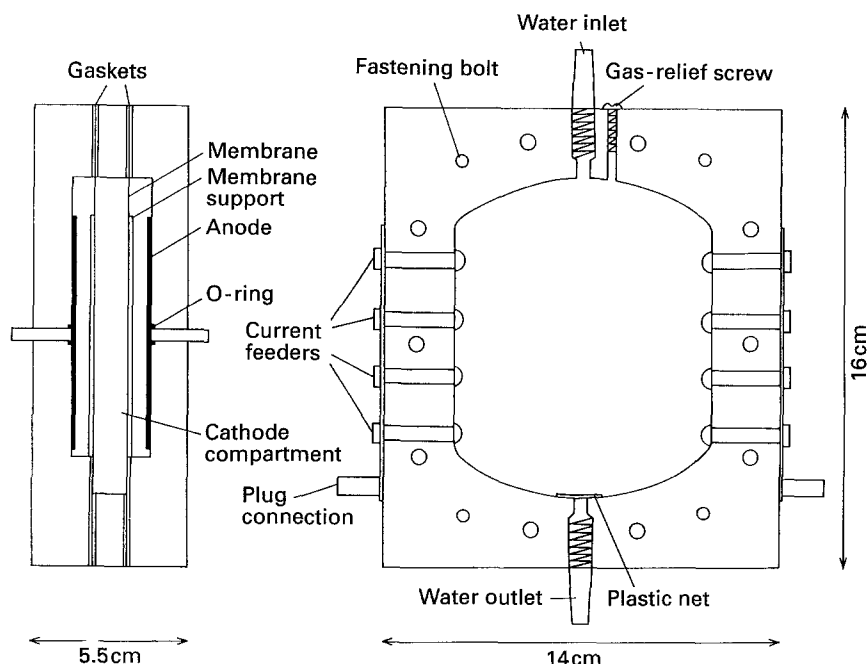


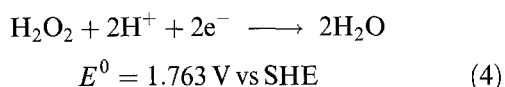
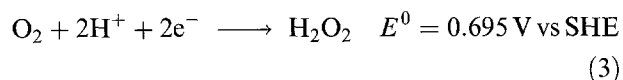
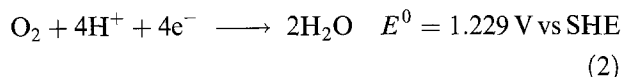
Fig. 1. Design of the cell for oxygen removal.

oxygen analyzer (Orbisphere 2713) and a pH-meter to the drain.

2.2. Deoxygenation method

In all experiments the oxygen-rich water flowed downwards in the cathode compartment (Fig. 3). The water flow was 2 g s^{-1} ($= 2 \text{ ml s}^{-1}$). The cell voltage was adjusted to about 2.0 V.

Oxygen molecules were reduced when they contacted the bed material. There are various hypotheses concerning this reaction. According to Tarasevich *et al.* [5] oxygen can be electrochemically reduced either to water (Equation 2), or to hydrogen peroxide, which can be further reduced to water (Equations 3 and 4). Equations 2–4 show these reactions in acidic media. The corresponding reactions in alkaline media give hydroxyl ions (OH^-) and hydrogen peroxide ions (HO_2^-).



Thus, water (or hydroxyl ions, depending on pH) and hydrogen peroxide were produced at the cathode

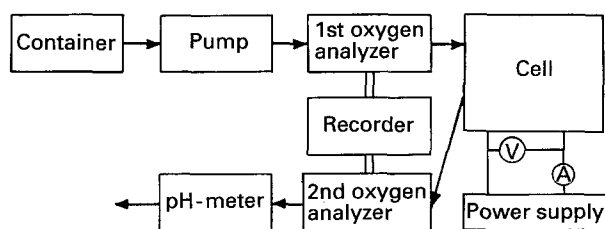


Fig. 2. Schematic picture of the research apparatus.

when oxygen was reduced. In addition, hydrogen evolution was possible when using high cell voltages.

The anodic reaction was oxygen evolution:



The oxygen gas produced did not reach the cathode compartment, but was released into the air through an outlet. In oxygen evolution the same amount of hydrogen ions was produced as was consumed in the reduction of oxygen. Therefore electrochemical deoxygenation did not affect the pH of the treated water (except in the initial phase [6]).

The (theoretical) cell current, I , needed for oxygen reduction can be calculated as follows:

$$I = [\text{O}_2]zFm/M \quad (6)$$

where $[\text{O}_2]$ is the mass fraction of dissolved oxygen in water, z the number of electrons required per oxygen molecule (4), F the Faraday constant ($96\,500 \text{ A s mol}^{-1}$), m the water flow (2 g s^{-1}) and M the molecular mass of oxygen (32 g mol^{-1}).

For example, at room temperature the oxygen content of saturated water is about $8000 \mu\text{g}$ oxygen per kg of water. At a water flow of 2 g s^{-1} complete oxygen reduction requires 0.19 A.

2.3. Experimental procedure

To find which combination of particle material, particle size and cell voltage is optimal, the bed material and cell voltage were varied systematically. The quantities measured were the oxygen content, hydrogen peroxide content and pH of the treated water, as well as the cell current. When using a copper bed the copper content of the water was also measured. The hydrogen peroxide and copper contents were measured by colorimetric methods [6]. The hydrogen evolution was estimated by comparing the measured cell current to the theoretical cell current. The difference was assumed to be the hydrogen evolution current.

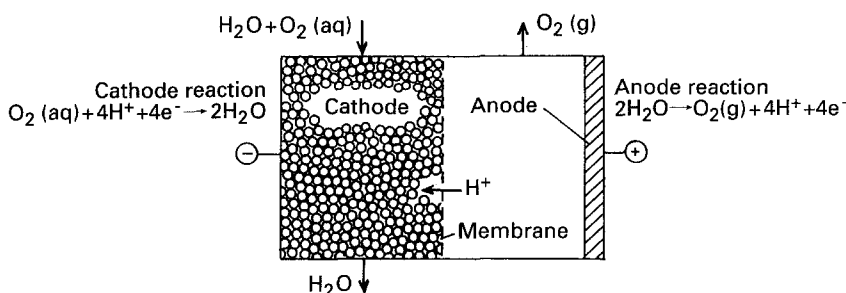


Fig. 3. The reactions in the cell.

3. Results

3.1. Graphite

The results obtained with the graphite bed are shown in Table 1. The bed consisted of 1.0–1.4 mm grains (Desulco, purity 99.7%). Because of the irregularity of the grains it was not possible to calculate the geometric bed surface. The bed voidage was 0.55.

On the surface of the graphite, oxygen was mostly reduced to hydrogen peroxide. This corresponds with results in the literature [5]. As hydrogen peroxide is a strong oxidant and a corrosive agent, graphite is not well suited as the cathode of an electrochemical deoxygenation cell.

3.2. Nickel

For the nickel bed spheres of 0.6–0.85 mm were used (Cerac, purity 99.9%). The geometric bed surface was calculated to be 0.5 m² and the bed voidage was 0.40. The results are shown in Table 2.

At first, the nickel bed functioned efficiently, but subsequently its activity declined drastically. This is probably due to the tendency of nickel to oxidation [7]. To avoid oxidation such high voltages are needed that hydrogen evolution is unavoidable. This makes nickel beds unsuitable for oxygen removal.

3.3. Copper

The copper beds consisted of copper spheres (Cerac, 99.95%). Three particle sizes were examined. The bed voidages were 0.40. The results are shown in Tables 3–5.

Copper reduced oxygen well and produced very little hydrogen peroxide. Copper resisted oxidation better than nickel and maintained its activity during the experiments. Nevertheless, slight oxidation was

detected after some time, especially when using 1.8 V cell voltage. The oxidation product, presumably Cu₂O, stayed at the particle surface [8]. The copper content of the outgoing water never exceeded the detection limit of 100 μg kg⁻¹.

The results show the effect of grain size on the efficiency of the cell. The more fine-grained the cathode material, the greater the surface area and, thus, the oxygen reduction capacity. Even when using the smallest spheres, the pressure drop caused by the bed is insignificant, of the order of 0.01 bar.

The most advantageous cell voltage is 2.0 V (Fig. 4). If the voltage is lower, the bed loses activity. At higher voltages hydrogen evolution becomes significant.

The bed with the smallest spheres was also used in long-term experiments. For 16 days, oxygen saturated-water (8200 μg kg⁻¹) was fed to the cell with a voltage of 2.0 V. The amount of residual oxygen never exceeded the detection limit of 3 μg kg⁻¹. In the end, the hydrogen peroxide content of the deoxygenated water was found to be lower than 10 μg kg⁻¹ and the hydrogen evolution current was estimated to be lower than 5%.

4. Discussion

The most restrictive factor in electrochemical oxygen removal is the uneven potential distribution in the three-dimensional cathode. Due to ohmic losses (*IR* drop) in the electrolyte, the cathode potential varies through the porous structure. The potential is most negative (about -0.5 V vs SHE, measured with a Luggin probe) near the membrane and at the bottom of the bed. Correspondingly, it is most positive (0.0 V) far from the membranes at the inlet of the cell. Too negative a potential leads to hydrogen evolution, whereas too positive a potential retards oxygen reduction (Fig. 5). An ideal potential distribution is achieved when the cathode potential in the middle

Table 1. Graphite grains, 1.0–1.4 mm. Oxygen and hydrogen peroxide contents of the treated water, and hydrogen evolution as a percentage of the cell current

Voltage /V	[O ₂] _{out} /μg kg ⁻¹	[H ₂ O ₂] _{out} /μg kg ⁻¹	H ₂ evolution /% of current
1.9	900	5700	<5
2.0	480	6300	<5
2.1	210	5700	<5
2.2	120	4700	8
2.3	70	4900	25

Table 2. Nickel spheres, 0.6–0.85 mm, bed surface 0.5 m². Oxygen and hydrogen peroxide contents of the treated water, and hydrogen evolution as a percentage of the cell current

Voltage /V	[O ₂] _{out} /μg kg ⁻¹	[H ₂ O ₂] _{out} /μg kg ⁻¹	H ₂ evolution /% of current
1.9	360	500	9
2.0	100	220	15
2.1	25	85	30
2.2	13	55	45

Table 3. Copper spheres, 1.0–1.4 mm, bed surface 0.3 m². Oxygen and hydrogen peroxide contents of the treated water, and hydrogen evolution as a percentage of the cell current

Voltage /V	[O ₂] _{out} /μg kg ⁻¹	[H ₂ O ₂] _{out} /μg kg ⁻¹	H ₂ evolution /% of current
1.9	300	300	<5
2.0	150	190	<5
2.1	90	185	<5
2.2	70	70	15
2.3	60	65	30

Table 4. Copper spheres, 0.6–0.85 mm, bed surface 0.5 m². Oxygen and hydrogen peroxide contents of the treated water, and hydrogen evolution as a percentage of the cell current

Voltage /V	[O ₂] _{out} /μg kg ⁻¹	[H ₂ O ₂] _{out} /μg kg ⁻¹	H ₂ evolution /% of current
1.8	>400	185	<5
1.9	100	85	<5
2.0	8	20	9
2.1	5	14	12
2.2	<3	15	25
2.3	<3	11	35

Table 5. Copper spheres, 0.3–0.6 mm, bed surface 0.8 m². Oxygen and hydrogen peroxide contents of the treated water, and hydrogen evolution as a percentage of the cell current

Voltage /V	[O ₂] _{out} /μg kg ⁻¹	[H ₂ O ₂] _{out} /μg kg ⁻¹	H ₂ evolution /% of current
1.8	200	90	<5
1.9	7	10	<5
2.0	<3	<10	7
2.1	<3	<10	17
2.2	<3	<10	35
2.3	<3	<10	45

of the bed is η_1 and at the membrane η_2 . Thus, the maximum potential drop is $\eta_1 - \eta_2 = \Delta\eta$.

The optimum bed depth of the packed cathode can be evaluated by Equation 7 [9]:

$$h_{\text{opt}} = \left[\frac{e\chi d_p \Delta\eta}{3(1-e)kzFc} \right]^{1/2} \quad (7)$$

where h_{opt} is the optimum bed depth (cm), e the bed voidage (0.4), χ the electrolyte conductivity (0.01 S cm⁻¹), d_p the particle diameter (0.045 cm), $\Delta\eta$ the maximum potential drop (0.3 V) [6], k the

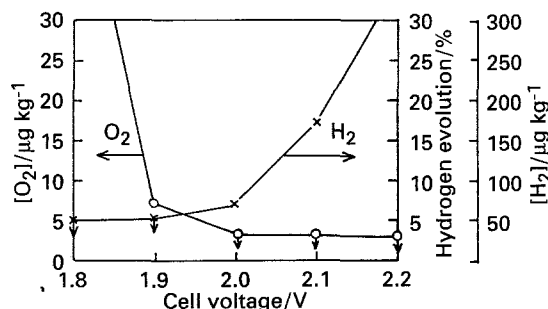


Fig. 4. Oxygen and hydrogen contents of the treated water as a function of cell voltage.

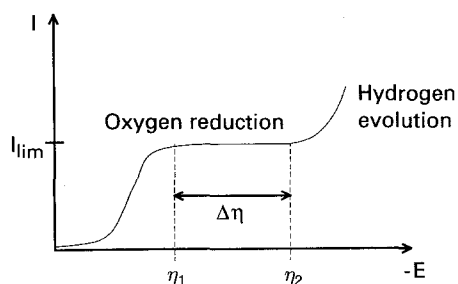


Fig. 5. The maximum potential drop.

mass transfer coefficient (0.0099 cm s⁻¹) [6], z the charge number (4), F the Faraday constant (96 500 A s mol⁻¹) and c the oxygen concentration (0.25 × 10⁻⁶ mol cm⁻³).

The result is multiplied by two when the counter electrodes are on both sides of the packed electrode.

These values give an optimum bed depth of 0.35 cm which is less than the 1.2 cm used in this study. Very thin electrodes are difficult to use because of channelling. They are the subject of ongoing work.

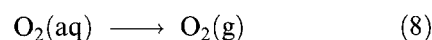
The potential drop necessitated high conductivity in the electrolyte, 50–100 times higher than in tap-water. This limits possible applications of electrochemical deoxygenation. For example, the treatment of boiler feed is not possible at the moment.

5. Conclusions

Water treated by the electrochemical method described contains less than 3 μg oxygen per kg of water when the initial level is 8000 μg kg⁻¹. The amount of residual oxygen is lower than the 10 μg kg⁻¹ achieved by physical methods, and is consistent with the levels lower than 5 μg kg⁻¹, achieved by chemical methods.

A packed bed is well suited as the cathode of a deoxygenation cell. The bed material must be fine-grained; it has to prevent the formation of hydrogen peroxide and it must maintain activity. Copper spheres fulfill these demands.

As the cathode reaction is oxygen reduction and the anode reaction is oxygen evolution, the overall reaction in the electrochemical deoxygenation is simply



Thus, the dissolved oxygen is converted into oxygen gas and is released outside the cell. No species other than oxygen are either formed or consumed. The amount of energy consumed is insignificant, 0.05 kWh per cubic metre of oxygen-saturated water.

The advantages of the electrochemical method are high efficiency and low energy consumption. Moreover, it is advantageous to avoid the use of toxic deoxygenation chemicals.

This electrochemical deoxygenation method has been found to be practical in laboratory work, when small amounts of oxygen-free water are needed. Possible industrial applications can be found in cooling and heating systems, and in chemical processing.

This laboratory scale research has been successfully continued on a pilot-plant scale [10].

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