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Scale-up of an electrochemical cell for oxygen removal from water

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In a previous paper an electrochemical method for the removal of dissolved oxygen from water was described. In that work the oxygen-rich water was passed through a three-dimensional cathode and the dissolved oxygen was reduced on the cathode surface to water. In the present study electrochemical oxygen removal and, especially, the scale-up of the deoxygenation cell were investigated. The volume of the three-dimensional cathode was enlarged and suitable cathode materials and membranes were tested. The maximum flow rate and the optimum cell voltage were determined. Finally, two cathodes were connected in parallel flow. A flow rate ten times higher than that of the former laboratory-scale cell was achieved. Over 99.95% of the dissolved oxygen was removed. No significant amount of by-products, hydrogen or hydrogen peroxide, was observed.

Nomenclature

A	area of the membrane (m^2)
D	hydrodynamic permeability ($g\,s^{-1}\,m^{-2}\,bar^{-1}$)
F	Faraday number ($96\,500\,A\,s\,mol^{-1}$)
I	current (A)
I_{meas}	measured current (A)
I_{theor}	theoretical current (A)
M_i	molecular mass of species i ($g\,mol^{-1}$)
$\dot{m}$	flow rate ($g[water]\,s^{-1}$)
m_{de}	mass of water decomposed on the anode (g)
m_{eo}	mass of water transported through the membrane by the electroosmosis (g)
m_{ev}	mass of water evaporated with the gaseous oxygen (g)
m_p	mass of water transported through the membrane due to the pressure (g)
m_{tot}	total mass change of the anolyte (g)
N_w	water transference number (2.2)
p	pressure of the gas bubble (pressure of the air, 101 300 Pa)
p_{H_2O}	water vapour pressure at room temperature (3000 Pa)
ΔP	pressure difference between catholyte and anolyte (bar)
$[O_2]$	mass fraction of dissolved oxygen ($g[O_2]\,g[water]^{-1}$)
t	time (s)
z_i	number of electrons needed per species i

1. Introduction

Removal of dissolved oxygen from water has a significant role in corrosion protection. In addition, oxygen is removed in the food and chemical industries in order to prevent undesirable oxidation reactions. Conventionally the oxygen is removed by physical (e.g. heating) or chemical (e.g. hydrazine) methods. The disadvantages of these methods are high capital cost (physical methods) or environmental and occupational risks (chemical methods).

An electrochemical deoxygenating method was reported in a previous paper [1]. In that work oxygen levels lower than $3\,\mu g\,kg^{-1}$ were achieved. The result was better than that obtained by physical methods and was equal to those obtained by chemical methods. The advantages of electrochemical deoxygenation were high efficiency and low energy consumption. The method was found to be very practical in the laboratory when small amounts of oxygen free water were needed.

The electrochemical cell for oxygen removal consists of a three-dimensional cathode that is separated from two oxygen evolving anodes by cation exchange membranes. During electrochemical deoxygenation, molecular oxygen is reduced in the cathodic reaction of the cell. The reaction in acidic medium is the formation of water:

$$O_2(aq) + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (1)$$

In neutral and alkaline media, oxygen reduction produces hydroxyl ions (OH^-). The reduction mostly occurs via a hydrogen peroxide intermediate stage.

The anodic reaction is the decomposition of water and the evolution of oxygen:

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \qquad (2)$$

The hydrogen ions are transported through a polymer cation exchange membrane into the cathode chamber. Regardless of the pH of water, the overall reaction of the electrochemical deoxygenation is the transfer of

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oxygen molecules from water to atmosphere:

$$O_2(aq) \rightarrow O_2(g) \qquad (3)$$

The work described in this paper is an experimental study of a scaled-up version of the electrochemical deoxygenation cell and it is closely related to the study on the laboratory-scale cell [1].

2. Apparatus

2.1. *Cell*

The cell used in the present study was a commercial plate and frame type Electro MP-Cell (ElectroCell AB) [2]. The cell was assembled from modules (frames) that were pressed together. Separate electrolytic flow channels to the anode and the cathode were formed in the modules. The MP-cell was easily expanded by assembling several single cells in parallel flow. In this study current was fed to the cathode by four copper current feeders. The flow in the cell was in a downward direction and the electric field in the cathode was perpendicular to the water flow (flow-by). Cross-sectional figures of the laboratory-scale cell and the scaled-up cell are shown in Fig. 1.

2.2. *Cathode*

The cathode used in the removal of oxygen was a packed bed. Previous studies determined copper as a suitable cathode material. Best results were achieved with 0.3–0.6 mm copper spheres [1]. In the scale-up, spherical particles were not considered for economical reasons. Irregular copper particles (Outokumpu Oy, 99.9%) were examined in the laboratory-scale cell and were found to be almost as good as small spherical particles [3]. Copper particles (size 0.2–1.2 mm) were chosen as the cathode material in the scaled-up cell. The bed voidage was determined to be 0.64 by the Archimedes method. The cathode area measured $0.075\,m^2\,g^{-1}$ by the BET method. The total BET area of the cathode was $40\,m^2$. A scanning electron microscope picture of the particles is shown in Fig. 2.

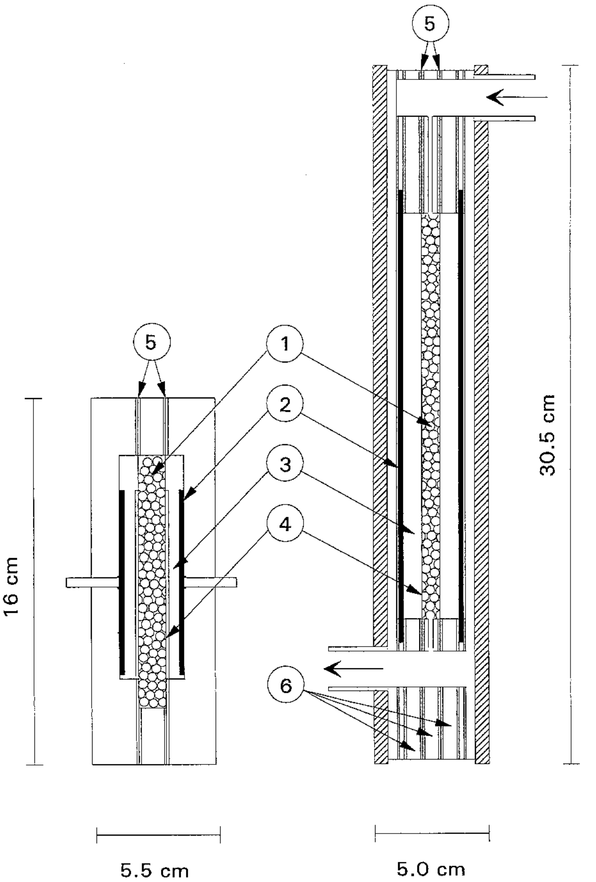

Fig. 1. The laboratory-scale cell and the Electro MP-Cell: (1) cathode compartment filled with the three-dimensional cathode, (2) anodes, (3) anode compartments, (4) membranes, (5) gaskets and (6) frames.

The length of the cathode (in the direction of the water flow), the depth (in the direction of the electric field) and the width were 17.3, 0.8 and 12.5 cm, respectively. The total volume of the cathode bed was $173\,cm^3$. The depth of the cathode in the scaled-up cell was, in fact, 0.4 cm less than in the laboratory-scale cell. This was accomplished as a consequence of the previous problems that were caused by the voltage drop in the electrolyte inside the cathode bed (*IR* drop).

2.3. *Membranes*

Cation exchange membranes were placed on both sides of the cathode bed. It was essential that the membrane used in the deoxygenation cell was impermeable to molecular oxygen. For the scale-up, oxygen permeability of various membranes was studied. The smallest oxygen leakage amongst the cation exchange membranes tested was with the IONAC® MC-3470 membrane [3]. This membrane was thus chosen for the scaled-up cell.

2.4. *Anodes*

Anodes were DSA®-type oxygen evolution anodes made of titanium, covered with iridium-based oxide. The anodes were placed on both sides of the cathode. The interelectrodic gap between the anode and the cathode bed was 0.8 cm. The total area of one anode was $216\,cm^2$. Supporting nets were placed in the

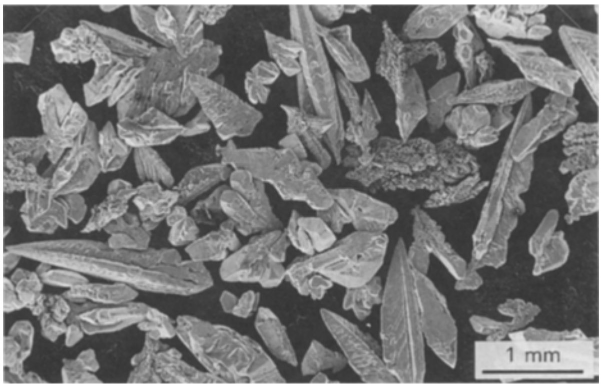

Fig. 2. SEM picture of the cathode bed particles, copper grain size 0.2–1.2 mm.

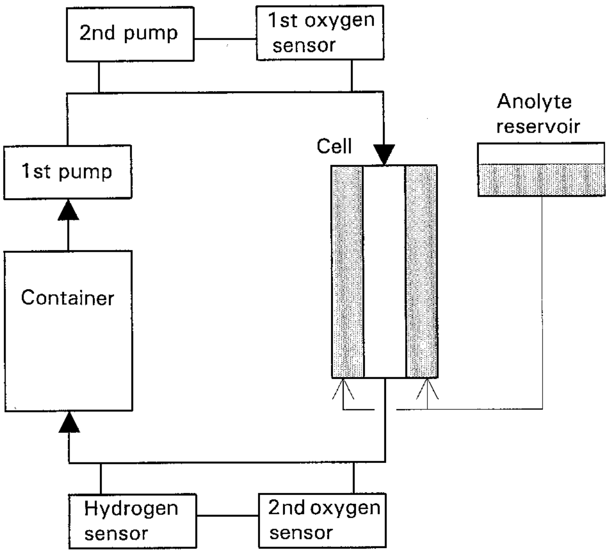

Fig. 3. Schematic picture of the flow system.

anode compartment so that the cathode retained its shape.

2.5. *Electrolytes*

To increase the conductivity of the electrolyte 0.05 mol dm^{-3} of sodium sulphate was added to distilled water. The conductivity of the solution was 0.9 S m^{-1} (20 °C). This solution was chosen in order to be able to compare the results of this and previous studies [1, 3]. Sodium sulphate solution was used both as anolyte and catholyte. Oxygen was removed from the catholyte.

A slight change in the pH of the electrolytes was observed. Some sodium ions in the anolyte were transferred through the membrane to the catholyte, and were replaced by hydrogen ions. Thus the anolyte became acidic and the catholyte became slightly alkaline.

2.6. *Flow system*

The performance of the cell was studied using a closed water circuit (Fig. 3). Oxygen saturated water was pumped from a container to the cell. Water flowed only through the cathode compartment. The flow through the first oxygen sensor (Orion research 1808) was adjusted to 100 g min^{-1}. The flow through the second oxygen sensor (Orbisphere 2713) and the hydrogen sensor (Orbisphere 27321) was adjusted to 150 g min^{-1}. After leaving the cell, water was fed back to the container, where it was again saturated with oxygen by mechanical stirring.

Anode compartments were filled from a separate anolyte reservoir.

3. Experiments and results

3.1. *Maximum flow rate*

Maximum flow rate was examined in a cell with one cathode. The aim was to study how much water the scaled-up cell could treat without losing its deoxygenation efficiency. A series of experiments was carried out during which the flow rate was varied and the oxygen content at the outlet was measured. The treated water was alkaline (pH 9–10). All the experiments were made at room temperature (20–25 °C).

Two initial conditions were fixed: (a) the current efficiency of the cell had to be constant at all flow rates to keep the rate of side reactions constant and (b) the oxygen content at the inlet of the cell had to be constant in all experiments.

Each experiment consisted of the following steps: (i) the flow rate was changed, (ii) the oxygen content at the inlet was adjusted, (iii) the theoretical current was calculated, (iv) the cell voltage was adjusted, and (v) the oxygen content at the outlet was measured.

The oxygen content at the inlet was controlled by a mechanical stirrer in the container. The oxygen content used (7450 $\mu g\,kg^{-1}$) was close to the equilibrium solubility of oxygen.

The theoretical current, I_{theor}, was calculated according to Equation 4:

$$I_{theor} = \frac{[O_2]z_{O_2}F\dot{m}}{M_{O_2}} \qquad (4)$$

The cell voltage was adjusted so that the cell current was 10 per cent higher than the theoretical current and thus the current efficiency was 0.9. The extra current was consumed in the hydrogen evolution reaction.

The oxygen content at the outlet was measured after it had settled at a constant value, in most cases after 30 min. The results are shown in Table 1. Two separate series of experiments were made. The cell voltage was reproducible within the limits ±0.1 V and the oxygen content within the limits ±3 $\mu g\,kg^{-1}$.

The oxygen content was under 3 $\mu g\,kg^{-1}$ below the flow rate of 500 g min^{-1}. At higher flow rates the content of unreduced oxygen grew rapidly. The cell voltage increased fairly smoothly. If the aim of the oxygen removal method is high deoxygenation efficiency, the maximum flow rate is about 500 g min^{-1}. At this flow rate the total pressure drop at the cathode was about 0.1 bar.

Table 1. The outlet content of oxygen at various flow rates. The cell voltage (and the current) was adjusted to maintain a constant current efficiency I_{theor}/I_{meas} = 0.9

Flow rate /g min^{-1}	*Cell voltage* /V	*Current* /mA	$[O_2]_{OUT}$ /$\mu g\,kg^{-1}$
100	1.90	170	<3
160	2.05	270	<3
240	2.19	400	<3
330	2.26	540	<3
420	2.43	700	<3
500	2.49	830	<3
540	2.51	890	4
590	2.56	970	5
670	2.61	1100	9
710	2.63	1170	17

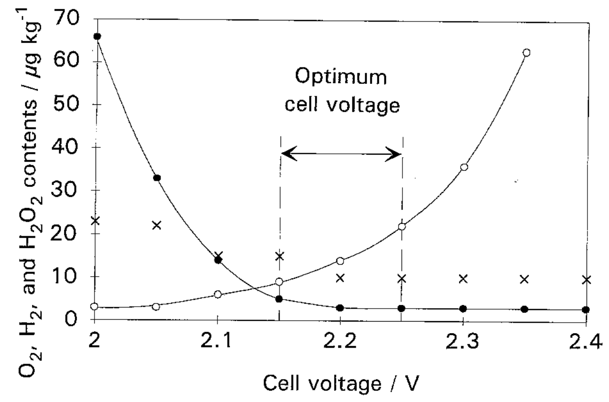

Fig. 4. Oxygen (●), hydrogen (○) and hydrogen peroxide (×) contents as a function of cell voltage at flow rate 500 g min^{-1}

3.2. *Optimum cell voltage*

The optimum cell voltage was determined by changing the voltage (and the current). Apart from the oxygen content, the by-products, hydrogen and hydrogen peroxide were also measured. The flow rate through the cell was kept at 500 g min^{-1}.

The oxygen content at the cell inlet was adjusted to a constant value of 7450 µg kg^{-1}. The pH of the water was 9. The experiment started at the highest cell voltage and ended at the lowest.

In Fig. 4, oxygen, hydrogen and hydrogen peroxide contents are shown as a function of the cell voltage. Oxygen was reduced almost completely when the cell voltage was higher than 2.2 V. A lower voltage caused an increase in the oxygen content. The hydrogen evolution was not significant below 2.3 V. Hydrogen peroxide was formed when voltages under 2.2 V were used. The optimum operating voltage was 2.15–2.25 V. In this region, the current efficiency was better than 0.95, and the oxygen reduction conversion was over 99.9%.

Copper and hydrogen sulphide contents were determined by colorimetric analysis. Both contents were below the detection limit of 100 µg kg^{-1}.

3.3. *Cell with two parallel cathodes*

To examine the possibility of a parallel scale-up, two cathodes and three anodes were combined to form a double-cathode cell with parallel flow. The anode in the middle served as the counter electrode for both cathodes. It was of special interest to establish whether an equal flow was formed through both cathodes.

An experiment was carried out in which the function of the double-cathode cell was studied at a flow rate of 1000 g min^{-1}, otherwise the experiment was identical to that described in Section 3.1. Results are shown in Table 2. The extra current (Equation 5) is the part of the cell current that was consumed in side reactions.

$$\text{Extra current} = [(I_{meas} - I_{theor})/I_{meas}] \times 100\% \tag{5}$$

This experiment shows that the water flow in the double-cathode cell was divided evenly between the two cathodes. A double flow rate was achieved with two cathodes, compared with a single-cathode cell. No deoxygenation capacity was lost.

Table 2. Double-cathode cell, flow rate 1000 g min^{-1}, oxygen content at the inlet 7450 µg kg^{-1}

Cell voltage /V	*[O_2]$_{OUT}$* /µg kg^{-1}	*[H_2O_2]$_{OUT}$* /µg kg^{-1}	*[H_2]$_{OUT}$* /µg kg^{-1}	*Extra current* /%
2.10	30	14	< 5	< 5
2.15	15	10	6	< 5
2.20	< 3	< 10	10	< 5
2.25	< 3	< 10	20	< 5
2.30	< 3	< 10	30	< 5
2.35	< 3	< 10	40	< 5
2.40	< 3	< 10	70	6
2.45	< 3	< 10	80	6
2.50	< 3	11	> 100	9
2.55	< 3	< 10	> 100	12
2.60	< 3	< 10	> 100	16

A seven-day experiment was carried out in order to study the possible oxidation of copper or other factors that might decrease the deoxygenation capacity of the cell in long-term use. During this experiment the flow rate through the double-cathode cell was 1200 g min^{-1}. The oxygen content at the inlet was about 7500 µg kg^{-1}. The current efficiency was kept at 0.95. The copper cathode did not lose activity. The oxygen content at the outlet remained under 3 µg kg^{-1}.

3.4. *Water balance*

The water balance of the electrochemical deoxygenation cell was examined by following the volume of the anolyte for 120 h. At a flow rate of 500 g min^{-1} (current 0.80 A) the amount of the anolyte increased by 85 g (0.71 g h^{-1}). Factors affecting the water balance are electrochemical reactions, evaporation, electroosmosis and hydrodynamic permeability. The values of these factors may be calculated to a certain extent.

The amount of water decomposed on the anode can be calculated accurately. For every reduced oxygen molecule two water molecules are decomposed in the anode reaction. The amount of water decomposed on the anode (Reaction 2) is calculated by Faraday's law when the quantity of electricity is known:

$$m_{de} = \left(\frac{It}{Fz_{H_2O}}\right) M_{H_2O} = It \times 9.33 \times 10^{-5}\,g\,C^{-1} \tag{6}$$

The gaseous oxygen produced on the anode is released into the atmosphere. The amount of evaporation is calculated assuming that this oxygen gas is saturated with water vapour:

$$\begin{aligned} m_{ev} &= \frac{p_{H_2O}}{(p - p_{H_2O})} \left(\frac{It}{Fz_{O_2}}\right) M_{H_2O} \\ &= It \times 0.14 \times 10^{-5}\,g\,C^{-1} \end{aligned} \tag{7}$$

Electroosmosis is the flow of water molecules that are transferred with the ions through the membrane. The effect of electroosmosis may be evaluated by assuming that every hydrogen ion is accompanied by about two molecules of water [4]. A value of 2.2 has been reported for the IONAC® MC 3470 membrane in 0.1 mol dm^{-3} HCl (25 °C) [5]. Thus, in this case, the transport from anolyte to catholyte is

$$m_{eo} = N_w \left(\frac{It}{F z_{H^+}} \right) M_{H_2O} = It \times 41.04 \times 10^{-5}\,g\,C^{-1} \qquad (8)$$

However, the higher pressure on the cathode side forces water molecules to move through the membrane in the opposite direction, from catholyte to anolyte. The water flow depends on the pressure difference and on the hydrodynamic permeability of the membrane, but not on the current. The mass of water transport due to this pressure difference is

$$m_p = DAt\Delta P \qquad (9)$$

According to the manufacturer's information the hydrodynamic permeability (D) of the IONAC® MC 3470 membrane is 0.174 $g\,s^{-1}\,m^{-2}\,bar^{-1}$.

The change in the mass of anolyte is

$$m_{tot} = -m_{de} - m_{ev} - m_{eo} + m_p \qquad (10)$$

Values of m_{de}, m_{ev}, m_{eo}, m_p and m_{tot} were calculated to be 0.27, 0.004, 1.18, 1.98 and 0.53 g, respectively, for the following conditions: $t = 3600$ s, $\dot{m} = 500\,g\,min^{-1}$, $I = 0.8$ A, $N_w = 2.2$, $\Delta P = 0.073$ bar and $A = 2 \times 0.0216\,m^2$. The calculated value for the change in the mass of anolyte (0.53 g) is, in fact, of the same magnitude to the observed value 0.71 g. However, the value is insignificant in view of the fact that 30 kg of water have been deoxygenated at the same time.

3.5. *Cathode potential*

The cathode potential was measured against a saturated calomel electrode. The electrode was placed in the water flow either at the inlet or the outlet of the cell. Potentials measured in this way corresponded to local potentials of the cathode at the top of the bed (in the middle in the direction of the electric field) and at the bottom of the bed (in the middle).

At the optimized flow rate of 500 g min^{-1} (one cathode) and at a cell voltage of 2.20 V the potential at the top of the cathode was −0.27 V vs NHE and at the bottom of the cathode −0.51 V vs NHE. The pH of the catholyte was kept at 10. The difference between the measured potentials was caused by the *IR* drop. The *IR* drop was higher at the top of the cathode due to the higher oxygen reduction current density.

4. Discussion

A common problem in three-dimensional electrodes is the uneven potential distribution along or through the porous electrode. This potential distribution is a consequence of the *IR* drop. Potential distribution may lead to situations where parts of the electrode become 'dead' or unwanted side reactions take place. In the case of electrochemical deoxygenation the side reactions are primarily copper oxidation at less negative cathode potentials and hydrogen evolution at the most negative cathode potentials.

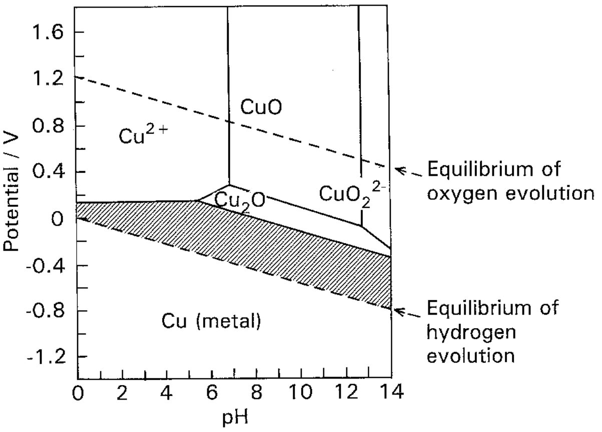

Fig. 5. The potential-pH (Pourbaix)-diagram of copper. The ideal potential range is shaded.

At an optimized flow rate of 500 g min^{-1} (one cathode) and at a cell voltage of 2.20 V the cathode remained active and the hydrogen evolution was minimized. The cathode potential stayed in the ideal potential range. In the potential-pH diagram [6] of the copper electrode (Fig. 5) this ideal range is shaded. In this range neither hydrogen evolution nor copper oxidation take place.

If the treated water were extremely conducting the deoxygenation capacity would be remarkably higher. On the other hand, if the water were extremely pure the *IR* drop would inhibit the cathode bed from reducing the oxygen molecules.

To be able to use electrochemical deoxygenation in all possible water systems the problems arising from potential distribution have to be solved. Therefore, the attention of the ongoing study is focused on the *IR* drop problem in electrochemical deoxygenation of water that contains considerably less dissolved salts than the solution in the present work.

At the present stage the electrochemical deoxygenation can be useful in applications where there is a need for effective, small-size and non-toxic oxygen removal.

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