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# Application of a three-dimensional ion-exchange electrolyte in the deoxygenation of low-conductivity water

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A solid ion-exchange electrolyte has successfully been used in the electrochemical deoxygenation of low-conductivity water. A packed bed three-dimensional cathode was mixed with ion-exchange resin. Oxygen-rich low-conductivity water was passed through the three-dimensional cathode and the dissolved oxygen was reduced to water. A sufficient ionic conductivity in the three-dimensional electrode was obtained for both distilled water and tap water by small-size strong cation exchange resins in the $H^+$ and $Ca^{2+}$ forms, respectively. Deoxygenation efficiencies of over 99.9% were achieved.

## 1. Introduction

A nonuniform potential distribution is a common result of ohmic loss (*iR*-drop) in three-dimensional, flow-by, packed bed cells [1]. As a consequence of the nonuniform potential distribution the bed may become partly inactive or undesirable side reactions may take place. These effects are especially observed in situations where the conductivity of the electrolyte is not adequate. It has been estimated [2] that, to get satisfactory current efficiencies, the application of flow-by electrodes should be restricted to solutions with conductivities above $1\,\mathrm{mS\,cm^{-1}}$.

In most applications where dilute solutions are treated electrochemically, a supporting electrolyte is added to increase the conductivity of the solution and thus to avoid the unwanted nonuniform potential distribution. For example, the recovery of dilute metal solutions is often performed in concentrated sulfate solutions. However, in some cases it is not desirable to increase the conductivity of the treated solution. In such cases, to minimize the *iR*-drop, the three-dimensional electrodes must be very thin (effective bed depth < 1 cm).

A previous paper [3] presented a new electrochemical method for treating solutions of low conductivity. In that work it was shown that a three-dimensional electrode mixed with ion-exchange resin works well in low-conductivity water (conductivity less than $1\,\mathrm{mS\,cm^{-1}}$). Inside the packed bed electrode the charge is transported in the resin, in which the ions can migrate. The ion-exchange electrolyte can be considered as a three-dimensional solid electrolyte.

In the present study a cathode of this kind has been adapted to the electrochemical deoxygenation of distilled water and tap water. This is of special interest in corrosion protection. The effect of particle size, geometry and structure of an ion-exchange electrolyte on the deoxygenation efficiency is reported.

## 2. Experimental details

### 2.1. *Deoxygenation method*

A schematic presentation of the method is shown in Fig. 1. The oxygen-rich water flows through a three-dimensional cathode where the oxygen molecules are reduced to hydroxyl ions (or to water at low pH values). The reduction mostly occurs via a hydrogen peroxide intermediate stage. The anode reaction is the decomposition of water to oxygen molecules and hydrogen ions. The oxygen gas is released from the anode compartment into the atmosphere. The hydrogen ions are transported through a cation exchange membrane to the cathode chamber. The overall reaction of the electrochemical deoxygenation is the transfer of oxygen molecules from water to atmosphere:

$$O_2(aq) \longrightarrow O_2(g) \tag{1}$$

The electrochemical deoxygenation method itself has been described in a previous paper [4].

### 2.2. *Electrolytes*

The low-conductivity flowing electrolytes (catholytes) used in this study were distilled water and tap water. The conductivities (at 25 °C) of distilled water and tap water were about $0.003\,\mathrm{mS\,cm^{-1}}$ and about $0.150\,\mathrm{mS\,cm^{-1}}$, respectively. The pH of the waters was neutral. The oxygen content used ($8300 \pm 500\,\mu\mathrm{g\,kg^{-1}}$) was close to the equilibrium solubility of oxygen. This was reached by stirring the flowing electrolyte thoroughly in a container. Tap water, which came from the general water supply for

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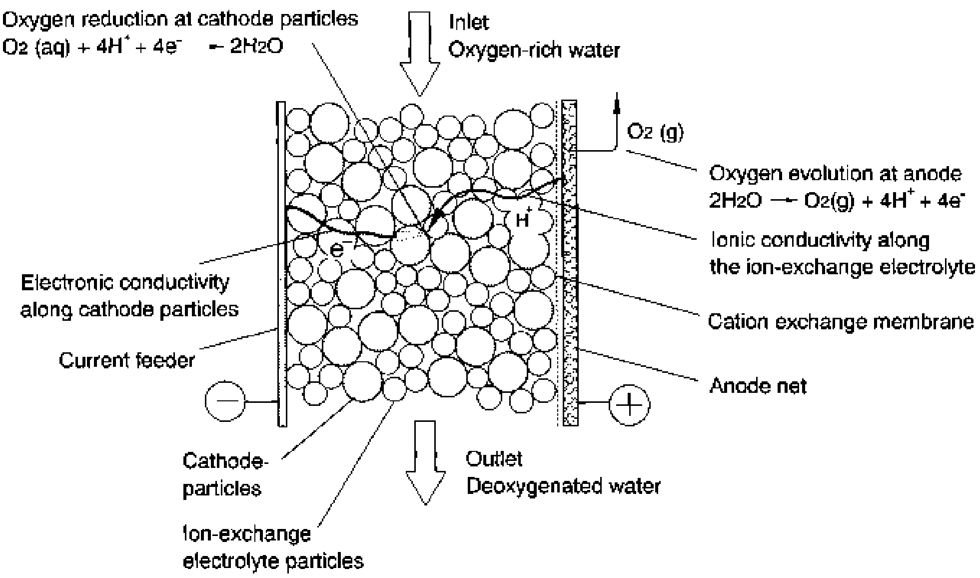

Fig. 1. A schematic presentation of the deoxygenation method of low-conductivity water using an ion-exchange electrolyte in the three-dimensional cathode.

the Helsinki area, was taken from the tap in the laboratory. The main ions in tap water were $Ca^{2+}$ ($17\,mg\,kg^{-1}$), $Na^+$ ($5\,mg\,kg^{-1}$), $SO_4^{2-}$($9\,mg\,kg^{-1}$), $Cl^-$ ($23\,mg\,kg^{-1}$) and $HCO_3^-$ ($41\,mg\,kg^{-1}$).

The anode compartment was filled with a $0.1\,mol\,dm^{-3}$ $HNO_3$ solution (anolyte).

The ion-exchange electrolytes used were commercially available, strong cation exchange resins. The suitability of ion-exchange electrolytes in three-dimensional electrodes depends on the following factors: counter-ions, degree of cross-linkage in the resin structure as well as particle size and geometry [3]. In accordance with these factors a group of resins, shown in Table 1, was chosen for this study. In the experiments where the dissolved oxygen was removed from distilled water the resins were in the $H^+$-form because hydrogen ions have the best conductivity. In tap water experiments the resins were in the $Ca^{2+}$-form, since otherwise the free $Ca^{2+}$-ions in tap water would have replaced the counter-ions. The resin must be in such an ionic form that no replacement of the counter-ions by the free ions can occur.

### 2.3. *Cell*

The deoxygenation cell was a three-compartment, flow-by Electro MP-Cell (ElectroCell AB) [5]. The middle compartment was filled with the three-dimensional cathode bed. It was separated from the two anode compartments by cation exchange membranes. A cross-sectional picture of the cell is shown in Fig. 2.

The cathode particles were 0.2–1.2 mm irregular copper particles (Outokumpu Oy). In a previous study [4] copper was found to be a suitable electrode material for oxygen removal. The packed bed was prepared in the following sequence: (i) cathode particles were cleaned with 10% sulfuric acid and rinsed with distilled water; (ii) the resin was regenerated to the desired cation form ($H^+$ or $Ca^{2+}$) with a 10% chloride solution; (iii) copper particles, $65\,cm^3$, were mixed with the resin to make a total volume of $130\,cm^3$; (iv) the electrode-resin mixture was packed into the middle compartment of the cell. The length of the cathode bed (in the direction of the electrolyte

*Table 1. Ion-exchange resins*

| *Resin and geometry* | *Structure Cross-linkage*[*] | *Dimensions* | *Intrinsic conductivity of the resin /mS cm$^{-1}$* [3] | |
|---|---|---|---|---|
| | | | *$H^+$-form* | *$Ca^+$-form* |
| Spherical | | | | |
| Dowex 50X2-100[†] | styrene + 2% DVB | 0.15–0.3 mm | 350 | 29 |
| Dowex 50X4-100[†] | styrene + 4% DVB | 0.15–0.3 mm | 325 | 20 |
| Dowex 50X4-50[†] | styrene + 4% DVB | 0.3–0.84 mm | 325 | 20 |
| Dowex 50X8-100[†] | styrene + 8% DVB | 0.15–0.3 mm | 270 | 8.3 |
| Fibrous | | | | |
| Smopex-101[‡] | polypropene + styrene + 0% DVB | length 4 mm<br>dia. 40 $\mu$m | 340 | 16 |

[*] Cross-linkage is expressed as a percentage of divinylbenzene (DVB).

[†] Dowex is a trademark of DOW Chemicals.

[‡] Smopex is a trademark of Smop Tech.

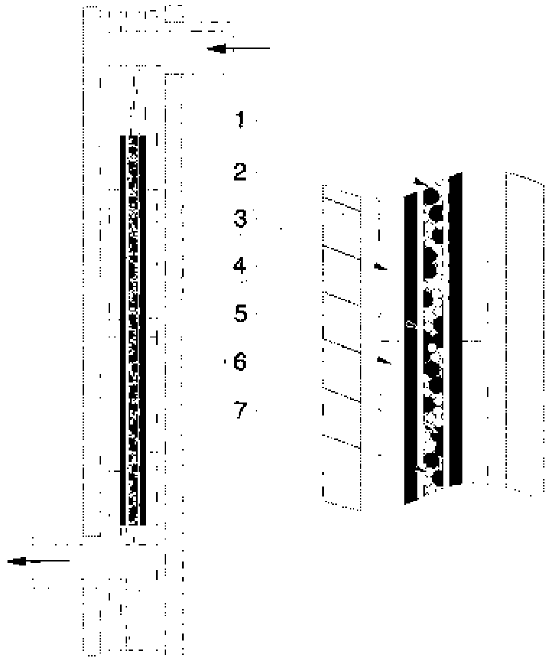

Fig. 2. The deoxygenation cell: (1) cathode compartment, (2) anode net, (3) anode compartment, (4) membrane, (5) anode support, (6) copper particle and (7) ion-exchange resin.

flow), the depth (in the direction of the electric field) and the width were 17.3, 0.6 and 12.5 cm, respectively. The total area of the cathode (copper particles) was 15 m$^2$, measured by the BET method. Four copper current feeders fed the current into the cathode compartment.

IONAC® MC-3470 cation exchange membranes were placed on both sides of the cathode bed. The DSA®-type oxygen evolution anode nets were placed in contact with the membrane. The interelectrodic gap was therefore only the thickness of the membrane, 0.4 mm. The oxygen gas was released into the atmosphere from the top of the anode compartment.

### 2.4. *Experimental procedure*

Oxygen saturated water was fed from a container through an oxygen sensor (Orion 1808), into the cell. The water flowed downwards through the cathode bed and was deoxygenated. After leaving the cell, the deoxygenated water flowed through a second oxygen sensor (Orbisphere 2713) into the drain. The oxygen content at the outlet was measured after it had settled at a constant value, in most cases after 30 min. The detection limit of oxygen measurements was 3 $\mu$g kg$^{-1}$. Besides oxygen measurements, conductivity, pH and hydrogen peroxide content were determined. The hydrogen peroxide content was determined spectrophotometrically by an iodide method [6]. The detection limit of that method was 100 $\mu$g kg$^{-1}$.

The cell current was dependent on the oxygen content and the flow rate. The theoretical cell current was calculated according to Equation 2:

$$I = [\mathrm{O_2}]\, z\, F\, \dot{m}/M \qquad (2)$$

where [O$_2$] is the mass fraction of dissolved oxygen in water, $z$ the number of electrons required per oxygen molecule (4), $F$ the Faraday number (96500 As mol$^{-1}$), $\dot{m}$ the water flow (g s$^{-1}$) and $M$ the molecular mass of oxygen (32 g mol$^{-1}$). The cell voltage was adjusted so that slightly more current was consumed. In most cases the current efficiency was 0.9. The difference between the measured current and the theoretical current was assumed to be the hydrogen evolution current.

Different electrode-resin mixtures were compared by experiments recording the oxygen content at the outlet as a function of the water flow rate. The experiments were carried out at room temperature, 20–25 °C.

## 3. Results

### 3.1. *Distilled water*

The results obtained with distilled water are shown in Fig. 3 and Table 2. In Fig. 3 the oxygen content at the outlet is presented as a function of flow rate for various resins. Both Dowex 50X2-100 and Dowex-50X4-100 (particle sizes 0.15–0.30 mm), worked well in distilled water. With these resins the unreduced oxygen remained low up to a flow rate of 300 g min$^{-1}$. Dowex 50X4-50 (particle size 0.3–0.84) and Dowex 50X8-100 (high divinylbenzene content) did not work in the three-dimensional electrode.

Table 2 presents cell voltage, and oxygen and hydrogen peroxide content at the outlet at a constant flow rate of 200 g min$^{-1}$ for various resins. The cell voltage slightly increased with an increasing degree of cross-linking. The formation of hydrogen peroxide was only observed when using Dowex 50X4-50.

The fibrous Smopex 101 was mechanically unstable in distilled water. It formed an almost impermeable slurry, and deoxygenation at flow rates over 175 g min$^{-1}$ failed due to the high pressure drop (up to 4 bar). However, the deoxygenation efficiency at low flow rates with the fibrous resin was good.

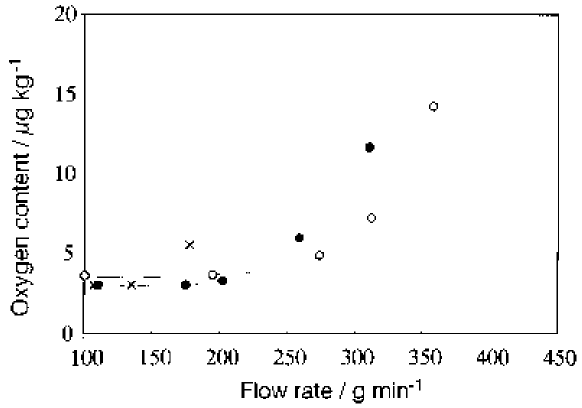

Fig. 3. Deoxygenation of distilled water. The oxygen content at the outlet is shown as a function of flow rate at a constant current efficiency of 0.9. Various resins: (●) Dowex 50X2-100, (○) Dowex 50X4-100 and (×) Smopex 101.

*Table 2. Deoxygenation of distilled water at a constant flow rate of 200 g min$^{-1}$ and a current efficiency of 0.9*

| *Resin* | *Cell voltage* /V | *Oxygen content* /$\mu$g kg$^{-1}$ | *Hydrogen peroxide* /$\mu$g kg$^{-1}$ |
|---|---|---|---|
| Dowex 50X2-100 | 1.79 | 3 | < 100 |
| Dowex 50X4-100 | 1.85 | 4 | < 100 |
| Dowex 50X4-50 | 2.02 | 600 | 400 |
| Dowex 50X8-100 | 1.96 | 50 | < 100 |

*Table 3. Deoxygenation of tap water at a constant flow rate of 200 g min$^{-1}$ and a current efficiency of 0.9*

| *Resin* | *Cell voltage* /V | *Oxygen content* /$\mu$g kg$^{-1}$ | *Hydrogen peroxide* /$\mu$g kg$^{-1}$ |
|---|---|---|---|
| Dowex 50X2-100 | 2.02 | < 3 | < 100 |
| Dowex 50X4-100 | 2.08 | < 3 | < 100 |
| Dowex 50X4-50 | 2.08 | 14 | 100 |
| Dowex 50X8-100 | 2.13 | 4 | < 100 |
| Smopex 101 | 2.20 | < 3 | < 100 |

In all experiments the conductivity at the outlet was 0.003 ± 0.001 mS cm$^{-1}$ and the pH stayed constant at pH 7 ± 1.

### 3.2. *Tap water*

Figure 4 shows the oxygen content at the outlet as a function of flow rate for various resins. The highest deoxygenation capacity was achieved with the Dowex 50X2-100 resin. The oxygen content was less than 3 $\mu$g kg$^{-1}$ up to a flow rate of 440 g min$^{-1}$. The deoxygenation efficiency was also very good with Dowex 50X4-100 and Smopex 101. In the Ca$^{2+}$-form Smopex did not lose its mechanical stability.

As in the experiments with distilled water, the deoxygenation efficiencies were lowest when resins with a large particle size (Dowex 50X4-50) or a high cross-linkage degree (Dowex 50X8-100) were used.

Table 3 gives the results for various resins at a constant flow rate of 200 g min$^{-1}$. The lowest cell voltage was achieved with Dowex 50X2-100 and the highest with fibrous Smopex 101. Hydrogen peroxide was observed only when using Dowex 50X4-50.

For the best resin, Dowex 50X2-100, two additional experiments were carried out at a constant flow rate of 200 g min$^{-1}$. In the first experiment the oxygen content and the extra current were recorded as a function of cell voltage. The results are shown in Fig. 5. The deoxygenation efficiency was excellent at cell voltages over 1.90 V. The optimum cell voltage was 1.90–2.10 V. The bed lost its activity at lower cell voltages. At higher voltages, hydrogen evolution became significant. The second experiment was a seven-day test. It was carried out at a constant current efficiency of 0.9. During the seven days the outlet content of oxygen never exceeded 4 $\mu$g kg$^{-1}$ and the hydrogen peroxide content stayed under the detection limit of 100 $\mu$g kg$^{-1}$. The cell voltage remained constant at 2.05 ± 0.05 V. Neither the conductivity nor the pH changed during the experiment. The pressure drop was 0.4 bar.

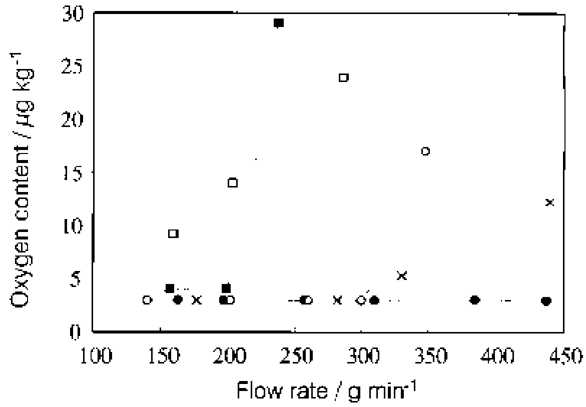

Fig. 4. Deoxygenation of tap water. The oxygen content at the outlet is shown as a function of flow rate at a constant current efficiency of 0.9. Various resins: (●) Dowex 50X2-100, (○) Dowex 50X4-100, (■) Dowex 50X4-50, (□) Dowex 50X8-100 and (×) Smopex 101.

## 4. Discussion

In this work the ohmic loss inside a three-dimensional electrode was minimized by using a solid ion-exchange electrolyte. The ionic current passed mainly through an ion-exchange resin. The average length of the path of the ions was 1.5 mm (about 5–10 resin particles). Because of the poor interparticle contact, the effective ionic conductivity inside the three-dimensional electrode is considerably lower than the intrinsic conductivity of the resin. In this work it can be assumed that the effective conductivities of the ion-exchange electrolytes in the three-dimensional electrode were in the same range as in the previous study [3]. For example, the conductivity of Dowex 50X2-100 resin in the H$^+$-form and in distilled water is about 3 mS cm$^{-1}$, and the conductivity in the Ca$^{2+}$-form and in tap water is about 1 mS cm$^{-1}$.

Even though the conductivities of the strong cation exchangers are higher in the H$^+$-form than in the Ca$^{2+}$-form the deoxygenation capacities in distilled water were lower than those in tap water. This can be explained by the fact that in distilled water the

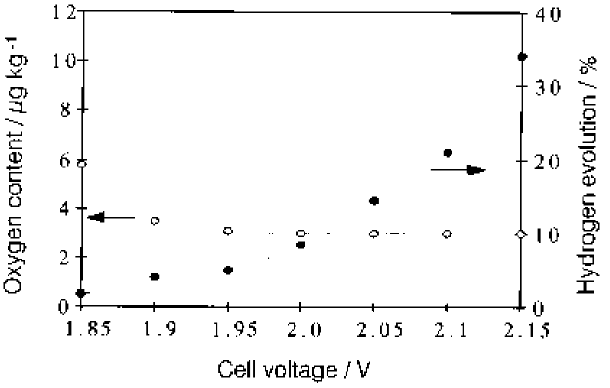

Fig. 5. Deoxygenation of tap water. Oxygen content (○) and hydrogen evolution (●) as a function of the cell voltage at a flow rate of 200 g min$^{-1}$. Resin: Dowex 50X2-100.

electroactive surface of a cathode particle is restricted very close to the electrode-resin contact point (interface). In tap water the electroactive area is much larger due to the fiftyfold higher conductivity of the solution. It can also be assumed that the poor deoxygenation efficiency caused by a larger particle size (Dowex 50X4-50) is a consequence of the lack of electroactive area.

The conductivity of the ion-exchange electrolyte inside the three-dimensional electrode allows a moderate (300–440 $\mathrm{g\,min^{-1}}$) deoxygenation capacity and prevents the copper from oxidation. A three-dimensional cathode that does not contain an ion-exchange electrolyte fails to deoxygenate distilled water or tap water and is oxidized within a few minutes. If a supporting electrolyte can be used, higher deoxygenation capacities are reached. For example, when using 0.05 $\mathrm{mol\,dm^{-3}}$ sodium sulfate as the supporting electrolyte (conductivity 9 $\mathrm{mS\,cm^{-1}}$), the deoxygenation capacity of the cell is 1200 $\mathrm{g\,min^{-1}}$. However, this demands 7 kg $Na_2SO_4$ per cubic metre of water.

In one study [7] the ohmic loss was minimized by a very short ionic route. In that work the low-conductivity (deionized) water was deoxygenated electrochemically in a flow cell where the mesh screen cathode was pressed against the membrane. The low-conductivity water flowed between the cathode and the membrane. Therefore, the ionic current had to pass through only a few tenths of millimetres in low-conductivity water. A reduction to 70% (deoxygenation efficiency 30%) of the initial oxygen concentration was reported. If this is compared to the results presented in this paper the advantages of a three-dimensional structure and an ion-exchange electrolyte are obvious.

## 5. Conclusions

A three-dimensional electrode can be mixed with an ion-exchange electrolyte. The packed bed cathode described is found to be very useful in the electrochemical removal of oxygen from low-conductivity water, such as distilled water. The best results are achieved by a strong cation exchange resin of a small particle size and a low cross-linking degree. The oxygen content at the cell inlet, 8000 $\mu\mathrm{g\,kg^{-1}}$, is reduced to levels lower than 3 $\mu\mathrm{g\,kg^{-1}}$ at the outlet, the mean residence time being ten seconds. The current efficiency is high (0.9) and the energy consumption is very low, only 0.06 kWh per cubic metre of oxygen-saturated water.

At the present stage of this research electrochemical oxygen removal can be applied to several water systems, including potable and boiler waters. At the moment the cell is being studied in a district heating system where the dissolved oxygen is removed from the make-up water.

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