Electrochemical detoxification of waste water without additives using solid polymer electrolyte (SPE) technology

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Abstract

Ion exchange membranes as solid polymer electrolytes (SPE) facilitate the electrochemical detoxification of waste water without addition of supporting electrolyte. Cation exchange membranes as H^+ ion conductors or anion exchange membranes as OH^- ion conductors were used in combination with different electrode materials. A variety of cell configurations were investigated which differ in the direction of the electro-osmotic stream (EOS). This is a characteristical property of SPE technology, caused by the solvation shells of the ions during their migration through the membrane. Dependent on cell configuration mass transfer at the electrodes can be hindered or enhanced by EOS. In the latter case it is appropriate to increase EOS by preparation of Nafion® membranes in order to decrease energy consumption per m^3 waste water. Using a perforated membrane, which operates in this case only as ion conducting solid polymer electrolyte but not as cell separator, flow rates through the cell can be adjusted independent of the EOS and a further decrease of energy consumption is possible. The best results were obtained using anodic oxidation followed by cathodic reduction: 2-chlorophenol as example compound was destroyed almost completely and more than 80% of the chlorine was mineralized to chloride ions. By-products were detected in very low amounts, less than the remaining traces of 2-chlorophenol.

Abbreviations

AEM: anion exchange membrane; CEM: cation exchange membrane; CHQ: chlorohydroquinone; 2-CP: 2-chlorophenol; DMF: *N,N*-dimethylformamide; EOS: electro-osmotic stream; FEP: fluorinated ethylene propylene co-polymer; MEA: membrane electrode assembly; MF: *N*-methylformamide; PEMFC: proton exchange membrane fuel cell (polymer electrolyte membrane fuel cell); PTFE: poly(tetrafluoroethylene); SPE: solid polymer electrolyte

1. Introduction

Electrochemical methods for waste water detoxification usually need no additional chemicals [1]. This is an important advantage in comparison with the large variety of chemical processes in this area. For example, chlorinated organic compounds are typically toxic or at least biologically difficult-to-degrade. A previous electrochemical elimination of one or more chlorine atoms by cathodic reduction and/or anodic oxidation often results in compounds with reduced toxicity which can finally be removed by biological waste water treatment. However, conventional electrochemical processes require a conductive liquid. In practice, the conductivity of waste water will often not be sufficient. In such cases a supporting electrolyte, e.g. a salt, has to be added which may cause additional environmental problems.

Thus, a direct electrochemical treatment of non-conductive waste water without addition of supporting electrolyte is desirable for environmental protection. This is enabled by using ion exchange membranes as solid polymer electrolytes. "SPE technology" was developed primarily for efficient production of hydrogen as energy carrier by electrolysis of pure water and also for fuel cells, as in the PEMFC = polymer electrolyte membrane fuel cell or proton exchange membrane fuel cell (e.g. [2]).

First applications of SPE technology for electro-organic reactions without addition of supporting electrolyte were published by Ogumi et al. [3]. Meanwhile many reactions have been successfully performed (e.g. [4, 5]).

Recent examples of electrochemical degradation of water-borne pollutants using SPE technology may be mentioned here. The cathodic treatment of chlorofluorocarbons was reported by Kyriacou et al. [6] and, additionally enhanced by light radiation, by Ogumi and co-workers [7]. Iwakura et al. [8] investigated the cathodic dechlorination of 4-chlorophenol at palladium layers on a membrane surface. Liu et al. [9] used a modified PEMFC for cathodic treatment of gaseous chlorinated hydrocarbons. Johnson et al. [10] oxidized 4-chlorophenol at oxide coated anodes in an SPE cell. The group of Scott et al. published systematic investigations of the hydrodehalogenation of halogenated phenols in aqueous solutions and in paraffin oil for comparison of conventional and SPE electrolysis, especially using palladium as cathode material (e.g. [11] and several previous papers). SPE cells were used also for oxidative decolourization of dye polluted water by Yamane et al. [12] and for removal of e.g., alcohols by Simond and Comninellis [13] and phenol by Grimm et al. [14].
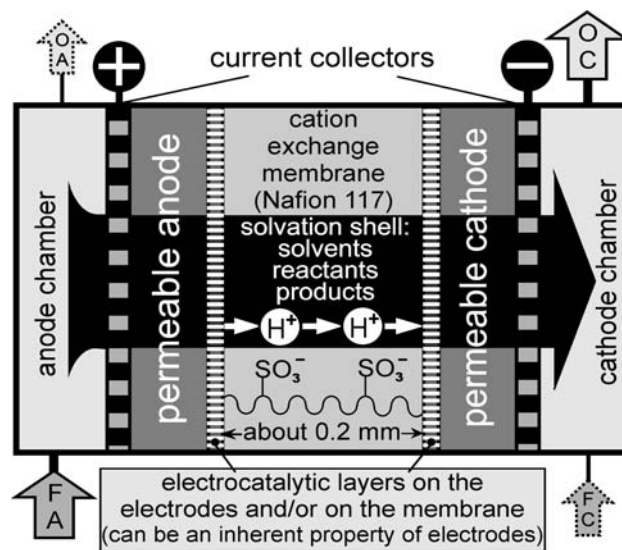
The aim of this work is the discussion of the characteristics and potential of SPE technology in different configurations for electrochemical detoxification. Here, particularly, the conversion of organic chlorinated compounds, using 2-chlorophenol (2-CP) as a water soluble chlorinated model substance, has been investigated in various continuously operated flow through cells with constant current [15, 16].

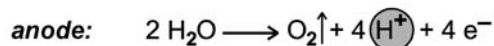## 2. Principles and operational alternatives of SPE technology

Figures 1 and 2 show the operating principle of SPE technology as examples of waste water treatment. The electrode reactions take place at the interfaces between the electrodes and the membrane. The produced ions can enter directly – without a conductive liquid – into the ion conducting membrane: cations e.g. H^+ in the case of a cation exchange membrane (Figure 1) or anions e.g. OH^- in the case of an anion exchange membrane (Figure 2).

For optimal function at minimal energy consumption the electro-catalytically active electrode areas must be in close contact with the current collectors for electron transfer and with the ion exchange membrane for ion transfer. Simultaneously unhindered mass transfer of reactants and products must occur. Therefore, membrane electrode assemblies (MEAs) may be applied, using methods known from fuel cell technology (e.g. [2]).

Nevertheless, many successful experimental examples have confirmed that porous electrode materials may also be simply pressed onto the membrane surfaces, for easy and cost-saving application (e.g. [4, 5]). An additional advantage of this inexpensive operation mode is that SPE technology can even be used under conditions where increased swelling of the membrane would destroy a sophisticated MEA immediately.
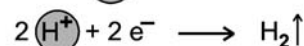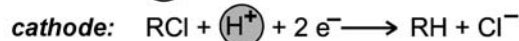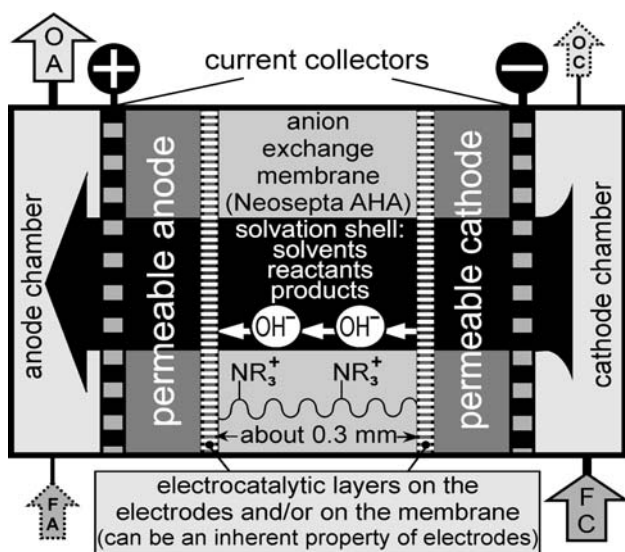

Fig. 1. Principle of solid polymer electrolyte technology using a cation exchange membrane as H^+ ion conductor as an example of cathodic dechlorination of a chloroalkane.
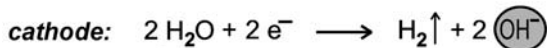
An inherent effect of SPE technology is the electro-osmotic stream (EOS, electro-osmotic drag). This is caused by the solvation shells of migrating ions inside the membrane (see arrows in Figures 1 and 2) because only ions of one type, cations or anions, are mobile while the others are fixed to the polymer. Therefore, EOS in a cation exchange membrane flows from the anode to the cathode (e.g. Nafion® 117 (Du Pont) with sulfonic acid groups as fixed ions, Figure 1). In an anion exchange membrane EOS flows in the opposite direction (e.g. Neosepta® AHA (Tokuyama) with quaternary ammonium groups as fixed ions, Figure 2).

The EOS unselectively contains solvents, remaining reactants and products in the same concentrations which are present at the membrane–electrode interface where the EOS is formed. The magnitude of the EOS is nearly proportional to the cell current and is a function of the composition of the cell fluid. Further, it is strongly dependent on the type of membrane and can possibly be increased by appropriate preparation of the membrane [5]. The effect of EOS on the electrode reactions is an essential aspect of this paper (see Section 4.1.2).

The different cell configurations in Figure 3 result from the combination of cation or anion exchange membranes (CEM or AEM) with a reactant feed either into the anode or into the cathode chamber. EOS causes significantly different behavior of these operational alternatives. The undesirable influence of EOS in specific
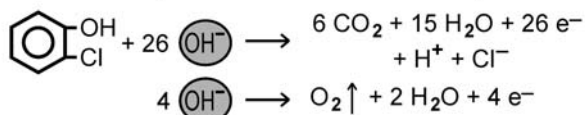
Fig. 2. Principle of solid polymer electrolyte technology using an anion exchange membrane as OH⁻ ion conductor as an example of anodic total oxidation of 2-chlorophenol.

cell configurations can be reduced by membrane perforation. Then the membrane is only used as an ion conducting solid polymer electrolyte – which is essential in non- or low-conductive solutions – but not as cell separator. The flow through the perforated membrane can be controlled independent of EOS.

The cell in Figure 3A is equivalent to Figure 1 and the cell in Figure 3E is equivalent to Figure 2. In both cases one electrode is used for the dechlorination (only a small amount of reactant permeates the membrane, counter-current to EOS of water). The reaction of the inert solvent water at the counter electrode supplies the ions (H^+ or OH^-, respectively) which are needed for migration through the membrane.

Figure 1 and 2 show examples of a desired dechlorination reaction, coupled with water decomposition at the counter electrode. In practice a wide variety of partial reactions and additional side-reactions may be expected. In all processes discussed small amounts of contaminants have to be converted within a large amount of water. Thus, the current efficiency is usually low and the main part of the cell current is used for evolution of hydrogen at the cathode and of oxygen at the anode. In both cell configurations A and E the direction of EOS retards the diffusion of the reactants within the permeable electrode material to the active electrode area at the membrane surface. Therefore reaction efficiency is decreased, particularly with increasing current density, because the EOS is proportional to the cell current.

On the other hand, EOS enables the cell configurations D and H in Figure 3. Here it works like a pump to
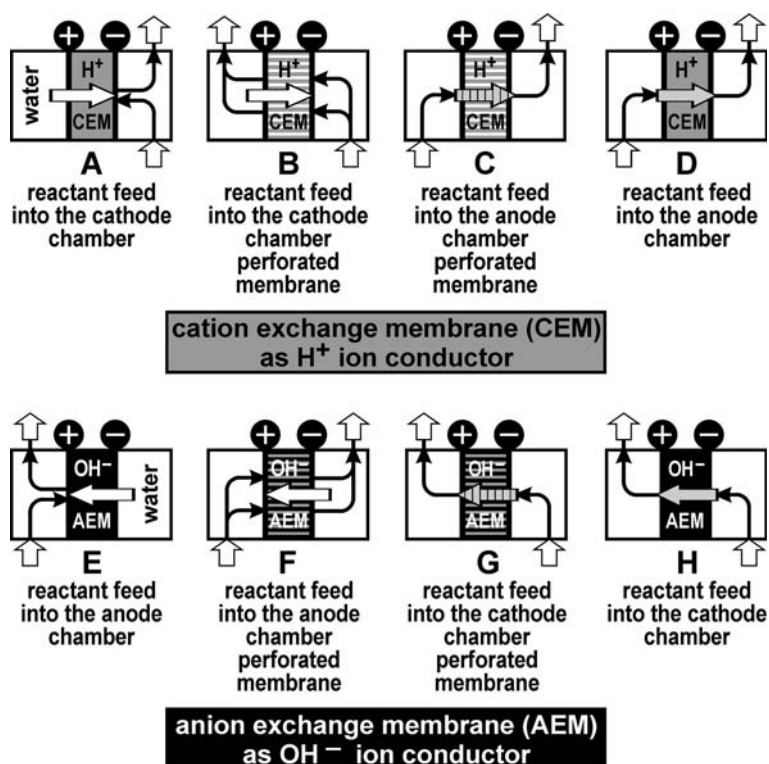

Fig. 3. Possible cell configurations of SPE technology. Arrows in membrane area show direction of EOS.

transport the feed through the cell and allows very easy operation. The (chlorinated) reactants (and their products) can be converted at the anode as well as at the cathode. The succession of these reactions depends on the usage of a CEM (D) or AEM (H). While in alternatives A and E EOS retards the mass transfer into the reaction zones here in alternatives D and H it enhances the transfer of reactants and products at the electrodes and therefore has a beneficial effect on the reactions. An important advantage is that the magnitude of EOS can be controlled to a certain extent, at least in case of Nafion® cation exchange membranes, by appropriate preparation procedures ([4, 5] and Section 4.1.2.1).

The perforation of the membrane in alternatives B and C or F and G of Figure 3 enables additional operation possibilities. The membrane functions as an ion conducting solid polymer electrolyte between the electrodes and the microscopic effect of EOS in the reaction zones at the membrane surfaces may be only minimally influenced by the macroscopic holes. The advantage of these configurations is that the flow direction and the flow rate through the cell can be adjusted to the requirements of the detoxification process, independent of EOS. The configuration B is a fundamental change in comparison with A. It allows the hindrance of reactant transfer to the cathode, which is caused by EOS in configuration A, to be overcome. But additionally, after cathodic reactions anodic reactions take place. Thus, a behavior like in configuration H is realized, but using a CEM. The configuration C is similar to D, but the flow rate in all alternatives with a perforated membrane can be adjusted according to needs and is not directly coupled with EOS. In configurations F and G equivalent modifications as in B and C are realized, but using an AEM.

3. Experimental

Figure 4 shows a cross-sectional view of the applied experimental SPE cell (three examples were used simultaneously, see also [17]). The body was made of stainless steel and was heated on both sides by two regulated water circuits. On the anode side all parts in contact with the anolyte and which could be attacked by chlorine were made of titanium.

The central components were the ion exchange membrane (3, in Figure 4 a Nafion® cation exchange membrane) and the permeable electrodes (2,4). The anode material must be corrosion resistant during oxygen evolution in acidic media. In most experiments it was a fine mesh of platinum/iridium (90:10 wt%, 0.1 mm wire diameter, 600 mesh per cm^2). The cathode material needs a high hydrogen overvoltage in order to provide a high current efficiency for the dechlorination reaction. Highly porous graphite is a suitable material. It was applied, e.g. as graphite felt (Sigratherm® GFA-5, KFA-5 and GFA-n of SGL Carbon, 5 mm thick) or
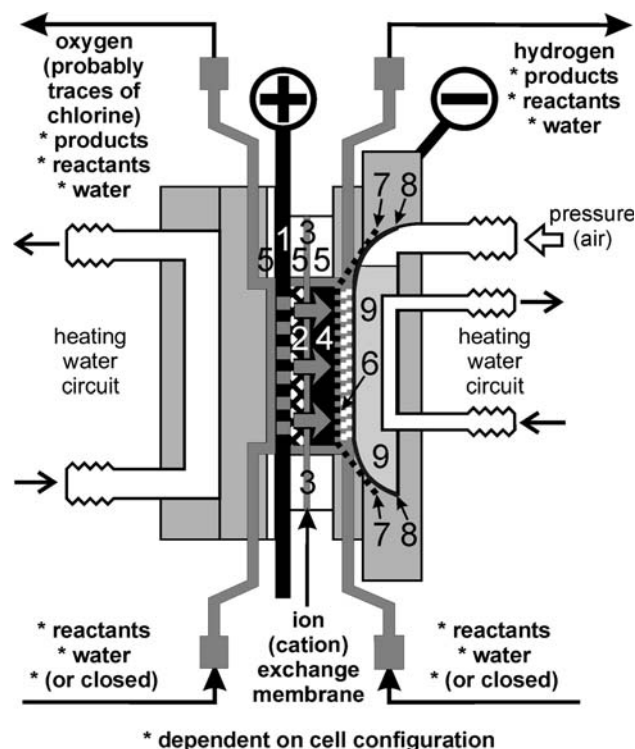
Fig. 4. Experimental SPE cell (22 cm^2 active membrane area) 1 = anode current collector (perforated titanium plate + titanium wire mesh), 2 = anode (wire mesh, Pt/Ir 90:10 wt%), 3 = ion (cation) exchange membrane, 4 = cathode (graphite felt or graphite paper), 5 = PTFE isolating rings (cell wall), 6 = polypropylene grid, 7 = cathode current collector (stainless steel knitted mesh), 8 = FEP film and silicon rubber membrane, 9 = water filling for better heat transfer.

graphite paper (Toray TGH-H-090, 0.5 mm thick, known as gas diffusion layer for electrodes of PEMFCs).

The electrodes were surrounded by PTFE rings (5) as cell walls. The membrane was to be mounted after the preparation (Section 4.1.2.1) in order to avoid later expansion or shrinking during the operation. Nevertheless, in order to allow a small change of membrane dimensions without wrinkling, a ring-shaped gap of 2 mm between the electrodes (58 mm diameter) and the cell wall (62 mm diameter) was provided. The active membrane and electrode area was limited to 53 mm diameter (22 cm^2) by two pore-free thin polymer films (FEP) on both sides of the membrane (not shown in Figure 4). Therefore, only in the active membrane area, where the cell current was flowing, was mass transfer through the membrane possible, but any diffusion outside was blocked. For all flat gaskets in contact with reaction solutions Gore-Tex® PTFE sealing band (1 mm thick) was used.

A perforated titanium plate (1), additionally a fine titanium mesh on the anode side and a highly flexible stainless steel knitted mesh (7) on the cathode side were used as current collectors. Sheets of polypropylene grid (6) behind the cathode current collector provided the transport space for fluid and gas. The complete flexible arrangement was pressed together via a silicon rubber membrane (8) by compressed air (0.5 bar) in order to

provide close and uniform contact. The rubber was shielded against cell fluid by pore-free FEP film. The space behind the rubber membrane was filled with water (9) for better heat exchange. The heating water circle was electrically isolated from the cathode by the rubber membrane so that one thermostat was used for anode and cathode heating without danger of corrosion due to potential differences inside the cell.

The cell was operated at constant cell current (galvanostatically) in steady state flow through mode with constant feed concentrations. Depending on the different operational alternatives of Figure 3 water or feed solutions were pumped into the various inlets (see Figure 4) by membrane dosing pumps (ProMinent). The outlet solutions were collected and a mass balance of all liquids was made by weighing. Liquid samples were analyzed by gas chromatography (Hewlett-Packard 6890 GC System with an autosampler, a flame ionization detector for quantitative analyses and a mass selective detector for product identification, 30 m HP5 column). The outlet gases were cooled for condensation of vapors and the condensates were recycled into the cell. The gases were collected and measured volumetrically and then analyzed by gas chromatography for oxygen, nitrogen, hydrogen, carbon monoxide, carbon dioxide (Hewlett-Packard 5918 with a thermal conductivity detector and a 3390 A integrator, columns (Chrompack): molecular sieve 5 Å, 10 m, and Poraplot Q, 30 m).

The success of dechlorination of organic compounds was measured by automated potentiometric titration of chloride ion content in the cell effluent using silver nitrate solution (Metrohm Titrino with AgS chloride ion specific electrode).

4. Experimental results

First measurements were performed using various chlorinated organic compounds (aliphatic, cyclic, aromatic) but the results were insufficient, mainly due to very low solubility in water. For comparison of the different cell configurations in Figure 3 a better water soluble model substance was needed and 2-chlorophenol (2-CP) was chosen.

4.1. Dechlorination using Nafion® 117 membranes

Nafion® perfluorosulfonic acid membranes are known from chlor-alkali electrolysis and from fuel cells for their excellent chemical and thermal stability. This was also confirmed in these experiments, even after the aggressive pretreatment, discussed in Section 4.1.2.1.

4.1.1. Dechlorination using cell configuration A
Figure 5 shows measurements for a cell of configuration A, using a Nafion® 117 membrane and reactant feed into the cathode chamber. The progress of chlorine mineralization with increasing operation time is shown

for different graphite cathode materials at various temperatures. For all cathode materials a significant increase in dechlorination activity with increasing temperature was observed.

Comparison of the two graphite felt types shows that GFA-n was much more active than GFA-5, although no considerable difference in the material properties is known. The increasing activity of GFA-n and the decreasing activity of GFA-5 is noteworthy. Even an influence of the production batch of the membrane samples was noticed in many experiments: in the dechlorination activity as well as in the contact between membrane and electrodes which is visible after the experiment [16]. Obviously, there are complex interactions between electrode material und membrane which are not well understood.

The best results in Figure 5 give above 70% dechlorination for the Toray graphite paper at 95 °C, i.e. slightly below the boiling point. At 65 °C this material started at almost zero activity and showed a remarkable long running-in period until it achieved 55% dechlorination.

For solvent comparison measurements were also carried out in methanol under conditions of Figure 5. Dechlorination of 2-CP in methanol at 45 °C was only about one quarter of that in aqueous solution.

In cell configuration A only cathodic dechlorination is possible. This reaction is retarded by EOS because it flows in the opposition to reactant transfer to the electrode. The evolved hydrogen gas may also hinder the
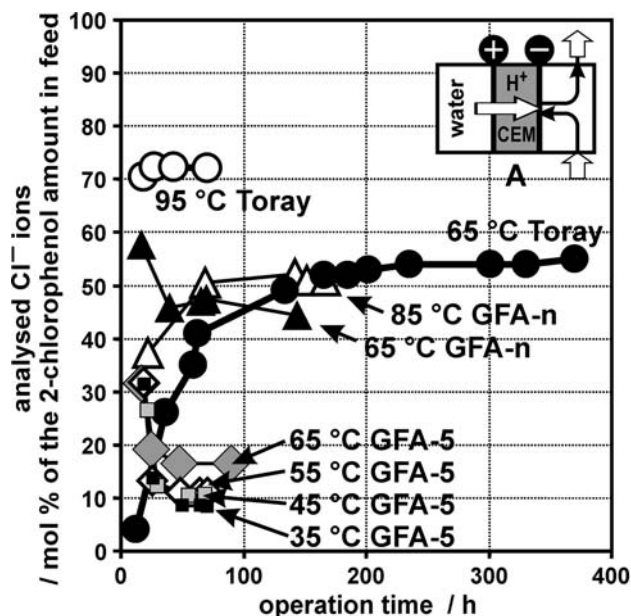
Fig. 5. Influence of temperature and cathode material on dechlorination of 2-CP as a function of operation time, cell configuration A, membrane: Nafion® 117, prepared in water (1 h at 90 °C), active membrane area: 22 cm², cathode: different graphite materials (graphite felt GFA-5 and GFA-n, 5 mm thick, SGL Carbon, and graphite paper Toray TGH-H-090), anode: Pt/Ir mesh 90:10 wt%, current density: 500 A m⁻², cathode feed: 12 g h⁻¹ = 5.4 kg h⁻¹ m⁻² aqueous solution 0.01 mol kg⁻¹ = 0.13 wt% 2-CP.

reactant transfer. Thus, the better results in Figure 5 for thin graphite paper (0.5 mm) in comparison to 10 times thicker graphite felt (5 mm) were expected.

The important influence of EOS on mass transfer is confirmed by experiments with decreased current density: at 50 A m^{-2} (low EOS rate and low hydrogen evolution) the dechlorination increased to 63% in comparison with 60% at 500 A m^{-2} (cathode Toray TGH-H-090, 85 °C, other conditions see Figure 5). In further experiments with increased cathodic feed rate the dechlorinated part of the feed was decreased. These results show that the reaction possibilities at the cathode are limited – particularly because for all experiments the cell was used according to Figure 4 in order to obtain comparable results. For a practical application of cell configuration A an optimization of the flow profile in the cathode chamber is necessary and possible in order to enhance the reactant transfer to the cathode and to allow better dechlorination rates.

4.1.2. Dechlorination using cell configuration D

Cell configuration D also uses a Nafion® 117 membrane but the reactant is fed to the anode chamber. In contrast to configuration A anodic, as well as cathodic, dechlorination is possible. The flow through the cell in this configuration is caused only by EOS which works like a dosing pump and enhances the mass transfer in the reaction zones at the electrode/membrane interfaces. The EOS is nearly proportional to the cell current; consequently the energy consumption per m^3 waste water is almost independent of current density. But EOS is strongly influenced by the type and condition of the membrane. Therefore, the preparation of Nafion® 117 membranes, carried out to increase EOS, will be described.

4.1.2.1. *Nafion® membrane preparation.* EOS of unchanged Nafion® cation exchange membranes is known to be about 2 molecules of water per migrating H$^+$ ion in a PEMFC. For applications in low concentration aqueous solutions and after membrane preparation by boiling in water values up to 4 H$_2$O per H$^+$ may be observed. Preparation of Nafion® membranes in *N,N*-dimethylformamide (DMF) or other amides at elevated temperatures increases EOS dramatically. Thus, the enhanced mass transfer favors the desired reactions, for synthesis applications e.g. alkoxylations in non-aqueous media, probably up to almost 100% selectivity [4, 5, 17].

An interesting result of measurements [16] is that the increased EOS of Nafion® membranes due to such preparation remains even after change to an aqueous solution. This enables new possibilities in waste water treatment for cell configuration D.

EOS increases with more aggressive preparation conditions of the un-reinforced Nafion® 117 membrane. The increase in EOS is proportional to the area increase due to membrane swelling. Because Nafion® is a polymer without chemical cross-linking the area can increase up to more than 100% of the original dimen-

sions. The swelling is strongly dependent on temperature, duration and solvent type during preparation. Additionally the equivalent weight of the Nafion® membrane has a strong influence and even small variations between membrane samples of different production batches have to be considered [5].

Figure 6 shows measurements of EOS in cell configuration D of Figure 3 with aqueous solutions using Nafion® 117 membranes after preparation at different temperatures. With *N*-methylformamide (MF) as preparation solvent a limit of increasing EOS with increasing temperature was observed at 110 °C. Using *N,N*-dimethylformamide (DMF) an EOS up to 31 mol H$_2$O per mol migrating H$^+$ ions was possible.

The membrane becomes extremely soft during this preparation and may be destroyed very easily. Additionally, loss of membrane polymer, increasing up to more than 20% of the original weight with increasing temperature, is observed. A temperature limit, where the membrane is irreversibly damaged, must not be exceeded. This limit may also be influenced by the production batch of the membrane material, as mentioned above concerning the equivalent weight and the swelling grade during preparation.

Nevertheless, although Nafion® membranes are not designed for such applications which approach the limits of the material, the membrane can work very stably if it is handled and mounted carefully in the SPE cell. For example: 6000 h steady state operation for methoxylation of DMF were achieved [4, 17]. For applications like those of Figure 6 the membrane was transferred to water after preparation in order to rinse the solvent. Then the membrane shrank, but not to its original dimensions, and recovered its mechanical strength
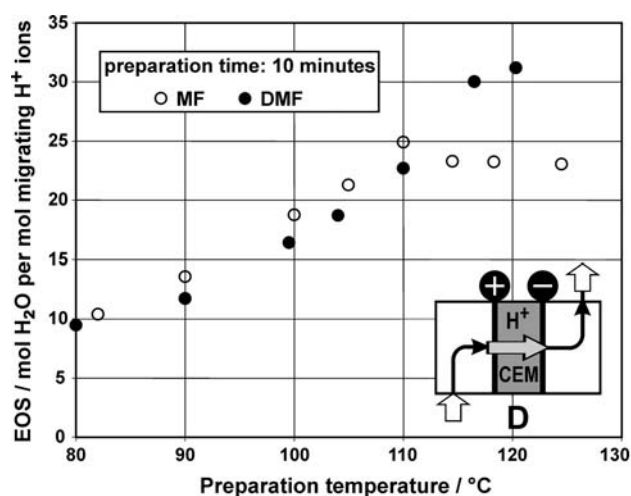
Fig. 6. EOS through prepared Nafion® 117 membranes, preparation solvent: MF = *N*-methylformamide, DMF = *N,N*-dimethylformamide, operation conditions (cell configuration D): active membrane/electrode area: 3.14 cm^2 (encircled using FEP film), anode: Pt/Ir mesh 90:10 wt%, cathode: Toray TGH-H-090, anode chamber feed: 0.01 mol l^{-1} = 0.13 wt% 2-CP in water, temperature: 85 °C, current density: 500 A m^{-2}, measurement time for each point: 20 h.

partially. No stability problems were observed during subsequent operation.

4.1.2.2. Dechlorination results of cell configuration D.
Figure 7 shows the results of dechlorination experiments using Nafion® membranes prepared in *N,N*-dimethylformamide at different temperatures. EOS was increased by more than a factor of 8 but the decrease of the mineralization to chloride ions was marginal.

An additional advantageous effect of the preparation is a significant decrease in cell voltage, probably due to better contact of the softened membrane with the electrodes. Under conditions of Figure 7 after 100 h constant operation with a membrane only prepared in water (EOS = 3.6 H_2O per H^+) a cell voltage of 2.5 V was observed and with a strongly prepared membrane (EOS = 20.2 H_2O per H^+) a cell voltage of 2.1 V.
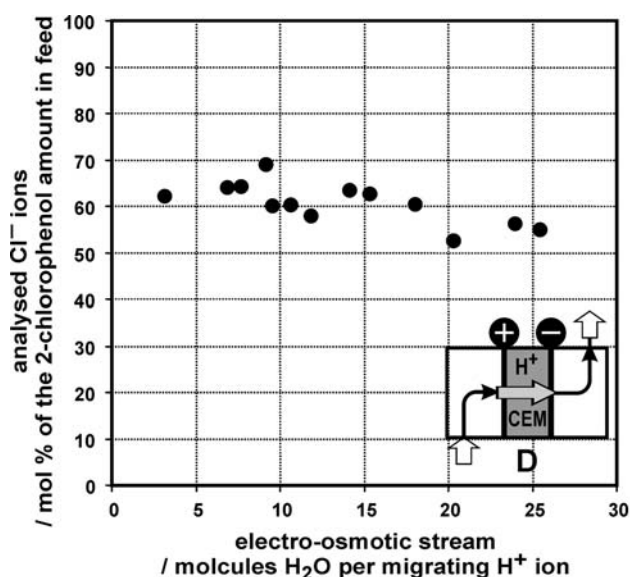

Fig. 7. Influence of EOS on dechlorination of 2-CP, operation conditions in cell configuration D: membrane: Nafion® 117, prepared under different conditions in DMF, active membrane/electrode area: 22 cm², anode: Pt/Ir mesh 90:10 wt%, cathode: graphite felt GFA-5, 5 mm thick, anode chamber feed: 0.01 mol l⁻¹ = 0.13 wt% 2-CP in water, temperature: 85 °C, current density: 500 A m⁻².

The most desired result of increased EOS in cell configuration D is reduced specific electrical power consumption (see Section 4.3.). But simultaneously an effective detoxification has to be achieved. An increased EOS, especially at high current densities, reduces the reaction time at the electrodes and incomplete or detrimental reactions may be the consequence. Therefore, experiments at different current densities with additional analysis methods were carried out (Table 1).

No problem occurred with the conversion of 2-CP: it was nearly 100% in all experiments using configuration D. Only traces of remaining 2-CP were detected.

At low current densities up to 200 A m⁻² about 70% of chlorine of the starting material 2-CP was mineralized to Cl^- ions. At 100 A m⁻² 3–4% were anodically oxidized to chlorate or perchlorate which were analyzed with inorganic titration methods in the liquid effluent. Chlorine in the anode gas was not detectable. An analysis of AOX (adsorbable organic bond halogen) resulted in an additional 7% chlorine. The remaining chlorine containing compounds could not be analyzed by gas chromatography. There was a large number of different unidentified peaks in the gas chromatogram but none of them was bigger than the small amount of unconverted 2-CP. Therefore, it may be assumed that the detoxification was successful and no hazardous amounts of toxic compounds remained.

At higher current densities, above 300 A m⁻², chlorohydroquinone (CHQ) became the main organic product. Obviously, the first anodic oxidation step of 2-CP is the introduction of a second OH-group in the para position. CHQ is an undesired by-product because it is more toxic than the starting compound 2-CP. Only at low current densities may there be enough time to decompose CHQ anodically to less toxic compounds. At current densities of 500 A m⁻² and higher the chlorine balance shows that chlorine was completely detected and practically all organic bound chlorine was included in CHQ.

At all current densities only about 80% of the carbon of the starting compound 2-CP is found in the balances of Table 1 which is based on analysis by gas chromatography. In an analysis of TOC (total organic carbon) in the cell effluent at 100 A m⁻² about 20% were found additionally to the 80% of carbon dioxide, i.e. all

Table 1. Experiments in cell configuration D at different current densities (cathode GFA-n, EOS = 22 H_2O per H^+, other conditions see Figure 7)

i/A m⁻²	2-CP/%	CHQ/%	Cl⁻/%	CO₂/%	ΣCl/%	ΣC/%
50	0.6	0.1	68.6	79.7	69.3	80.4
100	0.3	0.3	69.5	84.8	70.1	85.4
200	0.4	0.3	69.1	78.7	69.8	79.4
300	0.3	28.2	67.1	50.9	95.6	79.4
400	0.3	40.7	55.2	44.8	96.2	85.8
500	0.5	45.0	56.3	41.6	101.8	87.1
600	0.2	46.4	54.8	36.6	101.4	83.2
1000	0.1	51.8	48.2	28.5	100.1	80.4

i = current density, 2-CP = remaining 2-chlorophenol, CHQ = chlorohydroquinone, Cl^- = chloride ions in the liquid effluent, CO₂ = carbon dioxide in the outlet gas, ΣCl = sum of analyzed chlorine (as a sum of 2-CP, CHQ and chloride), ΣC = sum of analyzed carbon (as a sum of 2-CP, CHQ and CO₂).

organic compounds were detected. These compounds could not be extracted by dichloromethane or toluene; thus, they are well water soluble.

All results of balances in Table 1 show that the loss of summarized chlorine is most probably not included in highly toxic aromatic compounds which can be exactly analyzed by gas chromatography. Johnson et al. [10] report that they have found only 77% of the chlorine from 4-chlorophenol. They assume the residue of chlorine in chlorinated organic compounds of low molecular weight, which are difficult to analyze. Such compounds may be no problem for detoxification because they are less toxic than the starting material, 2-CP.

A very important influence of the initial concentration of 2-CP on the detoxification was observed. According to Table 1 for a feed concentration of 0.01 mol $l^{-1} = 0.13$ wt% 2-CP the current density should not exceed 100 A m^{-2} in order to avoid CHQ formation. This is a relatively high concentration for waste water detoxification. At a 10 times lower starting concentration of 0.001 mol $l^{-1} = 130$ ppm 2-CP the mineralization to Cl$^-$ ions increased to more than 80% and no CHQ was detectable. In contrast with this at a starting concentration of 0.1 mol $l^{-1} = 1.3$ wt% 2-CP the total conversion of 2-CP decreased to 96.5% and the mineralization to Cl$^-$ ions was only about 35% while 40% of 2-CP reacted to CHQ.

4.1.2.3. Dechlorination using other electrode materials.
Other experiments were carried out using cell configuration D with graphite paper, zinc modified graphite paper or palladium coating as cathode. But the expected better dechlorination results were not observed.

Thus, in order to get separate information about dechlorination activities of the anode and the cathode in cell configuration D, experiments were carried out with increased flow rates on the anode side and in consequence both anodic and cathodic effluents. From the effluent on the anode side information about the anode reactions was available. Only a part of the anode chamber feed flowed in EOS through the membrane and was additionally converted at the cathode. The effluent on the cathode side at different anode side feed rates also offered information about the cathode reactions.

The surprising result was that the mineralization to Cl$^-$ ions also, perhaps even mainly, takes place at the anode. Probably, the reactions at the cathode are less important.

Therefore, the anode material could have a significant influence. As an example a Pt/Ir mesh, which was usually applied as anode, was electrochemically coated with lead dioxide and used for cell configuration D [16]. Generally, PbO$_2$ is known to have limited stability. But in the SPE process, without aggressive electrolytes and without mechanical stress, due to the constant contact with the membrane, it is known to be very stable (e.g. [5]). Here, the PbO$_2$ anode was used over 2130 h at

various conditions [16]. At the PbO$_2$ anode as well as at the Pt/Ir anode conversion of 2-CP was almost complete. But significant differences in the product distribution were observed. For example, the mineralization to Cl$^-$ ions and the formation of CHQ was lower at the PbO$_2$ anode.

These results show that further investigations of electrode materials will be of interest, in order to identify more economic materials. Alternative materials may be on the anode side e.g. metal oxide coated titanium, like dimensionally stable anodes (DSA®), or boron doped diamond, and on the cathode side e.g. palladium. An additional aspect of the choice of anode material is possible poisoning of the cathode, e.g. lowering of the hydrogen overvoltage at the cathode by platinum which is dissolved from the anode.

4.1.3. Dechlorination using perforated membranes
Cell configuration B of Figure 3 was investigated using a Nafion® 117 membrane with holes of 0.2 mm diameter and 3.5 mm distance. Problems with shortcuts by graphite fibers can be avoided using Toray graphite paper as cathode material. The experiment was run for 5660 h at different conditions. The stability was confirmed by constant dechlorination rates at standardized conditions. For cell configuration C a Nafion® 117 membrane was also used with holes of 0.1 mm diameter and about 2 mm distance. Using a CNC machine (computer numeric control) 0.3 mm diameter and 1 mm distance was achieved for both cell configurations. Ideally, a large number of fine, close-packed holes should be used in order to allow a uniform flow distribution.

Dechlorination rates of about 80% and even higher were comparable to the best results of cell configurations A and D. Using perforated membranes it was possible, in contrast to alternative D, to decrease current density without an associated change in flow rate. Thus, the specific energy consumption could be decreased to lower values (see Section 4.3).

4.2. Dechlorination using Neosepta® AHA membranes

As shown in Figures 2 and 3 the application of an anion exchange membrane (AEM) as OH$^-$ ion conductor offers new possibilities for SPE technology because the reactions, or their sequence, and also the direction of EOS are changed. Therefore, investigations using AEMs for comparison with results using CEMs were included.

Common anion exchange membranes usually designed for electrodialysis applications include quaternary ammonium groups as fixed ions. Therefore, their stability in basic media is low and they are damaged quickly by OH$^-$ ions. The AEM Neosepta® AHA (Tokuyama) shows increased stability against OH$^-$ ions. Thus, experiments up to one week membrane durability at current densities up to 200 A m^{-2} were possible.

Table 2. Examples of energy consumption for different cell configurations

Cell configuration (see Figure 3)	Current density/A m^{-2}	Feed rate/kg h^{-1} m^{-2}	Dechlorination to chloride/%	Energy consumption /kW h m^{-3}	Details
A	500	5.4	60	216	Cathode: Toray
A	50	5.4	63	18	Cathode: Toray
D	500	1.0	62	960	Unprepared membrane
D	500	8.0	56	135	DMF-swollen membrane
D	100	1.9	67	104	DMF-swollen membrane
B	50	2.7	80	33	Perforated membrane
B	50	5.4	70	17	Perforated membrane
C	50	5.4	60	17	Perforated membrane

Membrane: Nafion® 117, anode: Pt/Ir mesh 90:10 wt%, active membrane/electrode area: 22 cm^2, temperature: 85 °C.

Cell configurations E, G and H of Figure 3 with an AEM were operated and checked [16]. None of these configurations showed significant better results than comparable configurations using a CEM. For mineralization to Cl$^-$ ions cathodic reduction is preferred, but this is not possible in configuration E. Using configuration H complete conversion of 2-chlorophenol was observed, as in configuration D with a CEM, but the mineralization to Cl$^-$ ions was lower. The cell voltage was higher in all experiments with an AEM compared to those with a CEM. With increasing operation time the cell voltage increased and the dechlorination activity decreased due to enhanced decomposition of the AEM.

Thus, the experiments confirmed that AEMs can be principally used for SPE technology in waste water detoxification, but currently this application makes no sense. It has to be considered that the investigated AEM Neosepta® AHA is not designed for this application and new membrane types may offer improvements.

4.3. *Energy consumption of the processes*

The most important criterion for an economically acceptable electrochemical waste water treatment process, in addition to the investment costs, is the specific energy consumption in kW h per m^3 of waste water.

Table 2 shows a few examples of energy consumption for different cell configurations with a Nafion® 117 cation exchange membrane. Using cell alternative A the energy consumption could be decreased to about 18 kW h m^{-3} by decreasing current density with unchanged dechlorination rates. But at the low current density investment costs will be very high. Using cell configuration D with low throughput due to the small EOS of an unprepared Nafion® 117 membrane an impracticably high energy consumption was needed. By membrane preparation in DMF, as shown in Figure 7, the energy consumption could be considerably decreased. Using perforated membranes in cell configurations B or C the energy consumption was also decreased down to 17 kW h m^{-3} (having 77 % 2-CP conversion).

For comparison: an on the market available electrochemical process for decomposition of 0.5 g l^{-1} phenol (90% conversion) using 5 g l^{-1} sodium sulfate as supporting electrolyte needs 90 kW h m^{-3} [18].

5. Conclusion

The investigations confirmed, using dechlorination of 2-chlorophenol as example reaction, that all possible cell configurations of SPE technology are in principle suitable for waste water detoxification without addition of supporting electrolyte. The best results, almost total conversion of fed 2-chlorophenol and mineralization of the largest part of the included chlorine to chloride ions, were obtained using the very stable Nafion® 117 cation exchange membranes (Du Pont). The electro-osmotic stream is used for waste water transport through the cell, first into anodic oxidation zones and then, after passing the membrane, into cathodic reduction zones.

There is a large variety of optimization possibilities for adapting the process to waste water detoxification. The advantages and disadvantages of different possible cell configurations have to be considered. Suitable electrode materials must be chosen. Additionally to the variation of the usual parameters, such as feed rate, temperature and current density, possibilities are offered by the preparation method and/or perforation of membranes.

Further investigations of operational possibilities will be necessary in order to develop an economically attractive detoxification process which uses the advantages of requiring neither chemicals nor supporting electrolyte.

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