



Electro-organic synthesis without supporting electrolyte: Possibilities of solid polymer electrolyte technology[☆]

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Abstract

The application of ion exchange membranes as solid polymer electrolytes (SPE) in fuel cells is state-of-the-art. This technology needs no supporting electrolyte; consequently it can be applied for electro-organic syntheses in order to save process steps. In this case the process is not predetermined to a maximized energy efficiency so that the selection of the cell design, of the electrode materials and of the operating conditions can be focused on a high selectivity of the electrode reactions. The electro-osmotic stream, which is caused by the solvation shells of the ions during their migration through the membrane, and hence is a typical property of SPE technology, has a significant effect on the electrode reactions. It generates enhanced mass transfer at the electrodes, which is beneficial for reaction selectivity. It can be influenced by the choice of, and possibly by the preparation of, the membrane. An additional remarkable advantage of SPE technology is the exceptional long durability of oxide coated electrodes. By combination of several process engineering methods stable operation of SPE cells has been realized, even for examples of non-aqueous reaction systems. Experiments up to 6000 h duration and in cells of up to 250 cm² membrane area show the potential for industrial application.

1. Introduction

The objective of this paper is to discuss the characteristics and the possibilities of solid polymer electrolyte technology (SPE) for electro-organic syntheses without a supporting electrolyte, a technique which is well known from its application in fuel cells. As a basis for the discussion a short elucidation of SPE principle is given, especially of properties where significant differences between applications as a fuel cell and as a synthesis reactor are significant.

Figure 1 shows the reactions and transport processes in a fuel cell at the surfaces of a proton exchange membrane. Catalyst particles, e.g. of platinum, are usually prepared on a carrier of carbon black and are electrically connected to the current collectors in this way. The hydrogen fuel reacts at the anodic catalyst, forming H⁺ ions and delivering electrons into the negative current collector. The H⁺ ions migrate through the membrane, which works due to its fixed ions (sulfonic acid groups) like immobilized sulfuric acid (20–200 μm thick). On the cathode side the H⁺ ions

react at catalyst particles with oxygen and electrons from the positive current collector, to produce water.

The performance of a PEMFC essentially depends on the quality of the membrane electrode assembly (MEA):

- maximal active catalyst surface available in three-phase reaction zones,
- unhindered gas transfer of H₂, O₂ and H₂O into and away from the reaction zones,
- minimal electrical resistance between the catalyst particles and the current collectors,
- direct contact of the reaction zones on the catalyst particles with the membrane for unhindered transfer of H⁺ ions in the absence of a conducting fluid (realized by implementation of membrane material into the MEA, initially as a solution, and usually completed by ‘hot pressing’).

The last item is of particular importance in a PEMFC. Any hindrance to ion transfer results, not only in an increased ohmic voltage drop, but additionally, differences in H⁺ ion concentration between the membrane phase and the electrode surfaces can occur, especially if further impurity ions are present. In combination with the small buffer capacity of pure water significant changes in pH and, therefore, differences in pH between the anode and cathode side are possible. The conse-

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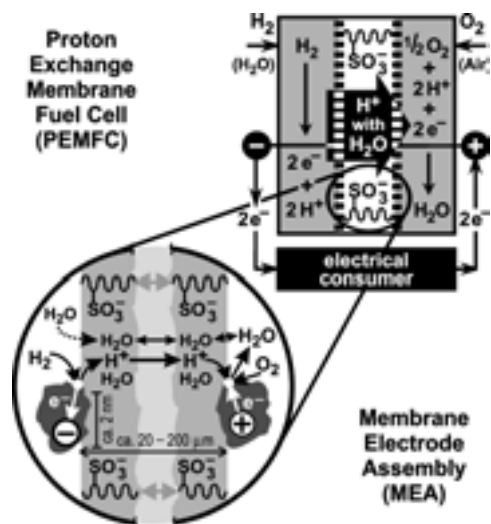


Fig. 1. Cation exchange membrane as SPE, here as example in a fuel cell, and details of mass, ion and charge transfer at the catalyst particles in the membrane electrode assembly.

quences are variations in electrode potential and major losses of energy.

Optimal operation of the PEMFC requires a well-adjusted water balance, considering the production of water at the cathode and its transport through the membrane (see Figure 1). As well as the diffusion, the electro-osmotic stream (EOS) is an important transport mechanism in ion exchange membranes: because only H⁺ ions are mobile within the membrane, the water in their solvation shells is simultaneously transferred through the membrane (ca. 2–4H₂O/H⁺, see Section 3). A sufficiently high water concentration has to be available for the solvation of the mobile and fixed ions in the membrane in order to achieve sufficient ion conductivity, and also for the EOS. Thus, humidification of the hydrogen gas feed is usually needed.

The applications of an electrochemical cell according to Figure 1 are not limited to the PEMFC. The reactions in Figure 1 can be reversed for the electrolysis of pure water, if the MEA is designed for a sufficient stability against gas evolution. Analogously, it is possible to use such a cell for organic reactions without supporting electrolyte.

Best known in this area is the direct methanol fuel cell (DMFC) which uses an aqueous solution of methanol as fuel, similarly to Figure 1. The methanol is oxidized at the anode forming H⁺ ions which migrate through the membrane and react at the cathode with oxygen to water. The EOS in this case is very unfavorable as it transfers, additionally to diffusion, water and methanol to the cathode. Thus, energy losses occur due to the mixed electrode potential and complicated removal of water. As the EOS is an inherent property of ion exchange membranes it is difficult to overcome this problem, though much research has been carried out in this area. The use of an anion exchange membrane as a potential alternative is discussed in Section 4.

2. SPE technology for electro-organic synthesis

A fundamental advantage of SPE technology for electro-organic syntheses is that no supporting electrolyte is required. Thus, process steps for separating and recycling of supporting electrolytes can be economized and the design of simple synthesis processes is enabled. Side-reactions with supporting electrolytes are impossible. SPE technology first was used for electro-organic synthesis by Ogumi about 20 years ago [1]. An overview up to 1996 is given in [2]. Examples of recent investigations are the electroreduction of 2-cyclohexene-1-one using various metals as SPE electrodes [3], the methoxylation of furan in an SPE fuel cell [4], the hydrogenation of edible oils in an SPE cell with a gas diffusion electrode [5], the electrosynthesis of *p*-methoxybenzaldehyde using a graphite SPE electrode [6], also investigations of mass transfer in the SPE membrane [7], the oxidation of various alcohols in an SPE cell with a Ti/IrO₂ anode [8] and the reduction of CO₂ to formic acid in an SPE reactor with metalized graphite electrodes [9]. A further application of SPE technology is the degradation of aqueous pollutants without supporting electrolytes. Examples are the electrochemical incineration of 4-chlorophenol [10], the electrochemical hydrodehalogenation of chlorophenols [11], the application of doped SnO₂ anodes, prepared by a sol-gel technique [12], the reduction of dichlorofluoromethane [13], the reductive dehalogenation of chlorinated solvents in the gas phase [14] and the electrolytic oxidation treatment of dye-containing waste water [15].

2.1. Differences in comparison with a fuel cell

The general structure of an SPE cell, suitable for electro-organic synthesis, corresponds to a fuel cell (Figure 1). But there are fundamental differences in the intention of the processes, with consequences for essential construction details of the cell:

- The product of a fuel cell is electrical energy, and so the main optimization criterion is a high energy efficiency, any loss of the (small) cell voltage has to be minimized.
- In the case of electro-organic synthesis a good product yield, a high reaction selectivity or a low by-product formation may be much more important than low energy consumption. Also the application of a suitable electrode material or a simple and stable cell construction can be predominant necessities.
- The energy consumption of many electro-organic conversions is often unfavorably high because the reaction path includes energy rich intermediate compounds, such as radical ions. In such cases the minimization of the energy consumption is less relevant.

Consequently, an SPE cell for electro-organic synthesis does not principally need a complex, energy optimized MEA, including the properties of a gas diffusion electrode, as demonstrated in Figure 1.

A beneficial result of these reduced requirements is the extended variety of electrode materials which can be applied, although it is not possible to connect them directly with the membrane, forming a MEA according to Figure 1. Even an assembly of permeable electrodes that are simply pressed to the surfaces of an ion exchange membrane can be sufficient (see Section 2.2). Such arrangements have been called 'zero gap cells'. Here, they are included in the discussion on SPE technology, because the determining property is the ion exchange membrane as the solely available electrolyte.

The possibility of using a simplified electrode-membrane combination also enables work in non-aqueous media, where increased swelling of the membrane would immediately destroy any regular MEA.

If the properties of the reaction medium do not allow realization of an optimal MEA with unhindered ion transfer, differences in H^+ ion concentration between the electrode surfaces and the membrane phase can occur, as discussed in Section 1. Thus, at the anode an acidic medium and at the cathode an alkaline medium is usually expected, independent of the acidic medium inside a cation exchange membrane or the alkaline medium inside an anion exchange membrane (proved by cyclic voltammetry of SPE water electrolysis [2]). This factor must be considered in the selection of electrode materials.

2.2. Variation range of suitable materials for SPE technology

The best chemical and mechanical stability and the lowest voltage drop, even in non-aqueous media, is achievable using the perfluorosulfonic acid cation exchange membrane Nafion[®] (Du Pont de Nemours), a standard membrane for fuel cells (e.g. Nafion[®] 117, equivalent weight = 1100 g of polymer per equivalent of fixed ions, 7 mil = 0.18 mm thick). For SPE cells it is usually applied without a fabric reinforcement, which would hinder ion transport and therefore will usually be unfavorable for SPE technology. Several types of cation and anion exchange membranes, including reinforcement, have been used.

Many electro-organic syntheses have been carried out successfully with permeable electrodes, which are pressed without further connection onto the surfaces of the membrane (at about 0.5 bar). Graphite (carbon) fiber felt (e.g. SGL GFA 5) is an interesting electrode material. It is inexpensive, has high porosity, conductivity and elasticity and, due to its soft surface, it ensures good contact with the membrane. Graphite itself is a common material for compact electrodes in industrial cells, especially for non-aqueous reaction media, e.g. for methoxylations.

Graphite felt is suitable in all reaction media as a cathode material for hydrogen evolution. Here, the overvoltage is relatively high and so the energy consumption is somewhat increased. But, on the other

hand, the low catalytic activity for hydrogenation reactions is advantageous in many cases.

On the anode side graphite felt has proved to be a favorable material for non-aqueous media. It suppresses undesired reactions with hydrogen gas. In aqueous solutions it is rapidly damaged by oxygen/carbon dioxide formation, however. A fine mesh of platinum (or e.g. Pt/Ir) is an anode material of almost universal stability. Connection to the membrane is sufficient, especially when, on the cathode side, the soft and elastic graphite felt guarantees a uniform contact pressure.

Porous layers of platinum or other metals, similar to a MEA (Figure 1), can be precipitated in the membrane surface by chemical [3, 16] or electrochemical methods [17]. They are mechanically stable, even after membrane swelling and with strong gas evolution, and they can be used as anode or cathode material. In this case suitable current collectors are very important. If a fine mesh of the same metal is used, equal results are achievable, even without a membrane coating [18].

Various oxide electrode materials show good stability, if they are used in combination with SPE technology, whereas they show less durability in conventional electrolytes (e.g. sulfuric acid). Ozone generators (e.g. [19]) are available, based on SPE water electrolysis, using a lead dioxide anode with a very long service life [20]. Moreover, experiments of several months duration, without deterioration of PbO₂ anodes, were carried out for the oxidation of propargyl alcohol (2-propyne-1-ol) to propargyl aldehyde and propiolic acid, using a cation exchange membrane (Nafion[®]), and for the oxidation of γ -butyrolactone to succinic acid, using an anion exchange membrane (Ionac[®], see Section 4) [2].

As carrier material for the oxide coating titanium is preferred (mesh, expanded metal or sintered metal, probably with a thin platinum intermediate layer). Such coated electrode materials are also commercially available. Sintered metal is a good material, because its smooth surface enables a large contact area with the membrane, under the precondition that there is no mass transfer limitation inside the electrode. Here, enhanced mass transfer by the EOS is useful (see Section 3).

Possible reasons for the increased stability of oxide electrodes using SPE technology may be:

- in the inert liquid of an SPE cell there is no aggressive electrolyte, like sulfuric acid, which could dissolve the oxide coating,
- no erosion is possible, because there is direct mechanical contact between the coating and the membrane and no convective flow occurs (only the slow and continuous EOS, see Section 3).

Metal oxide coatings on titanium, especially containing ruthenium and iridium, are used in industrial chlor-alkali electrolysis [21] and have also been applied for oxidations in SPE cells [8]. Beck has used this coating method for oxides of metals like chromium, cobalt and manganese, because their oxides are known as selective chemical oxidation reagents. But the service life of these electrodes in sulfuric acid solution was very short (e.g.

[22]). Such oxide coatings on titanium mesh, prepared by an optimized coating method with up to 40 thin layers, demonstrated a surprisingly long life time in an SPE cell. In experiments of at least 1 week of continuous operation, using the oxidation of methanol as test reaction, significant differences in product distribution have been demonstrated for various anode coatings. An electrochemically prepared manganese dioxide layer was used for two months in an SPE cell, whereas a similar electrode in sulfuric acid solution was destroyed after a short time [23].

The interesting electro-catalytic properties of oxide electrodes like PbO_2 , MnO_2 or new composites on titanium may be industrially applicable if their stability is increased by combination with SPE technology.

2.3. Example of a successful reaction

Numerous experiments were carried out in a cell with about 21 cm^2 membrane area [24].

Figure 2 shows as example the methoxylation of *N,N*-dimethylformamide (DMF), which runs nearly perfectly: 98% current efficiency and selectivity for the target product, 2% formic acid methyl ester, cell voltage about 4 V ($30 \text{ }^\circ\text{C}$, 50 mA cm^{-2}). Graphite felt electrodes, pressed onto the surfaces of a Nafion 117[®] membrane, were used in a pure non-aqueous solution of methanol and DMF without additives. The cell was operated continuously, with the reactant feed only into the anode chamber. The entire liquid flows as EOS through the membrane (see Section 3) and leaves the cell from the cathode chamber, together with the hydrogen gas. On the anode side there is only a small outlet of hydrogen which diffuses through the membrane. With graphite as

anode material instead of platinum there are no current efficiency losses due to oxidation of hydrogen gas. Also other amides and another alcohol (2-propanol) react similarly well [2]. These results are better than literature data [25] for the same reactions in batch operation, using a supporting electrolyte, like e.g. the expensive, toxic and difficult to separate liquid tetrabutylammonium tetrafluoroborate.

2.4. Membrane pretreatment

The surprisingly beneficial results of the example in Figure 2 can be realized after pretreatment of the membrane in an amide like DMF. In Nafion[®] there is no cross-linking and its swelling in amides is much stronger than in water, especially at elevated temperatures [2]. During this pretreatment the membrane material is partially dissolved, and at higher temperatures it can be totally solubilized. The swelling is also very dependent on the equivalent weight (grams membrane mass per mole of fixed ions), even the small changes in different production batches have an influence. In practice, suitable pretreatment conditions have been achieved for all types of Nafion[®], if the membrane swells to twice its area in the original state (about $80 \text{ }^\circ\text{C}$ and 6 min in DMF).

Such pretreatment of the Nafion[®] membrane appears to be a precondition for successful application of SPE technology in non-aqueous media, as was shown for various reactions [2, 24]. Benefits of the pretreatment are:

- reduced cell voltage, probably due to better contact between the softened membrane and the electrodes,
- requirement for a smaller quantity of the expensive membrane material,
- enhancement of the EOS, which increases proportional with the increasing membrane area (see Figure 6), leading to enhanced mass transfer at the electrodes which causes high selectivity of the electrode reaction.

This pretreatment method may seem at a first look to be suspicious and not reproducible, but it has confirmed its reliability in many experiments with various reactions. Figure 3 shows as example the results of a long time test of 6000 h using the reaction of Figure 2: only minor increase of the cell voltage and nearly constant high selectivity for the target product have been observed [26].

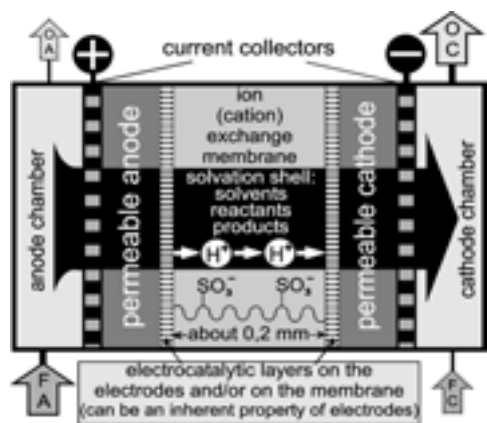


Fig. 2. Scheme of an SPE cell using a cation exchange membrane for the methoxylation of *N,N*-dimethylformamide [24].

3. Mass transfer in ion exchange membranes

3.1. Mechanism of the electro-osmotic stream (EOS)

Figure 4 shows the transport of solvated ions at the surface of one particle of a porous anode, e.g. at a single graphite fiber (not to scale). This is surrounded by a laminar diffusion layer where convection in the bulk phase of the liquid electrolyte is not present. In a conventional electrolyte (top of Figure 4) cations and

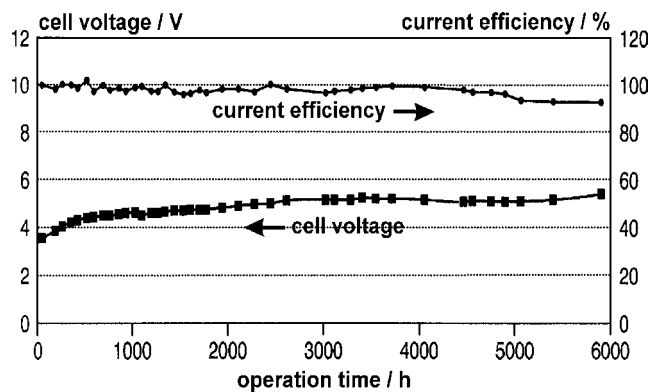


Fig. 3. Long time test of the methoxylation of DMF, molar ratio methanol:DMF = 10:1, 60 °C, 50 mA cm⁻², graphite felt electrodes, Nafion 117[®], pretreated in *N*-methylformamide [26].

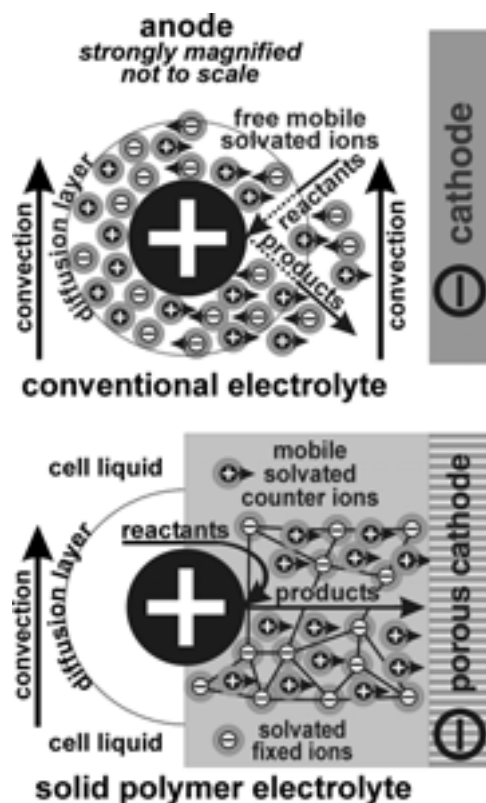


Fig. 4. Transport model of solvated ions at the anode surface in a conventional electrolyte and using the SPE technology.

anions are moving in opposite directions and no effective mass transfer is generated by their solvation shells. Therefore, uncharged reactants and products can be transferred by diffusion alone. Limited diffusion rates for reactants and/or products of the desired anode reaction can enable side reactions, and consequently give reduced reaction selectivity.

In SPE technology the cell liquid is free from ions, which are present only in the membrane (bottom of Figure 4). The fixed ions (here, in a cation exchange membrane, anions) are bound to the polymer and are thus immobile, including their solvation shells which are

formed due to the swelling of the membrane. Charge transfer is effected only by counter ions (here H⁺ cations) and their solvation shells generate the EOS.

In consequence, convective mass transfer in the membrane is caused, which is typical of SPE technology. The H⁺ ions are formed during reaction at the anode surface and therefore they have to be solvated at this location for further transport through the membrane. This requires molecules – not only products but also reactants and solvents – which are flowing from the cell liquid to the anode surface. Thus, in contrast to a conventional electrolyte with a diffusion layer at the electrodes, in SPE technology convective mass transfer occurs directly at the electrode surfaces.

Independent of the EOS, diffusion takes place (in the same or opposite direction) if a concentration gradient is present. If all mass transfer is carried out by EOS, as in Figure 2, the concentrations on both sides of the membrane are equal and no diffusion occurs.

3.2. Properties of the electro-osmotic stream (EOS)

The EOS obviously transfers all (uncharged) solvents, products and unconverted reactants unselectively. It contains the concentrations which are present in the reaction zone, i.e. at the interface between the electrode and the membrane. This has been shown in numerous measurements. It is additionally confirmed by investigations of the oxidation of methanol/water mixtures. Compared with the bulk concentrations in the anode chamber, the concentrations in the EOS are slightly lower for the reactant methanol and increased for the products (formaldehyde, formaldehyde dimethyl-acetal, formic acid and formic acid methyl ester) [27].

The strength of the EOS is very dependent on the composition of the liquid. Figure 5 shows the number of molecules in the solvation shell of the H⁺ ions during their migration through the membrane Nafion 117[®] for the above mentioned oxidation of methanol/water mixtures. The size of the solvation shell increases linearly from about 2 molecules per H⁺ ion in pure water up to ca. 10 molecules in pure methanol.

In these experiments the cathode chamber contained only the liquid which arrives within the EOS through the membrane (no cathode chamber feed, see Figure 2). Thus, there are almost no concentration differences and, consequently, no diffusion is possible. Under these conditions no temperature influence is observed.

Additionally the type and, especially, the preparation of the membrane has a significant effect on the quantity of the EOS. After pretreatment of a Nafion[®] membrane in amides according to Section 2.4 the solvation shell in a reaction mixture of methanol and amides (see Figure 2) attains up to 20 molecules per H⁺ ion and more [2]. Figure 6 shows that the solvation shell increases proportionally with the increasing area of the membrane during pretreatment, without influence of the equivalent weight of the membrane [28]. This effect of pretreatment is not limited to reaction mixtures including amides; it

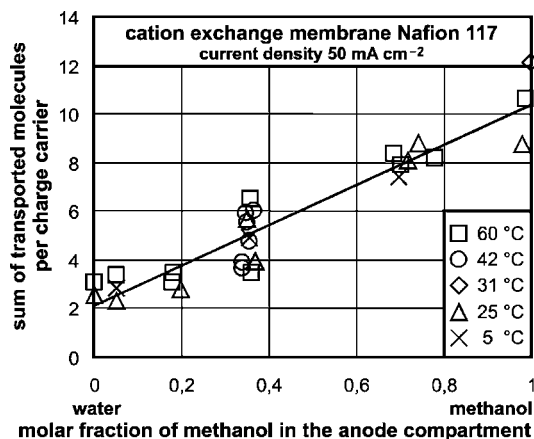


Fig. 5. EOS = transport in the solvation shells of the H^+ ions during the oxidation of methanol/water mixtures in an SPE cell as function of the concentration in the anode chamber (=outlet of the anode chamber in continuous operation after achieving a stationary state, cathode chamber outlet = EOS, see Figure 2), anode: platinum/iridium mesh (90/10), cathode: graphite felt [27].

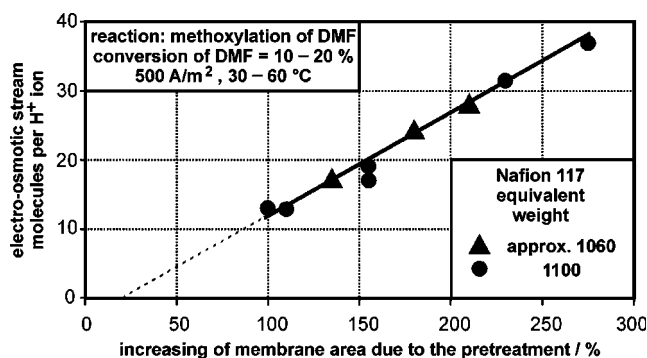


Fig. 6. Influence of increasing membrane area (Nafion®) due to the pretreatment in amides (see Section 2.4) on the EOS, i.e. on the solvation shells of the H^+ ions, during the methoxylation of DMF (see Figure 2) [28].

can also be applied in aqueous solutions [29 and A. Kornouchova, in preparation].

All measurements have demonstrated that the size and composition of the solvation shells is obviously independent of the current density. In consequence, the quantity of the EOS increases proportionally with increasing current density, without observable changes in composition.

3.3. Effects of the EOS on the selectivity and conversion rate of the electrode reactions

As shown in Figure 4 the EOS assures:

- a sufficient supply to the electrode reaction of reactants,
- a rapid removal of the products from the reaction zone, before undesired consecutive reactions can occur.

Therefore, the enhanced mass transfer caused by the EOS is understood to be the reason for the surprisingly high selectivity of anode reactions as in Figure 2. It is

better than in a conventional solution with supporting electrolyte, where mass transfer at the electrode surface is limited to diffusion. A convincing argument for this conclusion is that the high selectivity is achievable only after the above mentioned pretreatment of the Nafion® membrane, when the EOS is increased by strong swelling of the membrane [2].

An additional confirmation is the fact that the current density can be increased without reduction in selectivity: mass transfer by the EOS increases proportionally to the increasing current density and, thus, a mass transfer limitation is avoided. Continuously operated experiments with the reaction of Figure 2 were carried out, each for at least 2 days, at current densities which were very high for electro-organic syntheses (up to 150 mA cm^{-2}) without any loss of selectivity (nearly 100%) and up to 250 mA cm^{-2} with only a few percent decrease in selectivity [26].

A further consequence of the EOS is the limitation in the conversion rate of the electrode reaction. Usually, the solvation shell of each charge carrier (here H^+ ions) includes more molecules than are converted by the reaction that generates this charge carrier. In the example of Figure 2 the entire transport of reactants and products is carried out by the EOS. In this case, for one pass through the membrane in continuous operation, the conversion rate of DMF is about 10%. It can be increased by partial recycling of the product stream from the cathode chamber outlet into the anode chamber feed [26]. Additionally, it can be influenced by the feed composition and, via the quantity of the EOS, by membrane pretreatment (see Figure 6).

4. Chemical engineering possibilities for optimizing SPE technology

4.1. Practical consequences of the EOS for application of SPE technology

SPE technology uses the ion exchange membrane primarily as an ion conductor. The common membrane function as a cell separator is restricted due to the transport properties, especially due to the EOS. Consequently, a precondition for SPE technology is that there are no detrimental subsequent reactions of the reactants and products at the counter electrode. It is essential, that such reactions can be suitably used or, if they are undesirable can be prevented or minimized.

Fortunately, many electro-organic reactions run irreversibly. For example, the products of an anodic oxidation are usually not subject to cathodic reduction, at least if an appropriate cathode material is chosen. This has been realized for many published reactions, e.g. for the various investigations in the author's group [2, 24], as in Figure 2, where there is no risk of cathodic reduction and only hydrogen is evolved at the cathode.

But mass transfer through the membrane can also be detrimental, as in the well known example of methanol and water transfer ('cross over') to the cathode in a DMFC.

Mass transfer in continuously operated SPE cells, and its consequences for the electrode reactions, can be significantly influenced by the different cell configurations shown in Figure 7. The configurations result from the use of cation (CEM) or anion exchange membranes (AEM) in combination with the alternative reactant feeding into the anode or cathode chamber. In addition two DMFC designs are included, as usual with a CEM and as a potential substitute with an AEM. Significant differences between these configurations are influenced by the direction of the EOS.

Configuration A in Figure 7 relates to Figure 2 which shows an excellent example of the successful application of SPE technology. As mentioned above, a strong EOS promotes the target anode reaction; undesired reactions at the cathode do not occur. Under these conditions the best method is to add reactant feed to the anode chamber and to remove product on the cathode side. Thus, the membrane here works additionally as a dosing pump. The conversion rate for one pass through the cell is low, but can be increased by recycling from the cathode to the anode chamber.

In configuration A all compounds in the feed are exposed to both anode and cathode reactions. However, if a cathodic reduction is exclusively desired, configuration B may be interesting. At the anode an inert reaction takes place which generates the required H^+ ions, e.g. oxidation of water including oxygen evolution. The EOS (water) can be used to repel the diffusion of reactants to the anode and thus to minimize their undesired oxidation. But additionally the EOS can impede mass transfer of the reactants to the cathode.

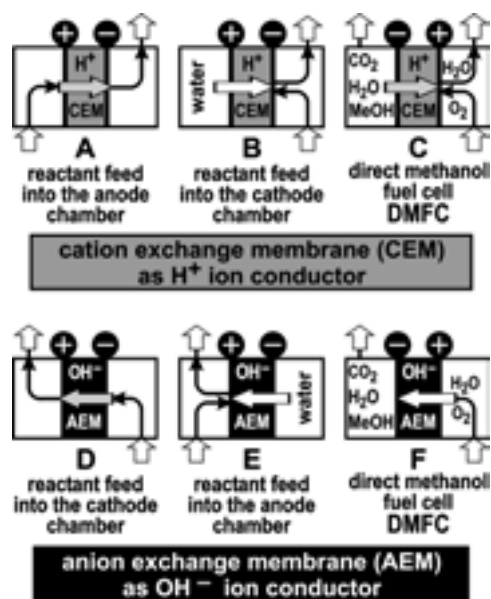


Fig. 7. Cell configurations for the SPE technology.

Configuration C shows the usual version of a DMFC. Due to the change from hydrogen evolution at the cathode (configuration B) to oxygen consumption the polarity of the cell is reversed, but no effect on the membrane and anode behavior is expected.

It can be useful to change the direction of the EOS by application of AEM.

An example for a successful use of configuration D with an AEM (Ionac MA 3475[®]) is the oxidation of γ -butyrolactone in aqueous solution [2]. At the cathode the lactone ring is opened by OH^- ions to γ -hydroxy butyrate anions which migrate through the membrane and are oxidized at the anode to succinic acid. Transfer through the AEM directly onto the anode was proved to be beneficial for the anode reaction, compared with the application of a CEM. As mentioned above, the cell was continuously operated with a PbO_2 anode for four months without deterioration [2].

Configuration E is interesting, analogously to B, if only an anodic reaction is desired, because the EOS can hinder reactant diffusion through the membrane.

While the long-time stability of AEMs in neutral or acidic solutions is state-of-the-art, upto now most AEM materials are rapidly damaged by OH^- ions. But the increased stability of Neosepta AHA[®], an electro-dialysis membrane of the Tokuyama Corp., for several days as OH^- ion conductor was sufficient to demonstrate the effect of the EOS in an AEM (Table 1).

Table 1 shows some experimental results of methanol transfer for comparison of CEM and AEM in different cell configurations. The base value is a methanol diffusion rate of $51.5 \text{ g h}^{-1} \text{ m}^{-2}$ through a Nafion 117[®] CEM without current (line 1). At 40 mA cm^{-2} current density in cell configuration A the methanol transfer is increased by the EOS to $100.1 \text{ g h}^{-1} \text{ m}^{-2}$ (line 2, under the chosen conditions the anode feed is completely exhausted by the EOS). If the methanol is fed into the cathode chamber (configuration B), i.e. the diffusion is directed to the anode, opposite to the EOS, the methanol transfer rate is decreased to $40.5 \text{ g h}^{-1} \text{ m}^{-2}$ (line 3). Thus, there is a repelling effect on diffusion through the Nafion 117[®] membrane, but under the chosen conditions it is small.

More evident is the effect using the AEM Neosepta AHA[®] in configuration E. Methanol diffusion without current is similar to that for Nafion 117[®] ($53.1 \text{ g h}^{-1} \text{ m}^{-2}$, line 4). The methanol transfer significantly decreases with increasing current density, much more than the change in the concentration difference (caused by intensified anodic methanol conversion) could reduce the diffusion (line 5–9). No influence of electrode material is visible (line 6/7) and a temperature effect may be in the range of experimental error (line 8). At 60 mA cm^{-2} the methanol transfer rate is greatly suppressed ($4.9 \text{ g h}^{-1} \text{ m}^{-2}$, line 4).

Considering these results, a DMFC with application of an AEM according to configuration F, could be interesting. A precondition would be the development of AEMs with better stability and conductivity.

Table 1. Methanol transfer in various SPE cell configurations with anion and cation exchange membranes (see Figure 7), at different current densities (hydrogen evolving cathode, cathode feed: ca. 5.5–7.0 g h⁻¹, anode feed: ca. 2.7 g h⁻¹) [30, and A. Kornouchova, in preparation]

Cell configuration (Figure 7)	Anode (mesh)	Cathode (felt or mesh)	Temperature /°C	Current density/ mA cm ⁻²	Methanol concentration /wt. %				Methanol transfer /g h ⁻¹ m ⁻²	
					Anode chamber		Cathode chamber			
					Feed	Outlet	Feed	Outlet		
Cation exchange membrane Nafion 117 [®] (Du Pont de Nemours)										
1	A	(Pt/Ir)	(graphite)	50	–	10	5.7	0	2.1	51.5
2	A	Pt/Ir	graphite	50	40	10	–	0	2.7	100.1
3	B	Pt/Ir	graphite	50	40	0	0.4	10	2.7	40.5
Anion exchange membrane Neosepta AHA [®] (electrodialysis membrane Tokuyama Corp.)										
4	E	(Pt/Ir)	(graphite)	50	–	10	5.4	0	2.1	53.1
5	E	Pt/Ir	Pt/Ir	50	20	10	6.1	0	0.7	17.5
6	E	Pt/Ir	Pt/Ir	50	40	10	2.6	0	0.6	14.1
7	E	Pt/Ir	graphite	50	40	10	2.0	0	0.5	14.6
8	E	Pt/Ir	graphite	65	40	10	2.1	0	0.6	12.0
9	E	Pt/Ir	graphite	50	60	10	1.7	0	0.3	4.9

Another example of experimental comparison of the cell configurations in Figure 7 is the detoxification of 2-chlorophenol in aqueous solution without supporting electrolyte [29, and Kornouchova, in preparation]. The best results were obtained using configuration A, i.e. first anodic oxidation and then cathodic reduction. It was possible to convert 2-chlorophenol completely (initial concentration 0.01 mol kg⁻¹) and to mineralize the included chlorine up to 80% as chloride ions. The known stability of the Nafion 117[®] membrane remained even after intense pretreatment (see Section 2.4 and Figure 6), which caused a change in the EOS from ca. 4 to 25H₂O molecules per H⁺ ion. Due to the strong pumping effect through the membrane the energy consumption (cell voltage ca. 2.4 V at 50 mA cm⁻²) is decreased to ca. 140 kWh m⁻³ of treated water. This is not far away from a commercial process for phenol degradation with sodium sulfate as supporting electrolyte (90 kWh m⁻³, [31]). Thus, there will be a chance to optimize the process for industrial applications.

4.2. Special methods for non-aqueous media

Ion exchange membranes are commonly designed for aqueous media. But SPE technology may also be of industrial interest for non-aqueous media. The examples of the methoxylation of furan [4] and the hydrogenation of edible oils [5] have been mentioned in Section 2. Methanol is often used as solvent in industrial reactions. Fortunately, it has been possible to show that SPE technology also can be applied in methanol containing non-aqueous solutions, at least when using Nafion[®] membranes. Ion exchange membranes can only work as ion conductors if the reaction mixture is able to solvate the different ions inside the membranes, in order to ensure the mobility of the counter ions. This presumes sufficient polarity of the compounds. Obviously, mixtures of alcohols and amides are suitable for SPE technology: the membrane voltage drop of the reaction in Figure 2 is < 1 V at 30 mA cm⁻², 50 °C [24].

Various ethers can be methoxylated if an increased voltage is accepted [32]. The methoxylation of *p*-methoxytoluene (*p*-methylanisol), which is industrially carried out using a supporting electrolyte, was initially found to be impossible using SPE technology. This seemed plausible and inevitable. Nevertheless, combination of the following procedures enabled similar product yields as in the industrial process and a steady operation of 1700 h at 4–5 V (30 mA cm⁻²) [24]:

- optimized pretreatment of the Nafion[®] membrane,
- use of *N,N*-dimethylformamide as co-solvent; in this case it is completely inert, although it can be very easy methoxylated itself (see Figure 2),
- permanent and uniform boiling of the fluid at the anodic membrane surface,
- addition of a very small concentration of sulfuric acid (only 2% of the usual amount as supporting electrolyte), which has no effect on the reaction and is easy to neutralize.

A cell voltage analysis, using galvanostatic current interruption measurements [24], suggests that the initial high voltage in this example is not the result of insufficient ion conductivity in the membrane. The most probable reason may be the formation of very thin polymer layers at the interface between anode and membrane. Their influence is minimized and further growth is hindered by the aforesaid procedures.

This example shows that it is not the behavior of the membrane itself that is the limiting factor for SPE technology and that its application in non-aqueous media may also be enabled if the operating conditions are optimized using chemical engineering methods.

4.3. Scale up for industrial applications

The reaction in Figure 2 was also carried out in continuous operation in a cell of 250 cm² membrane area [2]. Investigations of the distribution of current, temperature and residence time within the cell and of the

heat dissipation, showed that there is no obstacle to the application of SPE technology on the industrial scale [33].

For reactions such as those in Figure 2, which need no separation of the anode and cathode chamber, an interesting, uncomplicated cell construction has been proposed by BASF AG [34]. Comparable with the well known capillary gap cell, graphite felt discs work as a stack of bipolar electrodes between ion exchange membranes as ion conductors. This stack is compressed by current feeders at the bottom and top of the cell. The reaction fluid is pumped from a central channel, formed by holes in the electrodes and membranes, through the porous graphite felt electrodes to the outer surface of the bipolar stack, where it trickles down. Because the fluid is non-conductive reactions occur only at the interfaces between the electrodes and the membranes. This cell was successfully used at laboratory scale for the methoxylation of ethers [32]. Its properties make it suitable for scale-up for industrial applications.

5. Conclusions

SPE technology for electro-organic synthesis without supporting electrolyte enables an extended area of potential applications because it is not limited by the need to maximize energy efficiency as in the direct methanol fuel cell DMFC. Possibilities and advantages of SPE technology have been demonstrated for several reaction systems, e.g. using cation or anion exchange membranes, aqueous or non-aqueous media, various electrode materials and different cell configurations.

The EOS, an inherent property of SPE technology, can be used to enhance mass transfer at the electrodes and can increase reaction selectivity. Thus, in contrast to the DMCF, the EOS can be beneficial to the process.

The extended life time of oxide electrodes, combined with SPE technology, will enable new ways of using their special electro-catalytic properties.

The success of an application of SPE technology is not only dependent on the electrochemical properties of the cell, but also on the optimization of the operating conditions using chemical engineering methods. As shown in the discussed examples SPE technology, especially the ion exchange membrane as the central component, may permit more interesting possibilities than have been explored up to the present.

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