Hydrogen Economy and Polymer Membranes

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Summary: Hydrogen can be separated from its mixtures using polymer foams with closed cells. Each cell serves as a gas container which is filled through its walls – separation membranes. Foam, as a manifold membrane system, utilizes transient states of permeation and thus takes advantage of fastest diffusion of hydrogen. Large scale manufactured polystyrene foams were chosen to demonstrate the phenomenon. Novel proton conducting membranes containing ionic liquids are being developed. They can perform in intermediate-temperature fuel cells (FC).

Keywords: foams; gas permeation; hydrogen; ionic liquid; membranes

Introduction

Hydrogen economy is a concept which should shift world economy from the current state of almost complete dependence upon hydrocarbons for energy.[1] In its rather complicated scheme membranes can be found on some strategic positions. Polymer membranes for gas separation can be utilized during hydrogen production, recovery and separation. Proton-conducting membranes are the vital part of fuel cells – devices which convert hydrogen energy into electricity.

Polymer Membranes for Hydrogen Separation

Polymer membranes are very suitable for the separation of hydrogen from its mixtures. Hydrogen is usually the most permeable gas through polymers. Its permeability is many times higher than that of most of the other gases.[2] The composition of mixtures to be separated depends on the source of hydrogen. The product of the steam reforming of fossil fuels contains, besides hydrogen, CO_2 and CO and some other minor components.[3] Biological methods of hydrogen production provide mixtures containing CO_2 and N_2. While the separation of H_2 from N_2 using polymeric membranes is an easy task, the separation of H_2 from CO_2 is a rather difficult one. Hydrogen permeates at best 10 times faster than CO_2 as can be seen on diagrams in ref. [2].

However, the diffusion rates of hydrogen in various polymers can be hardly beaten. It is given by the size of hydrogen molecule,[4] the smallest besides helium. However, the advantage of fast diffusion is difficult to utilize in steady state permeation. Therefore transient states during permeation should come into focus. These can be studied on a manifold membrane system which are well represented by polymer foam with closed cells. Each cell is a small gas container which is filled through its walls – separation membranes. Gas diffusion in closed-cell foams is well described [5,6] and can be numerically modeled.[7] However, found effects regarding hydrogen diffusion and permeation are described further.

First, transport of above gases through a dense layer and through polymer foam was compared. Quite suitable is polystyrene (PS) for the purpose, as many sorts of the foam are industrially produced. Extruded polystyrene (EPS) board, utilized as facade thermo-insulation, was chosen. A module

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Table 1.
Gas transport properties of polystyrene (PS).

Material – PS	Time lag τ [minutes]		
	H_2	CO_2	N_2
dense layer – 0.11 mm thick	0,1	4,7	4,5
EPS foam – channels 30 mm appart	220	400	880

was prepared simply by drilling two parallel channels (feed + retentate channel; product channel) into the block of EPS 30 mm apart. The outermost walls of the block were gas-tightly sealed using a glued aluminum foil. Feed channel was pressurized with a gas. The passing gas in the foam should not only go through thin polymer walls but also had to fill the cells. Then it liberated into the product channel from which it was collected. Steady state permeability of the foam is two orders of magnitude higher then that of the dense layer as expected.[8] Transient characteristics show very long time-lags as shown in Table 1. Pure hydrogen can be collected for a long time before other gases appear.[8]

Another feature of the above module can be observed at the end of the permeation experiment – when the gas supply into the feed channel is closed. Gases continue to be liberated from the foam for longer time. The foam serves not only for hydrogen separation but also for hydrogen storage.

Hereby can be seen that hydrogen diffuse through the foam faster than most of the other gases. Hence, the mixture of gases in the feed channel is depleted from hydrogen. Hydrogen can be ''absorbed'' in the foam. The feature can be demonstrated better on expanded polystyrene (XPS) samples. A module was prepared so that a pipe was filled with pieces of XPS which are utilized for packaging of goods. The pipe had on opposite ends a feed channel and an output channel. Then gas mixture containing hydrogen was brought into the feed of the module. While the mixture was passing through open pores of XPS, hydrogen as a most permeable component, started preferably fill the beads of XPS which contain closed pores (cells). See the scheme in Figure 1a. Concentration of hydrogen in the gas mixture at the output was low until the foam in the module was filled with hydrogen. In such way ''absorbed'' hydrogen could be later obtained simply by decreasing the pressure in the module (Figure 1b) - while the feed channel was closed the output channel was connected to vacuum pump. Concentration of hydrogen at the output was higher than that of originally fed into the module.[9] Hydrogen enrichment depends on pressures during filling (feed pressure) and during liberating (product pressure) as seen in Table 2.

It can be concluded that closed cell polymer foams are suitable for separation of hydrogen (or helium). Besides selectivity in steady state permeation we can utilize

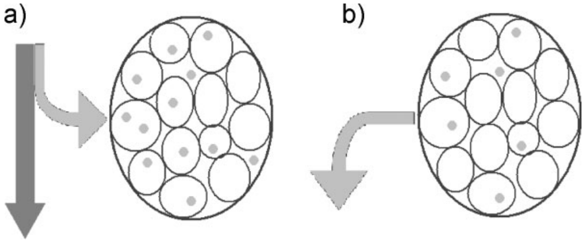

Figure 1.
a) ''Absorption'' of hydrogen from gas mixture into a XPS bead. b) ''desorption'' of hydrogen from the XPS bead.

Table 2.
Hydrogen recovery with XPS module.

Feed pressure	Product pressure	Feed concentration	Product concetration
[kPa]	[kPa]	[%]	[%]
400	100	66	75
400	20	66	86
250	15	33	61

transient effects – difference in timelags. The foams can be also utilized as selective ‘‘absorbers’’ of hydrogen from its diluted mixtures. This can be utilized for hydrogen recovery from off-gas of PSA process or from biohydrogen fermentation products. An important advantage of the concept is also given by the low price of polymer foams manufactured on a large scale.

Polymer Membranes for Fuel Cells

A hydrogen/oxygen fuel cell is a device that continuously converts the chemical energy of hydrogen and oxygen into electricity (Figure 2). The fuel cell generally consists of a fuel electrode (anode) and an oxidant electrode (cathode) separated by an electrolyte. On the catalytic surface of the anode, the hydrogen brought into the cell is split into hydrogen ions and electrons. The hydrogen ions permeate across the electrolyte to the cathode while the electrons flow through an external circuit and produce electric power. Oxygen, usually in the form of air, is supplied to the cathode and combines on its catalytic surface with the electrons and the hydrogen ions to produce water. Proton exchange membrane fuel cells (PEMFC) use a solid polymer membrane as the electrolyte.

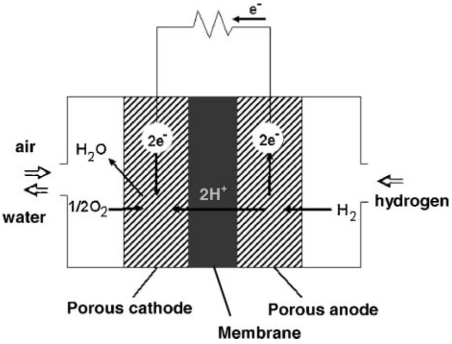

Figure 2.
Principle of a fuel cell.

The proton-conducting membrane is a vital part of PEMFC. The membrane must be a good conductor for hydrogen ions, but nonconductor for electrons, it must have low permeabilities to hydrogen and oxygen, it must show sufficient mechanical strength and it must be chemically and thermally stable under cell operation conditions.

Low-Temperature Fuel Cell Membranes

Proton-conducting membranes suitable for application in fuel cells have been prepared from a variety of polymer materials. First membranes were based on sulfonated phenol-formaldehyde resins (lacking hydrolytic stability) or on sulfonated copolymers of styrene with divinylbenzene (with poor oxidation stability).

Current membrane materials used in fuel cells are perfluorinated polymers with sulfonic acid groups in side chains,[10,11] such as Nafion (DuPont), which have excellent chemical stability. However, such membranes are expensive, which limits their use in large-scale applications. Therefore, there is a demand for new chemically and thermally stable polymer membranes combining the properties of perfluorinated membranes with a lower cost. Most of these membranes prepared in laboratories are based on sulfonated (or phosphonated) aromatic polymers. Aromatic polymers exhibit, in many cases, very good thermal, hydrolytic and general chemical resistance.[12] Polystyrene is the most common aromatic polymer. It contains, however, C–H bonds, which are particularly susceptible to oxidative attack.[13] Fuel cells with poly(styrenesulfonic acid) membranes were used in the Gemini spacecraft in the 1960s. The Gemini 5 flight faced serious problems due to the membrane degradation. Since then many aromatic polymers have been tested for the preparation of fuel cell membranes. The membrane properties depend on the degree of sulfonation: the membranes of highly sulfonated polymers show usually excellent conductivities but poor mechanical strength. The most suitable aromatic polymer for fuel cell membranes is probably sulfonated poly(etheretherketone).[14,15] The membranes prepared from this polymer were found nearly as durable under fuel cell operating conditions as the Nafion membrane.

The solution to the problem of mechanical strength may be the membranes based on two polymers: one with good mechanical strength and chemical stability and the other one with electrochemically active sulfonic (or phosphonic) acid groups. The condition is that the concentration of the electrochemically active polymer is high enough to form a protonic conduction path, i. e. it must be higher than the percolation threshold. These composite membranes can be prepared: (a) by grafting suitable monomers to a (fluorinated) polymer film with subsequent sulfonation;[16,17] (b) by blending an acid polymer with a basic one (e.g., polybenzimidazole);[18,19] and (c) by dispersing micron-sized or larger proton-exchange particles in an inert matrix. These membranes with proton-exchange particles (called heterogeneous membranes) are usually prepared by blending proton-exchange particles with a binder polymer and then calendering, extruding or compression molding the membrane[20,21] or by suspending the particles in a solution of an inert polymer, casting the membrane and evaporating the solvent.[22,23] In general, heterogeneous membranes have very good mechanical properties while being somewhat less ion-conductive. Their great advantage consists in their behavior in aggressive, in particular, oxidative environments: while homogeneous membranes at early stages of polymer degradation become brittle and develop cracks, heterogeneous membranes of the same ion-active material still keep their good mechanical strength.[21]

Low-temperature fuel cell membranes are based on hydrated acid polymers. Their proton conductivities decrease considerably with the decreasing levels of their acid groups dissociation, i.e., the membranes are almost non-conductive at low relative humidities. This means that the membranes can only be used at the temperatures below the boiling point of water.

Intermediate-Temperature Fuel Cell Membranes

The fuel cell operation at intermediate temperatures (100–200 °C) is desirable mainly because:

- higher reaction rates and thus higher fuel cell efficiencies can be achieved; and because
- catalyst poisoning with catalytic poisons is reduced. This is of importance as *bio-hydrogen* may contain traces of sulfur-containing compounds.

The most developed membranes which can operate in fuel cells at intermediate temperatures are based on polybenzimidazole (PBI) that is doped with phosphoric acid. [24,25]. The PBI/H_3PO_4 membranes are prepared by immersing PBI films into phosphoric acid for a prolonged time. Highly doped membranes contain 5–6 mol H_3PO_4 per PBI monomer unit and exhibit proton conductivities suitable for the use in fuel cells. The mechanism of conductivity of these membranes is rather complex and depends on H_3PO_4 doping levels, on the presence of water and temperature.[26,27] Phosphoric acid however leaks from the membranes which brings about the decrease in conductivities and the danger of the fuel cell corrosion.

Another solution to the problem of intermediate-temperature fuel cells may be the use of polymer membranes whose

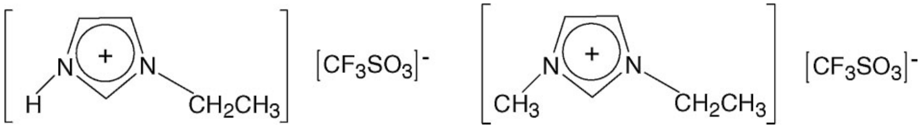

Figure 3.
A protic ionic liquid (1-ethylimidazolium trifluoromethanesulfonate) and an aprotic ionic liquid (1-ethyl-3-methylimidazolium trifluoromethanesulfonate).

proton-conducting component is an ionic liquid. Ionic liquids[28,29] are liquid salts consisting of bulky organic cations and organic or inorganic anions. Ionic liquids may be either protic or aprotic in nature (Figure 3). Protic ionic liquids are formed by proton transfer between molecules that are, respectively, Bronsted acids and bases. Aprotic ionic liquids are formed by transfer of an alkyl or similar group to the site occupied by a proton in a protic ionic liquid.

Most of the ionic liquids so far prepared contain imidazolium cation though pyridinium, ammonium, pyrrolidinium, phosphonium and sulfonium-based ionic liquids are also currently available. Most of the ionic liquids are ion-conductive, have negligible vapour pressure even at elevated temperatures and exhibit good thermal and electrochemical stabilities. Polymer membranes containing ionic liquids can be prepared by: (a) imbibing a polymer membrane with an ionic liquid,[30] (b) dissolving a polymer and an ionic liquid in one solvent, casting the film and evaporating the solvent [31] or (c) polymerizing monomers in the presence of an ionic liquid.[32] The prerequisite of the conductive membrane preparation is the compatibility of a polymer and an ionic liquid used. A compatible system polymer/ionic liquid and an incompatible one, respectively, are shown in Figure 4.

We have prepared the membranes of the fully compatible systems listed in Table 3.

The conductivities of the prepared membranes depended on the concentration of the ionic liquid in the polymer, on the conductivity of a neat ionic liquid, on the type of a polymer and on temperature. The best ionic conductivity we obtained so far was 24 mS/cm at 160 °C with the Nafion membrane containing 60 wt. % of 1-butyl-3-methylimidazolium trifluoromethanesulfonate. In a typical case, an addition of an inert polymer decreases the ionic conductivity of an ionic liquid by one order of magnitude. (Figure 5).

Selected membranes showing most promising properties were tested in the laboratory fuel cell at the operational

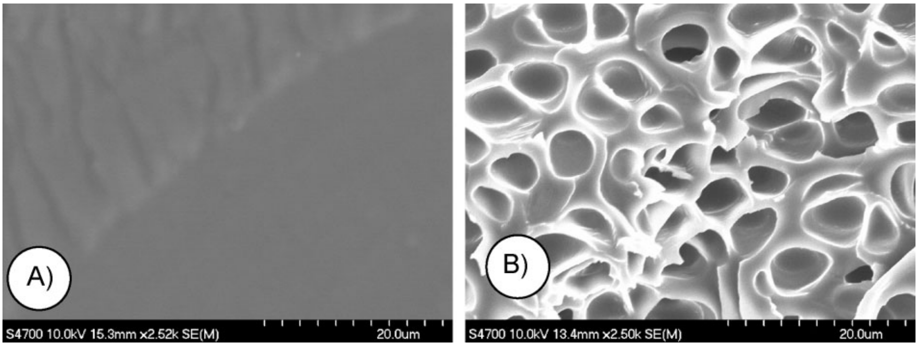

Figure 4.
SEM micrographs of the cross sections of membranes containing 50 wt. % of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. (A) Matrix polymer: poly(vinylidene fluoride-co-hexafluoropropylene); (B) matrix polymer: polybenzimidazole (J. Schauer and K. Bouzek, unpublished results).

Table 3.
Fully compatible systems polymer - ionic liquid used for the membrane preparation.

Polymer	Ionic liquid	Type of the ionic liquid
Poly(vinylidene fluoride-*co*-hexafluoropropylene)	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	Aprotic
Poly(vinylidene fluoride-*co*-hexafluoropropylene)	1-Butyl-3-methylimidazolium trifluoromethanesulfonate	Aprotic
Poly(vinylidene fluoride-*co*-hexafluoropropylene)	1-Hexyl-3-methylimidazolium trifluoromethanesulfonate	Aprotic
Poly(vinylidene fluoride-*co*-hexafluoropropylene)	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Aprotic
Poly(vinylidene fluoride-*co*-hexafluoropropylene)	1-Ethylimidazolium trifluoromethanesulfonate	Protic
Poly(acrylonitrile-co-vinylphosphonic acid)	1-Ethyl-3-methylimidazolium trifluoromethanesulfonat	Aprotic
Nafion	1-Butyl-3-methylimidazolium trifluoromethanesulfonate	Aprotic
Nafion	1-Ethylimidazolium trifluoromethanesulfonate	Protic
Poly(vinyl alcohol) crosslinked with maleic acid	1-Butyl-3-methylimidazolium trifluoromethanesulfonate	Aprotic
Poly(vinyl alcohol) crosslinked with maleic acid	1-Ethyl-3-methylimidazolium hydrogensulfate	Protic

temperatures up to 160 °C. In the first instance commercial gas diffusion electrodes (GDE) HT ELAT by E-TEK were used during fuel cell tests. Extremely poor performance was attained at the temperatures above 120 °C. This was due to the presence of Nafion binder in the structure of the GDE catalytic layer. Since dry gasses were used, Nafion phase dried out and turned into the insulation state. It was thus necessary to prepare new electrodes compatible with the novel membranes. First trial has involved polybenzimidazole as a binder. This electrode required impregnation by phosphoric acid prior the fuel cell assembly. This was necessary in order to make the catalytic layer proton conductive and to enhance the utilization of Pt catalyst by improving occurrence of the three phase contact. This approach is, however, not suitable from the point of view of testing of polymer bonded ionic liquid. It is because the phosphoric acid included in the electrode may increase proton conductivity of the ionic liquid incorporated into the membrane and thus influence the results. Therefore new generation of GDE was prepared based on the Teflon binder. In combination with a phosphoric acid doped polybenzimidazole based membrane the electrodes have reached power output of 250 mW cm^{-2} at 0.6 V (160 °C, dry gases). Unfortunately, when using the novel membranes based on the polymer supported ionic liquids the fuel cell power output did not exceed 10 mW cm^{-2}. The most probable reason for this behavior consists in low proton conductivity of the membrane under current load, as indicated by the results of electrochemical impedance spectroscopy.

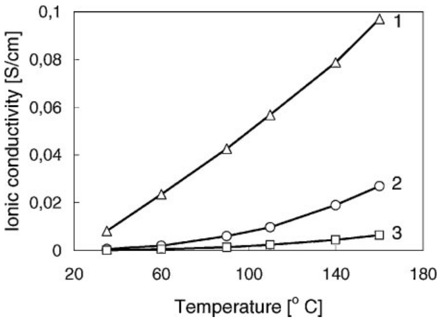

Figure 5.
Dependence of ionic conductivity on temperature. (1) neat ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate; (2) poly(vinylidene fluoride-co-hexafluoropropylene) membrane containing 60 wt. % of this ionic liquid; (3) the same membrane containing 40 wt. % of this ionic liquid (J. Schauer and K. Bouzek, unpublished results).

Conclusion

The membranes containing ionic liquids can work in hydrogen/oxygen fuel cells at temperatures above 100 °C but much research into membrane development and into gas diffusion electrodes has to been carried out to achieve power outputs suitable for practical application.

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