

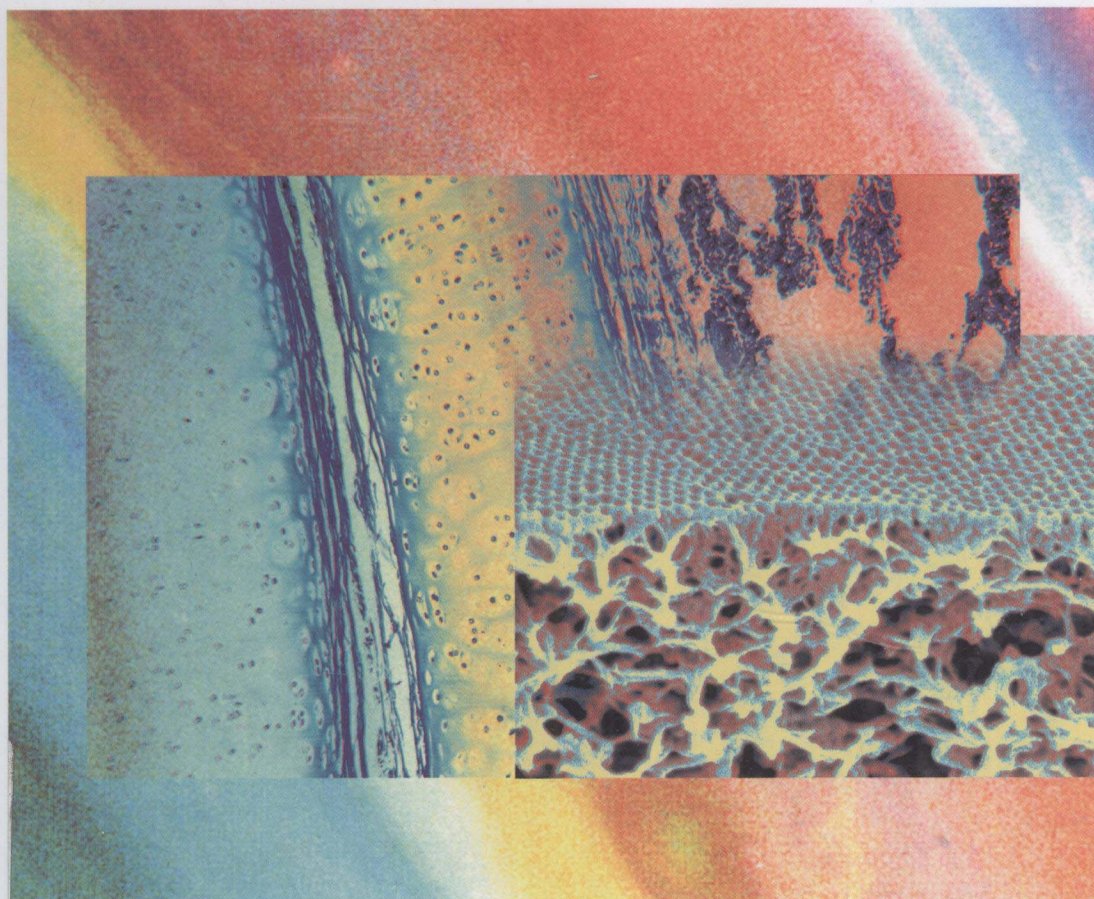
**Membrane Technology**

**Edited by Klaus-Viktor Peinemann  
and Suzana Pereira Nunes**

 **WILEY-VCH**

# **Membranes for Energy Conversion**

**Volume 2**



# Membranes for Energy Conversion

Volume 2

*Edited by*

*Klaus-Viktor Peinemann and Suzana Pereira Nunes*



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## Preface

The energy strategy is changing all over the world. There are different reasons for this: Fossil fuels will become rare in less than 50 years; more than 64% of the current petroleum reserve is located in the Middle East, while less than 14% is available in Europe, USA and the former USSR region together. Energy independence is a security issue. At least as important as these arguments is the undeniable evidence of climate change resulting from excessive emission of greenhouse gases. As a consequence different low emission renewable energy technologies are being implemented, favoring the use of biofuels and hydrogen to power our future. At the same time the modernization of conventional power plants and refineries is being stimulated to reduce their emission of CO<sub>2</sub> in a transition period when petroleum and coal are still the predominant fuel sources. In all these new technologies and transition steps, membranes have a huge opportunity to become a key player.

A clear example is the vision of a society moved by hydrogen. Hydrogen is currently produced on a large scale from natural gas. Membrane technology can offer several advantages for hydrogen separation, like for instance the possibility of integration of different processes so that hydrogen shift and purification or possibly reforming could be carried out in a single, simplified, compact membrane reactor system.

While the US has just a small part of the world's available oil, the US coal reserves are nearly equivalent to the total world oil reserve. A large program was recently launched to produce hydrogen from coal with near zero emission, using a series of clean technologies, which also include membranes.

Membranes for hydrogen separation are available for different temperature ranges. Two classes of inorganic membranes for hydrogen separation are treated in this book: palladium membranes (temperature 300–450 °C) and mixed proton and electron conductive materials (above 600 °C). For temperatures up to 550 °C molecular sieve membranes based on silica or zeolite are the state-of-the-art (M. C. Duke et al., *Advanced Functional Materials* 16 (2006) 1215–1220). For temperatures higher than 250 °C polymer membranes cannot compete but for the low temperature range they have some advantages, being easy to produce and manufacture in modules on a large scale. A potential application for this temperature range is the

recovery of hydrogen from fuel gas and platform off gas. Glassy polymers with high temperature stability like some polyimides are suitable for membranes for preferential hydrogen transport (S. Shishatskiy et al., *Advanced Engineering Materials* 8 (2006) 390–397). The best currently available polymer membranes have a  $\text{H}_2/\text{CH}_4$  selectivity of about 100 and a hydrogen permeance of  $8 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ .

A renewable source of hydrogen is water, which can be split using electrolyzers powered by wind energy. In 2006 wind farms with a total capacity of  $20.6 \times 10^3 \text{ MW}$  were available in Germany, which corresponds to about 28% of the world capacity (D. Fairless, *Nature* 447 (2007) 1046–1048). A fundamental part of the electrolyzer is a polyelectrolyte membrane.

A polyelectrolyte membrane is also the core of the low temperature fuel cell. Fuel cells are the main zero emission energy converters fed with hydrogen or renewable fuels like methanol and ethanol to power vehicles, portable devices or to supply electricity to buildings. Six chapters of this book are devoted to fuel cell membranes, covering some of the most promising material classes currently under investigation besides the more conventional Nafion-type materials. Two main challenges for membranes are connected to fuel cells for portable and automotive application: low alcohol crossover for membranes with direct feed of methanol or ethanol (portable application) and new materials for operation at  $100^\circ\text{C}$  and low humidity levels in hydrogen fuel cells (automotive application).

As mentioned above an important challenge for membranes is also the separation of  $\text{CO}_2$  from other gases as in its removal from flue gas. In modern coal power plants, potential tasks for membranes are the separation of  $\text{CO}_2$  from other combustion gases and separation of  $\text{H}_2$  from  $\text{CO}_2/\text{H}_2$  mixtures from gasification processes.  $\text{CO}_2$  separation using inorganic membranes is also a topic of this book. A big issue is  $\text{CO}_2$  separation with polymeric membranes. Different approaches for material development for membranes with preferential  $\text{CO}_2$  transport include functionalized polymers and polymer composites containing polar ether oxygens (H. Lin and B. D. Freeman, *Journal of Molecular Structure* 739 (2005) 57–74) and/or amine groups. An approach which is under investigation by different groups is the use of polymers with ethylene oxide segments. A commercial block copolymer of amide and ethylene oxide, Pebax, has a  $\text{CO}_2/\text{N}_2$  selectivity of about 60 (I. Blume and I. Pinnau *US Patent* 4 963 165). Recently, highly branched, cross-linked poly (ethylene oxide) was reported (H. Lin et al., *Science* 311 (2006) 639) with particularly high selectivity (up to 30) for  $\text{CO}_2/\text{H}_2$ .

The main competitor of fuel cells, at least in the automotive sector, is a battery system with high energy density like Li-ion. A critical component of batteries is the separator, which is also a membrane placed between the positive and the negative electrode to prevent physical contact between them, providing electronic insulation but allowing free ionic transport (S. S. Zhang, *Journal of Power Sources* 164 (2007) 351–364). The separator should also be able to activate a thermal shutdown avoiding fire or excessive heating. This is a large market for membranes. The requirements for a good separator are: (i) thickness lower than  $25 \mu\text{m}$  to reach high energy and power density, but still high enough for good mechanical strength and safety; (ii) porosity for sufficient ionic conductivity but not too high to allow shutdown in

the case of heating; (iii) good wettability for the electrolyte; (iv) low cost. The separator usually has a semi-crystalline polyolefin microporous layer like the Celgard membrane or preferably a bilayer system with layers with different melting temperatures. An interesting inorganic composite separator is the Separion, which is a flexible perforated polymeric non-woven material coated with porous ceramic layers.

The last chapter of this book deals with a quite innovative membrane technology for power production from the entropy change of mixing of fresh water and sea water, the osmotic power.

October 2007

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## 1

## Sulfonated Poly(aryl ether)-type Polymers as Proton Exchange Membranes: Synthesis and Performance\*

Baijun Liu, Dae-Sik Kim, Michael D. Guiver, Yu Seung Kim, Bryan S. Pivovar

### 1.1

#### Introduction

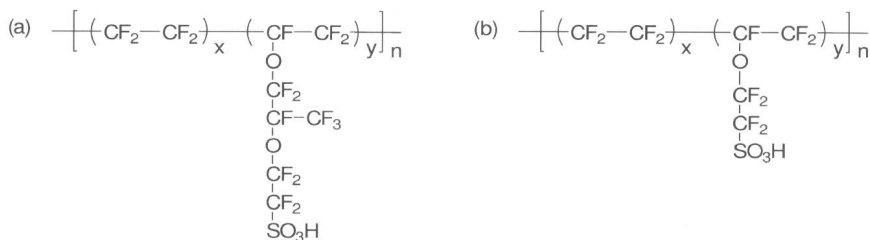
Fuel cells, which are devices for efficiently transforming chemical energy directly into electricity, are regarded as promising future clean power sources. Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) utilize polymeric proton exchange membranes (PEMs), which are a key component for transferring protons from the anode to the cathode as well as providing a barrier to fuel cross-over between the electrodes, are attracting increasing attention for use in automotive, stationary and portable electronic applications [1–3].

The PEM or solid polymer electrolyte fuel cell (SPEFC) was initially developed at General Electric by Grubb and Niedrach to provide on-board electrical power for the Gemini Earth-orbiting program in the early 1960s. The initial PEMs utilized did not exhibit long-term stability, due to the poor oxidative stability of the sulfonated polystyrene-divinylbenzene. The most practical PEM material to emerge having improved stability was Nafion, developed by the DuPont de Nemours Company in the late 1960s. This was initially used as the permselective separator in chlor-alkali electrolyzers [3,4]. The present-day Nafion series of membranes possess some attractive properties, such as excellent chemical and mechanical stabilities, and high proton conductivity because of the unique chemical structure of perfluorosulfonic acid (Scheme 1.1). The excellent performance of Nafion has promoted the further development of other PEMs with similar chemical structure to Nafion, and some of these are now commercially available. However, the high cost, low operation temperature ( $\leq 80^\circ\text{C}$ ), propensity for dehydration, high methanol crossover, and environmental recycling uncertainties of Nafion and other similar perfluorinated membranes are limiting their widespread commercial application in PEMFC and DMFC [5,6].

Apart from polymer–inorganic hybrid materials, we consider that there are three approaches for the design of alternative PEMs. The first involve polymers with a perfluoroalkyl backbone and stable side-group-acid pendants, such as aromatic pendant groups bearing sulfonic acids, which might combine the good properties

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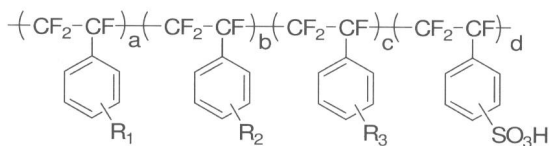




**Scheme 1.1** Chemical structures of perfluorinated polymers from DuPont (a) and Dow Chemical (b).

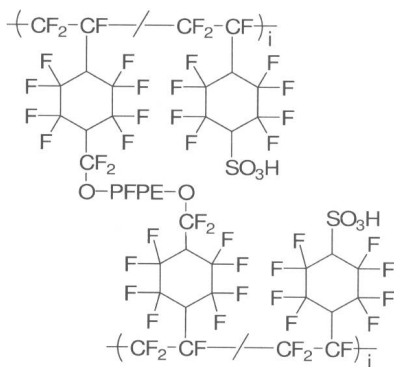
of Nafion with aromatic systems. A typical example is a polymer developed by Ballard Advanced Materials Corporation, as shown in Scheme 1.2 [7].

A few polymers with Teflon backbones and stable non-aromatic side-group acid may also show attractive performance, and a typical structure of fluorinated cross-linked polymers is given in Scheme 1.3 [8]. There are some partially fluorinated



$\text{R}_1, \text{R}_2, \text{R}_3$  = alkyls, halogens, OR,  $\text{CF}=\text{CF}_2$ , CN,  $\text{NO}_2$ , OH

**Scheme 1.2** Chemical structure of PEM with Teflon backbone and aromatic side group bearing a sulfonic acid.



**Scheme 1.3** Claimed chemical structure of crosslinked polymers with Teflon backbone.