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Preparation of ion-exchange materials and membranes

Claus Vogel, Jochen Meier-Haack *

Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany

HIGHLIGHTS

- Methods for preparation of anion- and cation-exchange materials are reviewed.
- Fuel cells are one driving force for development of stable anion-exchange materials.
- Cation-exchange materials for mid-temperature operation are available on lab-scale.
- Cost reduction in fuel cell technology by the use of anion-exchange materials

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ABSTRACT

Electro-membrane processes are successfully applied in desalination of sea and brackish water, waste water treatment, chemical process industry, and food and pharmaceutical industry. Key compound is the ion-exchange membrane, which enables the selective transport of ions. The intention of this paper is to briefly review synthetic aspects in the development of new ion-exchange materials for both anion-exchange and cation-exchange purposes.

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1. Introduction

Today membrane-based separation processes are state-of-the-art in industry. They are used in water treatment like wastewater treatment, drinking water production, ultraclean water production e.g. in semiconductor industry, in food and pharmaceutical industry and chemical industry (e.g. chlor-alkali electrolysis). For most applications non-charged membranes from chemically inert materials like polypropylene (PP), polyethylene (PE), poly(vinylidene fluoride) (PVDF), poly(tetrafluoro ethylene) (PTFE), polysulfone (PSU), poly(ether sulfone) (PES), polyacrylonitrile (PAN), (aromatic) polyamide (PA) or cellulose acetate (CA) are employed. However, charged membranes might be beneficial for some of the various separation processes listed in Table 1, but are a necessary prerequisite for electro-driven applications such as electrodialysis, electrodeionization or energy conversion and storage (fuel cells, reverse electrodialysis, redox batteries). A

list of commercially available ion-exchange membranes and their basic properties can be found for example in [1–3].

Typical cation-exchange groups are sulfonic acids ($-\text{SO}_3\text{H}$), carboxylic acids (COOH), phosphonic acids ($-\text{PO}_3\text{H}_2$) and phenolic hydroxide groups. Materials with such groups fixed to a polymer backbone reject anions but allow the passage of cations. On the other hand ion-exchange materials containing ammonium ($-\text{NR}_3^+$; with R = H or organic residue) or phosphonium ($-\text{PR}_3^+$; with R = alkyl or aryl) groups are anion selective and allow the selective transport of anions through the respective material [4]. In general ion-exchange membranes should show the following properties:

High permselectivity: ion-exchange membranes should be highly permeable for counter-ions and impermeable for co-ions for high efficiency

Low electrical resistance: as high as possible permeability of the counter-ions under the driving force of an electrical potential gradient for high efficiency

Good form and mechanical stability: the membrane should not swell or shrink too much during operation in order to avoid mechanical stress and should be mechanically strong

* Corresponding author. Tel.: +49 351 4658 519; fax: +49 351 4658 290.
E-mail address: mhaack@ipfdd.de (J. Meier-Haack).

Table 1
Survey of important membrane-based separation processes.

Membrane process	Driving force	Type of membrane
Microfiltration (MF)	ΔP	Porous
Ultrafiltration (UF)	ΔP	Porous
Nanofiltration (NF)	ΔP	Porous
Reverse osmosis (RO)	ΔP	Dense
Dialysis	Δc	Porous
Electro membranes processes	ΔE	Dense
Electrodialysis (ED)		
Electrodeionization (EDI)		
Reverse electrodialysis (RED)		
Fuel cells (FC)		
Pervaporation (PV)	Δc (partial pressure)	Dense
Gas separation (GS)	Δc (partial pressure)	Dense
Membrane distillation	ΔT	Porous

Good chemical stability: the membrane material has to withstand operations in a wide pH-range and temperature in the presence of oxidizing species.

Most studies dealing with electro-membrane processes employ commercial membranes. However, evaluating new membrane materials opens up the opportunity to further improve the related processes. There have been some reviews in the past concerned with the preparation of ion-exchange materials but with focus either on cation-exchange membranes or anion-exchange membranes for fuel cell applications [5–8]. Nasef and Güven published a more general review on ion-exchange materials and membranes but with focus on irradiation-grafted materials [9]. The above mentioned reviews mainly describe the preparation and properties of ion-exchange materials but to a lesser extent procedures for the introduction of ionogenic groups into the polymer backbone. Therefore, this contribution is aimed at reviewing synthetic strategies towards new ion-exchange materials covering both anion and cation-exchange materials. The main focus is put on the introduction of ionogenic groups into an existing polymer backbone rather than the preparation of the polymeric material itself. A second focus is set on temperature stable anion-exchange materials, since these are very important for the development of cost-efficient alkaline fuel cell systems.

2. Preparation of cation-exchange membranes

2.1. Sulfonic acid containing ion-exchange materials

A large variety of cation-exchange materials including membranes are described in the literature. Among the possible cation-exchange groups (Fig. 1) sulfonic acid groups are mostly used in cation-exchange materials.

The most prominent representatives are polystyrene sulfonic acid and perfluoroalkyl sulfonic acids. Cross-linked polystyrene sulfonic acid is mainly used as beads in ion-exchange columns but also as membranes in the early days of fuel cell applications (Fig. 2A). Although proton conductivity is high, polystyrene sulfonic acid suffers from

chemical instability of the tertiary carbon in the polymer backbone [10]. In order to enhance the chemical stability of polystyrene sulfonic acid Ballard introduced poly(α,β,β -trifluorostyrene sulfonic acid) (Fig. 2B) as ion-exchange membrane material for fuel cell applications [11], which is known as BAM-3 (Ballard Advanced Material, generation 3). Although a vinyl residue is mentioned in the patent [11], only noncross-linked polymers were described in the examples. However, upon sulfonation cross-linking might occur by formation of sulfone bridges, depending on the applied reaction conditions [12]. The advantage of this polymer besides its better chemical stability compared to polystyrene sulfonic acid is its solubility in common dipolar aprotic solvents like dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP).

Perfluoroalkyl sulfonic acids (PFSA) are well known under the trade name Nafion® from DuPont or other companies like Asahi Glass (Flemion®, Selemion®), Asahi Kasei (Aciplex®), FuMa Tech (Fumion F®) or Solvay (Aquivion®). Most of the perfluoroalkyl sulfonic acids (and perfluoroalkyl carboxylic acids (PFCA)) were developed for the membrane based chlor-alkali electrolysis. Nowadays these materials, especially the PFSA, are also widely used in fuel cell applications due to their high chemical stability and high proton conductivity under highly hydrated conditions. The major differences between the various PFSA materials are the length of the sulfonic acid bearing side-chain and the number of side-chains, both determining the equivalent weight (EW) or ion-exchange capacity (IEC) (Fig. 3). However, the complex synthesis and safety measures during production of monomers and polymers makes these materials quite expensive (Fig. 4). Furthermore, the maximum operation temperature considering mechanical stability and conductivity of the Nafion-type membranes is well below 100 °C under highly humidified conditions, which is disadvantageous in fuel cell powered vehicles. From automotive industry an operation temperature above 100 °C at ambient pressure is requested in order to simplify the water and temperature management [13]. Shortening the side-chain like in the Aquivion membranes (or formerly Dow membranes) turns the mechanical properties more towards PTFE and might allow for a higher operation temperature [14].

Especially the demand for highly conducting membranes at temperatures above 100 °C and/or at low humidity as well as cost effective alternative materials for fuel cell applications has initiated world-wide research activities. As a result, a vast number of publications has appeared (and still do), which have been summarized in numerous review articles and books [15–18]. These materials are not only suitable for fuel cell applications but may also be applicable in other electro-membrane processes [19,20].

The sulfonic acid group is the most often used cation-exchange group in fuel cell applications due to its high acidic strength (low pK_A) leading to high proton (ion) conductivities [21]. On the other hand the phosphonic acid group is thought to be more suitable for medium or high temperature membrane based fuel cells due to its amphoteric character and the ability to transport protons even under anhydrous conditions by the Grotthuss mechanism [22]. For other electro-membrane processes the use of polymeric phosphonic acids or carboxylic acids might be sufficient. The

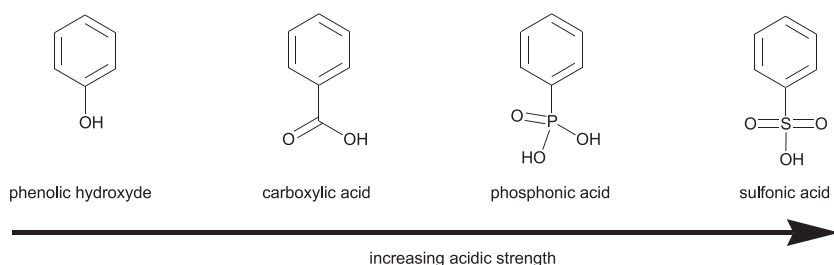


Fig. 1. Possible cation-exchange groups.

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