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# High pressure synthesis and transport properties of a perfluorinated sulfocationic exchange membrane

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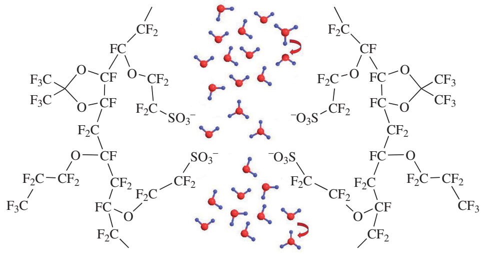
**A new perfluorinated sulfocationic polymer and a membrane based thereon have been produced using the thermally initiated high-pressure polymerization. The proton conductivity of obtained material is higher than that of commercial Nafion membranes and reaches 57 mS cm$^{-1}$ at 21 °C and 114 mS cm$^{-1}$ at 79 °C.**

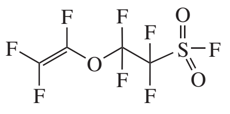


Renewable energy sources play a significant role in the modern world, hydrogen energetics being an important component.[1–3] Low-temperature fuel cells are the most cost-effective and popular in this field. Proton-conducting membranes are their main component. Of these, the dominating role belongs to perfluorinated Nafion materials that possess a high chemical stability and good transport characteristics.[4,5] However, they also have some drawbacks, such as a fast decrease in the conductivity along with decreasing the humidity as well as expensiveness. The latter is mainly due to the complexity of technology of polymerization and production of membranes. At this end, efforts to develop novel technologies for the membrane production are underway, and a number of analogues has already appeared on the market. The development of new synthetic methods for the membranes possessing a combination of the high conductivity and selectivity is in progress.[6–8]

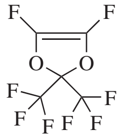
In recent years, approaches to the production of hybrid membrane materials based on commercially available products have been developed. Some methods include a modification of the membranes with inorganic fillers, such as silicon dioxide[9] or heteropolyacids[10] and their acid salts.[11] In addition, new methods for the synthesis of perfluorinated membranes were also explored, *e.g.*, a method for the polymerization in an emulsion was suggested.[12] A method for polymerization of perfluoromonomers at high pressures with thermal initiation, which allows previously inert monomers[13] to be involved in the reaction, was also proposed. It was demonstrated that under these conditions, the difference in the reactivity of monomers leveled off to a considerable extent.[14]

In light of this, the purpose of this work was to obtain perfluorinated sulfocationite polymers, employing the effect of high pressure, and to study the transport properties of resulting membranes.

The following starting materials were selected for the synthesis of perfluorinated polymers: perfluoro(3-oxapent-4-ene)sulfonyl fluoride **1**, perfluoro-2,2-dimethyl-1,3-dioxole **2**, and perfluoropropylvinyl ether **3**. Monomer **3** was purified by the extractive rectification.



**1**



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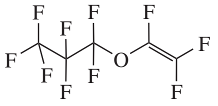
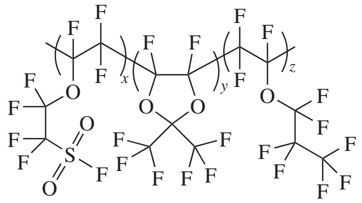


**3**

These monomers were introduced in the synthesis[†] according to the procedure similar to that reported previously.[14] The yield of three-component copolymer **4** was 85–87%.



**4**

The molar ratio of monomer moieties in the copolymers was determined using $^{19}$F NMR spectroscopy (300 MHz), taking into account the ratio of integral intensities of the signals at +40 (F in sulfonyl fluoride) and at ~ –79 ppm (trifluoromethyl groups). The molar content of monomer moieties in the 1 : 2 : 3 three-component copolymer was ~4 : 3 : 3. The $^{19}$F NMR and IR spectra of the obtained polymer **4** are given in the Online Supplementary Materials (Figures S1 and S2).

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[†] *Synthesis of polymer* **4**. Sulfoester **1**, dioxole **2**, and perfluoropropylvinyl ether **3** were preliminarily distilled under argon atmosphere and evacuated at –196 °C in order to remove any dissolved $O_2$. After that, the mixture of monomers in the molar ratio of 1 : 1 : 1 was placed into a Barostat unit at 10 °C in a Teflon tube. The reaction mixture was maintained at 150 °C under the pressure of 104 atm for 20 h.

**Table 1** Water uptake, proton conductivity, and conductivity activation energy in polymer **4** at various relative humidities (RH).

| RH (%) | $H_2O$ content (%) | Proton conductivity[a]/ mS cm$^{-1}$ | Conductivity activation energy/kJ mol$^{-1}$ |
|---|---|---|---|
| 100[b] | 59 | 59 | 10.4 ± 0.3 |
| 95 | 29 | 13 | 17.1 ± 0.6 |
| 75 | 9.4 | 2.2 | 30.0 ± 0.7 |
| 58 | 6.2 | 0.42 | 39 ± 1 |
| 32 | 1.4 | 0.0084 | 49.1 ± 0.4 |

[a] At 25 °C. [b] In a contact with water.

The polymer was used for a production of the membrane.‡ The disappearance of peaks at 1470, 820–790 and 606 cm$^{-1}$ in the IR spectrum corresponding to the vibrations of $SO_2F$ group[15] indicated the completeness of hydrolysis into the acid form. After the hydrolysis and hydration, a broad band of OH stretching vibrations, which belongs to $H(H_2O)_n^+$ proton-containing groups contained in the membrane, appeared in the region of 3000–3700 cm$^{-1}$ in the polymer spectrum. Moreover, a peak at 1650 cm$^{-1}$ corresponding to the deformation vibrations of $H_2O$ molecules appeared with its shoulder at high frequencies due to the presence of hydrated proton forms in the membrane.

Table 1 summarizes data on the water uptake and activation energy for the proton transfer in the produced polymer. Commercial Nafion with an equivalent weight of 1200 was selected for the comparison. The water uptake for polymer **4** (59%) upon a contact with $H_2O$ exceeds that in Nafion (22%) almost three-fold. This indicates a higher elasticity of the membrane matrix, which results in a higher volume of pores and channels system in the obtained membrane. When the relative humidity (RH) decreases down to 32%, the polymer is dehydrated to the $H_2O$ content of 1.4%.

Copolymer **4** demonstrated a high proton conductivity that was 57 mS cm$^{-1}$ at 57 °C and reached 114 mS cm$^{-1}$ at 79 °C (Figure 1). The conductivity of membrane at 25 °C decreases from 13.2 mS cm$^{-1}$ to 8.4 μS cm$^{-1}$ along with decreasing in RH from 95 to 32%, while the activation energy increases from 17.1 ± 0.6 to 49.1 ± 0.4 kJ mol$^{-1}$ (see Table 1). These observations match a change from the Grottgus mechanism to the hopping mechanism of proton conductivity.[16] Upon a decreased humidity and the corresponding decrease in the water uptake in the membrane, the distance between the $H_2O$ molecules increases, and the activation energy of proton hops rises, thus this stage becomes the limiting step.

The diffusion permeability of HCl for the studied membranes is rather high, *viz.* $9.73\times10^{-7}$ cm$^2$ s$^{-1}$ (Table 2). It characterizes the transport rate of anions $\sigma$ whose concentration in the membrane is much lower. It is known that the transport of anions across a membrane proceeds through an electrically neutral solution localized in the center of a pore,[5] since a double electric layer formed by dissociation of sulfonic groups, which excludes anions, is located along the pore walls. Due to the increase in the volume of the system of pores and channels as compared with commercial Nafion, the volume of this electrically neutral solution grows and, accordingly, the diffusion permeability of HCl increases.

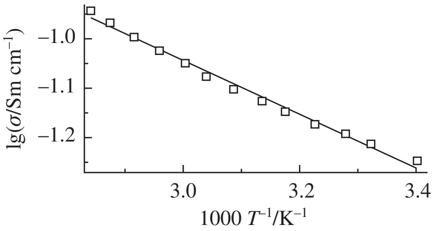

**Figure 1** Dependence of the conductivity of the resulting membrane on temperature upon its contact with water.

**Table 2** Diffusion permeability and coefficients of mutual diffusion of HCl and NaCl solutions through the membrane.

| Diffusion permeability of 0.1 M HCl solution/cm$^2$ s$^{-1}$ | Diffusion permeability of 0.1 M NaCl solution/cm$^2$ s$^{-1}$ | Mutual diffusion coefficient of 0.1 M HCl/NaCl solution/cm$^2$ s$^{-1}$ | Anion transfer number |
|---|---|---|---|
| $9.73\times10^{-7}$ | $5.54\times10^{-7}$ | $4.75\times10^{-6}$ | 0.17 |

In conclusion, it has been demonstrated that the method of thermally initiated high pressure polymerization is promising for the synthesis of membrane materials based on perfluorinated sulfocationite polymers. The membranes obtained in this work possess the high proton conductivity that reaches upon a contact with water 57 mS cm$^{-1}$ at 21 °C and 114 mS cm$^{-1}$ at 79 °C.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.019.

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‡ *Procedure for the membrane production.* The polymer in its sulfonylfluoride form was dissolved in perfluorotoluene (10 ml) at room temperature. The resulting solution was cast on a Petri dish and dried overnight at 50 °C on a heating table. The obtained film was boiled four times for 2 h in 1 M NaOH solution to hydrolyze the sulfonylfluoride. After that, the membrane was consistently conditioned with $H_2O_2$ solution (3 wt%), HCl solution (3 wt%), and with deionized $H_2O$ ($\sigma$ = 18.2 MSm cm$^{-1}$) at 80 °C.