Membranes

Copolymerization of Ethylene, Tetrafluoroethylene, and an Olefin-Containing Fluorosulfonyl Fluoride: Synthesis of High-Proton-Conductive Membranes for Fuel-Cell Applications**

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Fuel cells, which are devices that convert the chemical energy stored in the fuel directly into electricity, are one of the most important technologies in the 21st century. They not only provide pollution-free clean energy, but also give high-quality and more-reliable power.[1] Of all the types known today, the technology based on proton-exchange membrane fuel cells (PEMFC) is the most attractive for various applications, especially transportation and for stationary and portable devices.[2] The most important component of the PEMFC is the membrane electrode assembly (MEA), at the heart of which is the proton-conductive membrane. The key functions of the membrane are to transport protons from the anode to the cathode of the cell and to separate the fuel and the oxidant.

Significant resources have been devoted worldwide to the development of high-performance and reliable membranes.

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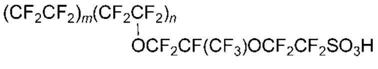
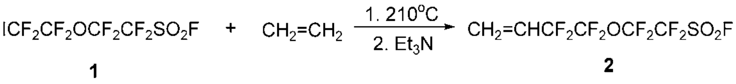
Academic researchers are working on the development of new membrane materials, while government and industry are driving the commercialization of fuel-cell technology.[3] Although many proton-exchange membranes have been developed, the perfluorinated-ionomer membrane nafion is still the best known today.[4] Nafion, which was invented and introduced by DuPont in the early 1960s, revolutionized fuel-cell technology, and is synthesized by copolymerization of tetrafluoroethylene (TFE) and a perfluorovinyl ether (PSEPVE) containing a sulfonyl fluoride.[5] Although nafion is the most widely used membrane in fuel cells and provides the best overall performance at temperatures below 100 °C, it is relatively expensive. The high cost of nafion is primarily attributed to the difficult polymerization and the need for an expensive monomer (PSEPVE). In addition, perfluorinated nafion is difficult to further modify to improve its desired properties. We report here a new, potentially lower cost and high-performance proton-conductive membrane for fuel-cell applications.



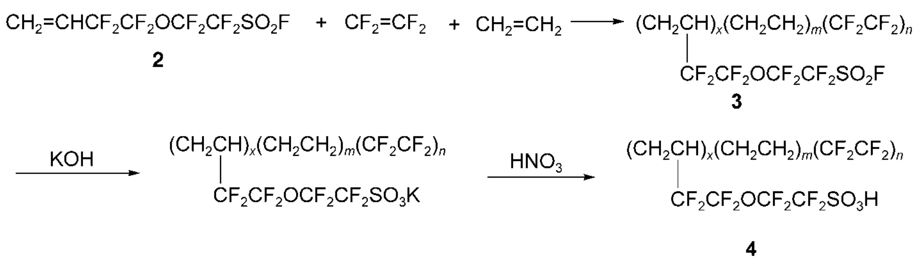
$(CF_2CF_2)_m(CF_2CF_2)_n$ with $OCF_2CF(CF_3)OCF_2CF_2SO_3H$

TFE/PSEPVE, nafion

Although perfluorinated polymers provide the best combination of both thermal and chemical properties, selective introduction of H atoms into polymers does not affect the stability dramatically.[6] In fact, a copolymer of ethylene and tetrafluoroethylene (ETFE), tefzel®, made by DuPont, still has excellent thermal and chemical stability and has better mechanical properties than perfluorinated polymers.[7] In addition, the ETFE portion can be cross-linked readily to further improve its properties, whereas perfluorinated polymers are extremely difficult to modify.[8] More importantly, TFE and ethylene copolymerize mostly alternately, which may help in the incorporation of olefins other than expensive perfluorovinyl ethers.[9] If this is the case, we might be able to design a low-cost, fluorinated monomer containing a sulfonyl fluoride group. Monomer **2** was readily synthesized from ethylene and **1**, which is commercially available, or by reaction of TFE, FSO_2CF_2COF, and I–Cl in one step.[10]



Although copolymerization of **2** and TFE was unsuccessful, and only a small amount of **2** was incorporated into the polymers, we found that copolymerization of TFE, ethylene, and **2** was more effective. Copolymerization in the presence of an organic peroxide, such as lupersol 11, as an initiator in 100 mL of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113) in a 240-mL shaker tube at 60 °C for seven hours provided the terpolymers shown in Table 1.



All polymerizations proceeded smoothly to give polymers in good yields. The remarkably high conversion of termonomer **2** makes this polymerization system particularly attractive for practical applications. In most cases, conversions of **2** were up to 90 %. The polymerization pressure drops with polymerization time, while the rate of polymerization decreases with an increase of monomer **2** in the presence of given amounts of TFE and ethylene. Incorporation of termonomer **2** increases in the polymers with an increase of the pre-charged amount of **2**. It is interesting to note that the ratio

Table 1: Coolymerization of TFE, ethylene (E), and **2**.

Entry	Monomers [g, mol]	(TFE + E)/**2** [mol]	ΔP[a] [psi/7 h]	Yield [g]	Analysis[b] (TFE + E)/**2**	EW	Conductivity[c] [mS cm^{-1}]
1	TFE (22, 0.22) E (7, 0.25) **2** (10, 0.031)	15.2	316	35.7	$(E)_{7.7}(TFE)_{6.5}(\mathbf{2})$ 14.2/1	1192	40
2	TFE (22, 0.22) E (7, 0.25) **2** (13, 0.040)	11.8	247	33.5	$(E)_{7.3}(TFE)_{5.5}(\mathbf{2})$ 12.8/1	1080	75.7
3	TFE (22, 0.22) E (7, 0.25) **2** (14, 0.043)	10.9	282	35.8	$(E)_{6.4}(TFE)_{5.5}(\mathbf{2})$ 11.9/1	1055	77.8
4	TFE (22, 0.22) E (7, 0.25) **2** (15, 0.046)	10.2	222	30.2	$(E)_{6.2}(TFE)_{3.7}(\mathbf{2})$ 9.9/1	870	94.6
5	TFE (22, 0.22) E (7, 0.25) **2** (16, 0.049)	9.6	244	35.5	$(E)_{5.7}(TFE)_{4.0}(\mathbf{2})$ 9.7/1	886	99.6
6	TFE (22, 0.22) E (7, 0.25) **2** (20, 0.061)	7.7	186	35.6	$(E)_{5.4}(TFE)_{3.3}(\mathbf{2})$ 8.7/1	807	102
7	TFE (22, 0.22) E (7, 0.25) **2** (25, 0.077)	6.1	152	30.6	$(E)_{3.6}(TFE)_{3.0}(\mathbf{2})$ 6.6/1	727	122

[a] Pressure change between beginning and end of polymerization in 7 h. [b] Based on elemental analysis. [c] At room temperature.

of TFE plus ethylene to **2**, (TFE + E)/**2**, in the polymers is similar to that of the precharged monomers.

Terpolymers **3** show excellent thermal stability. As observed in the TGA studies, the polymers start to decompose at about 370 °C and a 10 % weight loss occurs up to 425 °C. DSC analysis indicated that the polymers have no melting points, except for the polymer of entry 1, which has a broad melting point at 210 °C, although X-ray diffraction studies showed that the polymers have some degree of crystallinity. The degree of crystallinity decreases with increasing amounts of incorporated **2** in the polymers. These polymers are insoluble in common organic solvents at room temperature, so it is difficult to obtain their molecular weights.

All terpolymers **3** were readily pressed to transparent, strong and tough films at 220–250 °C, thus indicating their high molecular weight. The films were hydrolyzed with 10 % KOH in MeOH/H_2O/DMSO (4:5:1, *v*/*v*/*v*) at 60 °C to give the potassium salt of the ionomer membrane. The films became light yellow in color when hydrolysis was carried out above 100 °C. This is probably a consequence of the attack of the hydroxy anion on the backbone of the polymers. The potassium ionomers were immersed in 10 % HNO_3 at 60 °C for two hours twice, and then washed and boiled with deionized water several times to obtain membranes **4**.

The proton conductivity of **4** is, in general, similar to, or higher than that of nafion, and depends on the amount of incorporated termonomer **1**. It was found that the conductivity follows a linear relationship with the ratio of units of (TFE + ethylene)/**2**, or with equivalent weight (EW), as indicated in Table 1. Interestingly, the conductivity of the new membranes is higher than that of nafion samples containing the same mol percent of PSEPVE. For example, membranes containing less than 10 mol % of **2** (entries 4 or 5 of Table 1) have the same conductivity as nafion 117, which contains 15 mol % PSEPVE. Membranes containing 15 mol % of **1** (entry 7) have a conductivity of 122 $\mathrm{mS\,cm^{-1}}$, which is 22 % higher than that of nafion 117.

Although the exact reason for the high conductivity of membrane **4** is not fully understood, the more-polar and flexible backbones of the polymer and lower equivalent weight may, in part, be responsible for the proton conduction, as a result of higher water uptake.[11] In fact, the membrane in entry 5 takes-up 49 % (by weight) water compared with 39 % water for nafion under the same conditions. A clear phase-separation in **4** (entry 5) between the hydrophilic sulfonic acid and the hydrophobic hydrofluorocarbon backbone was observed by atomic-force microscopy (AFM; Figure 1), which is very similar to the images generated from nafion.[12]

The experimental membrane **4** from entry 5 in Table 1 without any optimization was tested in a direct MeOH fuel-cell. The membrane and electrode assembly required for the fuel-cell evaluation was fabricated using a standard method.[13] The anode and cathode catalysts were Pt–Ru and Pt black, respectively, and the loadings were kept close to 4 $\mathrm{mg\,cm^{-2}}$. Commercial carbon cloths—E-Tek's ELAT and Zoltek's plain carbon cloth—were used as the cathode and anode gas diffusion backing, respectively. The anode was fed with a 1 M methanol/water mixture at a rate of 25 $\mathrm{mL\,min^{-1}}$, and the cathode with oxygen (3 $\mathrm{L\,min^{-1}}$). The cell was heated to 80 °C, and the fuel-cell performance data were recorded. The fuel-cell performance of the membrane **4** is compared with the performance of commercial nafion 115 under the same conditions in Figure 2. The new 5-mil (127 µm) membrane exhibits a similar power output to a 5-mil commercial nafion membrane, although it has 9 % higher methanol crossover ($10.9\times10^{-4}\,\mathrm{g\,min^{-1}\,cm^{-2}}$ for membrane **4** and $9.9\times10^{-4}\,\mathrm{g\,min^{-1}\,cm^{-2}}$ for 5-mil nafion). This difference is partly a consequence of the variation in the thickness of the new membrane. We anticipate that higher EW samples may reduce the methanol crossover significantly. Of course, the high EW also affects the fuel-cell performance, although cross-linking may reduce MeOH crossover and further improve the fuel-cell performance.

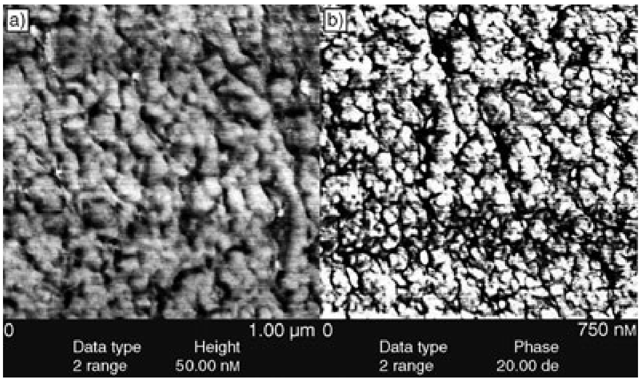


Figure 1. AFM images: a) Tapping-force height: 50 nm scale; b) phase: 750 nm scale.

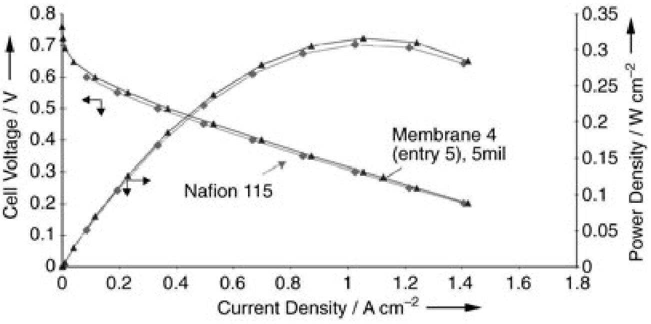


Figure 2. MeOH/O_2 fuel-cell performance with membrane **4** (entry 5) at 80 °C by monitoring cell voltage and power density versus current density. The anode was fed with 1 M methanol at a rate of 25 $\mathrm{mL\,min^{-1}}$ and the cathode was fed with oxygen at a rate of 3 $\mathrm{L\,min^{-1}}$.

In conclusion, we have discovered an effective copolymerization of tetrafluoroethylene and ethylene with **2** to give melt-processable terpolymers, which can be readily hydrolyzed and acidified to give membranes. The new membranes exhibit excellent conductivity and stability. The fuel-cell performance is comparable to, or slightly better than, that of nafion, although it is still to be optimized. Their polymeric lithium salts also exhibit excellent lithium-ion conductivity and are attractive candidates for lithium-battery applications. The new membranes could be produced more cheaply because of the simple polymerization process and the low monomer cost.

Experimental Section

General preparation of membranes: A 210-mL, stainless-steel tube was charged with F113 (100 mL), **2** (15 g), and lupersol 11 (0.5 g), and attached to a gas manifold. The tube was cooled in dry ice and the contents degassed by several cycles of evacuation and repressurization with nitrogen gas. After the final evacuation step, the tube was pressurized with ethylene (7 g) and TFE (22 g). The tube was then sealed and heated to 60 °C and held for 7 h to effect the polymerization. After completion of the polymerization, any remaining ethylene and TFE were removed by venting, and the remaining white solid was washed with MeOH and dried in a partial vacuum oven at 100 °C to give 30.2 g of polymer. IR(KBr): $\tilde{\nu} = 1464\ \mathrm{cm}^{-1}$ (SO_2F). Elemental analysis of the polymer indicated that its composition was $(CF_2CF_2)_{3.7}(CH_2CH_2)_{6.2}(CH_2CHCF_2CF_2OCF_2CF_2SO_2F)$ on a molar basis, based on C 34.68 %, H 2.64 %, F 50.65 %, and S 3.72 %. DSC showed that the polymer had no melting point. A 10 % weight loss was noted up to 430 °C under N_2 by TGA. A colorless, transparent, and tough film was pressed by placing a sample of the polymer between the platens of a hydraulic press and heated to 225 °C with a ram force 20000 lbs. This film was then immersed in a suspension of 10 % KOH in H_2O/MeOH/DMSO (5:4:1 *v*/*v*/*v*) at 60 °C for 6 h. The film was removed from the solution, washed with water many times, and then treated with 10 % HNO_3 at 60 °C for 2 h twice. It was then washed with deionized water until neutral, and then boiled in deionized water for 1 h.

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