



Fabrication of Aquivion-type membranes and optimization of their elastic and transport characteristics

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Abstract

The solution casting technology was applied to manufacture thin polymer films (~20–30 μm) from the ionomer solution of perfluorinated polymer with short side chains (an analogue of the commercial polymer Aquivion®). The influence of annealing temperature on the mechanical properties (elastic limit), proton conductivity, and heat capacity was investigated. The elastic limit, glass transition temperature, and proton conductivity of the samples were found to reach their maximum values at the annealing temperature 170 ± 5 °C. Comparative studies of membrane-electrode assemblies (MEA) using the commercial (Nafion NR212) and solution-casted membranes were carried out. MEA with optimized Aquivion-type membranes showed satisfactory values of fuel crossover and maximum output power. The results of the conducted studies show that the prepared Aquivion-type membranes are very promising for practical application in MEA.

Keywords Materials preparations · PEM-FCs · Polymer electrolytes · Proton conductors

Introduction

The current interest in proton-conductive polymers is largely due to their practical use as proton-exchange membranes in low-temperature hydrogen fuel cells. At present, the most widespread membranes are those developed in the mid-60s by DuPont™ using perfluorinated sulfonopolymer Nafion®. This polymer consists of long perfluorinated hydrocarbon chains with side branches ending with sulfogroups [1]. The Nafion® membranes

became the first stable and one of the most functional solid electrolytes in terms of basic fuel cells parameters, and now, Nafion® is the most common commercial membrane [2, 3]. The thickness of DuPont™ Nafion® membranes varies between 20 and 200 μm, the average proton conductivity at room temperature is about 0.1 S/cm, and the membrane retains the required functional parameters in the fuel cell up to 10,000 h [2, 3]. The water confined in the micropores of the membrane plays an important role in the proton transport [4, 5], and the operating temperature of the fuel cells with a Nafion membrane does not exceed 90 °C because of the rapid degradation of the electrolyte at a higher temperature, leading to a change in the polymer structure and a decrease in the proton conductivity [2, 3]. When a fuel cell with such a temperature limit is used, the platinum catalyst is poisoned on the electrodes due to impurities in hydrogen (especially, carbon monoxide). Since an increase in the operating temperature above 130 °C could significantly reduce the catalyst poisoning, many attempts have been made to modify Nafion®, as well as to develop alternative ionomers for proton-exchange membranes with a higher operating temperature [6–8].

In this respect, the development of perfluorinated polymers with shortened chains could be very promising. In particular, the Aquivion-type polymer is shown to have an improved water retention performance, a higher proton conductivity at the same temperature and humidity, and an increased mechanical and chemical resistance compared to Nafion® [9–11].

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Recently, a fuel cell using the Russian analogue of the Aquivion® polymer synthesized by the method of water-emulsion polymerization of fluoromonomers was investigated in [12, 13]. This method allows obtaining an Aquivion-type ionomer with a much lower cost than ionomers of other commercial proton-conducting polymers. Some electrochemical characteristics of membrane-electrode assemblies (MEA) using Aquivion-type membranes and commercial Nafion® membranes were measured and compared in ref. [13]. The Aquivion®-based MEA demonstrated higher output power and better thermal stability when compared with their Nafion-based analogues [14, 15]. Note also the advantage of Aquivion® membranes in other electrochemical cells, e.g., water electrolysis where these system operate stably at high potentials [16]. These encouraging results were not however supplemented with measurements of the mechanical strength and proton conductivity of the Aquivion-type membranes under different operating conditions, and the method used to obtain the membranes was not described. At the same time, this information is of primary importance for evaluating the advantages of perfluorohydrocarbonic short chain polymers in comparison with Nafion® for the use as electrolyte in the fuel cells.

The present work is aimed at obtaining Aquivion-type polymer membranes by solution casting method and studying their mechanical strength, transport, and calorimetric characteristics as function of the annealing temperature. The membranes with the optimal mechanical strength-conductivity properties were further used to fabricate MEAs, and their electrochemical characteristics were examined in a model fuel cell.

Experimental

The Aquivion-type polymer membranes studied in this work were prepared by the solution casting method. Aquivion type of copolymer powder was prepared using modified emulsion method described in ref [12]. Wet copolymer powder equivalent weight about 850–870 in SO₃H-form was dissolved in isopropanol by boiling with Liebig condenser for 2 h. Then, solution was cooled to 20 °C, filtered, and centrifuged.

To prepare a polymer film, 0.8 ml of the ionomer was casted onto a glass substrate 4 × 4 cm² in size, and the sample was air-dried for 1 h under normal conditions. The second and third layers of the ionomer were then applied in the same way and the resulting membranes were annealed for 20 h at different temperatures from 80 to 220 °C. Each annealed membrane was protonated and cleaned of organic residues in a 1-M solution of H₂SO₄ and a 3% solution of H₂O₂ at 80 °C for 4 h, and then triple-rinsed in deionized water for 1 h. All obtained samples were stored in deionized water.

The elastic strain limit was chosen as a criterion for the mechanical strength of the produced membranes. The samples in the form of rectangular fragments measuring 20 × 5 mm² were cut from different parts of the polymer film and dried at room temperature for 4 h. The experiments were carried out at room temperature on the TA Q800 DMA instrument. The length and width of the samples were determined with an accuracy of ±0.01 mm and the thickness was measured to within ±0.001 mm.

Within one experiment, measurements of multiple pieces of the same membrane (not less than 5 pcs.) were carried out, and those fragments were taken mainly from the central part of the membrane, where their thickness was more uniform. Then, the average mechanical stress dependence of the membrane, σ , versus its deformation ε was plotted.

The value of proton conductivity was determined from the impedance spectra measured in the longitudinal direction using four-probe method. For these purpose, 5 × 35 mm² sample of membrane was drained with filter paper and clamped between four contacts of platinum wire ($\varnothing = 1$ mm) in the cell [17]. The cell was placed in a sealed glass thermostatic container with water in order to reach 100% humidity conditions. The hydrogen was passed for an hour through the solution before the measurement and then workspace of the cell was heated to the desired temperature (20, 30, 50, and 70 °C). In some cases, the proton conductivity was measured directly in an electrochemical cell in order to check the isotropy of transport characteristics. The impedance spectra were measured with spectrometer Elins P-40 x in the range of 0.5 Hz to 50 kHz in potentiostatic mode. The amplitude of the applied voltage was equal to 100 mV.

Calorimetric studies were carried out during heating from 50 to 300 °C in argon atmosphere using a Perkin-Elmer DSC-7. Heating rate was 10 K/min; sample weight was varied in range of ~5–12 mg.

MEA of 22 × 22-mm² size was fabricated on the membrane which revealed the best characteristics of two parameters (mechanical strength and conductivity) simultaneously. The MEA was made by hot pressing method of the membrane and the gas diffusion layer (GDL) with inflicted catalyst. The pressure of 80 kg/cm² was applied for 3 min at the temperature 130 °C. The commercial product of Freudenberg Company (GDL I2C8) was used as GDL with inflicted catalytic Nafion ionomer-based ink and catalyst, produced by Inenergy LLC, with 29.75% Pt content and loading of Pt about 0.4 mg/cm².

The hydrogen crossover research was carried out by electrochemical method. The cell was connected by the 4-h contact pattern: current electrodes were connected to the current—collecting plates, the potential electrodes—to graphite bipolar plates. The cathode cell area was blown on by N₂ flow with the rate of 100 ml/min; the anode area was supplied by H₂ with the same flow rate. Measurements were started when open-circuit voltage dropped to 200 mV. A constant 400 mV

potential was set up by potentiostat and the cell current time dependence was measured. A typical obtained crossover curve is shown in Fig. 1. It can be seen from the figure that the measured current changes during 6–10 min then becomes stationary on its value which accepted as a specific leakage current i . The active square of the MEA in this study consisted of 1 cm².

MEA polarization curves (U - I characteristics) were got by means of the measuring cell at the Electrochem measuring stand. The MEA activation process prior the measurement was carried out at 65 °C. The cathode was supplied with O₂ at 200 ml/min flow rate, the anode, with H₂ at 200 ml/min flow rate. Both gases were applied at 100% relative humidity; the cyclic potential was applied to the cell in the range of 0.1–0.9 V with scan frequency 10 mV/s. Activation was carried out until U - I curves had not become more less the same from cycle to cycle. Total activation lasted for 1 h. For U - I data measurement in potentiostatic mode, the 30-s duration step of 50 mV was applied.

Experimental results

Figure 2 shows a typical deformation curve measured for three different experimental samples annealed at $T_{an} = 150$ °C. The point corresponding to the intersection of the two approximated elastic and plastic deformation lines was chosen as the elastic limit characteristic.

The values of elastic deformation for membranes, produced with different thermal conditions, are presented in Fig. 3. It can be seen that with the increase of annealing temperature from 80 °C to 110 °C, the mechanical strength of the membrane slightly increases. Then, with the annealing

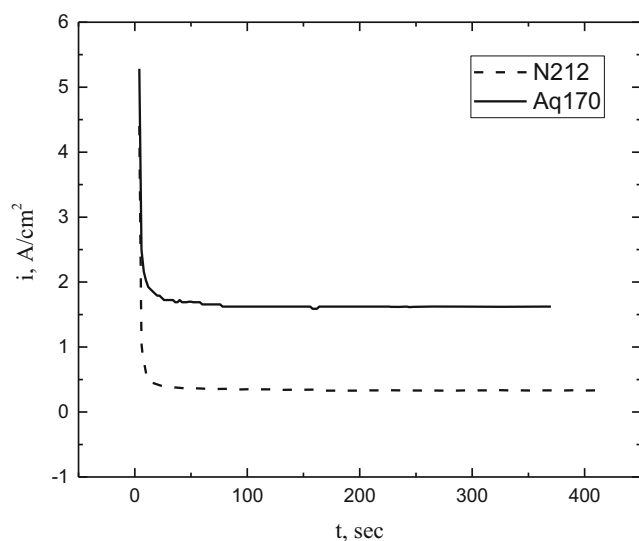


Fig. 1 Dependence of leakage current density i from time t for commercial pattern Nafion 212 (1) and Aq170, annealed at 170 °C (2), with the best mechanical-transport features

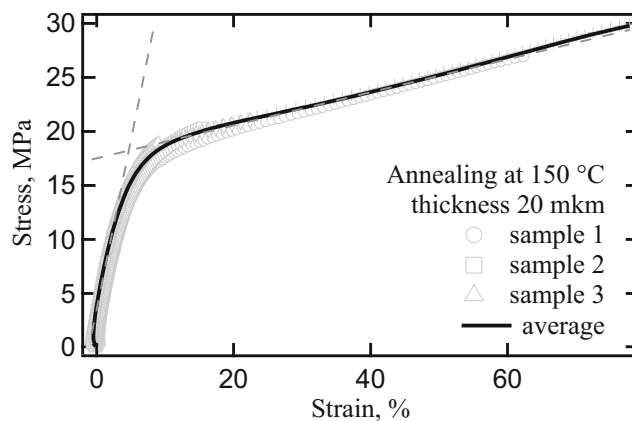


Fig. 2 Dependence of mechanical stress σ from deformation ϵ for three samples annealed at 150 °C. Straight lines correspond to approximation of elastic and plastic parts of deformation curve and their intersection point has been adopted for the elastic deformation limit

temperatures from 120 to 170 °C, the mechanical strength plot almost reaches a plateau. Maximum elastic deformation limit value was obtained for a sample annealed at 170 °C. Further increase of annealing temperature produced a negative impact on the mechanical strength of the samples. The limit of elastic deformation goes rapidly down at the level of membranes strength, annealed at 120 °C.

The measurements of proton conductivity for membranes, annealed at temperatures of 100, 120, 140, 150, 170, and 200 °C, and for the commercial Nafion NR212 membrane were carried out. As can be seen from Fig. 4, the conductivity of all membranes increases with temperature, and the relative conductivity increases with the temperature of annealing at $T \leq 170$ °C, afterwards begins to decrease nonmonotonic, so that is why the membrane, annealed at 200 °C, has the lowest conductivity. It is worth noting that the conductivity of

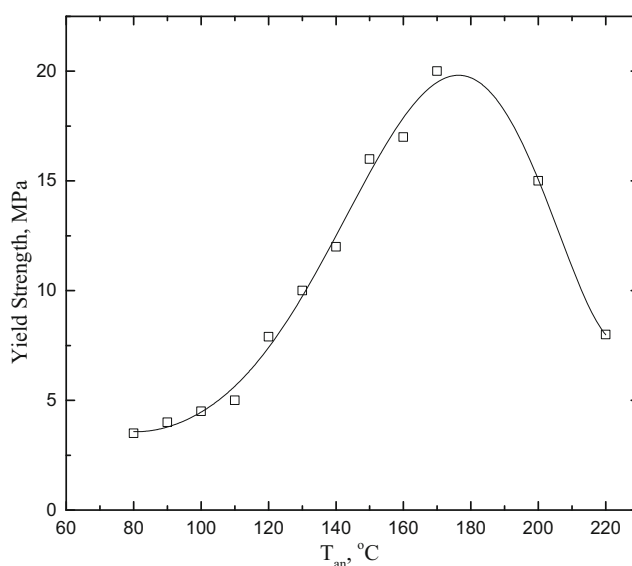


Fig. 3 Elastic deformation limit dependence on temperature annealing. The solid curve corresponds to polynomial approximation

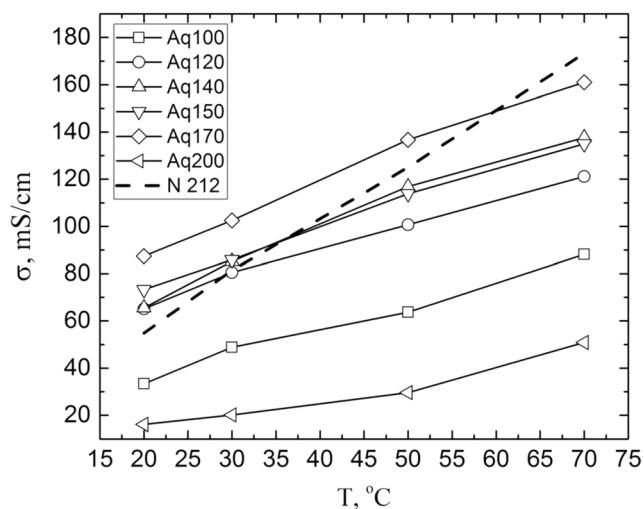


Fig. 4 Proton conductivity temperature dependence of membranes, annealed at different temperatures

membranes annealed in the temperature range of 140–170 °C is comparable to the conductivity of the commercial sample Nafion NR212. The values of the activation energy compared to commercial sample Nafion NR212 are shown in Table 1. It can be seen that the activation energies of membranes, annealed at temperatures $T_{an} = 120$ –170 °C, are almost twice less than the energy of activation of the membrane, annealed at 200 °C and the commercial sample Nafion NR212.

Figure 5 shows a typical calorimetric curve for the studied samples. It can be seen that there is an abnormal growth of heat capacity associated with the glass transition process at the temperature range ~ 150 –190 °C. The glass transition temperature for membrane annealed at 160 °C was $T_g = 175$ °C and was defined by the average height of heat capacity step; the heat capacity change for this sample in the glass transition point was $\Delta C_p = 1.14$ J/(K*gr). Data analysis showed that the glass transition point T_g strongly and non-monotonically varies depending on the annealing temperature of the membrane (Fig. 6), whereas heat capacity change ΔC_p is about 1–2 J/(K*gr) for all investigated samples. In Fig. 6, it can be seen

Table 1 Values of the pre-exponential factor A, the activation energy E_a , and quantities of proton conductivity σ at room temperature for membranes annealed at different T and commercial membrane Nafion NR212

Sample	A, $\text{Ohm}^{-1} \text{cm}^{-1} \text{K}$	E_a , eV	σ , S/cm
Aq100	6.64	0.069	9.78
Aq120	4.47	0.045	5.05
Aq140	5.33	0.054	7.54
Aq150	4.48	0.046	5.53
Aq170	4.49	0.047	6.05
Aq200	8.2	0.084	12.94
N212	8.14	0.086	22.42

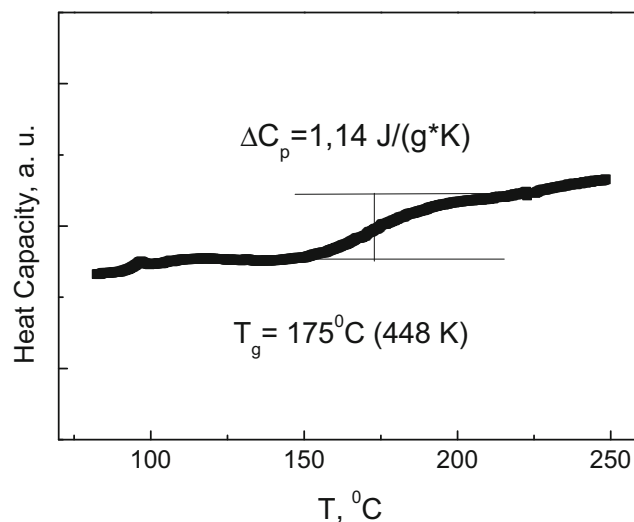


Fig. 5 Typical DSC dependence of studied membranes in the field of the glass transition temperature T_g . This curve corresponds to the sample, annealed at 160 °C

that maximum of glass transition temperature is within 165–175 °C temperature interval. This correlates well with data on mechanical strength, where maximum strength was also observed at annealing temperatures about $T_{an} \approx 160$ –180 °C, and data on transport characteristics, where the membranes, annealed at $T_{an} \approx 140$ –170 °C, had the highest values of conductivity. As we know, the higher values of T_g polymers are responsible for more stiffened polymer chains, which explains the observed correlation with mechanical properties. On the other hand, stronger polymeric chains allow the creation of an optimal structural polymer matrix with direct channels, increasing the mobility of protons. However, for more reliable conclusions, the additional detailed structural research is needed to be carried out.

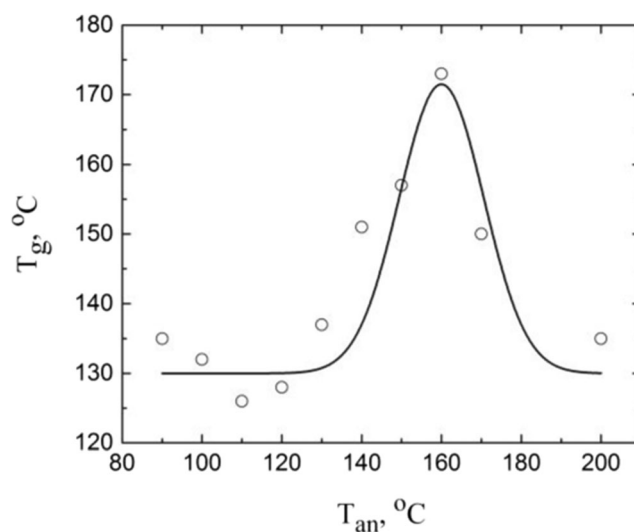


Fig. 6 Dependence of glass transition temperature T_g from annealing temperature T_{an} , of examined membranes

Thus, the analysis of physical characteristics (mechanical properties, conductivity, and calorimetry), measured in this study, indicates that annealing of this membranes at $T_{\text{an}} = 170 \pm 5 \text{ }^\circ\text{C}$ is optimal to achieve the best mechanical and proton conductivity characteristics. Therefore, all the next electrochemical measurements were carried out on the membrane, annealed at $T_{\text{an}} = 170 \text{ }^\circ\text{C}$.

The results of leak current (fuel crossover) measurement are presented in Fig. 1 for MEA based on solution-casted Aq170 and Nafion NR212 membranes. Specific leakage current for MEA based on the commercial sample was 0.34 mA/cm^2 , and for the MEA based on membrane Aq170— 1.71 mA/cm^2 . Despite the fact that the crossover of hydrogen through the membrane Aq170 in MEA was 5 times more than the crossover through Nafion membrane NR212, this value does not exceed the allowable world standard set by DOE— 2 mA/cm^2 [18]. It should be here noted that the crossover value can be down using radical scavengers in combination with recast Aquivion membranes which was experimentally demonstrated in ref. [19].

Figure 7 shows the current-voltage and output power characteristics of solution-casted membranes, annealed at $T = 170 \text{ }^\circ\text{C}$ (Aq170 in Fig. 7). It can be seen that the maximum output power at $T = 65 \text{ }^\circ\text{C}$ is equal to $\sim 0.2 \text{ W/cm}^2$. However, it should be noted that optimization MEA fabrications are necessary to increase maximum output power. This process includes catalytic ink layer deposition on gas diffusion layer (GDL) and thermal pressing of GDL layers on the membrane. However, these studies are the part of separate work.

Discussion

There are two main methods used to increase the mechanical and transport characteristics of the original proton-conducting polymers, which can be classified tentatively on physical and

chemical. In the first case, the applied effects are of physical cause: temperature [20–22], pressure [23, 24], electromagnetic fields [25–27], and so on. A significant effect on transport properties results from the water vapor treatment at elevated temperatures and pressures [26]. In the second case, different types of doping with organic and inorganic materials are applied to the original polymer [28–32]. The first way is relatively simpler and allows to find the limits of key fuel cell characteristics. In this study, the annealing method was used, which is widely distributed in materials science including a number of works on proton-exchange membranes [26–28, 33–36].

In one of the first studies, where the solution-casted Nafion membranes were subjected to the thermal treatment, it has been shown and experimentally proved that only annealing or solvent evaporation at high temperatures made the solution-casted membranes competitive with the extruded membranes [33]. The temperature treatment effect on the structure of perfluorinated solution-casted membranes and the relationships between the structure and basic membrane parameters were described in study [20]. The authors suggested that higher annealing temperature results in the more effective side chains restructure. The annealing processes in this study were conducted at 150, 170, 190, and 210 $^\circ\text{C}$. During this structure rearrangements, the hydrophobic polymer matrix sulfogroups shift in the direction of the ionic hydrophilic channels and thereby causing proton conductivity increase. Authors [34] performed comparison studies of the commercial and solution-casted Nafion membranes. It was found that the maximum conductivity values were reached at annealing temperatures $\sim 210 \text{ }^\circ\text{C}$ (commercial membrane) and $190 \text{ }^\circ\text{C}$ (solution-casted membrane). Various annealing procedures were proposed [34–36], which also demonstrated that there is some optimum temperature corresponding to the best transport characteristics of the samples under investigations.

This comprehensive study of mechanical and transport properties of solution-casted Aquivion-type membranes prepared at the different annealing temperatures was directed to the optimal annealing conditions determination, when the key characteristics (mechanical strength, conductivity, and glass transition temperature) proved to be near their extreme values.

It should be noted that we have used the elastic deformation limit as a criterion for mechanical strength of membranes although the specifications of commercial membrane samples indicate it as tensile strength. This was done in view of the fact that, despite the use of protocol ASTM D882, the stress-strain diagram had no plastic deformation characteristics and the limit of elastic deformation is also suitable for detection of the influence of heat treatment on mechanical properties of membranes manufactured by the casting solution method. According to technical specification, the tensile strength of commercial samples Nafion NR212 is equal to ~ 20 –

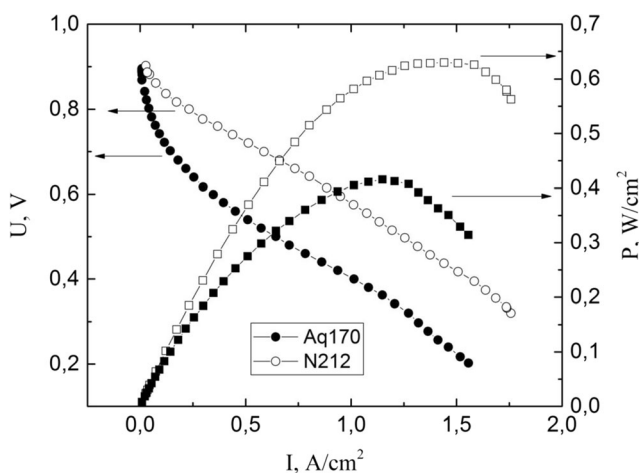


Fig. 7 U - I and output power characteristics of the MEA, with membrane annealed at $170 \text{ }^\circ\text{C}$ (Aq170)

30 MPa and for reinforced Nafion XL—~40–45 MPa. The elastic deformation limit of Aquivion-type membrane prepared at optimal conditions occur around 20 MPa (Fig. 3). Taking into account that the elastic deformation limit cannot exceed the tensile strength, it was concluded that elastic properties of prepared membranes are competitive with analogous parameter of commercial samples.

The dependence of the elastic strain limit of the obtained membranes on the annealing temperature (T_{an}) is nonlinear and passes through a maximum at $T_{\text{an}} \approx 170$ °C (Fig. 3). Similar dependences on T_{an} with a maximum at $T_{\text{an}} \approx 170$ °C are also observed for the glass transition temperature (Fig. 5) and for the isotherms of proton conductivity measured at $20 \leq T \leq 70$ °C (Fig. 4). This clearly indicates that the annealing temperature of 170 °C is optimal for achieving the best mechanical and transport characteristics for the membranes made of a perfluorinated polymer with a short side chain. Presumably, annealing at temperatures up to 170 °C results in a structural rearrangement of the polymer chains, whereas at higher temperatures, the polymer begins to decompose that leads to a degradation of its operating characteristics. This assumption is confirmed by results of our recent thermogravimetric measurements and X-ray scattering analysis, which are in progress now. Moreover, researchers [35, 36] demonstrated similar membrane behavior. Therefore, $T \approx 170$ °C is the limit for the reliable operation temperature of MEA with an Aquivion-type membrane. Many studies have shown that the protonic conductivity of these perfluorinated membranes increases with temperature and reaches 0.1–0.2 S/cm [21, 22]. At room temperature, the proton conductivity of the “optimal” membranes prepared in the present work is slightly higher than that of the Nafion NR212 membranes, and at temperatures around 80 °C, it has the same value as the commercial sample. Given the much higher decomposition temperature of our solution-casted Aquivion-type membranes, they are promising candidates for use in medium-temperature fuel cells (above 100 °C). The medium-temperature fuel cells allow the utilization of industrial hydrogen with a CO concentration of more than 10 ppm, which can significantly reduce the cost of the entire electrochemical generator with a proton-exchange membrane.

Conclusions

The solution casting technology was applied to manufacture thin polymer films (~20–30 μm) from the ionomer solution of perfluorinated polymer with short side chains (an analogue of the commercial polymer Aquivion®). Casting membranes were optimized by means of simultaneous measurement of three physical characteristics of the samples annealed for 20 h at temperatures from 80 to 220 °C. These three characteristics that were measured were the limits of elasticity, the

proton conductivity, and the glass transition temperature. Optimizing these characteristics plays a crucial role in obtaining high performance and a long lifetime in the membrane-electrode assembly (MEA). A comprehensive analysis of all of the physical characteristics that were investigated in the membranes showed that the characteristics obtain their maximum values when the samples are annealed in the temperature range 160–180 °C. Therefore, 170 °C was determined to be as the optimal annealing temperature for membranes created with a casting method. Moreover, the maximum achieved value of proton conductivity at room temperature of “optimal” membrane (Aq170) consists of 0.09 S/cm which is about 1.5 times higher than the conductivity under the same conditions of a commercial membrane Nafion NR212. To clarify the functional features of the optimal membrane, we carried out comparative measurements of gas permeability and the polarization characteristics of membrane-electrode assemblies on the basis both commercial membrane Nafion NR212 and Aq170. The gas permeability of the membrane (i.e., crossover) was measured by the method of leakage, which showed that the crossover of Aq170 membrane did not exceed 1.1 mA/cm². This value is fully consistent with the standard set by the DOE electrochemical community (Fuel Cell Technical Team Roadmap, website: https://energy.gov/sites/prod/files/2014/02/f8/fctt_roadmap_june2013.pdf) according to which the membrane crossover cannot exceed 2 mA/cm². The polarization characteristics demonstrated that the values of the output power maximum of MEA on the basis of Aq170 membrane was only 30% lower than the for MEA based on Nafion NR212, for which we previously optimized the whole MEA creation process with the best power characteristics. Thus, further optimization of MEA fabrication on the basis of a Aq170 membrane is necessary to improve power characteristics. However, these studies are the part of separate work.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

References

1. Dobrovolskii YA, Volkov EV, Pisareva AV, Fedotov YA, Likhachev DY, Rusanov AL (2007) Proton-exchange membranes for hydrogen-air fuel cells. *Russ J Gen Chem* 77(4):766–777
2. Carrette L, Friedrich KA, Stimming U (2001) Fuel cells—fundamentals and applications. *Fuel Cells* 1(1):5–39

3. Safronova EY, Yaroslavtsev AB (2016) Prospects of practical application of hybrid membranes. *Petroleum Chem* 56:281–293
4. Yaroslavtsev AB, Nikonenko VV (2009) Ion exchange membrane materials: properties, modification and application. *Nanotechnologies in Russia* 4(3–4):137–159
5. Nikonenko VV, Yaroslavtsev AB, Pourcelly G (2012) Ionic interactions in natural and synthetic macromolecules. N Jersey: Wiley 267 p
6. Yaroslavtsev AB, Dobrovolsky YA, Shaglaeva NS, Frolova LA, Gerasimova EV, Sanginov EA (2012) Nanostructured materials for low-temperature fuel cells. *Russ Chem Rev* 81(3):191–220
7. Wainright JS, Wang J-T, Weng D, Savinell RF, Litt M (1995) Acid-doped polybenzimidazoles: a new polymer electrolyte. *J Electrochem Soc* 142(7):L121–L123
8. Aricò AS, Blasi AD, Brunaccini G, Sergil F, Dispenza G, Andaloro L et al (2010) High temperature operation of a solid polymer electrolyte fuel cell stack based on a new ionomer membrane. *Fuel Cell* 10(6):1013–1023
9. Gebert M, Ghielmi A, Merlo L, Corasaniti M, and Arcella V. AQUIVION™—the short-side-chain and low-EW PFSA for next generation PEFCs expands production and utilization. *ECS J Solid State Sci Technol* 2010;26(1):279–83
10. Merlo L, Oldani C, Apostolo M, Arcella V (2012) PFSA Aquivion® membranes: general features and degradation mechanisms. *Solvay Specialty Polymers SPA*
11. Skulimowska A, Dupont M, Zaton M, Sunde S, Merlo L, Deborah JJ, Rozière J (2014) Proton exchange membrane water electrolysis with short-side-chain Aquivion® membrane and IrO₂ anode catalyst. *Int J Hydrog Energy* 39(12):6307–6316
12. Borekov Institute of Catalysis SB RAS, RU Pat, 2545182 C1, 2013
13. Kulvelis YuV, Ivanchev SS, Lebedev VT, Primachenko VS, Likhomanov VS, Török Gy Structure characterization of perfluorosulfonic short side chain polymer membranes. *Solid RSC Advances*, 2015; 5(90): 73820–26
14. Stassi A, Gatto I, Passalacqua E, Antonucci V, Arico AS, Merlo L, Oldani C, Pagano E (2011) Performance comparison of long and short-side chain perfluorosulfonic membranes for high temperature polymer electrolyte membrane fuel cell operation. *J Power Sources* 196(21):8925–8930
15. Park YC, Kakinuma K, Uchida H, Watanebe M, Uchida M (2015) Effects of short-side-chain perfluorosulfonic acid ionomers as binders on the performance of low Pt loading fuel cell cathodes. *J Power Sources* 275:384–391
16. Siracusano S, Hodnik N, Jovanovic P, Ruiz- Zepeda F, Šala M, Baglio V et al (2017) New insights into the stability of a high performance nanostructured catalyst for sustainable water electrolysis. *Nano Energy* 40:618–632
17. Korchagin OV, Bogdanovskaya VA, Tarasevich MR, Kuzov AV, Zhutaeva GV, Radina MV, Novikov VT, Zharikov VV (2016) Characteristics of nonplatinum cathode catalysts for hydrogen-oxygen fuel cell with proton-conductive and anion-conductive electrolytes. *Catalyst in Industry* 8(3):265–273
18. Department of Energy USA. Fuel cell technical team roadmap [Internet]. USA: Department of Energy; 2014 [cited 1 Nov 2017]. Available from: https://energy.gov/sites/prod/files/2014/02/f8/fctt_roadmap_june2013.pdf
19. D'Urso C, Oldani C, Baglio V, Merlo L, Aric AS (2014) Towards fuel cell membranes with improved lifetime: Aquivion® Perfluorosulfonic Acid membranes containing immobilized radical scavengers. *J Power Sources* 272:753–758
20. Luan Y, Zhang Y, Zhang H, Lei L, Li H, Liu Y (2008) Annealing effect of perfluorosulfonated ionomer membranes on proton conductivity and methanol permeability. *J Appl Polym Sci* 107:396–402
21. Junsheng L, Xi Y, Haolin T, Mu P (2010) Durable and high performance Nafion membrane prepared through high-temperature annealing methodology. *J Membr Sci* 361:38–42
22. Lee K, Ishihara A, Mitsushima S, Kamiya N, Ota K (2003) Effect of recast temperature on diffusion and dissolution of oxygen and morphological properties in recast Nafion. *ECS J Solid State Sci Technol* 151(4):639–645
23. Liu D, Lai X, Ni J, Peng L, Lana S, Lin Z (2007) Robust design of assembly parameters on membrane electrode assembly pressure distribution. *J Power Sources* 172:760–767
24. Freya Th, Linardi M. Effects of membrane electrode assembly preparation on the polymer electrolyte membrane fuel cell performance. *Electrochim Acta* 2004;50:99–105
25. Tong JY, Guo1 Q, Wang XX (2009) Properties and structure of SPEEK proton exchange membrane doped with nanometer CeO₂ and treated with high magnetic field. *Express Polym Lett* 3(12): 821–831
26. Safronova EY, Stenina IA, Yaroslavtsev AB (2017) The possibility of changing the transport properties of ion-exchange membranes by their treatment. *Petroleum Chem.* 57:299–305
27. Zhao Z, Hu J, Zhou Z, Zhong M (2007) The use of strong magnetic field treatment for preparation of proton exchange membrane doped by SeO₂ and its electrochemical properties. *Int J Electrochem Sci* 12:5450–5463
28. Yaroslavtsev AB, Yampolskii YP (2014) Hybrid membranes containing inorganic nanoparticles. *Mendeleev Communications* 24(6):319–326
29. Berezina NP, Kononenko NA, Timofeev SV (2002) Effect of conditioning techniques of perfluorinated sulphocationic membranes on their hydrophilic and electrotransport properties. *J Membr Sci* 209:509–518
30. Feng K, Tang B and Wu PA. «H₂O donating/methanol accepting» platform for preparation of highly selective Nafion-based proton exchange membranes. *J Mater Chem A* 2015;3:18546–18556
31. Li HY, Liu YL (2014) Nafion-functionalized electrospun poly(vinylidene fluoride) (PVDF) nanofibers for high performance proton exchange membranes in fuel cells. *J Mater Chem A* 2:3783–3793
32. Moore RB, Martin CR (1988) Chemical and morphological properties of solution-cast perfluorosulfonate ionomers. *Macromolecules* 21:1334–1339
33. Nicholas WD, Yossef AE (2006) Nafion/poly(vinyl alcohol) blends: effect of composition and annealing temperature on transport properties. *J Membr Sci* 282:217–224
34. Hensley E, Douglas W, Steven FD, Kent DA (2007) The effects of thermal annealing on commercial Nafion membranes. *J Membr Sci* 298:190–201
35. Osung K, Shijie W, Da-Ming Z (2011) Effect of thermal annealing on proton conduction in ion exchange membranes. *Mater Res Soc Symp Pro* 1330
36. Bruno RM, Cleveron AG, Elisabete IS, Muccillo R, Fabio CF (2014) Proton conductivity of perfluorosulfonate ionomers at high temperature and high relative humidity. *Appl Phys Lett* 104:091904