Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

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Structure and properties optimization of perfluorinated short side chain membranes for hydrogen fuel cells using orientation stretching

The calculations of specific conductivity of membranes were performed by impedance spectroscopy measurements using the formula: $\sigma_n = L / (R \times h \times b)$, where: L = 1.77 cm – the distance between the electrodes in the measuring cell; R – membrane resistance, found from impedance spectrum (fig. S1); h – average thickness of the membrane; b – average width of the membrane.

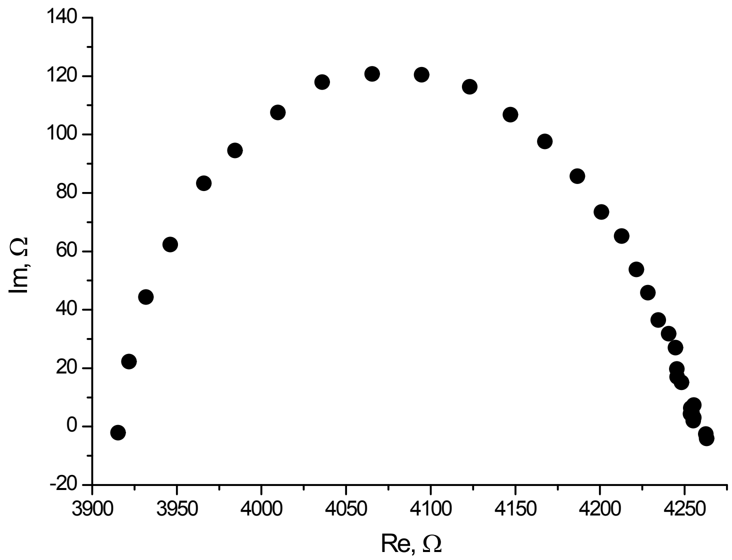

Fig. S1. An example of impedance spectrum for sample SSC-3, stretched for 200%, saturated with D_2O.

Table S1. Characteristics of initial samples measured by SANS.

Sample	Number of layers	Thickness, mm
SSC-5 dry	8	1.60
SSC-1 dry	8	1.71
SSC-3 dry	8	1.90
SSC-2 dry	12	1.70
SSC-6 dry	8	1.13
SSC-4 dry	5	0.86
SSC-5 H	8	2.00
SSC-1 H	8	2.16
SSC-3 H	8	2.30
SSC-2 H	12	2.02
SSC-6 H	8	1.41
SSC-4 H	11	1.81
SSC-5 D	8	2.05
SSC-1 D	8	2.46
SSC-3 D	8	2.18
SSC-2 D	12	1.80
SSC-6 D	8	1.36
SSC-4 D	6	0.88

Table S2. Fitting parameters for SANS on initial samples by the model (1).

Sample	SSC-5dry	SSC-1dry	SSC-3dry	SSC-2dry	SSC-6dry	SSC-4dry
I_0, a.u.	3.67±0.21	5.3±0.7	4.0±0.5	4.6±0.3	2.97±0.18	4.2±0.5
n	1.3	1.9	2.1	1.23±0.08	1.69±0.15	1.70±0.07
R_g, nm	0.339±0.019	0.20±0.03	0.21±0.04	0.291±0.019	0.33±0.04	0.24±0.03
C_1	-1.506±0.020	-1.621±0.016	-1.514±0.020	-1.412±0.024	-1.39±0.03	-1.336±0.022
R_1, nm	1.675±0.025	1.633±0.016	1.591±0.025	1.842±0.016	1.64±0.05	1.813±0.018
C_2	1.65±0.29	2.4±0.9	1.9±0.5	1.29±0.05	1.21±0.11	1.19±0.03
R_2, nm	3.53±0.07	3.45±0.08	3.53±0.08	3.534±0.025	3.56±0.06	3.585±0.023
C_3	-1.0±0.3	-1.7±0.9	-1.3±0.5	-0.51±0.05	-0.65±0.13	-0.560±0.027
R_3, nm	4.15±0.10	3.86±0.10	4.04±0.11	4.68±0.06	4.46±0.11	5.05±0.05
C_4	-0.042±0.005	-0.0085±0.0019	-0.0265±0.0023	-0.154±0.009	-0.083±0.015	-0.207±0.020
R_4, nm	11.9±0.4	10.9±1.0	10.2±0.3	11.05±0.14	10.40±0.19	9.62±0.09
C_5	0.033±0.008	0.0366±0.0029	0.0311±0.0025	0.083±0.022	0.046±0.020	0.166±0.027
R_5, nm	19.8±0.8	19.2±0.3	17.2±0.3	21.5±0.4	19.2±0.6	19.38±0.19
C_6	-	0.010±0.004	0.011±0.003	-	-	0.087±0.023
R_6, nm	-	30.0±1.7	31.3±1.2	-	-	29.7±0.5
B, a.u.	0.0892±0.0017	0.0778±0.0027	0.0756±0.0023	0.0692±0.0016	0.0772±0.0018	0.0545±0.0025

Sample	SSC-5H	SSC-1H	SSC-3H	SSC-2H	SSC-6H	SSC-4H
I_0, a.u.	8.50±0.05	7.65±0.04	8.42±0.04	8.96±0.03	9.12±0.06	7.90±0.03
n	1.82±0.15	2.6	2.4	1.90±0.10	2.07±0.14	2.2
R_g, nm	0.691±0.028	0.486±0.008	0.536±0.007	0.652±0.019	0.682±0.026	0.524±0.006
C_1	-1.795±0.020	-1.830±0.016	-1.880±0.018	-1.880±0.020	-1.834±0.021	-1.826±0.017
R_1, nm	3.02±0.03	2.812±0.013	2.774±0.013	2.885±0.023	3.02±0.03	2.580±0.011
C_2	1.44±0.05	1.51±0.05	1.53±0.04	1.61±0.03	1.55±0.03	1.568±0.026
R_2, nm	5.17±0.04	4.98±0.04	4.73±0.03	4.80±0.03	5.12±0.03	4.425±0.023
C_3	-0.56±0.06	-0.65±0.06	-0.61±0.04	-0.59±0.05	-0.59±0.05	-0.678±0.028

R_3, nm	6.79±0.10	6.33±0.07	6.26±0.06	6.42±0.08	6.86±0.08	6.07±0.04
C_4	-0.034±0.005	-0.015±0.005	-0.0255±0.0016	-0.084±0.011	-0.049±0.006	-0.0644±0.0023
R_4, nm	15.9±0.3	16.6±0.9	14.0±0.4	14.87±0.12	15.2±0.4	12.10±0.17
C_5	0.009±0.004	0.014±0.005	0.0214±0.0018	-	0.019±0.005	0.0413±0.0024
R_5, nm	24.2±1.7	21.1±1.1	21.1±0.4	-	20.9±1.1	19.04±0.29
C_6	-	-	0.0089±0.0023	-	-	0.0103±0.0027
R_6, nm	-	-	34.2±1.1	-	-	29.6±1.3
B, a.u.	0.2841±0.0014	0.2904±0.0016	0.2520±0.0013	0.2399±0.0011	0.2483±0.0013	0.1666±0.0010

Sample	SSC-5D	SSC-1D	SSC-3D	SSC-2D	SSC-6D	SSC-4D
I_0, a.u.	0.378±0.007	0.474±0.012	0.433±0.010	0.180±0.016	0.391±0.010	0.218±0.020
n	1.63±0.11	2.45±0.10	2.28±0.13	2.15±0.15	2.1±0.3	2.40±0.20
R_g, nm	0.80±0.03	0.602±0.029	0.63±0.04	0.37±0.08	0.74±0.31	0.38±0.14
C_1	-1.77±0.08	-1.88±0.05	-1.89±0.07	-1.90±0.10	-1.87±0.10	-2.21±0.20
R_1, nm	3.00±0.08	2.90±0.04	2.79±0.06	3.03±0.06	2.99±0.10	2.74±0.09
C_2	2.47±2.51	1.9±0.4	2.3±1.3	1.46±0.21	2.2±1.3	1.70±0.16
R_2, nm	5.5±0.4	5.17±0.15	5.03±0.26	4.97±0.19	5.4±0.3	4.36±0.16
C_3	-1.6±2.6	-1.0±0.5	-1.38±1.32	-0.48±0.26	-1.3±1.4	-1.0±0.8
R_3, nm	6.2±0.5	6.09±0.21	5.76±0.32	6.4±0.4	6.2±0.4	6.9±0.6
C_4	-	0.013±0.005	0.026±0.010	-	-0.013±0.008	0.5±0.9
R_4, nm	-	26.9±1.1	27.1±0.7	-	17.4±2.1	7.9±0.9
B, a.u.	0.04970±0.00028	0.03831±0.00025	0.2483±0.0015	0.0456±0.0005	0.0439±0.0003	0.0309±0.0009

Table S3. Characteristics of stretched samples measured by SANS. Samples SSC-3 and SSC-2 are 2 times stretched, SSC-6 – 3 times stretched.

Sample	Number of layers	Thickness, mm
SSC-3 dry	12	1.62
SSC-2 dry	21	1.75
SSC-6 dry	12	0.78
SSC-3 H	6	1.07

SSC-2 H	10	1.02
SSC-6 H	8	0.67
SSC-3 D	6	1.04
SSC-2 D	11	1.11
SSC-6 D	12	0.89

Table S4. Fitting parameters for SANS on stretched samples by the model (1).

Sample	SSC-3 dry	SSC-2 dry	SSC-6 dry
I_0, a.u.	4.86±0.22	6.2±0.4	3.00±0.08
n	1.83±0.15	1.31±0.13	1.70±0.16
R_g, nm	0.34±0.04	0.328±0.027	0.38±0.09
C_1	-1.56±0.05	-1.54±0.03	-1.84±0.14
R_1, nm	1.66±0.06	1.866±0.024	1.49±0.12
C_2	2.1±1.7	1.25±0.07	1.43±0.17
R_2, nm	3.58±0.20	3.51±0.04	2.5
C_3	-1.4±1.7	-0.47±0.08	-0.46±0.05
R_3, nm	4.01±0.26	4.58±0.10	3.70±0.22
C_4	-0.017±0.003	-0.070±0.006	-0.070±0.025
R_4, nm	11.0±0.8	11.1±0.3	7.46±0.20
C_5	0.030±0.014	-	0.036±0.020
R_5, nm	19.8±0.6	-	17.6±0.7
B, a.u.	0.116±0.003	0.0994±0.0028	0.0712±0.0029

Sample	SSC-3 H	SSC-2 H	SSC-6 H
I_0, a.u.	9.59±0.12	9.80±0.28	5.18±0.06
n	1.87±0.29	1.8±0.4	1.66±0.08
R_g, nm	0.71±0.05	0.74±0.06	0.496±0.017
C_1	-1.84±0.04	-1.84±0.05	-1.74±0.03
R_1, nm	2.99±0.06	2.96±0.07	2.158±0.025
C_2	1.43±0.06	1.53±0.08	1.61±0.06

R_2, nm	5.06±0.06	5.01±0.07	3.82±0.04
C_3	-0.50±0.09	-0.57±0.14	-0.77±0.08
R_3, nm	6.84±0.18	6.59±0.17	5.01±0.08
C_4	-0.040±0.011	-0.055±0.019	-0.020±0.004
R_4, nm	16.1±0.7	16.2±0.3	10.4±0.8
C_5	0.013±0.007	-	0.065±0.013
R_5, nm	22.2±2.5	-	17.5±0.3
B, a.u.	0.2856±0.0026	0.2675±0.0025	0.1027±0.0014

Sample	SSC-3 D	SSC-2 D	SSC-6 D
I_0, a.u.	0.399±0.012	0.13±0.04	0.050±0.013
n	1.62±0.19	2.2	2.1±0.4
R_g, nm	0.79±0.07	0.8	0.5
C_1	-1.76±0.18	-1.3±0.6	-1.16±0.15
R_1, nm	3.08±0.15	2.1±0.7	2.0±0.4
C_2	1.6±0.8	0.4±0.6	0.26±0.17
R_2, nm	5.4±0.5	3.9±1.1	5.2±1.3
C_3	-0.7±0.9	-	-
R_3, nm	6.5±0.8	-	-
C_4	0.048±0.043	-	-
R_4, nm	22.7±2.3	-	-
B, a.u.	0.0511±0.0007	0.0747±0.0006	0.0317±0.0005

Table S5. Calculation of nuclear contrast for membranes in different media.

Substance	Formula	Molar weight M, g mol^{-1}	Macroscopic density ρ, g cm^{-3}	Scattering length density B= $\sum b_C$, 10^{-13} cm	Contrast factor $K = \frac{BN_A\rho}{M}$, 10^{10} cm^{-2}	Contrast $\Delta K = K_X - K_{SSC}$, 10^{10} cm^{-2}
The entire polymer	$C_{14}F_{27}OC_2F_4SO_3H$	878	2.2	303.93	4.57	ΔK_{dry} = -4.57 ΔK_H = -5.129 ΔK_D = 1.80

Backbone	$C_{14}F_{27}$	681	2.2	245.702	4.76	ΔK_{dry} = -4.76 ΔK_H = -5.319 ΔK_D = 1.61
Side chain	$OC_2F_4SO_3H$	197	2.2	58.228	3.90	ΔK_{dry} = -3.90 ΔK_H = -4.459 ΔK_D = 2.47
Side chain without sulfonic group	OC_2F_4	116	2.2	41.711	4.75	ΔK_{dry} = -4.75 ΔK_H = -5.309 ΔK_D = 1.62
Sulfonic group	SO_3H	81	2.2*	16.517	2.70*	
Light water	H_2O	18	0.998	-1.675	-0.559	
Heavy water	D_2O	20	1.105	19.145	6.370	

The measured membranes density is 1.95 g cm^{-3}, however they are porous. Therefore the solid Teflon density of 2.2 g cm^{-3} was used for calculations.
Considering the contrast of channels in the entire polymer:
Dry channels have ΔK_{dry} = (0 - 4.57)×10^{10} cm^{-2} = -4.57×10^{10} cm^{-2};
H_2O-saturated channels have ΔK_H = (-0.559 - 4.57)×10^{10} cm^{-2} = -5.129×10^{10} cm^{-2};
D_2O-saturated channels have ΔK_D = (6.37 - 4.57)×10^{10} cm^{-2} = 1.80×10^{10} cm^{-2}.
In air-dry samples, measured by SANS, dry channels contain some amount of bound water. If we take into account that typical water volume in air-dry membrane reduces to 5% from saturated level, and channel volume reduces 4-6 times (channel radius reduces 2-2.5 times), the channels will be filled with water at ~ ¼ of their volume. Then air-dry channels will have contrast ΔK ~ (-0.559*0.25 - 4.57)×10^{10} cm^{-2} = -4.71×10^{10} cm^{-2}, close to the contrast calculated above for for absolutely dry channel. This will be also true for unavailable for water channels in case of partially saturated by H_2O samples, studied by SANS. In case of partial saturation by D_2O, even if we consider the complete replacement of bound H_2O to D_2O molecules, we should have the contrast ΔK ~ (6.37*0.25 - 4.57)×10^{10} cm^{-2} = -2.98×10^{10} cm^{-2}, that does not make the situation qualitatively worse. On the contrary, the contrast compensation from filled and partially filled channels with the reducing of ionomer peak intensity becomes more possible (1.8×10^{10} is better compensated by -2.98×10^{10}, than by -4.57×10^{10}).
If we take into account different parts of membrane separately, they will result in different contrast mainly due to sulfonic acid groups in side chains. The backbone and the side chain excluding sulfonic group have a similar content with similar values of contrast factor. Only the presence of sulfonic group makes a change in contrast factor of the side chain and the entire polymer. Since water filling the channels mainly contacts with sulfonic groups and side chains, rather than with the backbone, the contrast calculations for the individual parts of the polymer matrix are also performed. It does not qualitatively change the scattering character.
* Another, more correct way of calculation the contrast for sulfonic groups in terms of their volume (since the density of Teflon is not relevant to sulfonic group). To obtain the sulfonic group volume we should subtract the volume of OH-group from the volume of sulfuric acid molecule. Sulfuric acid has ρ = 1.836 g cm^{-3}, M = 98 g mol^{-1}, single molecule volume $M\rho^{-1}N_A^{-1}$ = 8.90×10^{-23} cm^3. Volume of OH-group is V_{OH} = 9.79×10^{-24} cm^3, calculated from the known ion radii for O (132 pm) and H (54 pm). Thus the sulfonic group volume turns V = 7.9×10^{-23} cm^3. Scattering length density for sulfonic group = B/V = 2.1×10^{10} cm^{-2}, that differs from the entire polymer and may cause additional features in the scattering, since water in saturated samples is localized in the channels with sulfonic groups on their surface.