Self-assembly in Nafion membranes upon hydration: water mobility and adsorption isotherms.

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SUPPORTING INFORMATION

I. Relative volumes of the beads

Table S1.

Bead	W	C	E	S	S
Fragment	$(H_2O)_{4.5}$	$(-CF_2-)_4$	$-O-CF(CF3)-CF2-O$	$(-CF_2-)_2SO_3K$	$(-CF_2-)_2SO_3^-$
Σr_i [a]	4.14	4.04	3.67		
Representative compound [b]	H_2O	$H(CF_2)_4H$	$CF_3OCFOCF_2H$	$H(CF_2)_2SO_3K$	$H(CF_2)_2SO_3^-$
V_{COSMO}	29.1	141.1	112.7	124.2	140.7
Effective volume, Å^3	134.5	131.3	117.1	119.3	136.5

(a) sum of volume parameters r_i for the functional group forming the fragment
(b) molecule, for which the COSMO volume was calculated using PQS ab-initio; correspondingly V_{COSMO} is the volume of the molecule, rather than the bead volume

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II. Details of MD simulations for DPD parameter fitting

The simulation procedures were similar to those employed in refs. [1-3] We used MDynaMix [4] software package. In the initial configuration, molecules were arranged in a lattice order at a low density of 0.005 g/cm^3. The system was then gradually contracted in a series of constant-temperature MD simulations at $T = 303K$ maintained by a simple velocity scaling. After the density of 1.0g/cm^3 (aqueous solutions) or 1.7 g/cm^3 (perfluorohexadecane) was achieved, the simulation proceeded at a constant pressure $P = 1atm$. T and P were maintained by the Nose-Hoover thermostat. [5, 6] System equilibration was performed for 200 ps followed by additional 10 to 1 ns MD simulation, over which the system configuration was periodically saved to disc for analysis. The distribution of distances between the beads in DPD simulations were fitted to the distances between the centers of mass of the corresponding fragments (see Table 1 in the main text and Table S1). In order to maintain symmetry in Nafion model, we assumed that some fluorocarbon groups were divided between the two neighboring beads. In particular, the location of bead C1 from the MD trajectories of the Nafion fragment shown in Figure S1(a) was calculated as

$$\mathbf{r}_{C1} = (\mathbf{r}_3 * M_{CF} + \mathbf{r}_2 * M_{CF2} + \mathbf{r}_4 * M_{CF2} + 0.5 * \mathbf{r}_1 * M_{CF2} + 0.5 * \mathbf{r}_5 * M_{CF2})/(M_{CF} + 4 * M_{CF2})$$

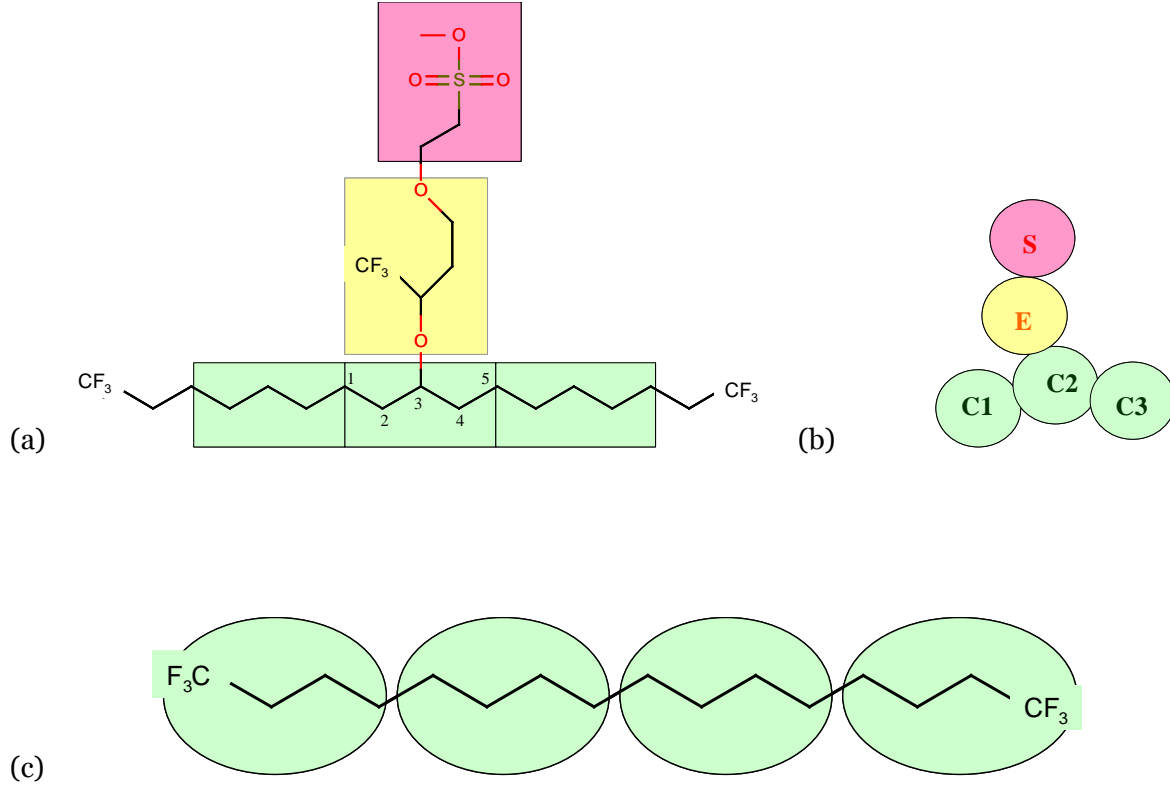The indexes of fluorocarbon groups are also shown in the Figure.

Figure S1. (a) Nafion fragment modeled in aqueous solution by molecular dynamics in order to obtain distribution of distances between the bead centers (b) coarse-grained model of Nafion fragment simulated by DPD (3) molecular and coarse-grained models of perfluorohexadecane

III. Details of DPD simulations.

Nafion was presented by oligomers each containing 20 monomers. Bead density $\rho * R_c^3$ in the system was set to 3, a common choice for aqueous solutions. The random force, which accounts for thermal fluctuations, is taken proportional to the conservative force that is also acting along the vector between the bead centers: $\boldsymbol{F}_{ij}^{(R)}(r_{ij}) = \sigma w^R r_{ij} \theta_{ij}(t) \boldsymbol{r}_{ij}$, where $\theta_{ij}(t)$ is a randomly fluctuating in time variable with Gaussian statistics. The drag force is velocity-dependent: $\boldsymbol{F}_{ij}^{(D)}(\boldsymbol{r}_{ij}, \boldsymbol{v}_{ij}) = -\gamma w^D(r_{ij}) (\boldsymbol{r}_{ij} * \boldsymbol{v}_{ij})$, where, $\boldsymbol{v}_{ij} = \boldsymbol{v}_j - \boldsymbol{v}_i$, $\boldsymbol{v}_i$ and $\boldsymbol{v}_j$ are the current velocities

of the particles. We assume the common relationship between the drag and random force parameters $w^D(r) = [w^R(r)]^2$. σ and γ are parameters that determine the level of energy fluctuation and dissipation; they are related as and $\sigma^2 = 2\gamma kT$ that allows to maintain constant temperature in the course of simulation. We assumed $\gamma = 4.5$, a common value fitted to the diffusion coefficient of water. In the initial configuration, all beads were assigned random locations in the box. Starting from this random configuration, we performed a steepest descent energy minimization taking in account only harmonic bond and short-range conservative forces. The minimization was followed by 10000 step preliminary MD simulation ($\gamma = 0$, no drag or random forces) at temperature fixed by velocity scaling on each step. DPD simulations started from the final configuration obtained in that preliminary MD run. In-house DPD program was used.

III.A. Simulations of Nafion fragments employed in forcefield fitting.

The systems exactly mimicked the MD simulations (Tabke S2). Simulations were 150000 DPD steps long, time step in reduced time units was $0.02(m_W R_c^2/kT)^{1/2}$. First 50000 steps were discarded. After that the coordinates of all beads except solvent beads were dumped to disk every 100 steps. The distributions of intramolecular distances and angles were calculated from this trajectory. In first simulations, we used reasonable bond parameters approximately evaluated from average distances and dispersions obtained in MD simulations. Then, the bonds were optimized from one simulations to another in order to improve the agreement with the MD results similarly to ref [8]

III.B. Simulations of hydrated Nafion

Nafion was presented by oligomers each containing 20 monomers. Simulations were conducted in cubic boxes of $30R_c$ (22.3nm) in size, the total number of beads was around 81000 in each simulations. The total numbers of bneads of each type is given in the table at the botoom of this section. On the minimization and preliminary scaled-velocity MD stages, all beads were uncharged. Before DPD simulations started, S beads were converted to S- (at low hydration, the beads for conversion were chosen randomly), and randomly chosen W beads were converted to M+ beads, according to the targeted system composition. The total number of DPD steps was 800000 in each simulation. The initial configuration was created by placing all beads at random coordinates within the simulation box. Then the energy was minimized using a primitive steepest descent algorithm, which lead to a segregated system with small hydrophilic clusters of several W, S and M beads. The minimization was followed by 10000 step preliminary MD simulation (γ = 0, no drag or random forces) at temperature fixed by velocity scaling on each step. DPD simulations started from the final configuration obtained in that preliminary MD run. DPD simulations were started from these configurations. First 200000 DPD steps were performed with no long-range correction (electrostatic interactions were cut off at $5R_c$), and after that, Ewald summation was turned on to account for the long-range electrostatics. The structural evolution was characterized using the number of overlapping pairs of mobile (W and M+) beads as a criterion. The initial portions of each trajectory characterized by a persistent upward trend (about 400000 steps) were discarded. Over the last 400000 steps, the system configuration was dumped to disk every 1000 steps. In so doing, we collected 400 configurations for structural analysis and the calculation s of chemical potentials of water via Widom insertions.

Table S2. Numbers of beads of different types in each simulation. The number of M$^+$ (hydrated counterion) beads equals the number of S$^-$ beads. There were no W beads in all simulations for λ=2.24

λ =	2.2			4.5			6.8		
PEW	S-	S	C	S-	W	C	S-	W	C
945	11172	6284	52371	15511	3447	46532	17153	12388	51459
1145	9191	5170	57447	13018	2893	52071	14155	10223	56621
1345	7807	4392	60994	11215	2492	56077	12050	8702	60248
1745	6000	3375	65625	8783	1952	61482	9287	6707	65006

9.0			13.5			18.0		
S-	W	C	S-	W	C	S-	W	C
15511	18957	46532	13018	28929	39054	11215	36138	33646
13018	15911	52071	11215	24923	44862	9851	31743	39405
11215	13708	56077	9851	21892	49257	8783	28301	43916
8783	10735	61482	7924	17609	55467	7218	23257	50525

III. C. Electrostatic interactions: comparison between smeared and point charges.
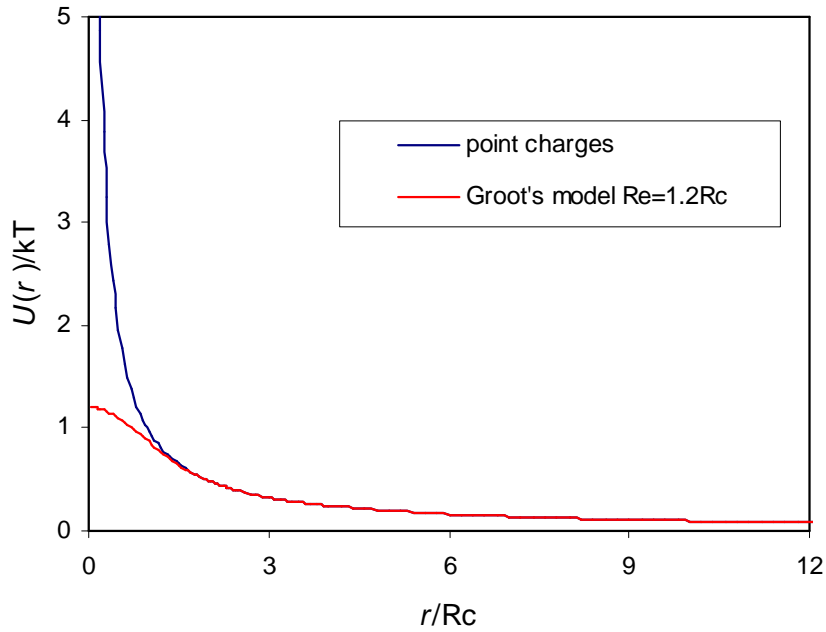

Figure S2. Comparison of electrostatic potential between two +e point charges and linearly smeared charges with smearing radius of R_e=1.2R_c in a dielectric medium of ε = 78, which corresponds to .water at room temperature.

IV. Water sorption and diffusion in hydrated Nafion

Table S3. Main results.

$\lambda =$	9			13.5			18		
PEW	m_W/m_{pol}, %	ϕ_W, %	D_W/D_{pure}	m_W/m_{pol}, %	ϕ_W, %	D_W/D_{pure}	m_W/m_{pol}, %	ϕ_W, %	D_W/D_{pure}
945	16.5	28.6	0.12	24.7	37.5	0.11	32.9	44.4	0.04
1145	13.7	25.0	0.014	20.5	33.3	0.009	27.4	40.0	0.002
1345	11.7	22.2	0.0009	17.6	30.0	0.0002	23.4	36.4	0
1745	9.1	18.2	0	13.6	25.0	0	18.2	30.8	0

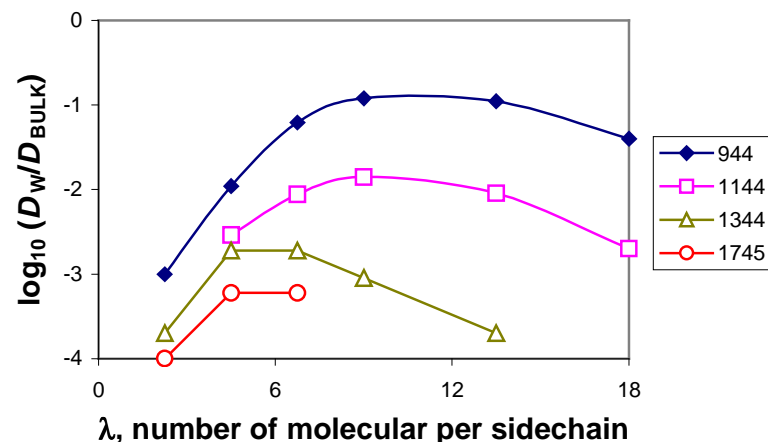| $\lambda =$	2.24			4.5			6.75		
PEW	m_W/m_{pol}, %	ϕ_W, %	D_W/D_{pure}	m_W/m_{pol}, %	ϕ_W, %	D_W/D_{pure}	m_W/m_{pol}, %	ϕ_W, %	D_W/D_{pure}
945	4.1	9.1	0.001	8.2	16.7	0.011	12.3	23.1	0.062
1145	3.4	7.7	0	6.8	14.3	0.0029	10.3	20.0	0.0087
1345	2.9	6.6	0	5.9	12.5	0.0002	8.8	17.6	0.0019
1745	2.3	5.2	0	4.5	10.0	0.0001	6.8	14.3	0.0006

m_W/m_{pol} are calculated assuming K^+ as cation

Figure S3. Self-diffusion coefficient of water in hydrated Nafion reduced to the diffusion coefficient of pure water for polymers of hydration level λ.

References

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