Supporting Information File

Parameterization of a coarse-grained model with short-ranged interactions for modeling fuel cell membranes with controlled water uptake

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1. Potential forms.

Interactions between water molecules are described by the mW water model[1], which is based on the Stillinger-Weber (SW) potential form:

$$U = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{i\square k}), \quad \text{(S1)}$$

$$\phi_2 = 7.049556277\epsilon \left[0.6022245584 \left(\frac{\sigma}{r_{ij}}\right)^4 - 1\right] \exp\left(\frac{\sigma}{r_{ij}-1.8\sigma}\right), \quad \text{(S2)}$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda\epsilon\left[\cos\theta_{ijk} - \cos\theta_0\right]^2 \exp\left(\frac{1.2\sigma}{r_{ij}-1.8\sigma}\right) \exp\left(\frac{1.2\sigma}{r_{ik}-1.8\sigma}\right) \quad \text{(S3)}$$

The screened Coulomb (Yukawa) potential for chloride-chloride interactions:

$$E = \sum_{i<j} \left[A \frac{e^{-\kappa r_{ij}}}{r_{ij}}\right], r_{ij} < r_c, \quad \text{(S4)}$$

where the sum is over the pairs of Cl.

$$E_{\text{smooth}} = \sum_{i<j} \left[E(r_{ij}) f(r_{ij})\right] \quad \text{(S5)}$$

The 12-6 Lennard-Jones (LJ) potential with addition of a taper function[2] that ramps the energy and force smoothly to zero between an inner and outer cutoff:

$$E(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{\square j}}\right)^6\right] \quad \text{(S6)}$$

$$f(r_{ij}) = 1.0, \quad r_{ij} < r_{\text{inner}}, \quad \text{(S7)}$$

$$f(r_{ij}) = (1-x)^3(1+3x+6x^2), r_{\text{inner}} < r_{ij} < r_{\text{outer}}, \quad \text{(S8)}$$

$$f(r_{ij}) = 0.0, r_{ij} > r_{\text{outer}}, \quad \text{(S9)}$$

where $x = \frac{(r_{ij} - r_{\text{inner}})}{(r_{\text{outer}} - r_{\text{inner}})}$, r_{ij} is the distance between particle i and j, $r_{\text{inner}} = 7.0$ Å and $r_{\text{outer}} = 10.0$ Å are the inner and outer cutoff, respectively.

2. Parameters for the coarse-grained force field FF_{pavp} of hydrated PPO/TMACl.

The parameters for the polyphenylene oxide (PPO) fragment are from our previously developed coarse-grained force field FF_{comp}. We highlight in yellow the parameters of FF_{pvap} that are different from those of FF_{comp}.

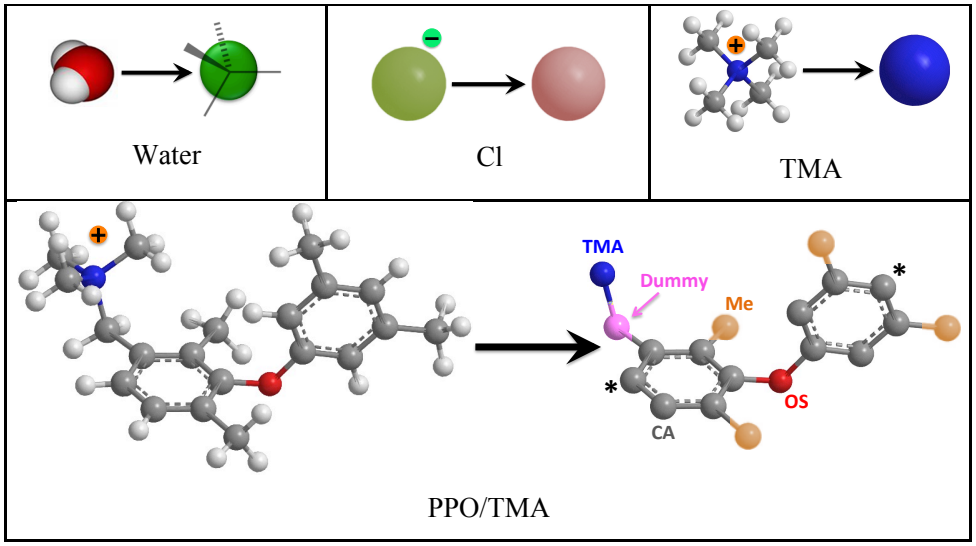

Figure S1. Mapping from the atomistic to the coarse-grained models. In the atomistic model, the white balls represent H, the gray ones C, the blue ones N, and the red ones O. CG water, chloride, and TMA are represented by single particles. CG PPO is represented at the united atom level, with all heavy atoms. A dummy atom is added to control the relative position of the cationic group with respect to the backbone. The PPO/TMA structure of this figure is a PPO/TMA dimer. The sites marked with * indicate the positions which dimers can be linked through OS to create PPO/TMA polymers.

Parameters that have modified from FF_{comp} are displayed in red in the tables that follow.

Table S1. Atom types and their definitions

CG Atom type	Description
mW	Water molecule
Cl	Chloride anion
TMA	Tetramethyl ammonium cation
CA	Aromatic carbon
Me	Methyl group bonded to aromatic carbon
Dummy	Dummy atom to connect the aromatic carbon to TMA
OS	Ether oxygen linking the aromatic rings

Table S2. Two-body parameters for the SW potential, equation S2

Atom type		Parameter	
i	j	ϵ_{ij} (kcal/mol)	σ_{ij} (Å)
mW	mW	6.189	2.3925
mW	TMA	0.65	4.60
mW	Cl	15.0	2.60
TMA	**Cl**	**3.133**	4.60
TMA	TMA	0	0
Cl	Cl	0	0

Table S3. Three-body parameters[a] for the SW potential, equation S3

Atom type			Parameter		
i	j	k	ϵ_{ijk} (kcal/mol)	λ_{ijk}	$\cos\left(\theta_{0ijk}\right)$
mW	mW	mW	6.189	23.15	−1/3
mW	mW	Cl	15.0	16.0	−1/3
mW	Cl	Cl	15.0	13.0	0.258819
Cl	mW	mW	15.0	16.0	−1/3

[a] Three-body interactions for all the other triple combinations that are not listed here are zero.

Table S4. Pair parameters for the Yukawa potential for (Cl,Cl), equation S4

Atom type		Parameter		
i	j	A (kcal/mol)	κ (Å^{-1})	r_c (Å)
Cl	Cl	1107	1.2	10.0

Table S5. Pair parameters for the LJ potential for (TMA, TMA), equations S5 to S9

Atom type		Parameter[a]	
i	j	ϵ_{ij} (kcal/mol)	σ (Å)
TMA	**TMA**	0.005	**6.5**

[a] Inner and outer cutoffs for the tapper function (equations S7 to S9) are 7.0 and 10.0 Å, respectively.

Table S6. Pair coefficients of the LJ potential for the pair-wise interactions between the atom types in PPO, and between PPO and mW/Cl, equations S5 to S9

Atom type		Parameter[a,b]	
i	j	ϵ_{ij} (kcal/mol)	σ (Å)
CA	CA	0.11	3.75
Me	Me	0.118	3.905
OS	OS	0.17	3.00001
CA	Me	0.11393	3.8275
CA	OS	0.1367	3.375
Me	OS	0.14163	3.45251
CA	mW	0.185	3.336
Me	mW	0.22	3.4
OS	mW	0.25	3.036
CA	Cl	0.47	3.61
Me	Cl	0.50	3.61
OS	Cl	0.043	4.699
CA	TMA	0.15	4.3
Me	TMA	0.15	4.3
OS	TMA	0.20	4.3

[a] The inner and outer cutoffs for the tapper function (equation S7 to S9) are 7.0 and 10.0 Å, respectively.

[b] The pair coefficients for interactions of CA-Me, CA-OS, and Me-OS are derived from the pair coefficients for interactions of CA-CA, Me-Me, and OS-OS based on the arithmetic mixing rule; the pair coefficients for all other interactions are parameterized explicitly.

Table S7. Bond parameters, equation 10 in ref [3]

Bond	K_r (kcal mol^{-1} Å^{-2})	r_0 (Å)
CA-CA[a]	31.0	1.4
CA-Me	31.7	1.513
CA-OS	32.0	1.373
Dummy-TMA	29.36	1.51

[a] Note that the aromatic rings are treated as rigid bodies, with internal structure minimized with GAFF in vacuum before mapping it to the CG model.

Table S8. Angle parameters, equation 10 in ref [3]

Angle	K_θ (kcal mol^{-1} radian^{-2})	θ_0 (degrees)
CA-CA-CA[a]	30	120
CA-CA-Me	28	120
CA-CA-OS	27.92	119.2
OS-CA-CA	27.92	119.2
CA-dummy-TMA	25	114.54
CA-OS-CA	25.32	119.95

[a] Note that the aromatic rings are treated as rigid bodies, with internal structure minimized with GAFF in vacuum before mapping it to the CG model.

Table S9. Dihedral parameters, equation 10 in ref [3]

Dihedral	Divider	No. of terms of Fourier series	K (kcal mol^{-1})	n	d (degrees)
CA-CA-CA-CA[a]	1	1	5.3	2	180
CA-CA-CA-Me	1	1	5.3	2	180
CA-CA-CA-OS	1	1	5.0	2	180
Me-CA-CA-CA	1	1	5.3	2	180
Me-CA-CA-OS	1	1	5.3	2	180
OS-CA-CA-CA	1	1	5.0	2	180
OS-CA-CA-Me	1	1	5.3	2	180
CA-CA-OS-CA	1	1	0.9	2	180
CA-OS-CA-CA	1	1	0.9	2	180
Me-CA-CA-Me	1	1	5.3	2	180
CA-CA-dummy-TMA	1	1	4.5	2	0

[a] Note that the aromatic rings are treated as rigid bodies, with internal structure minimized with GAFF in vacuum before mapping it to the CG model.

3. Calculation of the heat of sorption Q_{sorp} in the TMACl solution modeled with FF_{pvap}.

We calculate Q_{sorp} from the Clapeyron-Clausius plot

$$Q_{sorp} = -R\left[\frac{\partial(\ln p_v)}{\partial(1/T)}\right]_{N_w,N_{ions},p},$$

where R is the gas constant, p_v is the vapor pressure of water in the solution, T is temperature, p is pressure, N_w and N_{ions} are the number of water molecules and ions in the solution, respectively. The Clapeyron-Clausius plot is linear, i.e. Q_{sorp} does not change significantly in the temperature range we explore (figure S2).

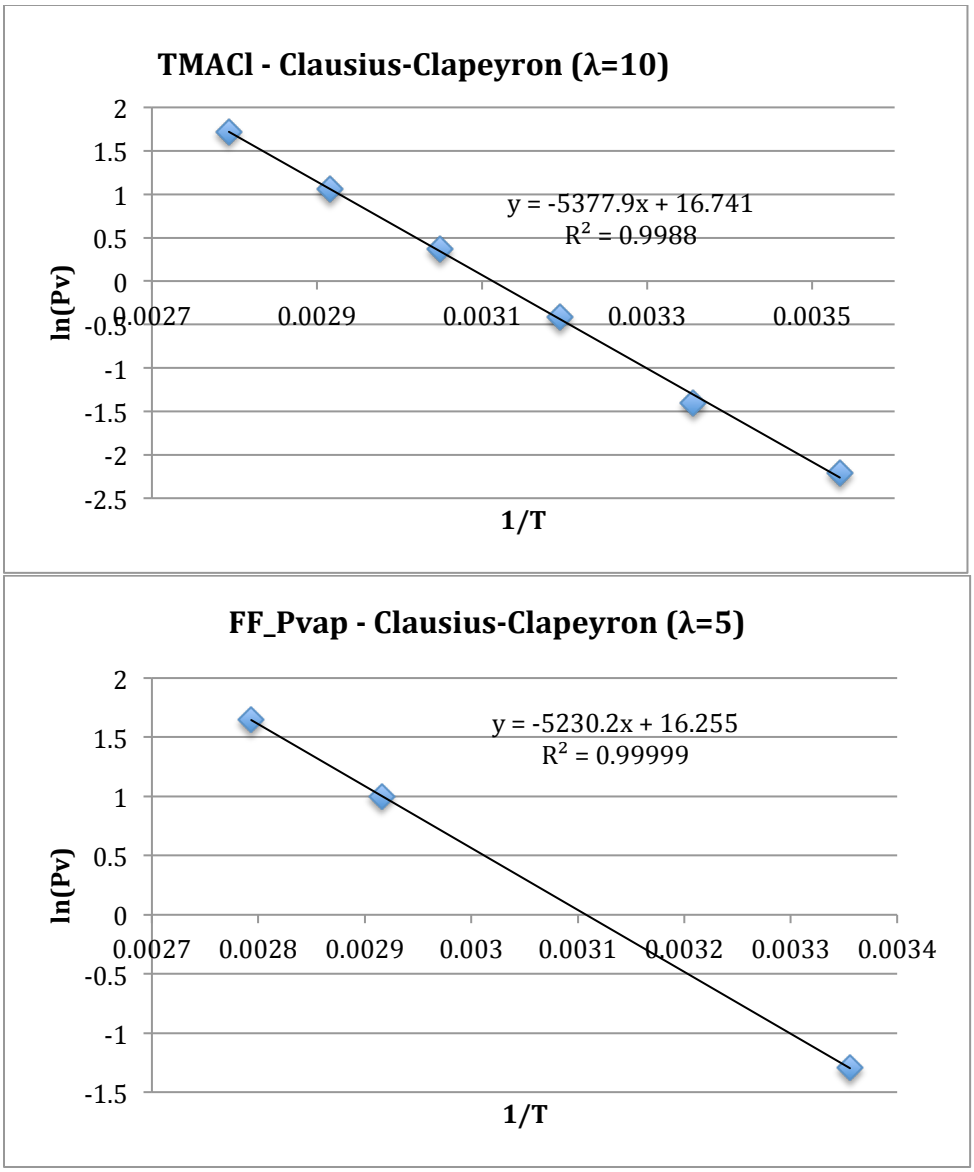

Figure S2. Clausius–Clapeyron relation for TMACl solution at (a) $\lambda = 10$ with FF_{comp}, (b) $\lambda = 5$ with FF_{pvap}. The heat of sorption Q_{sorp} calculated from (a) and (b) are10.69 and 10.40 kcal/mol, respectively.

References

1. V. Molinero and E. B. Moore, *J. Phys. Chem. B*, 2009, **113**, 4008-4016.
2. J. Mei, J. W. Davenport and G. W. Fernando, *Phys. Rev. B*, 1991, **43**, 4653-4658.
3. J. Lu, L. C. Jacobson, Y. A. Perez Sirkin and V. Molinero, *J. Chem. Theory Comput.*, 2017, **13**, 245-264.