SUPPORTING INFORMATION

Role of Water Environment in Chemical Degradation of Covalent Organic Framework tethered with Quaternary Ammonium for Anion Exchange Membranes

Siyao Qiu[a], Wei Wang[a], Jibao Lu[*a,b], Rong Sun[a,b]

[a] *Shenzhen Institute of Advanced Electronic Materials, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China*

[b] *Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China*

*Authors to whom correspondence should be addressed:
E-mail: jibao.lu@siat.ac.cn

COMPUTATIONAL METHODS

The water uptakes of the two COF structures are determined with Grand canonical Monte Carlo (GCMC) simulations at water fugacity of 101 kPa, with the atomic interactions described by the CVFF force field that has been used to model COF structure[1]. The maximum translation displace is 1 Å. The acceptance rules of GCMC simulation are based on Metropolis criterion. Probability of translation and rotate MC moves are 0.2 and 0.2, respectively. Number of steps of the GCMC simulations is 10e8 steps.The GCMC simulation were conducted by Large-scale Atomic/Molecular Massively Parallel Simulator (Lammps)[2]. As for ReaxFF simulation, the initial COF structures with fixed number of water molecules were constructed by Monte Carlo techniques with fix number of loading molecules. Then the ReaxFF simulation was performed for 800 ps with a temperature of 500K and a time step of 0.25 fs, and the last 200ps was used for the analysis of the residual numbers of hydroxide ions. The simulation was conducted by LAMMPS program[2], with a ReaxFF parameter provided in a previous work by van Duin et. al[3]. Also, MD simulations were performed for radial distribution functions (RDF) calculation with COMPASS II force field, a more updated force field confirmed with high reliability, by Forcite module under Material Studio program.[4] This force field is implemented in the Forcite module of the Material Studios software. Note that we use CVFF instead of COMPASS II for the simulation of the water sorption just because we do not have the license for the GCMC module in Material Studio program. To equilibrate the system, NVT ensemble simulation was conducted at 298 K for 2000ps, with a time step of 1 fs. Long-range atom-based method has been applied during the simulation, with 18.5 Å cutoff distance. The integration algorithm is Verlet algorithm. Period boundary condition of a, b, c vector of (25.9418, -14.9775, 0.00), (0.00, 29.955, 0.00), (0.00, 0.00, 29.955) for QA-2 and (26.6554 -15.3895 0.00) (0.00 30.779 0.00) (0.00 0.00 30.779) for QA-6 was used for all simulation. To obtain RDF analysis, frame of an interval of every 500 steps were outputted during the trajectories.

All the DFT calculations were studied via the unrestricted B3LYP functional by Gausian16 program.[5] Def2TZVPP basis sets have been applied for all models.[6] In all cases, the EDIIS/CDIIS procedure was applied for the self-consistent field (SCF) convergence. Also, frequency calculations were performed in order to confirm the nature of the stationary points and to obtain the zero point energy (ZPE) as well as the thermal correction terms. Therefore, all the energies reported below were Gibbs free energies under mild conditions. Also, the dispersion interaction

correction had been included during geometry optimization by using the Grimme's D3 damping function in all models.[7] The B3LYP functional is widely used in calculations of degradation of cations.[8-11] Besides, PBE functional were calculated to compare with B3LYP result.

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CHEMICAL DEGRADATION UNDER DIFFERENT WATER ENVIRONMENT
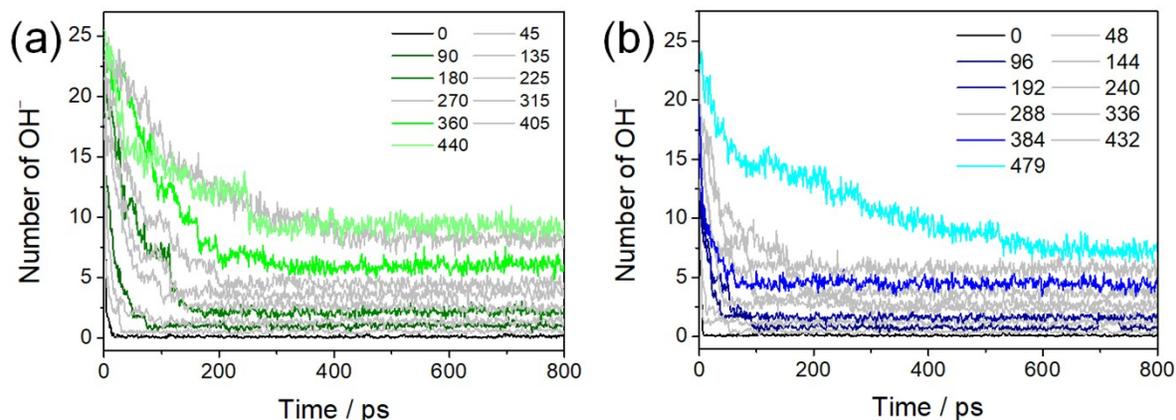
Figure S1. Time dependence of the residual number of OH⁻ in (a) COF-QA-2, and (b) COF-QA-6, under different water environment.

CHEMICAL DEGRADATION AT SAME DENSITY OF WATER
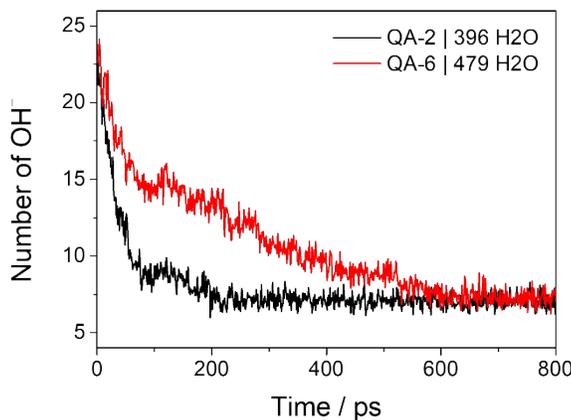
Figure S2. Time dependence of the residual number of OH⁻ in the COF-QA-2 and COF-QA-6 systems with 396 and 479 water molecules, respectively. The two systems have the same ρ_w^{eff} of 1.626 per nm³ (see ESI for detailed conversion of ρ_w^{eff})

Independent trajectories for the same model have been simulated,with the results shown in Figure S3. It can be seen that a system with independent initial COF structures and number of water molecules are very close to each other, demonstrating the reproducibility of the simulations.
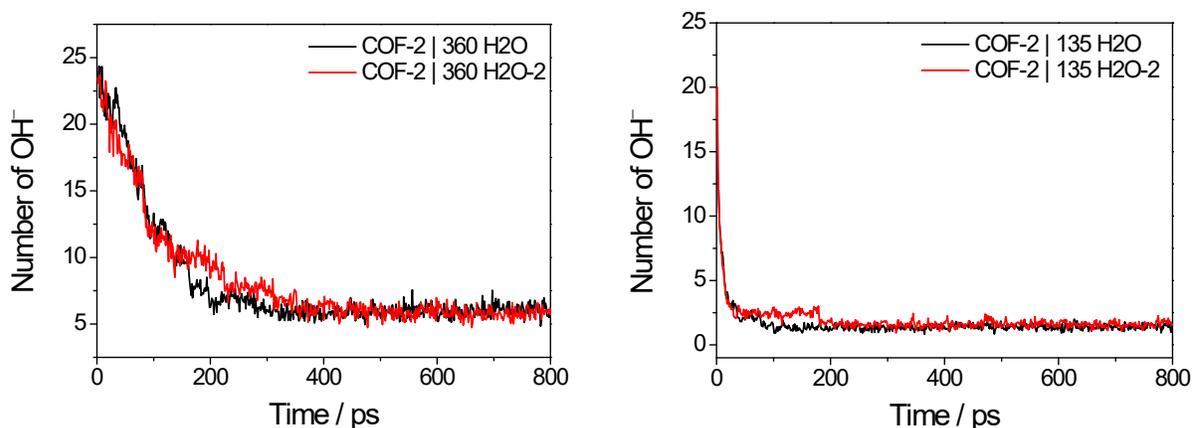
Figure S3. Time dependence of the residual number of OH⁻ in the COF-QA-2 with 135 and 360 water molecules.

SUPPLEMENTARY DFT CALCULATIONS

DFT calculations on the energy difference of QA-4

Number of water	Route	energy difference / eV
0	1	-2.15
	2	-1.79
1	1	-1.73
	2	-1.59
2	1	-1.39
	2	-1.28
3	1	-1.11
	2	-1.01

From the chart, we could learn that QA-4 shows similar energy change with QA-2 and QA-6.

DFT calculations on the energy difference of QA-2 with 4 and 5 water molecules
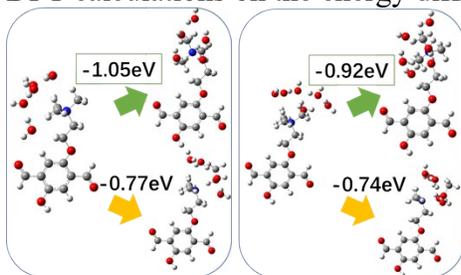
DFT calculations conducted by PBE functional on QA-2

Number of water	Route	energy difference / eV
0	1	-2.12
	2	-1.73
3	1	-1.26
	2	-1.20

From the chart, the PBE functional shows similar trend with B3LYP result.

DFT calculations with different initial configurations

	E1 / Hartree	E2 / Hartree	Delta E / eV
QA2-OH-3H2O	-1167.161907	-1167.161221	0.018667
QA2-OH-2H2O	-1090.687602	-1090.687594	8E-06
QA2-OH-H2O	-1014.213359	-1014.213229	0.00354
QA2-OH	-937.736577	-937.736546	0.000844
QA2-NCH3-3H2O	-1167.205456	-1014.281355	0.03197
QA2-NCH3-2H2O	-1090.742285	-1090.742173	0.00305
QA2-NCH3-H2O	-1014.281837	-1014.281355	0.01312
QA2-NCH3	-937.819519	-937.819219	0.008163

EFFECTIVE DENSITY OF WATER

Table S1. He void ratio detected by iRASPA program for QA-2 and QA-6.

	HE VOID RATIO [-]	ALPHA	BETA	GAMMA	A	B	C
COF2	0.47496	90	90	120	29.955	29.955	29.864
COF6	0.39877	90	90	120	30.779	30.779	34.648

The void ratio of two models is 0.43753 and 0.43171, and the volume of two models are 23.207 nm3 and 28.426 nm3. Therefore the void volume of two models are 10.154 nm3 and 12.272 nm3, and the ratio of number of water molecules between the two models would be 0.8274.

Assuming the number of waters in QA-6 remains 479, which is ρ_w^{eff} equals to 1.626 per nm3, the number of waters per void volume in QA-6 is 39. To keep a same number of waters per void volume in QA-2, the number of waters in QA-2 model would be 396.