Supporting Information

High-Throughput Molecular Simulations Reveal the Origin of Ion Free Energy Barriers in Graphene Oxide Membranes

Christopher D. Williams*, Paola Carbone and Flor R. Siperstein

Department of Chemical Engineering and Analytical Science, School of Engineering, The University of Manchester, Manchester, United Kingdom.

Data Tables

Table S1. Permeation free energy barriers, ΔF_i, and pull energies, U_{pull}, for each K^+ permeation pathway in GO membranes with a water content of 15% (average interlayer spacing, d = 0.79 nm). The final column shows the convergence of free energy barrier with number of pathways obtained by selecting the minimum energy pathway and averaging over the five membranes. Units: kJ mol^{-1}.

i	1		2		3		4		5		ΔF
	ΔF_i	U_{pull}	ΔF_i	U_{pull}	ΔF_i	U_{pull}	ΔF_i	U_{pull}	ΔF_i	U_{pull}	
1	193.7	10.1	104.5	3.4	151.9	6.4	77.7	3.0	42.6	8.9	114.1
2	53.6	7.7	86.8	4.1	162.8	6.0	59.8	2.9	204.6	12.0	79.0
3	129.2	8.6	67.6	4.1	174.7	6.9	206.0	4.5	50.4	10.4	75.1
4	208.9	8.4	57.8	3.4	169.8	6.3	132.1	3.7	101.4	12.8	73.2
5	113.2	8.9	245.4	6.6	46.0	5.4	124.5	3.2	129.6	12.5	52.0
6	78.0	7.9	450.2	8.5	134.5	6.7	205.8	5.2	157.2	8.5	52.0
7	161.7	11.5	104.6	3.5	89.4	6.4	261.7	5.6	69.3	9.4	52.0
8	71.5	8.5	112.7	3.9	78.9	7.7	58.9	2.3	71.1	9.0	51.8
9	125.5	10.6	88.3	3.9	359.5	11.6	137.8	3.7	89.0	7.6	51.8
10	140.5	9.6	89.5	3.5	172.1	8.8	41.7	2.3	42.4	7.7	48.3
11	224.6	9.9	136.7	5.6	178.3	6.0	137.5	3.3	72.9	8.9	48.3
12	169.8	9.3	96.5	4.8	463.9	10.2	66.3	3.0	145.5	8.9	48.3
13	171.1	11.6	98.8	3.6	109.3	6.1	169.7	5.8	71.4	8.7	48.3
14	194.5	8.8	193.7	5.7	53.9	5.8	50.4	2.4	160.8	9.5	48.3
15	146.3	8.5	107.5	7.2	119.0	7.0	346.6	10.4	95.7	15.0	48.3

Table S2. The two free energy barriers, ΔF_i, for each water content and each of the five membrane models. Units: kJ mol^{-1}.

H$_2$O content (%)	1		2		3		4		5	
10	49.1	107.0	66.4	66.1	56.7	88.2	105.2	105.6	138.1	98.7
15	53.6	78.0	57.8	104.5	46.0	53.9	58.9	41.7	89.0	42.4
20	40.1	57.5	56.4	35.9	46.6	33.9	34.5	60.4	46.0	41.1
25	30.4	46.1	22.4	17.3	24.3	30.4	48.9	44.0	30.7	27.5
30	47.9	22.1	64.4	33.6	47.4	28.5	38.5	27.0	18.7	24.9
35	22.4	25.1	11.2	37.2	10.7	21.1	21.2	28.9	22.8	29.0
40	13.6	45.6	19.6	16.7	38.3	14.7	25.7	12.7	19.3	23.2

Table S3. Average n_{KOw} from the lowest energy pathway from each of the five membrane models at each water content.

H$_2$O content (wt%)	10	15	20	25	30	35	40
d (nm)	0.76	0.79	0.87	0.96	1.06	1.19	1.35
1	3.9	4.0	5.0	5.9	5.8	6.0	6.3
2	4.3	4.3	5.3	5.7	5.1	6.1	6.0
3	3.9	4.9	5.2	5.8	5.4	6.3	6.3
4	4.0	4.4	4.8	5.2	5.7	6.0	5.9
5	3.6	4.7	4.9	5.5	5.7	6.2	6.1
average	3.9	4.5	5.1	5.6	5.6	6.1	6.1
% of bulk n_{KOw}	54	62	70	77	77	84	84

Table S4. Maximum n_{KOw} from the 50 umbrella sampling windows for the lowest energy pathway for each of the five membrane models at varying water content.

H₂O content (wt%)	10	15	20	25	30	35	40
d (nm)	0.76	0.79	0.87	0.96	1.06	1.19	1.35
1	5.7	4.8	6.4	6.3	6.6	6.5	6.7
2	4.9	5.8	6.6	6.3	6.4	6.4	6.7
3	5.2	6.5	6.1	6.7	6.1	6.5	6.7
4	5.9	5.8	6.4	6.5	6.5	6.5	6.8
5	5.0	5.9	6.4	6.3	6.4	6.6	6.8
average	5.4	5.8	6.4	6.4	6.4	6.5	6.7
% of bulk n_{KOw}	74	79	88	88	88	90	93

Table S5. Minimum n_{KOw} from the 50 umbrella sampling windows for the lowest energy pathway for each of the five membrane models at varying water content.

H₂O content (wt%)	10	15	20	25	30	35	40
d (nm)	0.76	0.79	0.87	0.96	1.06	1.19	1.35
1	1.0	2.7	3.1	4.4	4.4	3.9	4.7
2	3.1	2.7	3.1	4.1	3.8	4.2	3.1
3	2.8	3.6	3.2	4.9	3.9	5.4	5.1
4	1.4	3.3	2.4	3.4	3.6	4.1	4.4
5	1.6	3.1	2.7	3.6	4.3	4.1	4.4
average	2.0	3.1	2.9	4.1	4.0	4.1	4.3
% of bulk n_{KOw}	27	42	40	56	55	60	60

Table S6. Average n_{KO} for the lowest energy pathway, averaged over all 50 umbrella sampling windows for each of the five membrane models at varying water content.

H₂O content (wt%)	10	15	20	25	30	35	40
d (nm)	**0.76**	**0.79**	**0.87**	**0.96**	**1.06**	**1.19**	**1.35**
1	6.8	6.9	7.5	7.3	7.4	7.6	7.4
2	6.5	7.2	7.6	7.5	7.6	7.4	7.5
3	7.0	7.2	7.4	7.5	7.6	7.5	7.6
4	7.0	6.9	7.9	7.3	7.2	7.5	7.4
5	7.0	7.3	7.8	7.5	7.6	7.6	7.3
average	7.1	7.1	7.6	7.4	7.5	7.5	7.4
% of bulk n_{KOw}	95	97	105	102	103	104	102

Table S7. Maximum n_{KO} from the 50 umbrella sampling windows for the lowest energy pathway for each of the five membrane models at varying water content.

H₂O content (wt%)	10	15	20	25	30	35	40
d (nm)	**0.76**	**0.79**	**0.87**	**0.96**	**1.06**	**1.19**	**1.35**
1	8.7	9.0	8.5	8.7	8.5	8.6	8.4
2	8.9	9.5	8.6	8.8	8.7	8.5	9.6
3	8.6	8.6	8.4	8.6	9.5	8.4	9.3
4	8.8	8.5	9.2	9.2	9.0	8.7	8.2
5	8.8	9.3	9.2	8.5	8.6	9.4	8.6
average	8.8	9.0	8.8	8.8	8.9	8.7	8.8
% of bulk n_{KOw}	121	124	121	121	122	120	121

Table S8. Minimum n_{KO} from the 50 umbrella sampling windows for the lowest energy pathway for each of the five membrane models at varying water content.

H$_2$O content (wt%)	10	15	20	25	30	35	40
d (nm)	0.76	0.79	0.87	0.96	1.06	1.19	1.35
1	6.3	5.7	5.6	7.1	6.6	6.8	6.9
2	5.8	5.9	6.7	7.0	7.0	6.2	6.7
3	6.3	5.3	6.4	7.3	6.7	7.3	6.9
4	6.1	6.0	6.3	6.3	6.6	6.9	7.0
5	6.0	6.4	7.1	7.1	6.4	6.9	6.8
average	6.1	5.9	6.4	6.9	6.7	6.8	6.9
% of bulk n_{KOw}	84	81	89	96	92	94	94