Supporting Information for:

Selective ion transport in large-area graphene oxide membrane filters, driven by ion radius and electrostatic interactions.

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Figure S1. Picture of the experimental setup.
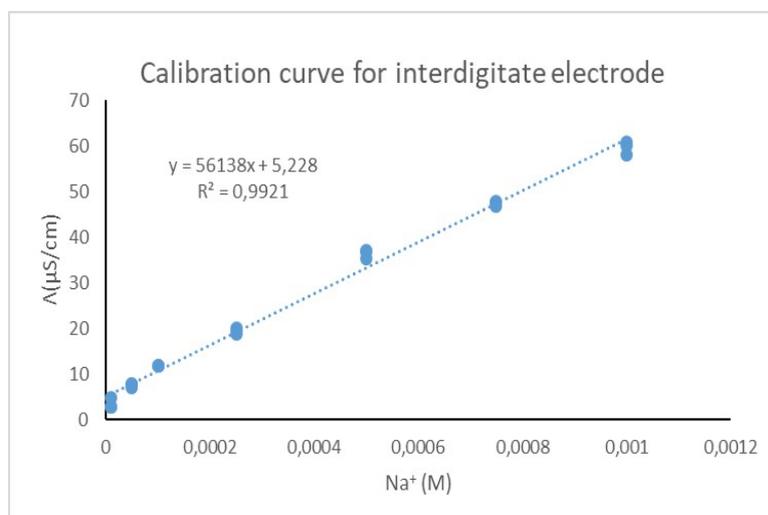
Figure S2. Correlation between the conductivity measured by EIS and the concentration of NaCl.
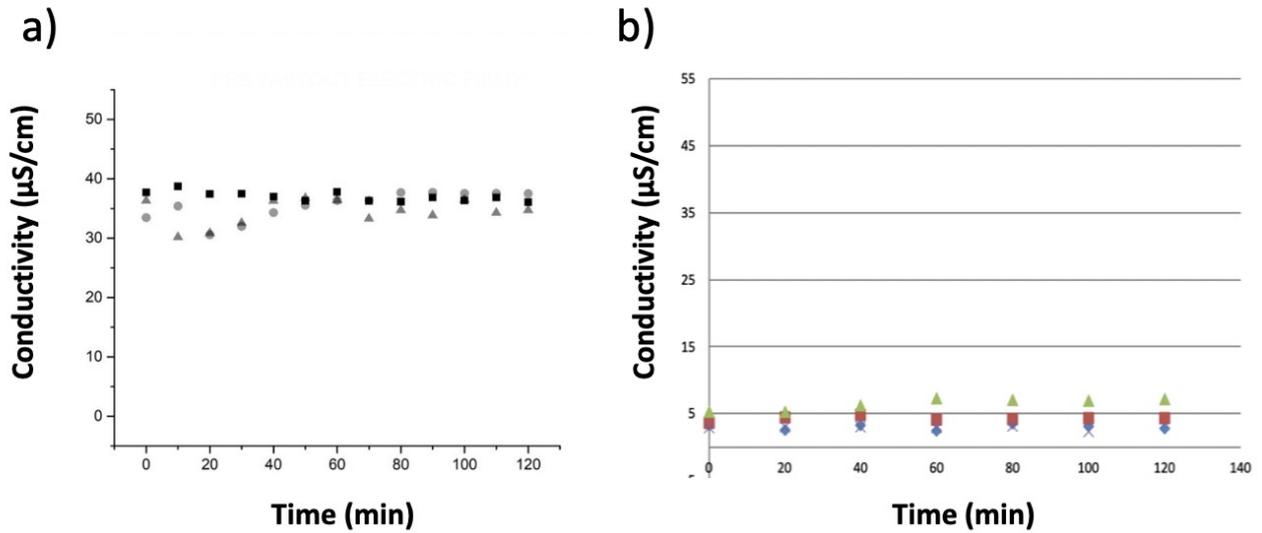
Figure S3. Values of conductivity measured in tank 2 while letting a 0.1 M solution of NaCl in tank 1 freely diffuse for 120 min in a) pristine PES with open nano-pores and b) PES-GO-5 hollow fibers. Three replicates for each test are reported.
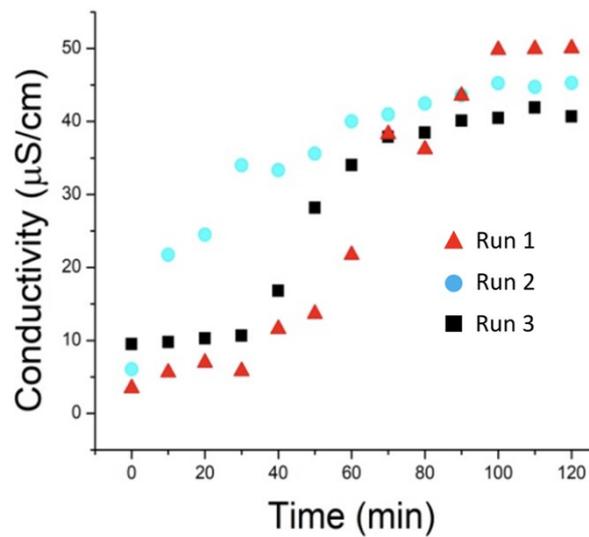
Figure S4. Evolution of the conductivity recorded by EIS in tank 2 due to ion transport of Na+ at constant potential difference of -1.0 V. Typical curves obtained in three different HF-GO-5 filters are shown.

Test of different coating thickness

We tested transport of both Na^+ and for Ca^{2+} in filters with varying GO membrane thickness. [1] We obtained a significant transport of ions for all coatings, and such transport was not inversely proportional to the GO thickness, as could be expected in a simple permeation process, as example for gases. [2]

Table S1. Amount of GO suspension filtered in each module in relation to the thickness of the GO membrane obtained and to the acronym used in the text

Volume filtered (mL)	% GO (w/w)	Film thickness $(\mu m)^1$	Sample name
5	1	0.5	HF-GO-1
7.5	2.5	1.0	HF-GO-2.5
15	5	1.5	HF-GO-5

Table S2. Percentage adsorption values of the selected cations on GO.

	KCl $[10^{-5}$ M$]$	SD	HCl $[10^{-5}$ M$]$	SD	HCl $[10^{-3}$ M$]$	SD	HCl $[10^{-1}$ M$]$	SD
Na^+	5.7	8.6	10.2	9.6	18.6	4.0	16.2	2.0
Ca^{2+}	64.9	2.8	21.2	3.2	20.9	3.7	21.9	4.3
Li^+	10.3	3.5	7.3	1.9	16.8	1.1	12.7	1.5
Mg^{2+}	33.7	0.6	34.3	1.7	39.5	4.0	9.8	0.8
K^+	91.8	3.2	87.0	5.8	98.8	0.2	40.7	4.5
Pb^{2+}	86.4	0.5	85.6	0.4	49.6	5.6	2.3	1.8

Table S3. Computed total binding affinity and its contributions *i.e.*, van der Waals, electrostatic (E_{El}) and non-polar solvation (E_{SURF}) for Na^+ and Ca^{2+} towards GO membrane. All energies are reported in kcal mol^{-1}. A column graph with the same numbers is also shown.

	Na$^+$	Ca^{2+}
van der Waals	12.0	28.9
Electrostatic	-50.8	-86.7
E_{SURF}	-0.5	-0.4
Total Affinity	-39.3	-58.2
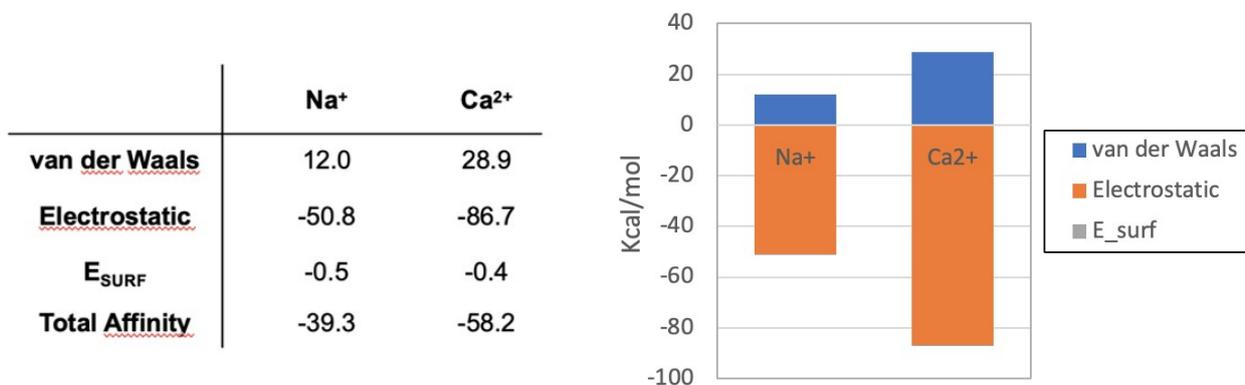
Table S4. Diffusion Coefficients of Na^+ and Ca^{2+} calculated by MD in bulk water, adsorbed on a nanosheet of GO in water, or intercalated between two nanosheets of GO with water (model shown in fig. 5a,b), in presence or absence of an electric field. All numbers are reported in $[10^9 \text{ m}^2/\text{s}]$ units.

	Na$^+$	Ca^{2+}
Bulk solution	6.63	1.28
Monolayer GO	Ion detached	Ion detached
Bilayer GO	0.026	0.018
Bilayer GO + 1V/cm electric field	0.038	0.0042
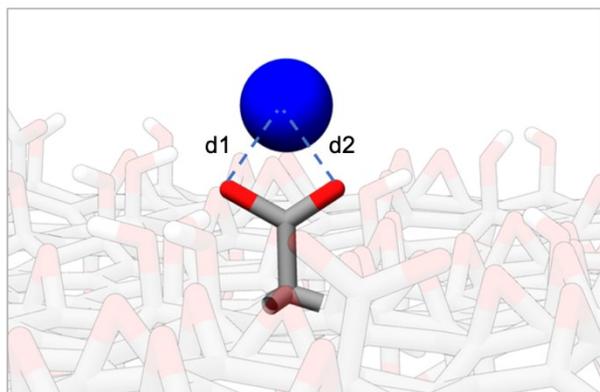
	D = (d1+d2)/2 [Å]
Na^+	2.36
Ca^{2+}	2.30
K^+	2.65
Li^+	2.04
Pb^{2+}	2.33
Mg^{2+}	2.03

Figure S5. Scheme showing the interaction of a ion with a carboxyl group of GO, as modelled by MD. b) Average distance between the oxygen atoms of the carboxylate and the different ions, where d1 and d2 distances correspond to what shown in the scheme in a).

Table S5. Chemical composition of GO membranes from XPS in atomic %. *GO membrane before use. All membranes after immersion in solution present some residuals of: i) PO4 ion (P 2p signal at 133.9 eV 0.2-0.3 at. %). ii) Al2O3 (Al 2p signal at 75 eV c.a. with 0.7-1.4 at. %). A slight amount of Al (Al 2p) was present due to a residual of Alumina filter used for the preparation of GO membranes.

Force	Solution	Na KLL 263.8 eV	Ca 2p 3/2 347.8 eV	C 1s 285.0 eV	O 1s 532.5 eV	N 1s 401 eV	Cl 2p 200 eV
none	*	-	-	70.8±0.8	27.9±0.5	0.7±0.2	0.3±0.1
Electric Field	H_2O	-	-	70.2±0.8	27.3±0.5	0.5±0.1	0.14±0.05
	Na^+	0.03±0.005	-	69.5±0.8	27.9±0.5	0.5±0.1	0.13±0.05
	Ca^{++}	-	0.18±0.05	69.7±0.8	27.2±0.5	0.9±0.2	0.21±0.05
Hydrodynamic Pression	H_2O	-	-	69.7±0.8	27.9±0.5	0.5±0.1	0.15±0.05
	Na^+	0.02±0.005	-	71.2±0.8	26.9±0.5	0.5±0.1	0.18±0.05
	Ca^{++}	-	0.42±0.05	69.7±0.8	27.9±0.5	0.4±0.1	0.51±0.05
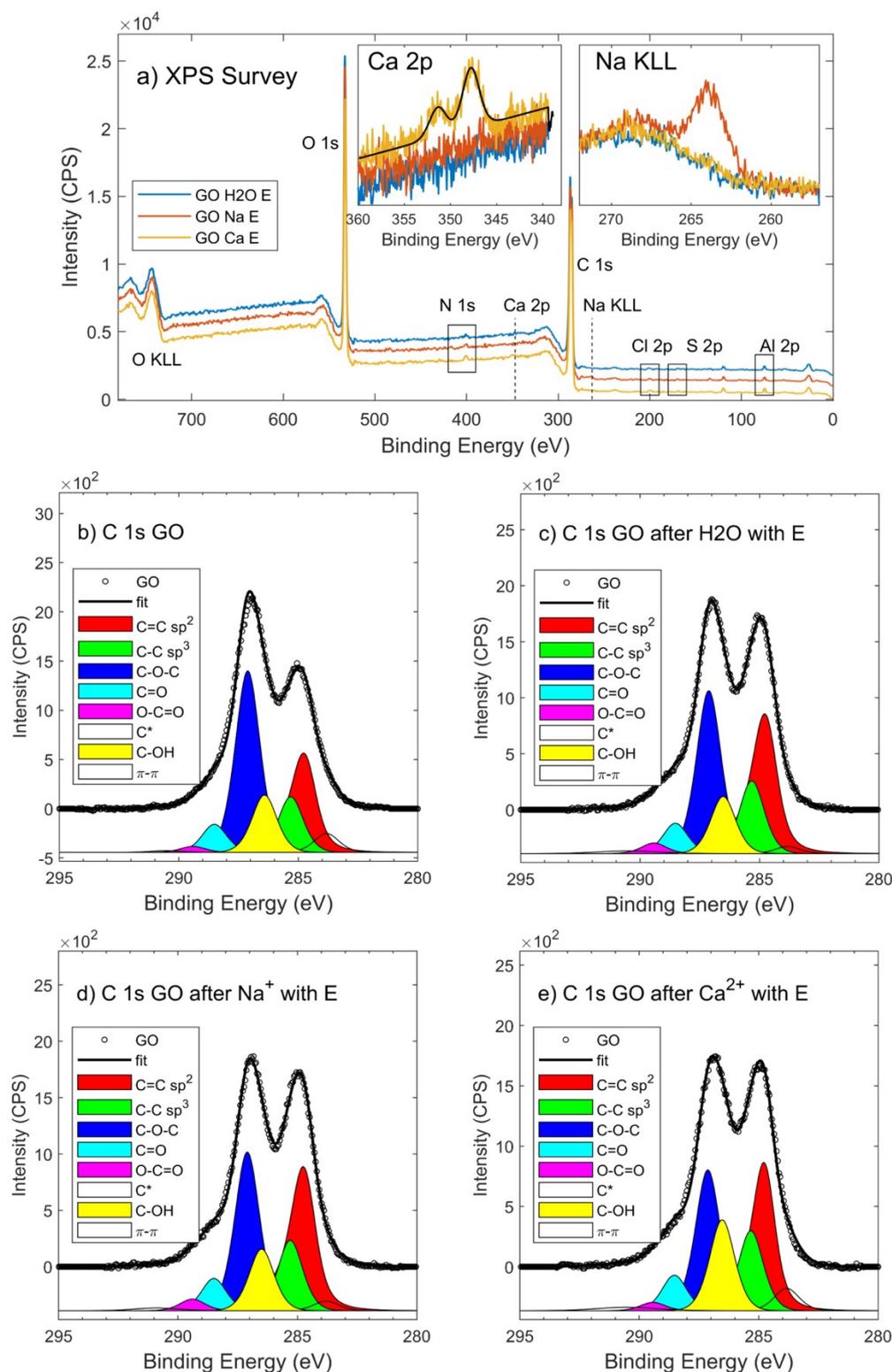
Figure S6. (a) XPS survey spectra of GO after exposure to pure water and electric field (GO H$_2$O E) and to a solution containing either Na$^+$ (GO Na E) or Ca^{2+} (GO Ca E) and the electric field. Spectra are vertically shifted for better visualization. Insets: Ca 2p and Na KLL signals, black line is Ca 2p fit. C 1s signal fit of (b) pristine GO membrane, (c) GO membrane after exposure to pure water and and electric field, (d) GO membrane after exposing to Na$^+$ (GO Na E) and the electric field, (e) GO membrane after exposing to Ca^{2+} (GO Ca E) and the electric field.

Characterization by XPS

XPS spectra were obtained using a Phoibos 100 hemispherical energy analyser (Specs GmbH. Berlin. Germany) and Mg Ka radiation (photon energy 1253.6 eV; power = 125 W) in constant analyser energy (CAE) mode, with analyser pass energy of 40 eV for survey and 10 eV for high resolution spectra. The overall resolution of 1.5 eV for survey spectra and (Na KLL and Ca 2p) was measured on Ag 3d 5/2 (368.3 eV) and analyser was calibrated using Au 4f 7/2 (84.0 eV) signals from freshly Ar^+ sputtered samples. Charging effects were corrected by calibration of binding energy on C 1s (285.0 eV) for all spectra. Before the measurements, the membranes were cleaved by using scotch tape (Magic Tape. 3M) in order to probe a fresh surface for XPS.

All line-shape were fitted with Voigts function, the only exception was the asymmetric pseudo-voigt used for sp^2 aromatic carbon.[1] All the doublets were fitted by a doublet with fixed spin orbit split of for Ca 2p (3.60 eV), Cl 2p (1.6 eV) and a fixed area ration between the two components. Data analysis and fitting were performed with CasaXPS software, after Shirley background subtraction.

Peak positions used for fit C 1s were: aromatic carbon (C=C sp^2 284.4 eV and C=C* 283.5 eV). aliphatic carbon (C-C sp^3 285.0 eV), hydroxyl (C-OH 286.2 eV), epoxy (C-O-C 286.8 eV), carbonyl (C=O 288.2 eV) carboxyl (O-C=O 289.1 eV). The relative abundances of C-O functional groups in pristine GO obtained from C 1s fit were: 30.2% C=C sp^2, 12 % C-C sp^3, 12 % C-OH, 39% C-O-C, 6.0 % C=O, 1.3 % O-C=O. The O/C ratio for GO was O/C=0.40±0.01, obtained from the area ratio of C1s and O 1s signal. this value were in agreement with those found by fit of C 1s (O/C fit =0.4) as described in our previous work.[2,3]

MM-GBSA calculations of the Na^+ and Ca^{2+} ions interaction with the HF-GO membrane.

We fully sampled the interaction energy of the Na^+ and Ca^{2+} cations in the inter-layer region of the HF-GO membrane (interactions with epoxides, hydroxyls, carboxylate and all the possible

combinations). We evaluated the MM-GBSA binding energy for 5000 snapshots taken from the MD simulations, sampling all the different positions that the cations can assume (Figure S7).
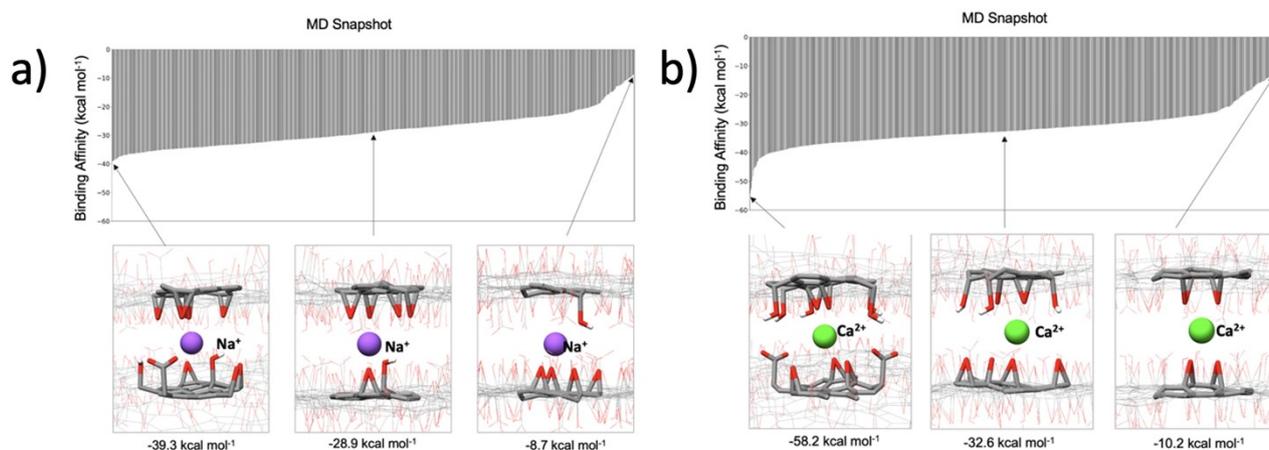
Figure S7. MM-GBSA calculations of the a) Na^+ and b) Ca^{2+} ion interaction with HF-GO membrane. The calculations were carried out on 5000 snapshots taken by the MD simulations and ordered from the most interacting to the less interacting snapshot. All the atoms within 6 Å from the ions are represented as sticks, otherwise as wires. Carbon atoms are in grey, oxygen atoms in red, hydrogen atoms in white.
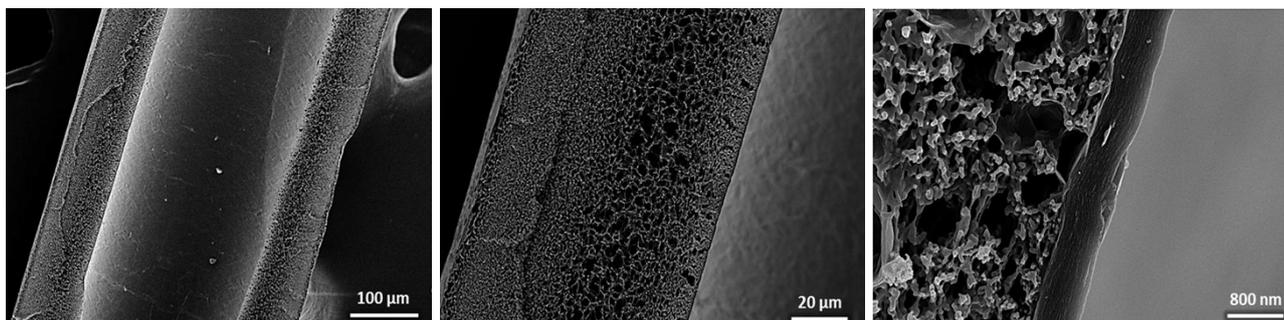
Figure S8. SEM micrograph of the cross section of HF-GO membrane taken along the long axis of the fibre (Z direction) at different magnifications. SEM operated at 5 kV, 5 mm working distance and secondary electron's signal was collected from In-Lens detector. Cross section was obtained by filling the HF-GO-5% cartridge with pure water and freezing it in liquid nitrogen for 5 min; then, it was broken using a rubber hammer; the broken fibers cross the Z direction were freeze-dried for 12 hours before being collected.

Bibliography

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