Two-dimensional adaptive membranes with programmable water and ionic channels

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Membranes are ubiquitous in nature with primary functions that include adaptive filtering and selective transport of chemical/molecular species. Being critical to cellular functions, they are also fundamental in many areas of science and technology. Of particular importance are the adaptive and programmable membranes that can change their permeability or selectivity depending on the environment. Here, we explore implementation of such biological functions in artificial membranes and demonstrate two-dimensional self-assembled heterostructures of graphene oxide and polyamine macromolecules, forming a network of ionic channels that exhibit regulated permeability of water and monovalent ions. This permeability can be tuned by a change of pH or the presence of certain ions. Unlike traditional membranes, the regulation mechanism reported here relies on specific interactions between the membranes’ internal components and ions. This allows fabrication of membranes with programmable, predetermined permeability and selectivity, governed by the choice of components, their conformation and their charging state.

The structure of our membranes with adaptive permeability is analogous to that of rigid cellular plant membranes\textsuperscript{13–15} with the function of the ionic channels played by the functional groups of polyamine macromolecules (PA) and graphene oxide (GO). The rigid walls\textsuperscript{13–15} and strong interactions in the van der Waals structure prevent swelling of hydrophilic components and provide structural stability to the membranes. Unlike typical membranes\textsuperscript{16–18} where water and ionic flow are controlled by pore size and the external pressure, the permeability through our membranes is determined solely by the charging (protonation) state of the components of the van der Waals structure and specific interactions with certain ions. Thus, water permeability is determined by the intrinsic osmotic pressure within the interior of the rigid membrane, which arises due to excessive proton concentration due to specific (competing) charging states of GO and PA. Similarly, the ionic transport is controlled by the competing interaction between protons and ions with the functional groups at the GO–PA interfaces, which has strong selectivity towards ions, thus allowing selective ionic pumping. Furthermore, we observe that the permeability of some ions can be regulated by the presence of other ions, creating a ‘transistor effect’ for selective ionic transport.

The ordered membrane structure was formed by self-assembly of GO and PA macromolecules (Fig. 1a,b). The preparation procedure is described in the Methods. Briefly, a suspension of GO (average size of flakes, 2 μm) was mixed with polyethyleneimine for 10 min. We used branched polyethyleneimine with low (25 kDa) and high (750 kDa) molecular weights. Due to the opposite charges on the GO and PA molecules and the low entropy of macromolecules, GO flakes become completely covered by the polymer, as confirmed by the atomic force microscopy (AFM) images in Fig. 1c–e,h–j. After thorough washing (which ensures that only one
monolayer of PA molecules is adsorbed on GO flakes) and a slow reduction of a volume of solvent via vacuum filtration, the suspension of PA-decorated GO particles is collapsed in a highly ordered composite membrane with a regular distribution of monolayers of PA and GO. The measurements of the surface potential of the membranes show that the outermost layer is formed by negatively charged GO (Supplementary Fig. 1).

Polyethyleneimine is a weak polycation and its degree of ionization strongly depends on pH25,26. The degree of ionization of GO is also pH dependent, and it can be considered a weak polyanion24. For control purposes, we also prepared bare GO membranes and membranes where GO is covered with poly(diallyldimethylammonium) chloride (PDADMAC), which is a positively charged strong polyelectrolyte with a dissociation that does not depend on pH25. Thermogravimetric analysis shows that the mass ratio of GO to PA (25 kDa) in our membranes is approximately 1:1 (Supplementary Fig. 2), and the differential scanning calorimetry curve (Supplementary Fig. 2) shows no step typical for a glass transition of PA at pH 10.2, and the GO without PA (bottom) with extracted interlayer distances. Schematic illustrations for the membranes’ structure depending on pH of the solution during assembly based on the X-ray diffraction data shown in Fig. GO and PA are represented in the same way as in b, h, i, AFM height (h) and phase (i) images of the GO flakes assembled with PA at pH 10.2. j, Height profile taken along the yellow dashed line in h. Scale for c, d, h and i is given by the scale bar in c, which is 0.5 μm. Z scale for c and h (height) from black to white is 0 to 20 nm. Z scale for d and i (phase) from black to white is 0 to 60 degrees.

The typical thickness of our membranes used in permeability experiments is 250 nm for GO–PA of 25 kDa and 500 nm for GO–PA of 750 kDa (Supplementary Figs. 2 and 3) and can be regulated by the concentration of the suspension used for vacuum filtration and the molecular weight of polymer (Supplementary Fig. 3). The X-ray diffraction and AFM data confirm (Fig. 1c–i) that the membranes obtained by this method indeed have a layered structure of alternating GO and PA monolayers. Note that the conformation of PA macromolecules depends on the pH of the suspension during the assembly. Depending on the pH of the suspension, it is possible to deposit PA in the form of coils (Fig. 1h, i) or stretched chains (Fig. 1c, d) and to obtain two different structures as illustrated in Fig. 1g. The X-ray diffraction measurements show that after assembly, the interlayer distance is insensitive to the humidity conditions (Supplementary Fig. 4).

We measured the water flux through our membranes by using them as a separator between two reservoirs—one with water (where we can control the pH by adding HCl or NaOH) and one with 2.5 M sucrose (standard osmosis experimental method26; Fig. 2a, e). The 2.5 M sucrose creates a large permanent external osmotic pressure (61 bar) across the membrane27 and accelerates the permeability. The water flux across the membrane as a function of pH is presented in Fig. 2a. Our GO–PA membranes are very permeable for acidic solutions and much less permeable for basic ones (Fig. 2f–h). The bare GO membranes behave in the opposite way compared to the GO–PA membranes: they are more permeable at basic pH and less permeable at acidic pH (though the change is dramatically smaller; Fig. 2c), and the GO–PDADMAC (strong polyelectrolyte) membranes show similar permeability to water as GO membranes; that is, the permeability is only weakly dependent on pH (Supplementary Fig. 5).

To check the stability of our GO–PA membranes and the reproducibility of the measurements, in a separate experiment we changed pH abruptly and measured the water flow for several hours (each measurement at a particular pH takes 24 h; Fig. 2c). One can see that such membranes are very stable (dramatically more stable than pure GO membranes), can survive multiple cycles of pH changing and can strongly adjust their permeability according to pH. Note that bare GO membranes of similar thickness decomposed after one cycle (the low stability of bare GO membranes is well documented in the literature28). We also see that water flux depends on the
Fig. 2 | Selective permeability of GO–PA membranes. a, Water flux as a function of pH for two of our GO–PA membranes (red squares, PA with molecular weight 750 kDa; blue circles, PA with molecular weight 25 kDa). We tested ten membranes. The measured water flux is fitted by the formula $c\ln(p_{\sigma_{\text{in}}}/p_{\sigma_{\text{out}}})$, where $c = 3.2 \text{ ml h}^{-1}\text{m}^{-2}\text{bar}^{-1}$ is the only fitting parameter connecting the water flux with the chemical potential drop defined in the text. Here, $p_{\sigma_{\text{in}}}$ and $p_{\sigma_{\text{out}}}$ are the H$^+$ concentrations between GO layers and near the outer wall of the membrane, respectively (see the main text). Black triangles show water flux for bare GO membranes demonstrating very weak dependence on pH. b, Dependence of surface charge density on pH for pristine GO flakes (black triangles), GO–PA flakes with PA of molecular weight 750 kDa (red squares), and GO–PA flakes with PA of molecular weight 25 kDa (blue circles). The measurements are fitted by the Henderson–Hasselbalch equation with $a = 4.5$ and $\sigma_0 = 0.2 \text{ C m}^{-2}$ for GO; $a = 4$ and $\sigma_0 = 0.175 \text{ C m}^{-2}$ for GO–PA (25 kDa); and $a = 5.5$ and $\sigma_0 = 0.4 \text{ C m}^{-2}$ for GO–PA (750 kDa). c, Water permeability through GO (black triangles) and GO–PA (red squares for membrane assembled at pH 2 and orange diamonds for membrane assembled at pH 10.2). Each point was measured for 24 h. GO membrane decomposed after 24 h of measurements. The measured water flux is fitted by the formula $I = \sigma_0^2 \rho_{\text{in}}/C_0/C_1$, where $I$ is the water flux, $\rho_{\text{in}}$ is the proton concentration near the negatively charged plane is constant due to protonation of PA chains. This charge results in the excessive ionic strength as well as the increased hydrophobic nature (Supplementary Fig. 6) of weakly charged PA coils compared to more strongly charged stretched chains. Thus, the permeability of water through our GO–PA membranes can be reliably regulated by external pH.

To understand the membrane’s water permeability mechanism, we first measured the surface charge density of GO–PA and GO flakes ($\sigma_{\text{GO–PA/GO}}$) using the potentiometric titration method and fitted the data by the Henderson–Hasselbalch equation, $\sigma_{\text{GO–PA/GO}} = \pm \sigma_0/(1 + 10^{(pH - pK_a)/a})$, with the saturated surface charge density $\sigma_0$ of the order of 0.1 C m$^{-2}$ (Fig. 2b). The fitting suggests that the charge density reaches half-saturation at pH = $pK_a$, with $pK_a = 7.7$ for pristine GO and $pK_a = 6.7$ for GO–PA. To fit each charge density curve with only one $pK_a$, we have used a smoothing parameter $a$. The parameter values are given in the caption of Fig. 2b. GO–PA flakes are strongly charged at acidic pH due to protonation of PA chains. This charge results in the excessive ionic concentration between GO planes where PA resides. We estimate this inner H$^+$ concentration as $\rho_{\text{in}} = \sigma_{\text{GO–PA}}/ed$, where $e$ is the elementary charge, $d \approx 2 \text{ nm}$ is the interlayer distance and $\sigma_{\text{GO–PA}}$ is shown in Fig. 2b for the two PAs used.

GO flake form the outer walls of the membrane and are therefore exposed to the environment. GO planes acquire a negative surface charge in water (Fig. 2b), and the outer GO plane determines the beginning of the diffuse layer in electrokinetic theory. The counterion concentration near the negatively charged plane is given by the Boltzmann distribution $\rho_{\text{out}} = \rho_{\text{in}}^\infty e^{\phi \infty/4kT}$ and exceeds the bulk value $\rho_{\text{out}}^{\infty} \approx N_0 10^{-7} \text{mol dm}^{-3}$ determined at infinity (fig
from the charged surface). Here, \( T = 300 \text{ K} \) is the temperature, \( k_b \) is the Boltzmann constant, \( N_A \) is the Avogadro number and \( \phi_0 \) is the electrostatic potential at the surface. The latter obeys the Grahame equation derived from the total (surface and electrolyte) electroneutrality condition\(^{30} \) and given by

\[
\frac{\sigma_{\text{GO}}^2}{8\varepsilon_0\varepsilon_kk_bT\rho_{\text{out}}} = \sinh^2\left(\frac{\phi_0}{2k_bT}\right),
\]

where \( \varepsilon_0 \) is the dielectric constant, \( \varepsilon \approx 80 \) is the water relative dielectric permeability and \( \sigma_{\text{GO}} \) is the GO surface charge shown in Fig. 2b by the black curve. As illustrated in Fig. 3 the inner counterion concentration is assumed to be homogeneous (determined by the protonation state of the PA), whereas the outer one depends on the distance from the membrane’s wall in accordance with the Poisson–Boltzmann equation. The outer counterion concentration acquires its maximal value \( \rho_{\text{out}} \) near the outer wall and then decreases into the bulk of water, approaching \( \rho_{\text{out}}^\infty \). The inner excess concentration \( \rho_{\text{in}} - \rho_{\text{out}} \) for PA with 25kDa reaches a maximum at pH \( \approx 2 \). At higher pH the difference between inner and outer concentrations gradually vanishes and eventually becomes negative.

The known inner and outer counterion concentrations allow us to estimate the chemical potential difference \( \Delta \mu = k_bT\ln\left(\rho_{\text{in}}/\rho_{\text{out}}\right) \), which has a maximum of about 100 meV at pH \( \approx 2 \) (Supplementary Fig. 7). The potential difference creates an excess osmotic pressure between the diffusion layer and interior of the membrane\(^{36} \). It is further tunable by adjusting the pH of the adjacent solution. The water flux is assumed to be proportional to \( \Delta \mu \), resulting in controllable water transport across the membrane (Fig. 2a,c).

The model suggests that water accumulates inside the membrane at pH \( \approx 2 \). To confirm this, we measured water uptake by the membrane using a quartz-crystal microbalance. We found that the same membrane uptakes water at acidic pH but does not at basic pH (Fig. 2d). The measurements on the same membrane can be repeated multiple times with very good reproducibility (Supplementary Fig. 8) by drying it in air and placing it back into water solution.

It is possible that the intake of water due to excess osmotic pressure at low pH promotes swelling of the membrane in the vertical direction and contraction in the lateral due to the Poisson effect. The in situ liquid cell transmission electron microscopy experiments show that the wrinkled GO flakes in our membranes are unfolded in the presence of water (Supplementary Fig. 9), showing the adaptivity of our membranes and forming potential for self-healing applications.

According to the quartz-crystal microbalance data (Supplementary Fig. 8), the maximum quantity of water that the membranes can absorb is approximately 12 wt% at low pH, which corresponds to the presence of \( 2 \times 10^{12} \) molecules of water per layer. A water molecule measures approximately 0.3 nm, thus covering an area \( 1.8 \times 10^{-14} \text{m}^2 \), which corresponds approximately to the area of our membrane. Hence, \( 2 \times 10^{12} \) water molecules form just a single monolayer per unit cell in the most hydrated state. This confirms again that the membrane retains a perfectly integrated layered structure even when it is soaked in water.

We also studied ionic permeability through the membranes. To this end, we used the same set-up as before (Fig. 2e), where the membranes separate two volumes: one with aqueous solution of monovalent cations (here we control the pH and concentration of the four ions Cs\(^+\), K\(^+\), Na\(^+\) and Li\(^+\)) and another one with the 2.5 M solution of sucrose. Note that the GO–PA 750kDa membranes were completely impermeable for any of the studied ions (Supplementary Fig. 10), probably due to a large positive charge density of PA and thus, the electrostatic rejection of cations typical for polyelectrolytes\(^{35,36} \). In addition, such low permeability of the membranes prepared with a high molecular weight polyelectrolyte can also be related to longer hopping paths for ions along long polymer chains. By contrast, GO–PA 25kDa membranes demonstrate measurable permeability. Thus, we can tune the ionic permeability of our membranes without sacrificing the water permeability.

Two sets of experiments were performed on GO–PA 25kDa membranes. In the first one, we used only one particular salt in solution (0.1 M solutions of either KCl, NaCl, CsCl or LiCl) and measured ionic permeability for different pH values (Fig. 4a). Concentration of ions was measured by inductively coupled plasma optical emission spectroscopy analysis 24h after the permeability test. We found that K\(^+\) permeability through the GO–PA 25kDa membrane is a strong function of the pH, whereas the permeability of Na\(^+\), Cs\(^+\) and Li\(^+\) remains low (20 times lower than that of K\(^+\)) and is almost independent of the pH (Fig. 4a). The transport of K\(^+\) (Fig. 4a) and water demonstrates similar dependence on pH (Fig. 2a). In general, the fast permeability of small ions in pure GO (Supplementary Fig. 11) is explained in terms of capillary pressure\(^{37-41} \).

In the second experiment we tested the permeability of a mixture of 0.1 M solutions of the four chloride salts at pH values of 2 and 5.5 (Fig. 4b). Surprisingly, when in the mixture, we observe a finite permeability for all four ions (not for only K\(^+\)), which also depends on the hydrated radius of the ion and on the pH: ions with low hydrated radius permeate more intensively than those with larger radius and the permeability is increased at low pH. We conjecture that the presence of K\(^+\) stimulates transport of other ions as well. To test this hypothesis, we performed the permeability experiment of Cs\(^+\) first on its own and then in the presence of K\(^+\). As in the previous experiments, Cs\(^+\) does not permeate when on its own in solution (Fig. 4c). After 12h, upon adding 0.1 M K\(^+\) to the solution (Cs to K ratio is 1:1) we started to observe a finite concentration of...
GO–PA membranes prepared at pH 10.2. 

Attenuated total reflectance Fourier transform infrared spectra of the GO, PA and GO–PA membranes. Potentiometric titration curves for suspensions of GO and GO–PA by 0.1 M base (NaOH, KOH, CsOH and LiOH).

Clearly not the case in the GO–PA membranes: Cs+ ions permeate more slowly than K+, which would indicate the hydrated ionic radii with the cut-off around 4.5 Å, which is the hydrated radius permeates more slowly than K+, and the radius of either is around 3.25 Å. Furthermore, interlayer spacing in our membranes is notably larger (1.9–2.5 nm) than in bare GO membranes (0.9–1.2 nm).

To explain the substantial difference in the permeability of K+ and other ions as well as the cumulative effect of ion permeability, we studied the interaction of GO and GO–PA with ions using potentiometric titration by 0.1 M NaOH, KOH, CsOH and LiOH (Fig. 4d,e). There is a very small difference for the titration of GO in the four different bases (Fig. 4d). However, we observe a strong shift in measured pK for the titration of GO–PA by KOH (Fig. 4e). The titration curve for GO–PA by KOH indicates that a large number of functional groups in GO–PA are accessible for K+. K+ replaces protons in such groups, releasing them to the medium, thus shifting the measured pK. Indeed, inductively coupled plasma analysis of the membranes immersed in salt solutions shows that the concentration of K+ inside of the membrane is higher than the concentrations of Na+, Cs+ and even Li+ (Supplementary Fig. 12).

We have several explanations of why our GO–PA membranes have such a strong affinity to K+. In nature, selectivity of potassium channels in biological membranes is explained by specific interactions of carbonyl oxygen atoms with K+. Coordination of carboxyls is also responsible for transport of K+ by a K+ selective ionophore, valinomycin. Na+ and Li+ cannot be transported because the dehydrated ions of Na and Li are too small to interact with the inward-facing carbonyls of peptides. To this end we use X-ray photoelectron spectroscopy and attenuated total reflectance Fourier transform infrared spectroscopy (Fig. 4f and Supplementary Fig. 13) to monitor the presence of carboxyls in the GO–PA membrane. Whereas the carbonyls’ corresponding peak is very weak in pure GO (Fig. 4f), such peak appears strongly in GO–PA membranes, which suggests that due to electrostatic interactions between GO and PA, carbonyl groups are exposed to their interface. Due to the specific affinity of K+ to carbonyl groups at the interfaces formed by GO and PA, the entire membrane acts as an ionic pump. Once the affinity is established (like in the case of GO–PA and K+) the ion hopping transport is possible along the interfaces that form the channels.

Based on these observations we suggest the following model for the ionic transport through GO–PA membranes. In the normal state GO–PA membranes are closed for the transport of hydrated ions due to strong repulsion between the cations and the positively charged PA. However, the chains of carbonyl groups at the interface of GO and PA act as selective ionic channels, allowing dehydrated K+ to permeate through. Large K+ ions might even replace protons on GO–PA interfaces, reducing the overall charge, thus opening both ions in the drain side. Thus, the system behaves as a chemical transistor, and adding the signalling component (K+) opens the flux of the main compound (Cs+).

Fig. 4 | The pH-regulated ion permeability through the GO–PA 25 kDa membrane. a, Ionic permeability of GO–PA membranes as a function of pH measured separately for K+, Na+, Cs+ and Li+ from 0.1 M aqueous solutions of corresponding salts. Red line, a fitting curve deduced from the combinatorial model explained in the Supplementary Information. b, Ionic permeability versus the hydrated radii of ions under osmosis conditions against 2.5 M sucrose solution for the 0.1 M mixture of ions adjusted to pH 2 and pH 5.5. We used 0.1 M solutions of corresponding chloride salts adjusted to a particular pH. Overall, in a and b three membranes were tested for each pH, and the statistical distribution is given by the error bars. The experimental time was 24 h.

c, Ionic permeability of GO–PA membranes for Cs+ only for 12 h; after 12 h, K+ ions were added and permeability was measured for both K+ and Cs+ for the mixed 0.1 M salt solution at pH 5.5. d, e, Potentiometric titration curves for suspensions of GO and GO–PA by 0.1 M base (NaOH, KOH, CsOH and LiOH). Titrations started from acidic solutions prepared by adding 0.1 M HCl. f, Attenuated total reflectance Fourier transform infrared spectra of the GO, PA and GO–PA membranes prepared at pH 10.2.
channels for hydrated ions of any species. Thus K⁺ acts as a sort of gate in an 'ionic transistor'. Furthermore, the sensitivity of such a 'transistor' to the presence of K⁺ ions can be regulated by the overall protonation state of PA, through the external pH.

The proposed model is highly phenomenological and thus it is very difficult to provide a quantitative description for it. The key mechanism that opens the ionic channels for the transport of hydrated ions is the replacement of a fraction of protons in the interlayer PA with K⁺ ions. The K⁺/H⁺ exchange can be treated as a stochastic process of competition between protons and potassium ions for the available sites on GO–PA. A simple combinatorial model suggests that the maximum of the K⁺/H⁺ exchange frequency should be achieved when the surface densities of H⁺ and K⁺ inside the membrane are approximately the same. The result of this model, presented in Fig. 4a, fits the dependence of potassium permeability as a function of pH reasonably well. The model also suggests that permeability for K⁺ is always higher than for Cs⁺ in the K⁺/Cs⁺ mixture because K⁺ can exchange with both H⁺ and Cs⁺ whereas Cs⁺ can exchange with K⁺ only. This is indeed observed in Fig. 4c: the permeability ratio for K⁺ and Cs⁺ is larger than one and does not depend on time. A similar effect can also be seen in permeability for Na⁺ and K⁺ (Supplementary Fig. 14). The model based on the fitted surface charge densities (Supplementary Fig. 15 and Supplementary Table 1) is further illustrated in Supplementary Figs. 16 and 17.

The biomimetic behaviour of our membranes in terms of controlled water transport and selective ionic permeability is a striking feature that is essential for the creation of adaptive membranes. Furthermore, our membranes are operational and highly dynamic even in physiological conditions. The ionic selectivity and permeability can be further programmed during the preparation stage (for instance, by the choice of strength of the polyelectrolytes and their charge density), opening multiple opportunities for applications. For instance, it should be possible to design membranes with regulated selective K⁺/Na⁺ pumping, for the extraction of Li⁺ or separation of Cs⁺. We also stress that our membranes use a novel mechanism of regulated water and ion permeability. Gaining further control of such mechanisms will be of fundamental importance for understanding and construction of stimuli responsive composite materials. Such membranes will allow building relatively simple artificial structures that reproduce such properties of living matter as switchable ionic permeability and selectivity and will lead to further advances in the formation of super-nanocapacitors, membranes with selective release of ions for biofilm growth, membranes for extraction of Li⁺ for lithium-ion batteries and extraction of radioactive Cs⁺ for water purification, as well as for iontrons and neuromorphic devices. Thus, membranes operating on the principles we discussed can be the key components for the construction of artificial membranes with intrinsic intelligence.

Online content

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The membranes were prepared by vacuum filtration of suspensions of GO flakes (GO, 2 mg ml⁻¹, dispersion in H₂O; Merck) covered by polyethyleneimine (branched, average molecular weight ~25,000 Da by light scattering, number average molecular weight ~10,000 by gel permeation chromatography; Merck) and polyethyleneimine (branched, number average molecular weight ~60,000 by gel permeation chromatography, average molecular weight ~750,000 Da by light scattering, 50 wt% in H₂O; Merck) on two types of filters: Anodisc 47 (pore size, 0.02 µm; diameter, 47 mm; Whatman) and polyethersulfon membrane (pore size, 0.03 µm; diameter, 47 mm; Sterlitech). The surface charge of GO and GO–PA flakes was estimated using a titration method. The titrations of 0.5 g GO or GO–PA were performed in 0.005 M NaCl background electrolyte. Titrations started either from lower pH (GO dispersion) or higher pH (GO–polyethyleneimine dispersion) using 0.1 M NaOH or 0.1 M HCl as base/acid titrants. Both dispersions were titrated in the pH range from 2 to 12. Water flux was measured by using a H1C side-by-side diffusion system equipped with an H1C magnetic stirrer and a heater/circulator (PermeGear). The membrane was placed between two compartments. In one half, we added 2.5 M solution of sucrose (99%; Merck) in water to create a pressure of approximately 61 bar. In the second half of the cell, we used water solutions at a particular pH that was adjusted using 1 M HCl or 1 M NaOH solutions. The permeability tests were conducted for 24 h. A Perkin Elmer Optima 5300DV was used to measure the concentration of ions by inductively coupled plasma optical emission spectroscopy.

Morphology was studied by atomic force microscopy using a Dimension FastScan AFM (Bruker). The cross-section was studied by scanning electron microscopy using a field emission scanning electron microscope FEI Verios460 (ThermoFisher Scientific) at an operating voltage of 2 keV. The structure was studied by X-ray diffraction using a Bruker D8 Advance X-ray transmission diffractometer (Bruker; CuKα radiation from the copper target using an in-built nickel filter, λ = 1.54056 Å). Swelling was studied by quartz-crystal microbalance measurements on an AWS A20 system (BioLogic) using Ti/Au polished-finish 5 MHz resonators.

Measuring proton concentration. We also directly measured how many H⁺ the GO–PA membrane could consume and accumulate from the electrolyte to show that amino groups of PA molecules in the membranes are accessible for H⁺ and provide their accumulation in the midplanes of the sandwiches. We used a two-compartment cell (for details, see the Supplementary Information) and placed our membrane between the compartments, which were filled with water at pH 2 and water at pH 11. Monitoring the pH in both compartments showed that 5 × 10⁻⁴ mol of protons were consumed from the water at pH 2 and 1.97 × 10⁻⁵ mol of protons were released into the water at pH 11 within 24 h; therefore, 3.03 × 10⁻⁵ mol of protons accumulated in the membrane. Knowing the weight of PA (~1.5 mg per membrane), we could calculate how many amino groups were actually available for H⁺ per membrane: 3.25 × 10⁻⁵ amino groups were available for H⁺ and could accumulate 3.03 × 10⁻⁵ mol of H⁺. Thus, these results support our hypothesis that PA is important for the accumulation of electrostatically attracted H⁺.

**Data availability**
The data that support the plots within this paper and other findings of this study are available from the corresponding author on reasonable request.

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**Author contributions**
D.V.A., M.T. and K.S.N. conceived and designed the experiments. A.N., M.C.F.C., P.V.C., M.H., K.Y., S.C., S.W.C. and U.M. performed the experiments. A.H.C.N. contributed the materials and analysis tools. D.V.A., M.T. and K.S.N. co-wrote the paper. All authors discussed the results and commented on the manuscript.

**Competing interests**
The authors declare no competing interests.

**Additional information**
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