ONE-ATOM-THICK CRYSTALS AS A NOVEL CLASS
OF PROTON CONDUCTING MATERIALS

A THESIS SUBMITTED TO
THE UNIVERSITY OF MANCHESTER
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (PHD) IN
THE FACULTY OF ENGINEERING AND PHYSICAL
SCIENCES

MARCELO LOZADA HIDALGO

SCHOOL OF PHYSICS AND ASTRONOMY

2015
List of Figures

Figure 2.1 Microchamber experiment. ...............................................................20
Figure 2.2 Energy dispersion of π electrons in graphene.................................24
Figure 2.3 Lattice structure of other 2D crystals............................................26
Figure 2.4 AFM images of a V₂O₅ monolayer in air......................................27
Figure 3.1 Hydrogen bond between two water molecules.............................30
Figure 3.2 Distance between hydrogen bonded species...............................32
Figure 3.3 Energy surface for a chemical reaction......................................36
Figure 4.1 Chemical composition of Nafion................................................38
Figure 4.2 Gierke model of Nafion...............................................................39
Figure 4.3 Hydrogen fuel cell........................................................................41
Figure 5.1 Fabrication process of free standing one atom thick crystal membranes. .46
Figure 5.2 Optical images of cleaved crystals.............................................47
Figure 5.3 Transfer techniques.....................................................................47
Figure 5.4 Final devices...............................................................................49
Figure 5.5 Optical images of two free standing graphene membranes...........50
Figure 5.6 Scanning electron micrograph of a suspended graphene membrane. ......51
Figure 5.7 Raman spectrum of our suspended graphene devices....................52
Figure 5.8 Microchamber experiment..........................................................53
Figure 5.9 Pt deposition on the membranes...............................................54
Figure 5.10 Set up for conductance measurements.......................................55
Figure 5.11 Gas flow experimental set-up....................................................56
## Contents

1. Introduction .................................................................................................................... 15

2. Graphene: basic properties .......................................................................................... 18
   2.1 Mechanical and impermeability properties ......................................................... 18
   2.2 Electrical properties ............................................................................................. 23
   2.3 Beyond Graphene .................................................................................................. 26

3. Proton Conductivity ...................................................................................................... 29
   3.1 The Hydrogen Bond .............................................................................................. 29
   3.2 Proton transport in hydrogen bond networks ...................................................... 31
   3.3 The hydrogen isotope effect .................................................................................. 34

4. Nafion and Fuel Cells .................................................................................................... 38
   4.1 Nafion .................................................................................................................... 38
   4.2 Fuel Cells ............................................................................................................... 40

5. Experimental Techniques ............................................................................................. 45
   5.1 Device Fabrication ................................................................................................. 45
   5.2 Device Characterization ........................................................................................ 50
   5.3 Electrical and Mass Spectrometry Measurements .............................................. 54

6. Proton Transport through One-Atom-Thick Crystals .................................................. 57

7. Isotope Selective Transport through 2D Crystals ....................................................... 91

8. Concluding Remarks ..................................................................................................... 124

9. References ..................................................................................................................... 126
Abstract

Graphene, a one-atom-thick sheet of carbon atoms, is impermeable to all atoms and molecules; the same can be expected for other 2D crystals like hexagonal boron nitride (hBN). In this work we show that monolayers of graphene and hBN are highly permeable to thermal protons. As a reference, we show that monolayers of molybdenum disulphide as well as bilayers of graphene and tetralayers of hBN are not. Moreover, we show that water plays a crucial role in the transport mechanism. Because of the zero point energy of vibration in the oxygen-hydrogen bonds in water, protons face energy barriers smaller than previously predicted by theory. The effect, revealed by substituting hydrogen for deuterium, also shows that protons and deuterons transport at different rates across the membranes; establishing them as membranes with subatomic selectivity. Beyond the purely scientific implications, our results establish monolayers of graphene and hBN as a promising new class of proton conducting materials with potential applications in fuel cells, hydrogen purification and isotope enrichment technologies.
Declaration

The University of Manchester

PhD by published work Candidate Declaration

Candidate Name: Marcelo Lozada Hidalgo

Faculty: Engineering and Physical Sciences

Thesis Title: One-Atom-Thick Crystals as a Novel Class of Proton Conducting Materials

Declaration to be completed by the candidate:

I declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Signed: Date:
Copyright

The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”)¹ and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

The ownership of certain Copyright, patents, designs, trademarks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

Further information on the conditions under which disclosure, publication and commercialization of this thesis, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see http://documents.manchester.ac.uk/DocuInfo.aspx?DocID=487), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on Presentation of Theses.

¹ This excludes material already printed in academic journals, for which the copyright belongs to said journal and publisher. Pages for which the author does not own the copyright are numbered differently from the rest of the thesis.
Acknowledgements

These three years have been some of the most rewarding I’ve had; not least, because during that time I learned how to do science. In that respect, I’d like to thank Prof. Andre Geim – from whom I keep learning how to do science – for his guidance throughout these years. But during these years I also had a great time. And for that I’d like to thank my colleagues at the lab: Colin Woods, James Chapman, Thanasis Georgiou, Artem Mishchenko, Sheng Hu, Sebastian Heeg, Axel Eckmann, Roshan Krishna Kumar, Liam Britnell and Mengjian Zhu to name but a few. Special thanks to Roshan Krishna Kumar for proof reading the thesis. But this experience was possible thanks to the people back home, especially Prof. Teresa Alonso and Mtra. Dolores Sánchez from CONACyT. I gratefully acknowledge support from CONACyT to carry out my PhD. Finally, and most important, I’d like to thank my family: my parents Marcelo and Gisela and my sisters, Daniela, Alejandra and Gisela. Their support got me to where I am today.
1 Introduction

The question of whether a proton – the nucleus of a hydrogen atom – can transfer across 2D crystals [1] is not *a priori* evident. Indeed, these crystals have so far been proven impermeable to all gases and molecules under ambient conditions [2]–[5]. Moreover, the existing theory had predicted that protons would face unsurmountable energy barriers while trying to cross these crystals’ electron clouds [6]–[8]. Notwithstanding, we find that thermally excited protons can transport with unexpected ease. We furthermore show that the disagreement with the theoretical predictions is not surprising. The existing theory has so far considered the transport properties of protons in vacuum. In that case, the large energies associated with a naked charge result in energy barriers as much as twice the height of the measured ones. However, protons are not in vacuum and therefore the proton donating medium should play a crucial role. And indeed, by substituting hydrogen for its heavy isotope deuterium, we have shown that to be the case.

The finding that protons can transfer through 2D crystals provides fresh insight into the much studied electron transport properties of these crystals [9]–[13]. Protons are charged particles 2000 times more massive than electrons; yet the proton and electron transport properties of these crystals are not correlated. In fact, the best proton conductor in this work is an electron insulator. But beyond the purely scientific implications, the proton permeation properties of these crystals may prove useful in a
number of hydrogen based technologies from fuel cells and purification membranes to isotope separation.

The outline of this work is as follows. In Chapter 2 we introduce graphene and its mechanical, electrical and impermeability properties. Because of its importance to this work, focus is placed in the experiments that prove its impermeability to all gases. We then proceed to review some basic properties of other crystals, in particular hexagonal boron nitride (hBN) and molybdenum disulphide (MoS$_2$).

In chapter 3, some basic elements of the mechanism of proton conduction are reviewed. We introduce the hydrogen bond and explain its relevance to the conduction mechanism in electrolytes. Finally, the effect of substituting hydrogen for deuterium in proton conducting systems is reviewed. In chapter 4 we briefly review some basic properties of fuel cells and Nafion (the proton conducting polymer used in this work).

Chapter 5 deals with the experimental techniques of this work. Device fabrication is discussed from crystal exfoliation to membrane production. Characterization and device measurement techniques are also reviewed; especially, the techniques used to show the absence of pinholes in our suspended crystal membranes.

The main body of results is presented in chapter 6. It includes all the results that prove that protons can transfer across monolayers of hBN and graphene but not MoS$_2$ or thicker layers of hBN and graphene. This chapter also includes all the control experiments behind that result as well as the molecular dynamics simulations performed by our colleagues in China.
In chapter 7, we present the effects of substituting hydrogen for deuterium on the transport properties of graphene and hBN. The results provide further insight into the proton transport mechanism and establish these crystals as competitive materials for isotope separation technologies.

In chapter 8 we summarize the main results and discuss some future work lines.
2 Graphene: basic properties

Graphene, a material isolated in 2004 has opened a new field of research of its own encompassing all sorts of disciplines in the natural sciences. Of particular importance to the present investigation are graphene’s mechanical, impermeability and electrical properties. Let us review some fundamental aspects of them.

2.1 Mechanical and impermeability properties

Previously thought not being stable enough to exist, graphene is the strongest material ever measured. Indeed, nanoindentation experiments [10], [14], [15] on suspended graphene membranes have established graphene’s intrinsic strength (the maximum stress it can sustain before breaking) at 130 GPa – over 500 times that of steel. Yet, despite boasting a Young’s modulus of 1 TPa, graphene can be strained up to 20% before breaking – more than any other crystal [10], [14]−[20]. In fact, it was precisely thanks to its maximal strength that graphene’s impermeability properties could be tested. And, because of its importance to our results, we will review them more carefully.

To test whether graphene was impermeable to gases, Bunch et al. [2] enclosed a very small volume of pressurized gas (~1µm³) inside a graphene sealed SiO₂ microcavity. If the pressure inside the cavity was larger than atmospheric, the membranes bulged upwards; if it was smaller, downwards. So, by measuring the height of the membrane
as a function of time with an AFM, they were able to determine the pressure inside the cavity and the leak rate of the enclosed gas. They found this leak rate far too small to be explained by effusion through holes in the membrane and far too large to be due to tunneling through the pristine membrane. They concluded then that the membranes did not have pinholes through which atoms could effuse and that the pristine membrane was impermeable to all gases. Let us study how they reached that conclusion.

Figure 2.1 shows a summary of the experiment (adapted from ref. [2]). Graphene was transferred on top of microcavities etched into Si/SiO$_2$ wafers. Typical volume of the cavity was 1μm$^3$. Then, leaving the substrates inside a pressurized chamber for 4 days resulted in the gas leaking out of the cavities through the SiO$_2$ layer until the pressure outside and inside the microchamber was the same. After this, the samples were taken out of the chamber and their height profiles were measured using an AFM.

By comparing the height of the membrane versus time, they were able to determine the leak rate of the gas using classical deformation theory. Hencky’s solution for a pressurized clamped elastic membrane dictates that the pressure difference across it ($\Delta p$) is related to the geometry of the deformation as [2]:

$$\Delta p = K(\nu)(Ew\delta^3)/a^4$$

where $K(\nu=0.16)=3.09$ is a coefficient that depends only on Poisson’s ratio $\nu$, $w$ is the membrane thickness (0.3 nm), $\delta$ is the maximum height of the membrane, $E$ is graphene’s Young’s modulus ($E=1$TPa) and $a$ is the radius of the membrane.
Figure 2.1 Microchamber experiment. (a) Schematic of the graphene sealed Si/SiO$_2$ microchambers. (b) Schematic of the pressurized chamber. (c) Typical AFM image of a pressurized membrane where the pressure inside was larger than outside the microchamber. (d) AFM image of a membrane. (e) Height profile of the membrane at different times. Adapted from ref. [2].

Now, from ideal gas law we know that $PV(\delta) = NkT$, where $P$ is the absolute pressure inside the cavity, $V(\delta) = V_0 + C(\nu)\pi a^2 \delta$ is the volume in the cavity (which depends on the volume of the SiO$_2$ cavity and the volume added by the deformation of the membrane $C(\nu = 0.16) = 0.52$ ), $N$ is the number molecules inside the chamber, $k$ is Boltzmann’s constant and $T$ is the temperature [2].

Inserting $P = \Delta p + p_{atm}$ into the ideal gas law, dividing both sides by $V(\delta)$ and inserting Hencky’s solution for the pressure difference, the equation is now:

$$\frac{K(\nu)(Ew\delta^3)}{a^4} + p_{atm} = \frac{NkT}{V_0 + C(\nu)\pi a^2 \delta}$$
Then, solving for \( N \) and taking the derivative against time, we get the leak rate from the cavity as a function of the change in membrane height (deflection rate) \([2], [3]\):

\[
\frac{dN}{dt} = \frac{3K(\nu)Ew\delta^2V(\delta)/a^4 + PC(\nu)\pi a^2}{kT} \cdot \frac{d\delta}{dt}
\]

Using this equation, their deflection rates were associated with leak rates of the order of \( \sim 10^3 \) atoms/second for air and argon. That means that typical chambers take one day to reach atmospheric pressure.

Now, what leak rates should be expected from atoms effusing through holes in the membrane? Using classical effusion theory, the number of atoms as a function of time in a cavity of volume \( V \) that has a hole of area \( A \) is given by \([21]\):

\[
N = N_0 \exp \left[ \frac{-A}{V} \sqrt{\frac{kT}{2\pi m}} t \right]
\]

where \( m \) is the mass of the particle, \( N_0 \) is the initial number of particles and \( t \) is the time. Taking the derivative of this equation one estimates the leak rates from the graphene sealed microcavities in the presence of a single atomic vacancy at \( \sim 10^9 \) atoms/second. That is, the cavities should deflate in less than a second; in stark contrast with the observed 24 hrs it takes for the membrane to deflate.

Moreover, the observed rates cannot be explained either by assuming tunneling through the membrane. The semiclassical WKB approximation (after G. Wentzel, A. Kramers and L. Brillouin) \([22]\) for the tunneling probability through a barrier of height \( V \) is given by:
Graphene: basic properties

\[ P \propto \exp\left( -\frac{2x\sqrt{2m(V-E)}}{\hbar} \right) \]

where \( x \) is the width of the barrier (0.3nm), \( V \sim 8.7 \text{ eV} \), \( E \) is the kinetic energy of the particle \( \sim kT = 25 \text{ meV} \) and \( \hbar \) is the reduced Planck’s constant. This results in a probability of transmission of the order of \( \sim 10^{-335} \). Even assuming a temporary breaking and reassembly of the carbon bonds, the probability is still \( \sim 10^{-212} \); still many orders of magnitude smaller than the ones observed [2].

How, then, are the atoms escaping the cavity? They found that their measured leak rates match what would be expected by diffusion through the SiO\(_2\) layer. So, the conclusion was that the membranes do not have pinholes that allow atoms to effuse and that the pristine membrane is impermeable to all gases.

Finally, we point out that the experiment described so far can be used for Ar and other gases but not for He since the leak rates through SiO\(_2\) are 2 orders of magnitude faster. So, to determine the leak rates for He, Bunch et al. used an optical setup to probe the resonant frequency of the membranes under pressure as a function of time. We did not replicate their results for He so we will not describe them. But, for the purposes of this work, it suffices to say that their set up led them to the same conclusions as for the other gases. Now, let us review some other impermeability properties of graphene.

Graphene is also impermeable to liquids. For example, water can be trapped using monolayers of graphene [23]–[25], allowing the study of a few layers of water using AFM or STEM. Moreover, its impermeability extends to ions and molecules. For
example, graphene has been shown to block large ions ($\text{Na}^+$, $\text{Cl}^-$, $\text{Li}^+$, $\text{Ru}^{3+}$, $\text{K}^+$, $\text{Cs}^+$) [26]–[29]. For this reason, when perforated with subnanometer accuracy, graphene has been shown to selectively sieve ions, gases and molecules [3], [26], [28]–[34].

The impermeability of graphene has also been studied theoretically [4], [5], [35], [36], usually with \textit{ab initio} molecular dynamics simulations or density functional theory. In these simulations, graphene was found to remain impermeable to all gases even when a few atomic vacancies were present. Nevertheless, experimental examination of mechanically exfoliated graphene and hBN has failed to find even single atomic vacancies with SEM or STEM [3], [37]–[39].

### 2.2 Electrical properties

Graphene’s structure is dictated by the in plane $\text{sp}^2$ orbitals that bond each carbon atom with its three nearest neighbors in a hexagonal lattice. But, since the $\sigma$ states form fully occupied bands, the unique electrical properties of graphene [9]–[13] stem from the off-plane $\pi$ orbitals. And so, solving the Hamiltonian for these two available electrons per unit cell (the hexagonal lattice is described as two triangular lattices) results in the famous energy dispersion relation (energy bands) for $\pi$ electrons in graphene. This relation is illustrated in Figure 2.2 (adapted from ref. [11]).

Now, the conductivity of any material depends on how the energy bands are populated with electrons. For example, in a metal, the conduction bands are not fully populated; this allows electrons to be excited with an electric field. On the other hand, in an insulator, the valence band is fully occupied and the next available energy band
is separated by a large energy gap. This precludes exciting electrons using an electric field and, hence, hinders the conductivity in the material. In graphene, however, the two $\pi$ bands are connected via a structure in the energy dispersion relation known as the Dirac cone. This structure is of paramount importance to graphene’s electrical properties because in most cases the bands are populated around the tip of the cone (the bands start to become non-linear around 1 eV [40]). This means that, for practical purposes, the electrical properties of graphene are dictated by this portion of the energy dispersion relation.

![Figure 2.2 Energy dispersion of $\pi$ electrons in graphene. Wavenumbers in units of $2\pi/a$, $a=1.42\text{Å}$. Energy in units of $t=2.7\text{eV}$. Adapted from ref. [11].](image)

Now, the filling of the energy bands is a mechanical statistical process dictated by the Fermi-Dirac distribution. Electrons will fill the energy levels up to a cut off value dictated by the chemical potential of the system. This value is known as the Fermi energy level and, crucially, it can be controlled experimentally. Indeed, because the cut off value is the chemical potential of the system, gating the substrate onto which graphene is deposited – and hence modulating the carrier concentration in graphene –
allows experimental control of the Fermi energy of the system. This, in turn, allows for the exploration of graphene’s electrical properties. Two of these properties worth mentioning are graphene’s high room temperature carrier mobility and its linear dispersion relation.

Graphene’s room temperature carrier mobility is around 140,000 cm$^2$ V$^{-1}$ s$^{-1}$ [41] and the carrier concentration can be continuously tuned between electrons and holes well up to $10^{13}$ cm$^{-2}$ [9]. This mobility value compares favorably with other materials; most semiconductors (GaAs, Si, GaN for example) have mobilities lower than 10,000 cm$^2$ V$^{-1}$s$^{-1}$ [42]. For this reason, this property, combined with graphene’s transparency to light (it only absorbs 2.3% of the light [12]), has attracted much attention due to its potential use as a transparent electrode.

The second property, and the one responsible for many of graphene’s exotic electrical phenomena, is its linear dispersion relation. Since the effective mass of the carriers is given by the curvature of the dispersion relation, charge carriers in graphene behave like massless fermions. Indeed, their behavior is best described using the Dirac equation rather than the Schrödinger equation (hence the name of the cone in the band structure) [43]. These properties have made graphene a starting material to study new Physics, turning graphene related studies into one of the most active research fields in science today.
2.3 Beyond Graphene

Graphene was the first truly two dimensional material to be discovered but it is by no means the only one. Indeed, as early as 2005, already monolayers of MoS$_2$, NbSe$_2$ and Bi$_2$Sr$_2$CaCu$_2$O$_x$ were isolated [1]; and the search for new materials still continues [44]. Of particular importance to our project are monolayers of MoS$_2$ and hBN. Let us have a closer look at both.

Figure 2.3 Lattice structure of other 2D crystals. Lattice structure of MoS$_2$, adapted from ref. [45]. Structure of hBN, adapted from ref. [46]. Electron tunneling across 1-4 layers of hBN, adapted from ref. [39].

Bulk MoS$_2$ is an indirect bandgap semiconductor (1.2 eV) whereas its monolayer is a direct bandgap semiconductor (1.8 eV). And, precisely because of its bandgap, it has recently attracted much attention as a material for atomically thin transistors [45]. Hexagonal boron nitride (hBN), on the other hand, is a wide band-gap insulator (5.97 eV) that remains stable up to 700°C and arranges itself in a hexagonal lattice that has
only a slight mismatch with graphene’s (1.8%). This material has, instead, attracted much attention due to its potential as a barrier in tunneling transistors and as a substrate for high quality graphene devices [47], [48].

Figure 2.4 AFM images of a V$_2$O$_5$ monolayer in air. (a) Height channel (b) phase channel. Roughness analysis shows that the height of the monolayer area is 1.14 nm, in agreement with the measured height of monolayer using AFM for other crystals [1].

One recent addition to the list of 2D materials is V$_2$O$_5$. This crystal represents the highest oxidation state of vanadium and is arranged as a layered orthorhombic lattice with constants $a = 11.51$ Å, $b = 3.56$ Å, $c = 4.37$ Å; the layers being held together by van der Waals bonds. It is a predominantly n-type, low mobility semiconductor ($\mu = 1$ cm$^2$V$^{-1}$s$^{-1}$) with carrier concentration of $\approx 1.34 \times 10^{20}$ cm$^{-3}$ and with a melting point of 963 K [49]. We isolated monolayers of this crystal by mechanical exfoliation and characterized them with AFM (Figure 2.4).

Using the same techniques, we have studied other crystals. We found that a few layers of other layered, van der Waals bonded oxides such as Sb$_2$S$_2$O and Sb$_2$O$_3$ are
stable in air; whereas a few layers of As₂O₃, PbO are not. Indeed, finding new atomically thin crystals is a very active area of research.

Now, having gone through some of the basic properties of one-atom-thick crystals, let us turn our attention to the basics of proton conductivity.
3 Proton Conductivity

Protons are unique among charge carriers. Their mass sets them apart both from the much smaller electrons ($\approx 2000$ lighter) and the much heavier ions. Indeed, protons’ mobility in water is much smaller than that of electrons in metals; yet higher than that of any ion in solution. Not surprisingly then, protons are in many ways an intermediate case between electrons and ions with fascinating properties; not least their transport properties. Let us go through some essential aspects of proton conductivity.

3.1 The Hydrogen Bond

Water exhibits unusual properties in all of its phases: negative melting volume; high boiling and melting points; increased fluidity at higher pressures; high dielectric constant; and high mobility of $\text{H}^+$ and $\text{OH}^-$ ion transport; to name but a few [50]–[52]. These properties come about because water has a high density of hydrogen bonds; indeed, liquid water has at least as many of these as it has covalent bonds [51]. A basic knowledge of the hydrogen bond, then, is crucial to our project. Let us review some basic aspects of the hydrogen bond.

The hydrogen bond is an intermolecular bond by means of which the atoms directly involved form linear structures of the form $\text{A-H}\cdots\text{A}$ and where the separation
between the A atoms is around 3 Å. The atom covalently bonded to H is known as the donor; the other one, as the acceptor. So, for example, the bond linking together two water molecules would be HO-H⋯OH₂ with the two oxygen atoms separated by 3 Å [53], [54].

![Figure 3.1 Hydrogen bond between two water molecules. The oxygen and hydrogen atoms form electrostatic dipoles that attract to each other forming a bond between the two molecules.](image)

Now, hydrogen bonds form when hydrogen covalently bonds to a very electronegative atom (O, F or N) to form a polar molecule which then interacts electrostatically with another one via a dipole-dipole attraction. Because of the nature of the interaction, the energy of the bond (~0.2 eV) lies between the very weak van der Waals interaction (~0.01 eV) and the strong covalent bond (~4 eV). This energy is enough to bond together clusters of water into networks but weak enough not to disrupt their structure. Additionally, since it is just ~10 kT (k, Boltzmann constant, T temperature), hydrogen bonds can be formed and broken by just thermal fluctuations [52], [53], [55], adding great versatility to the structures formed.

Solvated protons behave in exactly the same way. The proton is stabilized by a water molecule to form a hydronium ion (H₃O⁺) wherein the proton is embedded in the
electronic cloud of the molecule. This ion then interacts via hydrogen bonds with the surrounding water molecules to form structures that allow the proton to be transported. Let us have a closer look at this phenomenon.

3.2 Proton transport in hydrogen bond networks

Protons are unique amongst all other ions because of their very high mobility in water: twice that of the hydroxide ion and seven times that of sodium [55]. Not surprisingly, as early as 1806 [53], it was recognized that the transport mechanism for protons in water ought to be different from that governing the rest of the ions.

Indeed, all ions, except protons and the hydroxide ion, diffuse via the vehicular mechanism [55], [56]. When an ion is solvated in water, it strongly attracts water molecules around itself to form a solvation shell. This shell will move with the ion as it diffuses. In contrast, protons in water move via the Grotthuss mechanism [53], [54], [56], [57]. In this mechanism, protons diffuse in water by rapid “jumps” from one water molecule to the next, forming and breaking hydrogen bonds in the process. Let us take a closer look at this process.

The equilibrium position of a proton in a hydrogen bond depends on the separation of the two oxygen atoms. For small separations, the hydrogen atom will lie half way between them; for large separations, closer to one of them. Figure 3.2a, for a variety of compounds, shows the length of the covalent bond holding the donor oxygen and the proton together. This length is plotted against the length of the hydrogen bond connecting the proton to the acceptor (adapted from ref. [56]). The data shows that
longer bonds to hydrogen are associated with shorter covalent bonds and vice versa. The result of this is then a very uniform donor acceptor separation that ranges from 240 pm to rarely above 395 pm.

Figure 3.2 Distance between hydrogen bonded species. Distances between H and the two O atoms involved in a hydrogen bond of the form (R-O-H-R) for different hydrogen bonded systems. (R is an arbitrary atom or compound). Each point represents a different hydrogen bonded compound (a). Potential energy surfaces for proton transfer as a function of oxygen separation (Q) (b). Adapted from ref. [56].

But, as small as this spread in oxygen separation is, it has dramatic consequences for the proton transfer potential barriers. Figure 3.2b (adapted from ref. [56]) shows the potential energy surface a proton experiences when in between two hydrogen bonded molecules for different O-O separations (Q). For the shortest separation (~240 pm), the transfer is barrierless while already for 300 pm it experiences a double well potential with a height of 1 eV. Intuitively, this makes sense. If the two oxygen atoms are very close together, the proton does not really distinguish between them and, so, transferring from one to the other has no cost. As the separation increases, however, separating from the donor is more difficult as there is less electron cloud to screen.
the large electric field associated with the proton’s naked charge. Nonetheless, remaining close to the donor or acceptor still stabilizes the proton, hence the double well.

So far, we have explained how the proton “jumps” from one oxygen atom to the next for a given O-O separation. Nevertheless, this is not the only way a proton can transfer between two oxygen atoms. It is possible for the two oxygen atoms to get closer to each other in much the same way a baton is handed in a relay race. By getting closer, the oxygen atoms reduce the energy barrier that the proton must surmount. This, however, affects the transport rate. In the case where the oxygen atoms don’t “relay” the proton, the attempt frequency is of the order of $\sim 10^{14}$ s$^{-1}$, consistent with the vibration energy of the O-H bond. On the other hand, in the case where the oxygen atoms do “relay” the proton, the frequency is much slower; of the order of $\sim 10^{12}$ s$^{-1}$. In most cases, the transport will take place by a combination of both scenarios [56].

There is, however, another element at play in the process. It has long been recognized that the calculated activation energies for proton transport do not match the experimental observations [52], [55], [56]. Indeed, the measured barriers are consistently lower than those predicted by quantum chemistry. And, the reason for that is that protons are never at the bottom of the energy well. Indeed, the bond that connects the proton to the donor molecule has a fixed vibrational energy which, to a good approximation, can be modeled with a quantum harmonic oscillator. As a result, the bond has a minimum vibrational energy: its zero point energy. For the OH bond, this energy is very high ($\approx 200$ meV). As a matter of fact, for many oxygen
separation distances, it is already higher than the double well height shown in Figure 3.2 [54], [56]. This high quantization energy explains the mismatch between the calculated and the measured activation energies for proton transport in hydrogen bonded networks and, as we will see later on, it plays a crucial role in our proton transport experiments.

### 3.3 The hydrogen isotope effect

One very useful tool in elucidating the transfer mechanism of protons in chemical reactions is to substitute them for deuterons. This technique, for example, can identify the limiting step in proton transport processes [52], [58]–[61]. Let us have a look at some simple observations.

The basic idea behind all isotope effects is that substituting an atom for one of its isotopes does not change the electronic structure of the compound but it does change its vibrational energy levels [52], [62]–[64]. The simplest way to illustrate this is by studying a diatomic molecule A-H where A is any atom and H is hydrogen. For this molecule, the vibrational energy levels are given – to a good approximation – for the first energy levels [52], by

\[
E_n = \left( n + \frac{1}{2} \right) \hbar \sqrt{\frac{f}{\mu}}
\]
where $f$ is the force constant of the bond and $\mu$ is the reduced mass of the molecule, $h$ is Planck’s constant and $n$, which is an integer, is known as the vibrational quantum number. What would be the effect of substituting H for D in the energy levels?

The force constant of the bond is the same for the molecule both with H and with D because the electronic structure is the same. However, deuterium has twice the mass of H; therefore, substituting H for D lowers the energy levels. To illustrate this effect, suppose the mass of A is much larger than that of H or D. In such case, the ratio of reduced masses is: $\frac{\mu_H}{\mu_D} = \frac{m_A m_H / m_{AH}}{m_A m_D / m_{AD}} \approx \frac{m_H}{m_D} = \frac{1}{2}$. As a consequence, the energy levels of the system are lowered by a factor of $1/\sqrt{2}$ when H is substituted for D.

How then, does the isotopic substitution change the rate of a reaction? As we will explain, the substitution changes both the attempt rate and the energy barrier for the reaction. This change is quantified as the ratio of the reaction rates with H and D ($k_H/k_D$). Let us introduce the effect.

Classical statistical mechanics can be used to calculate the rate of a reaction as [65]:

$$k = \frac{kT}{h} \frac{Z'}{Z} e^{-\Delta E/RT}$$

where $Z'$ and $Z$ are the partition functions for the “activated complex” (the complex at the top of the energy barrier, see Figure 3.3) and reactants, respectively; $k$ is Boltzmann’s constant; $\Delta E$ is the energy difference between the activated complex and the zero point energy of the reactants; $R$ is the ideal gas constant; $h$ is Planck’s constant and $T$ is the temperature.
Now, as we saw in the last section, substituting hydrogen for deuterium changes the zero point energy levels of the compound. So, the isotopic substitution changes the reaction rate by modifying the excitation energy needed by the reactants to cross the energy barrier ($E$). With this simple model, already some useful general observations can be made. (1) If the shift of the energy levels at the activated complex ($T_1$, $T_2$ in Fig. 3.3) is the same as that for the reactants ($R_1$, $R_2$), then $\Delta E$ is the same for the complex with H or D and no isotope effect is observed. Conversely, if $T_1 \approx T_2$ but $R_1 \gg R_2$, a large effect would be observed. (2) The more tightly bound protons are in the donor side, the larger the energy split (since it depends on the force constant $f$). The isotopic substitution also changes the attempt rate since the partition functions ($Z$ and $Z'$) depend on the masses. The zero point energy shift, however, will normally dominate due to the exponential dependence of the rate on it.

Figure 3.3 Energy surface for a chemical reaction. $R_1$, $R_2$, $T_1$, $T_2$ stand for the energy levels with H (1) or D (2) for the reactants (R) and the activated complex (T).
In general, since the zero point energy for deuterium is lower, the isotope effect results in a slower rate of reaction when deuterium is substituted for hydrogen. A good example of this is water electrolysis. Electrolyzing water to form hydrogen ($H_2$) and oxygen ($O_2$) gas requires less energy than electrolyzing heavy water to produce oxygen and deuterium gas ($D_2$) [66].

Because of its importance in technical applications, the efficiency of the separation of hydrogen from deuterium has been carefully characterized for several processes. The parameter used to do this is known as the separation factor:

$$\alpha = \frac{([H]/[D])_{II}}{([H]/[D])_I}$$

where $([H]/[D])_{II}$ denotes the atomic fraction of H to D in the phase enriched with the lighter isotope; $([H]/[D])_I$ the fraction in the phase depleted of the light isotope.

Some of the most common methods to separate hydrogen from deuterium are [66]–[72]: liquid H$_2$O distillation ($\alpha \sim 1.05$), water electrolysis ($\alpha \sim 3$ to 10), ammonia-hydrogen exchange ($\alpha \sim 2.8$ to 6), liquid H$_2$ distillation ($\alpha \sim 1.5$), water hydrogen exchange ($\alpha \sim 2.8$ to 6), aminomethane hydrogen exchange ($\alpha \sim 3.5$ to 7), water hydrogen sulphide exchange ($\alpha \sim 1.8$ to 3) and laser isotope separation ($\alpha \sim 20,000$). All of these methods, except for the laser isotope separation, are used at some stage during the heavy water enrichment process.
4 Nafion and Fuel Cells

Perhaps the main application of this work is in improving the efficiency of fuel cells. These electrochemical devices are a very promising technology to harness the energy from fuels such as methanol and hydrogen. Now, as we saw in past sections, 2D crystals are impermeable to all gases and liquids. So, if they allow protons through, then the efficiency of this technology can be significantly enhanced. Let us study why.

4.1 Nafion

In order to study proton transport through graphene and other 2D crystals, a source of protons was needed. After trying several options, we settled for Nafion, a polymer that conducts protons but not electrons [73]–[78]. Let us discuss some of its basic properties.

\[
-\left[(\text{CF}_2\text{CF}_2)(\text{CF}_2\text{CF}_2)_m\right] - \\
\text{OCF}_2\text{CFOCF}_2\text{CF}_2\text{SO}_3^- - \text{H}^+
\]

Figure 4.1 Chemical composition of Nafion. The polymer is formed by long Teflon chains with a proton attached to a sulfonate group at the end of the tail.
Nafion is a fluoropolymer that consists of a long Teflon chain with a proton attached to a sulfonate (SO$_3$) functional group (see Figure 4.1). This group is responsible for Nafion’s proton conducting properties; the rest of the chain, for its mechanical and chemical stability properties [79]. When the polymer is cast to form membranes, it forms a network of water filled clusters with sulfonate groups at the boundary (Gierke model [73]) as shown in Figure 4.2. This boundary is responsible for the majority of the proton conduction in the polymer; the conduction process takes place via the Grotthuss mechanism (explained in the last section) [79].

Moreover – because of its Teflon backbone – Nafion is very resistant to chemical attack and can resist temperatures well over 200°C, albeit not without dehydrating and, consequently, hindering proton conductivity. In its hydrated form, however, the polymer is highly conductive (≈0.1 S cm$^{-1}$ [78], [80], [81]) due to its large proton concentration (~1.4 M) [74]. This high proton conductivity along with its resistance to chemical attack has positioned Nafion as the industry standard for polymer electrolyte fuel cells.

Figure 4.2 Gierke model of Nafion. Cluster network in extruded Nafion. The sulfonate groups (yellow) cluster around water pools (blue).
Commercially, Nafion can be found in either membrane form or solution form; the former being the most common. Additionally, depending on the application, Nafion of different thicknesses is desirable; usually somewhere between 20 μm to 300 μm. The thinner the membrane, the less resistance it has; but then, it will be more prone to fuel cross over (fuel diffusing across the membrane without being used – see next section). In our case, however, we used Nafion in its solution form because of our fabrication constrains: the polymer must be in direct contact with a micro-meter sized suspended crystal membrane. And, in its solution form, Nafion is easy to process with standard clean room techniques.

4.2 Fuel Cells

Fuel cells are electrochemical devices that convert the chemical energy stored in a fuel into electrical energy [82]–[87]. To do so, they transform the fuel into ions and electrons; the ions flow across an electrolyte and the electrons into a circuit where they are used. Finally, both electrons and ions are recombined in another reaction at the other end of the cell. Accordingly, fuel cells are classified depending on the electrolyte used and their operating temperature. The following table shows some commonly encountered ones [86]:

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Mobile ion</th>
<th>Operating temperature</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline</td>
<td>OH⁻</td>
<td>50-200°C</td>
<td>Space shuttles</td>
</tr>
<tr>
<td>Proton exchange membrane</td>
<td>H⁺</td>
<td>30-100°C</td>
<td>Vehicles and mobile applications</td>
</tr>
<tr>
<td>Direct methanol</td>
<td>H⁺</td>
<td>20-90°C</td>
<td>Low power but long running time devices</td>
</tr>
</tbody>
</table>
The hydrogen fuel cell is one the most commonly encountered and probably the one that has received more attention both by researchers and consumers. This cell works as follows: (1) hydrogen is fed to the cells through a porous electrode (carbon cloth or paper); (2) a Pt catalyst in the electrode breaks it down into protons and electrons; (3) the protons are injected into a Nafion membrane and the electrons flow through the electrode into an external circuit where they are used; (4) finally, the protons are collected by the cathode, where they recombine with the electron to form water. This process is illustrated in Figure 4.3.

**Figure 4.3** Hydrogen fuel cell. In a hydrogen fuel cell, hydrogen is broken down into protons and electrodes in the anode, protons then diffuse through the proton conducting membrane to the cathode where they combine with oxygen to form water.
But why are we interested in fuel cells? First, they are capable of converting chemical energy into electrical current much more efficiently than, for example, a gas electric station [85]. Second, the only waste of the process is water so carbon emissions for this technology are only associated with fuel production. Third, unlike batteries, as long as fuel is supplied, the cell will continue to operate. This makes fuel cells attractive for power supplies in submarines or remote locations. Fourth, their operation is silent; this is important in portable devices and domestic power generation. Let us take a closer look at the efficiency of fuel cells.

The efficiency of a fuel cell is defined as the ratio between the electrical energy obtained from it versus the heat that would be released if the fuel was burnt instead at constant temperature and pressure. Then, the efficiency ($\eta$) is defined as [86]:

$$\eta = \frac{\text{electrical energy}}{-\text{enthalpy of formation}}$$

This definition immediately shows that there is a thermodynamic upper bound to the efficiency of fuel cells, namely the energy obtained from a reversible process (the Gibbs energy). This limiting efficiency ($\eta_L$) is given then by:

$$\eta_L = \frac{\text{Gibbs energy of formation}}{-\text{enthalpy of formation}}$$

Now, because what can be actually measured from the fuel cell is its operating voltage (V), the practical definition of efficiency commonly encountered is given using operating voltages. This definition is just a simple arithmetic manipulation of the past definition to obtain voltages from energies using Faraday’s constant. Then,
let us note that the voltage associated with the Gibbs energy of formation ($V_G$) is obtained by dividing this energy by Faraday’s constant times the number of electrons transferred. The same is done for the enthalpy of formation ($V_h$) and so, the limiting efficiency is then:

$$\eta_L = \mu \frac{V_G}{V_h} \times 100\%$$

where $\mu$ is introduced to take into consideration fuel utilization (it stands for the ratio between used and fed fuel to the cell).

Now, for hydrogen, the relevant reaction is $H_2 + 1/2 O_2 \rightarrow H_2O$. The enthalpy of formation for this reaction is 285 kJ mol$^{-1}$ and, since two electrons are transferred (one for each H atom in the H$_2$ molecule) $V_h = 1.48$ V. In contrast, the Gibbs energy for this reaction is 237 kJ mol$^{-1}$ or 1.14 V. For this reason the maximum thermodynamic efficiency possible for this type of cell is around 60%-80%, depending on temperature; for methanol fuel cells this limit ranges between 52%-82%, depending on operating temperature. Notwithstanding, efficiencies for typical cells are not that high (they are obtained by using the actual operating voltage of the cell instead of $V_G$ in the past equation). They are usually around 50% for H$_2$ cells and around 30% for methanol cells [86]. Yet, as a benchmark comparison, the efficiency of gas electric stations is around 20% [85].

And so, because of their higher efficiency and lower emissions, it is very attractive to use fuel cells. However, their efficiency is still not high enough to justify the cost of the technology except in niche applications. For this reason, most research efforts are
directed towards increasing the efficiency of the cell closer to its thermodynamic limit and lowering the cost; especially that of the catalysts.

There are four main causes for voltage drop below the thermodynamic allowed one:

1. Activation losses. These are due to inefficiencies in driving the chemical reactions at the electrodes. Their optimization involves improving the cell’s catalysts and achieving higher operating temperatures.

2. Fuel crossover. Fuel that is not used but instead crosses through the cell. This is a major problem, particularly in methanol fuel cells.

3. Ohmic losses. Voltage drop due to electrical resistance in the cell. Their optimization requires more conductive or thinner membranes and more conductive electrodes.

4. Mass transport losses. As the fuel is used in the electrodes, products accumulate reducing the cell’s performance. Their optimization requires improving membrane and electrodes.

Reducing thickness would help with many of these issues, especially with ohmic and mass transport losses as resistance is proportional to membrane thickness [86]. Unfortunately, reducing thickness aggravates the fuel crossover problem so there’s usually a tradeoff between reducing ohmic losses and abating cross over. This is one of the motivations for introducing graphene and boron nitride into the fuel cell membrane. If protons can transport through these crystals, then, due to the impermeability of the crystals to everything else, this tradeoff can be bypassed.
5 Experimental Techniques

In this chapter the experimental techniques used in the study will be described. We start by discussing device fabrication; especially how to obtain fully suspended atomically thin crystal membranes. Next, the techniques to characterize such membranes are described emphasizing the search for subnanometer vacancies. Finally, we explain how the proton flux through the membranes is measured.

5.1 Device Fabrication

We measured the flux of protons and deuterons through mechanically cleaved, free standing boron nitride (BN), graphene and molybdenum disulphide (MoS₂) membranes suspended over 2-50 µm diameter through holes by two different methods: hydrogen gas flow and conductance measurements. Accordingly, two different kinds of devices were fabricated. The core of both kinds of devices, nonetheless, is the same: a suspended crystal membrane. Let us describe its fabrication.

The first step is to prepare a perforated substrate to suspend the crystal membranes. Due to the measurements to be performed on the device, there were two constraints to take into consideration while choosing an appropriate substrate. First, it had to be electrically insulating since electrical measurements were to be performed. And,
second, due to the gas flow measurements to be performed, it had to block all gases and liquids.

After trying several options, we settled for double coated Si/SiN\textsubscript{x} wafers (see Figure 5.1). To etch a through hole in the wafer, we first etch a square hole (1 mm\textsuperscript{2}) in the SiN\textsubscript{x} layer. To that end, a polymer resist mask (S1813, Nanochem) is patterned on the substrate using photolithography (Microtech LaserWriter) to protect the substrate but expose the square hole to be etched. After this, the hole is etched using reactive-ion etching (Oxford Instruments RIE System). This technique generates a plasma and then uses an electric field to bombard the substrate with the plasma ions. In our particular recipe, the SiN\textsubscript{x} is etched using sulfur hexafluoride by the following reaction: 

\[
\text{Si}_{3}\text{N}_4 (s) + 3 \text{SF}_6 \rightarrow 3 \text{SiF}_4 (g) + 3 \text{SF}_2 (g) + 2 \text{N}_2 (g).
\]

Figure 5.1 Fabrication process of free standing one atom thick crystal membranes. (1) Polymer mask to expose the 1mm\textsuperscript{2} square in the nitride layer. (2) Reactive ion etching of the top nitride layer. (3) KOH etching of Si. (4) Etching of the circular through hole in the top nitride layer. (5) Crystal transfer. Adapted from ref. [37].
This process leaves the underlying Si exposed. The next step then is to chemically etch the Si using a potassium hydroxide (KOH) solution. This proceeds according to the reaction: \( \text{Si} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4^{2-} + 2\text{H}_2\text{(g)} \) and produces an etching angle of \( \arctan(\sqrt{2}) \approx 55^\circ \). The effect of this angle is then a fully suspended top \( \text{SiN}_x \) layer of around 0.4mm\(^2\). Finally, in this layer, a circular hole (2-50µm diameter) is etched using reactive-ion etching again. This process is illustrated in Figure 5.1.

Figure 5.2 Optical images of cleaved crystals. Single layer of graphene (a) and boron BN (b) on SiO\(_2\). Single layer of MoS\(_2\) on PMMA/PMGI/Si substrate. Circles mark the monolayer area.

Figure 5.3 Transfer techniques. Wet transfer (a). PMMA – poly(methyl methacrylate) – is spun on the flakes and then released by etching the oxide layer with KOH. Dry transfer (b).
An underlying layer of PMGI – poly(methyl glutarimide) – is dissolved using MF319 to release the flake.

Now that the substrate is ready, a suitable crystal has to be suspended over the through hole. The atomically thin crystals in this study were obtained by mechanical exfoliation. In this method, the parent crystal is pressed between two surfaces: a substrate and a piece of adhesive tape. Both surfaces are then separated. This results in thin layers of the crystal being attached to the substrate. There are two main variations of this method: the wet and the dry transfer techniques. In the former, the substrate is a Si/SiO$_2$ wafer; in the latter, a double layer of polymer (PMMA/PMGI).

Figure 5.2 shows typical images of the resulting crystal flakes for graphene, hBN and MoS$_2$ obtained by the wet and dry transfer techniques [88]–[91]. In the former, the flake is transferred from the Si/SiO$_2$ by spin coating the flake with PMMA – poly(methyl methacrylate) – and then etching away the SiO$_2$ with KOH. In the latter, the PMGI – poly(methyl glutarimide) – layer is dissolved (MF319) releasing the flake on the PMMA layer. Both processes are illustrated in Figure 5.3.

At this point, the core of all devices (the suspended membrane) is finished and the remaining fabrication procedure depends on whether conductance or gas flow measurements will be performed. For conductance measurements, a proton conductive polymer (Nafion 117, 5% wt.) is drop cast on both sides of the membrane and PdH$_x$ or PdD$_x$ electrodes are mechanically attached [92]–[94]. PdH$_x$ and PdD$_x$ are obtained by leaving Pd foil (0.025mm thick) in a hydrogen or deuterium donating solution overnight (NaBH$_4$ or NaBD$_4$). The whole device is then baked in a humid
atmosphere at 130°C to crosslink the polymer and to bind all of the components together.

On the other hand, if gas flow measurement will be performed, prior to flake transfer a gold contact is patterned on the substrate using photolithography and e-beam evaporation (Moorfield e-beam system). After the flake transfer, a discontinuous layer of Pt (nominally 2 nm) is deposited by e-beam evaporation onto the suspended membrane to form a catalyst layer so that the transferred protons can evolve as hydrogen gas (H₂). On the other side of the membrane, Nafion is drop cast and a PdHₓ electrode is attached in the same way as before. This is illustrated in Figure 5.4.

Figure 5.4 Final devices. (a) For conductance measurements, Nafion is drop cast in both sides of the membrane and PdHₓ electrodes are attached on both sides. (b) For gas flow measurements Nafion is only cast on one side and a layer of Pt is deposited on the suspended flake. Adapted from ref. [37].
5.2 Device Characterization

In order to obtain reproducible results from different devices, we characterized them prior to measuring their electric conductance or gas flow properties. The main feature we looked for was the absence of holes in the membrane. To that end, we used optical, scanning electron and atomic force microscopy in addition to Raman spectroscopy.

Optical microscopy is used to rule out micron sized holes, to determine if the membrane is completely broken or to detect residues of PMMA or other contamination traces (see Figure 5.5). Scanning electron microscopy (SEM) is then used to detect nanometer sized holes. Figure 5.6 shows a scanning electron micrograph of a pristine graphene membrane. Small residues of contamination are visible but no holes can be found. This will be the case except if membranes are intentionally damaged (UV ozone etch for example [95]) or a mistake is made during device processing.

Figure 5.5 Optical images of two free standing graphene membranes. PMMA residue left from the transfer procedure in one intact membrane (a). A rip in a membrane is clearly visible under the optical microscope (b).
Figure 5.6 Scanning electron micrograph of a suspended graphene membrane. Small residues of contamination are visible in an otherwise pristine membrane.

Notwithstanding, SEM cannot detect holes smaller than $\sim 20$ nm. For that reason, we used Raman spectroscopy. This technique is a very powerful, non-invasive, characterization tool that can identify the number and relative orientation of layers in the crystal, strain, doping, defect density, functional group density among other properties [96]. The Raman spectrum of pristine graphene is dominated by two peaks: the 2D ($\sim 2700$ cm$^{-1}$) and the G peaks ($\sim 1580$ cm$^{-1}$). Importantly, the spectrum is very sensitive to the presence of defects – adatoms or vacancies – in the crystal. The most apparent feature when defects are present is yet another peak known as the D peak ($\sim 1350$ cm$^{-1}$).

Relevantly, the ratio of D and G peak intensities can be used to estimate the defect concentration in the membranes (higher D to G peak intensity ratio is associated with higher defect concentration) according to the formula [97], [98]:

$$L(\text{nm}) = 2.4 \times 10^{-10} \lambda(\text{nm})^4 (I_D/I_G)^{-1}$$

where $L$ is the distance between defects in nm, $\lambda$ is the laser wavelength and $I_D/I_G$ is the ratio of intensities of D to G peaks in the Raman spectrum. Our membranes, however, did not show a D peak (see Figure 5.7) and for that reason we were able to
place an upper bound on the defect concentration at $\sim 10^8 \text{cm}^{-2}$; that is, one hole per square micron. This is already a good bound since our devices were typically 1 $\mu$m in radius. There is, however, another way to characterize these membranes that is sensitive to the presence of atomic-sized vacancies.

Figure 5.7 Raman spectrum of our suspended graphene devices. The ratio of intensities of G to D can be used to estimate defect concentration in the membrane.

That sensitivity level can be accomplished by measuring the gas flow from a graphene sealed microcavity described in chapter 1: the microchamber experiment. The microcavities in this study were etched into a Si/SiO$_2$ wafer by a combination of photolithography and reactive ion etching and were sealed with a single layer graphene membrane. Next, the devices were left inside a chamber with Ar gas at 200 kPa above atmospheric pressure to pressurize the microchambers. After four days, when the devices were taken out of the chamber, the membranes bulged upwards and, over the course of a day, deflected downwards. Figure 5.8 shows the deflation over time of such membranes over 24 hrs.
Figure 5.8 Microchamber experiment. Maximum height of a pressurized graphene membrane as a function of time from the first measurement. It takes around a day for the membrane to deflate. Bottom inset shows typical AFM image of the membrane and top inset shows an optical image of the device; usually at least four cavities are etched on the Si substrate at one time.

Until now, we have described how to characterize the amount of defects in our crystalline membranes. However, it is also important to know how many layers of crystal we have. While Raman spectroscopy can be used to that end, we did it using an optical microscope. Indeed, it is straightforward to know how many layers of graphene or MoS₂ there are just by the optical contrast between the flake and the substrate. For hBN, however, that can be extremely challenging [99]. Nonetheless, by etching the SiO₂ substrate onto which the crystal is exfoliated, we can optically find very thin hBN.

Finally, as mentioned before, for the gas flow devices we evaporated (ebeam) a discontinuous layer of Pt to serve as catalyst. If the layer is continuous, the gas was trapped in between the graphene and the metal layer (Figure 5.9). For this reason we
made the layer discontinuous and characterized it using SEM. As shown in Figure 5.9, evaporating 2 nm Pt (nominally), results in a discontinuous layer of nanometer sized particles that allows for gases to evolve and escape without destroying the membrane.

Figure 5.9 Pt deposition on the membranes. Optical images of graphene membranes with a continuous layer of Pt (a) before and (b) after measuring the device. To prevent the formation of bubbles we evaporated discontinuous films of Pt. SEM micrographs of the membranes with Pt (c), (d).

5.3 Electrical and Mass Spectrometry Measurements

With devices characterized for the absence of pinholes, flux measurements could proceed. As mentioned before, we measured the flux of protons through atomically thin crystals by two methods: electrical conductance and hydrogen flow measurements.
To measure the electrical conductance through the membranes, devices were placed inside a chamber with a controlled atmosphere consisting of 10% H₂ in Ar at 100% relative humidity (this ensures Nafion’s proton conductivity). To provide the water and H₂ atmosphere, the chamber was pumped and then flushed with water vapor and hydrogen gas (see Figure 5.10).

Devices were bonded with gold wires and, using a Keithley 2636A sourcemeter, d.c. I-V measurements were recorded. The devices were biased between ±1 V at sweeping rates up to 0.5 V/min. To study the deuteron conductivity of the membranes, we replaced H₂ for D₂ and water for heavy water (D₂O) but, otherwise, the set-up remained the same.

![Figure 5.10 Set up for conductance measurements. Controlled atmosphere chamber (a) Image of final device (scale bar 1 cm) (b) and gold wire bonding (c). Adapted from [37].](image)

To measure proton transport using mass spectrometry, devices were glued with epoxy to a perforated Cu foil and clamped between two O-rings to separate two chambers: one with a gas mixture and another evacuated and connected to a mass
spectrometer (Inficon UL200); see Figure 5.11. Next, to check the impermeability of the membranes, the first chamber was filled with He at 1 bar pressure; the reading in the gas spectrometer was in the background level (∼10⁻⁸ bar cm³/s). Finally, the chamber was filled with a 10% H₂/Ar gas mixture at 1 bar and 100% relative humidity. The device was bonded with gold wires and connected to a Keithley source meter. By applying a potential bias, a controllable flow of H₂ of the order of 10⁻⁵ bar cm³/s was detected by the spectrometer.

The top chamber (see Figure 5.11) can be filled, alternatively, with an electrolyte. To study the transport properties of deuterons, we filled it with an electrolyte mixture containing protons and deuterons. In this way, the same set-up was used to measure transferred protons and deuterons as they evolved as hydrogen deuteride (HD) and deuterium gas (D₂) simply by tuning the spectrometer to masses three and four, respectively.

Figure 5.11 Gas flow experimental set-up. A graphene gas flow device was used to separate two chambers: one with a water/hydrogen atmosphere and another one evacuated and connected to a mass spectrometer. The electrical current across the device was monitored with a sourcemeter.
6 Proton Transport through One-Atom-Thick Crystals

Graphene is usually pictured as a mesh of carbon atoms arranged in a hexagonal lattice in a ball and stick picture. In reality, however, there is a dense electron cloud smeared all over the lattice (as described in Section 2.2) which prevents all gases, liquids and molecules from crossing the lattice [2]–[5]. Because of this property – along with its mechanical strength and thinness –, graphene has been extensively researched as a separation membrane. Indeed, when carefully perforated, gases, ions and molecules may be precisely separated [3], [26], [28]–[34].

Until recently, moreover, graphene was believed to be impermeable to bare hydrogen nuclei [6]–[8]. Then, only accelerated ions were able to cross [100], [101]. Notwithstanding, our work proves that graphene and monolayers of hBN are highly permeable to thermal protons; the measured areal conductivities at room temperature are of the order of 100 mS/cm². Moreover, as an Arrhenius activated process, proton areal conductivity through the membranes increases to well over 50 S/cm² above 200°C; the goal set by the US department of energy for proton conducting fuel cell membranes [102]. This property paves the way to thinner, more conductive and more efficient fuel cells: because of graphene’s impermeability, fuel crossover can be eliminated (see chapter 4); because of its thinness and high proton conductivity, fuel cells can be more conductive, light and cost effective.
But this result is not only interesting because of its potential application in fuel cells. These results show that subatomic particles can cross through atomically thin electron clouds with very low energies (< 1 eV). They also prove that two different proton accepting phases (electrolyte/electrolyte or electrolyte/gas) can correlate through the atomically thin electron cloud. This is by itself a new result. Before, proton transport reactions had been studied across molecules and interphases lying in direct contact (electrolyte/electrode or molecule/molecule). Perhaps, the only analogue phenomenon of our results is electron tunneling through insulating barriers.

So how exactly is the interaction established between the two phases? We have learned so far that this separating electron cloud must obey some restrictions. If it is too dense (as is the case for single layer MoS$_2$ and bilayer graphene) or if the two phases are too separated (as is the case for tetralayer hBN), the phases will not correlate. In all likelihood, the exploration of these rich interfaces will display new and interesting phenomena.

The results included in this section were published in the article S. Hu, et al., *Nature* **516**, 227–230 (2014). As stated in the acknowledgements section of the paper, A. K. Geim directed the project with help from S. Hu and myself. S. Hu and I did the experimental work, data analysis and were involved in the design of the experiments. H. A. Wu and F. C. Wang performed MD simulations. Along with H. A. Wu, I. V. Grigorieva and A. K. Geim, I was involved in writing the manuscript. H. A. Wu and myself are corresponding authors for this paper. The following version of the paper is the one submitted to the journal for peer review.
Proton Transport through One-Atom Thick-Crystals


Proton Transport through One Atom Thick Crystals

S. Hu\textsuperscript{1,2}, M. Lozada-Hidalgo\textsuperscript{1}, F. C. Wang\textsuperscript{3}, A. Mischenko\textsuperscript{1}, F. Schedin\textsuperscript{2}, R. R. Nair\textsuperscript{1}, E. W. Hill\textsuperscript{2}, D. V. Boukhvalov\textsuperscript{4}, M. I. Katsnelson\textsuperscript{4}, R. A. W. Dryfe\textsuperscript{5}, I. V. Grigorieva\textsuperscript{1}, H. A. Wu\textsuperscript{3}, A. K. Geim\textsuperscript{1,2}

\textsuperscript{1}School of Physics & Astronomy, University of Manchester, Manchester, M13 9PL, UK
\textsuperscript{2}Manchester Centre for Mesoscience & Nanotechnology, Manchester M13 9PL, UK
\textsuperscript{3}Chinese Academy of Sciences Key Laboratory of Mechanical Behavior and Design of Materials, Department of Modern Mechanics, University of Science and Technology of China, Hefei, Anhui 230027, China
\textsuperscript{4}Institute for Molecules and Materials, Radboud University of Nijmegen, 6525 AJ Nijmegen, The Netherlands
\textsuperscript{5}School of Chemistry, University of Manchester, Manchester, M13 9PL, UK

Graphene is impermeable to all gases and liquids\textsuperscript{1-3}, and even such a small atom as hydrogen is not expected to penetrate through graphene’s dense electronic cloud within billions of years\textsuperscript{3-6}. Here we show that monolayers of graphene and hexagonal boron nitride (hBN) are unexpectedly permeable to thermal protons, hydrogen ions under ambient conditions. As a reference, no proton transport could be detected for a monolayer of molybdenum disulfide, bilayer graphene or multilayer hBN. At room temperature, monolayer hBN exhibits the highest proton conductivity with a low activation energy of \( \approx 0.3 \) eV but graphene becomes a better conductor at elevated temperatures such that its resistivity to proton flow is estimated to fall below \( 10^{-3} \) Ohm per cm\(^2\) above 250\(^\circ\)C. The proton barriers can be further reduced by decorating monolayers with catalytic
nanoparticles. These atomically thin proton conductors could be of interest for many hydrogen-based technologies.

Graphene has recently attracted renewed attention as an ultimately thin membrane that can be used for development of novel separation technologies (for review, see refs. 7,8). If perforated with atomic or nanometer accuracy, graphene may provide ultrafast and highly selective sieving of gases, liquids, ions, etc.\textsuperscript{2,9-19} However, in its pristine state, graphene is absolutely impermeable for all atoms and molecules moving at thermal energies\textsuperscript{1-7}. Theoretical estimates for the kinetic energy $E$ required for an atom to penetrate through monolayer graphene vary significantly, depending on the employed model, but even the smallest literature value of 2.4 eV for atomic hydrogen\textsuperscript{3-6} is 100 times larger than typical $k_B T$ which ensures essentially an impenetrable barrier ($k_B$ is the Boltzmann constant and $T$ the temperature). Therefore, only accelerated atoms are capable of penetrating through the one atom thick crystal\textsuperscript{20,21}. The same is likely to be valid for other two dimensional (2D) crystals\textsuperscript{22,23}, although only graphene has so far been considered in this context. Protons can be considered as an intermediate case between electrons that tunnel relatively easily through atomically thin barriers\textsuperscript{24} and small atoms. It has been calculated that $E$ decreases by a factor of up to 2 if hydrogen is stripped of its electron\textsuperscript{4,5}. Unfortunately, even the latter barrier is still prohibitively high to allow appreciable transport of thermal protons ($E \approx 1.2$ eV is estimated\textsuperscript{5} to result in permeation rates of $\sim 10^9$ sec).

Despite the pessimistic prognosis, we have investigated the possibility of proton permeation through monocrystalline membranes made from mono- and few- layers of
graphene, hBN and molybdenum disulfide (MoS$_2$). The 2D crystals were obtained by mechanical cleavage and then suspended over micrometer size holes etched through Si/Si$_x$N$_y$ wafers. Details of fabrication procedures are described in Supplementary Information, section 1. The resulting free-standing membranes were checked for the absence of pinholes and defects (Supplementary Information, sections 1-3) and spin coated from both sides with Nafion, a polymer that exhibits high proton and negligible electron conductivity$^{25}$. Finally, two proton injecting PdH$_x$ electrodes$^{26,27}$ were deposited onto Nafion from both sides of the wafer (Supplementary Figs 1 and 2). As illustrated in the left inset of Fig. 1a, 2D crystals effectively serve as atomically thin barriers between two Nafion spaces. For electrical measurements, samples were placed in a hydrogen-argon atmosphere at 100% humidity, which ensured high conductivity of Nafion films$^{25,26}$. Examples of I-V characteristics measured for devices incorporating monolayers of graphene, hBN and MoS$_2$ are shown in Fig. 1a. This behavior is highly reproducible, as illustrated by statistics in Fig. 1b for a number of different membranes. The measured proton current $I$ is found to vary linearly with bias $V$, and the conductance $S = I/V$ to be proportional to the membrane area $A$ (Supplementary Figs 3-5). For devices prepared in the same manner but without a 2D membrane (‘bare hole’), $S$ was $\sim$50 times higher than in the presence of monolayer hBN (Supplementary Fig. 3). This ensures that the measured areal conductivity $\sigma = S/A$ is dominated by the 2D crystals and that Nafion gives rise only to a relatively small series resistance. In the opposite limit of thick barriers (e.g., a few nm thick graphite or thick metal or dielectric films evaporated between the Nafion spaces), we find a parasitic parallel conductance of $\sim$10 pS, which could be
traced back to leakage currents along SiN\(_x\) surfaces in high humidity. Within this accuracy, we could not detect any proton current through monolayer MoS\(_2\), bilayer graphene, tetra-layer hBN or thicker 2D crystals.

The difference in permeation through different 2D crystals can qualitatively be understood if we consider the electron clouds that have to be overcome by passing protons. One can see from the insets of Fig. 1b that monolayer hBN is more ‘porous’ than graphene, reflecting the fact that the boron nitride bond is strongly polarized with valence electrons concentrated around nitrogen atoms. For MoS\(_2\), the cloud is much denser because of the larger atoms involved (Supplementary Fig. 8). The absence of detectable \(\sigma\) for bilayer graphene can be attributed to its AB stacking such that ‘pores’ in the electron cloud in one layer are covered by density maxima within the other layer. In contrast, hBN crystals exhibit the AA’ stacking, which leads to an increase in the integrated electron density with increasing number of layers but allows the central pore in the cloud to persist even for multilayer hBN membranes.

It is instructive to emphasize that there is no correlation between proton and electron transport through 2D crystals. Indeed, hBN exhibits the highest proton conductivity but is a wide gap insulator with the highest tunnel barrier\(^{23,24}\). In contrast, monolayer MoS\(_2\) that shows no discernable proton permeation is a heavily doped semiconductor with electron-type conductivity\(^{22,28}\). Furthermore, numerous studies using transmission and tunneling microscopy and other techniques have so far failed to find even individual pinholes (atomic-scale defects) in graphene and hBN prepared using the same cleavage technique as employed in the present work (see, e.g., refs 1,2,24). Similar examination of our specific membranes is described in Supplementary
Information, section 3. In contrast, MoS\textsubscript{2} monolayers contain a high density of sulfur vacancies\textsuperscript{29} but nonetheless exhibit little proton conductivity. These observations combined with the high reproducibility of our measurements for different devices, the linear scaling with $A$ and the consistent behavior with increasing the number of layers assure that the reported $\sigma$ represent the intrinsic proton properties of the studied membranes.

**Figure 1 | Proton transport through 2D crystals.** a, Examples of I-V characteristics for monolayers of hBN, graphite and MoS\textsubscript{2}. The upper inset shows experimental schematics. Middle inset: Electron micrograph of a typical graphene membrane before depositing Nafion. Scale bar: 1 $\mu$m. In a scanning electron microscope, 2D crystals give rise to a homogenous dark background and can only be seen if contamination, defects or cracks are present (Supplementary Fig. 2). Small (pA) currents observed for MoS\textsubscript{2} membrane devices (lower inset) are due to parasitic parallel conductance. b, Histograms for 2D crystals exhibiting detectable proton conductivity. Each bar represents a different sample with a 2 $\mu$m diameter membrane. Left and right insets: charge density (in electrons per $\text{Å}^2$) integrated along the direction perpendicular to graphene and monolayer hBN, respectively. The white areas are minima at the hexagon centers; the maxima correspond to positions of C, B and N atoms.
To determine the barrier heights $E$ presented by graphene and hBN, we have measured $T$ dependences of their $\sigma$ (Fig. 2a) which are found to exhibit the Arrhenius-type behavior, $\exp(-E/k_B T)$. Note that conductivity of Nafion not only contributes little to the overall value of $S$ but also changes only by a factor of $\sim 1.5$ for the same $T$ range (Supplementary Fig. 5). The activation behavior yields $E = 0.78\pm0.03$, $0.61\pm0.04$ and $0.3\pm0.02$ eV for graphene, bilayer hBN and monolayer hBN, respectively.

![Image](image.png)

**Figure 2 | Proton barrier heights and their catalytic suppression.** a, $T$ dependences of proton conductivity for 2D crystals. The inset shows $\log(\sigma)$ as a function of inverse $T$. Symbols are experimental data; solid curves are the best fits to the activation dependence. The $T$ range is limited by freezing of water in Nafion, and we normally avoided $T$ above 60°C to prevent accidental damage because of different thermal expansion coefficients. b, Proton conductivity is strongly enhanced if 2D crystals are decorated with catalytic nanoparticles. Each bar is a different device. The shaded area indicates the conductivity range found for bare-hole devices (Nafion/Pt/Nafion: no 2D crystal but for full similarity the same amount of Pt was evaporated). Inset: Arrhenius-type behavior for graphene with Pt, yielding $E = 0.24\pm0.03$ eV. Monolayer hBN with Pt exhibits only a weak $T$ dependence (Supplementary Fig. 5) which indicates that the barrier becomes comparable to $k_B T$. 
The proton barrier for graphene is notably lower than the values of 1.2–2.2 eV, which were found using ab initio molecular dynamics simulations and the climbing image nudged elastic band method\textsuperscript{4-6}. We have reproduced those calculations for graphene and extended them onto monolayer hBN (Supplementary Information, section 5). Our results yield $E = 1.25$–$1.40$ eV for graphene, in agreement with refs 4-5, and $\approx 0.7$ eV for monolayer hBN. The disagreement between the experiment and theory in the absolute value of $E$ is perhaps not surprising given the complex nature of possible pathways and sensitivity of the calculations to pseudopotentials, the exchange-correlation functional, etc. Alternatively, the difference can arise due to the fact that protons in Nafion/water (Supplementary Information, section 6) move along hydrogen bonds\textsuperscript{25} rather than in vacuum as the theory has assumed so far.

**Figure 3 | Current-controlled proton flux.** Top inset: Schematics of our experiment. Monolayer graphene decorated with Pt nanoparticles separates a vacuum chamber from the Nafion/PdH$_x$ electrode placed under the same H$_2$/H$_2$O conditions as described above. Protons permeate through the membrane and rapidly recombine on the other side into molecular
hydrogen. The hydrogen flux is detected by a mass spectrometer (Inficon UL200). Different symbols refer to different devices, error bars are shown for one of them, and the red line is the theoretically expected flow rate. Bottom inset: Optical image of one of the devices. Graphene contoured by the dashed lines seals a circular aperture of 50 μm in diameter. Nafion is underneath the graphene membrane.

For certain applications, it is desirable to achieve the highest possible proton conductivity. For example, hydrogen fuel cells require membranes with $\sigma > 1$ S per cm$^2$. This condition is satisfied by monolayers of hBN and graphene above 80 and 110 °C, respectively (inset of Fig. 2a). Moreover, graphene remains stable in oxygen and humid atmosphere up to 400°C (ref. 30), and the extrapolation of our results to ‘very safe’ 250°C yields extremely high $\sigma > 10^3$ S/cm$^2$. Furthermore, noticing that platinum group metals have a high affinity to hydrogen, we have investigated their influence on proton transport through 2D crystals. To this end, a discontinuous layer of Pt or Pd (nominally, 1-2 nm thick) was evaporated onto one of the surfaces of 2D crystals (Supplementary Information). Fig. 2b shows that the added catalytic layer leads to a significant increase in $\sigma$. For monolayer hBN, the measured $S$ becomes indistinguishable from that of reference ‘bare hole’ devices (Fig. 2b). This shows that our measurements become limited by Nafion’s series resistance and Pt-activated monolayer hBN is no longer a bottleneck for proton permeation. On the other hand, for graphene and bilayer hBN activated with Pt, the series resistance remains relatively small and the measurements still reflect their intrinsic properties. By studying $\sigma(T)$, we find that Pt reduces the activation energy $E$ by as much as $\approx 0.5$ eV to $\approx 0.24$ eV (Fig. 2b). Our simulations of the catalytic effect yield a reduction in $E$ by $\approx 0.65$ eV, in qualitative agreement with the experiment (Supplementary Information).
The mechanism behind this barrier reduction can be attributed to attraction of passing protons to Pt (Supplementary Fig. 10). Note that the measurements in Fig. 2b set only a lower limit of \( \approx 3 \, \text{S/cm}^2 \) on room-\( T \) conductivity of catalytically-activated monolayer hBN and, if the membranes experience qualitatively similar reduction in \( E \) as observed for graphene, we expect essentially a barrier-less proton transport. It would require membranes with much larger area to determine intrinsic \( \sigma \) for catalytically-activated hBN.

Finally, we demonstrate directly that the observed electric currents are due to proton flux through the 2D membranes. To this end, we have prepared devices such as shown in the insets of Fig. 3. Here, one of the Nafion/PdH\(_x\) electrodes is removed, and the graphene surface decorated with Pt faces a vacuum chamber equipped with a mass spectrometer. If no bias is applied between graphene and the remaining PdH\(_x\) electrode, we cannot detect any gas leak (including He) between the hydrogen and vacuum chambers. Similarly, no gas flow could be detected for positive bias on graphene. However, by applying a negative bias we have measured a steady \( \text{H}_2 \) flux into the vacuum chamber. Its value is determined by the number of protons, \( I/e \), passing through the membrane per sec. Using the ideal gas law, one can easily derive the relation \( F = k_B T (I/2e) \) where the flow rate \( F \) is the value measured by the mass spectrometer tuned to molecular hydrogen. The latter dependence is shown in Fig. 3 by the solid red line, in excellent agreement with the experiment.

In conclusion, monolayers of graphene and hBN represent a new class of proton conductors. In addition to the fundamental interest in how subatomic particles transfer through atomically thin electron clouds, the membranes can find use in
various hydrogen technologies. For example, 2D crystals can be considered as proton membranes for fuel cells. They are highly conductive to protons and chemically and thermally stable and, at the same time, impermeable to $\text{H}_2$, water or methanol. This could be exploited to solve the problem of fuel crossover and poisoning in existing fuel cells. The demonstrated current-controlled source of hydrogen is also appealing at least for its simplicity and, as large-area graphene and hBN films are becoming commercially available, the scheme may be used to harvest hydrogen from gas mixtures or air.

References
#1 Experimental devices
Figure S1 explains our microfabrication procedures. We start with preparing free-standing silicon nitride (SiN$_x$) membranes from commercially available Si wafers coated from both sides with 500 nm of SiN$_x$. Reactive ion etching (RIE) is employed to remove a 1×1 mm$^2$ section from one of the SiN$_x$ layers (steps 1&2 in Fig. S1). The wafer is then exposed to a KOH solution that etches away Si and leaves a free-standing SiN$_x$ membrane of typically 300×300 m$^2$ in size (step 3). During step 4, a circular hole is drilled by RIE through the SiN$_x$ membrane using the same procedures as in steps 1&2. Next, a 2D crystal (graphene, hBN or MoS$_2$) is prepared by the standard micromechanical exfoliation [S1] and transferred on top of the membrane using either the wet or dry technique [S2,S3] to cover the aperture in SiN$_x$ (step 5).

After step 5, the suspended membranes could be examined for their integrity and quality in a scanning electron microscope (SEM). We did not, however, perform electrical measurements of any membrane that was imaged with SEM. As mentioned in the main text, pristine 2D crystals give little SEM contrast, and it requires some contamination to notice 2D membranes on top of the holes. Contamination can be accidental as in the case of Fig. S2a or induced by the electron beam (Fig. S2b). If cracks or tears are present, they are clearly seen as darker areas (inset of Fig. S2b).
Figure S1 | Microfabrication process flow. ① An etch mask is made by photolithography. ② RIE is used to remove the exposed SiN_x layer. ③ Si underneath is etched away by wet chemistry. ④ By repeating steps 1 and 2, a hole is drilled through the membrane. ⑤ 2D crystal is transferred to cover the hole. ⑥ Nafion is deposited on both sides of the wafer. ⑦ Palladium-hydride electrodes are attached. Bottom right: Optical photo of the final device. Scale bar: 1 cm.

The fabrication of devices for electrical measurements continues with depositing a proton-conducting polymer layer. A Nafion 117 solution (5%) is drop-cast or spin-coated on both sides of a suspended 2D membrane (step 6 in Fig. S1). Finally, palladium hydride (PdH_x) electrodes are mechanically attached to the Nafion layers. To synthesize such electrodes, a 25 µm thick Pd foil is left overnight in a saturated hydrogen-donating solution following the recipe reported in ref. S4. This leads to atomic hydrogen being absorbed into the crystal lattice of Pd turning it into PdH_x.
The resulting devices are placed in a water saturated environment at 130°C to crosslink the polymer and improve electrical contacts.

**Figure S2 | SEM images of suspended 2D membranes.** a, Monolayer graphene with some accidental contamination. One of the particles away from the edge is marked by the white circle. b, Suspended graphene with pillars of hydrocarbon contamination intentionally induced by a focused electron beam. The inset shows a crack in the membrane; scale bar: 100 nm.

The described experimental design is optimized to take into account the following considerations. First, electric currents in Nafion are known to be carried out exclusively by protons that hop between immobile sulfonate groups [S5]. Nafion is not conductive for electrons, which can be evidenced directly by, for example, inserting a gold film across a Nafion conductor, which then breaks down the electrical connectivity. Accordingly, protons are the only mobile species that can pass between PdH\textsubscript{x} electrodes. Second, PdH\textsubscript{x} is widely used as a proton injecting material that converts an electron flow into a proton one by the following process: \[ PdH_x \rightarrow Pd + xH^+ + xe^- \] [S6-S8]. This property combined with a large area of our electrodes (relatively to the membrane area \( A \)) makes the contact resistance between Nafion and PdH\textsubscript{x} negligible so that the circuit conductance in our experiments is...
limited by either 2D crystals or, in their absence, by the Nafion constriction of diameter $D$.

For the catalytically-activated measurements, 1-2 nm of Pt were deposited by e-beam evaporation directly onto the suspended membrane to form a discontinuous film prior to the Nafion coating. Thicker, continuous films were found to block proton currents, which could be witnessed as numerous hydrogen bubbles that appeared under Pt after passing electric current. Typically, our Pt films resulted in ~80% area coverage, which reduced the effective area for proton transport accordingly, as found by depositing such films between Nafion spaces but without 2D membranes (see below). Pd films were found to be less blocking and continuous films up to 10 nm in thickness did not significantly impede the proton flow. Otherwise, both Pd and Pt films resulted in similar enhancement of proton transport through 2D crystals.

#2 Electrical measurements
The devices described above were placed inside a metallic chamber filled with a forming gas (10% H$_2$ in argon) and containing some liquid water to provide 100% relative humidity. I-V curves were obtained by DC measurements recorded with a Keithley 2636A electrometer. We varied voltage in a range of typically up to 1 V at sweep rates up to 0.5 V/min. We avoided voltages higher than 1.5 V to prevent the membranes from delaminating from the SiN$_x$ substrate as a result of gas bubble formation from water electrolysis. Under these conditions, the curves were non-hysteretic and highly reproducible. The devices were stable for many weeks if not allowed to dry out.
To characterize our experimental setup, we first measured leakage currents in the absence of a proton conductive path. To this end, two metallic contacts were placed onto the opposite surfaces of a piece of a fresh Si/SiN$_x$ wafer and I-V characteristics were measured under the same humid conditions. Conductance of the order of $\sim 5$ pS was normally registered. We also used fully processed devices and then mechanically removed the Nafion film and electrodes. In the latter case, the parasitic conductance was slightly (by a factor of 2) higher, which is probably due to a residue left of SiN$_x$ surfaces during processing. In principle, it would be possible to reduce the leakage currents by using, for example, separate chambers at the opposite sides of the Si wafer [S9] but the observed parasitic conductance was deemed small enough for the purpose of the present work.

As a reference, we studied conductivity of ‘bare-hole’ devices that were prepared in exactly the same manner as our membrane devices but without depositing a 2D crystal to cover the aperture (step 5 in Fig. S1 is omitted). Figure S3 shows conductance of such devices as a function of their diameter $D$. Within the experimental scatter, conductance $S$ increases linearly with $D$, in agreement with Maxwell’s formula: $S = \sigma_N D$ [S10]. The latter is derived by solving Laplace’s equation for two semi-spaces that have conductivity $\sigma_N$ and are connected by a hole with $D$ much larger than the length $d$ of the opening. In our case, $d = 500$ nm and the condition is comfortably satisfied, except for possibly the smallest membranes in Fig. S3 with $D = 2 \mu$m.
**Figure S3 | Bare-hole devices with different apertures.** Their conductance exhibits a linear dependence on D as expected for this geometry. The inset illustrates schematics of such devices.

From the dependence shown in Figure S3, we can estimate conductivity of our Nafion films as $\approx 1$ mS/cm. As discussed in the main text, Nafion’s conductivity did not limit our measurements of proton transport through 2D crystals, except for the case of catalytically-activated monolayer hBN. Nonetheless, we note that the found $\sigma_N$ is two orders of magnitude smaller than values achievable for highest-quality Nafion [S11]. There are two reasons for this. First, solution-cast Nafion is known to lose typically one order of magnitude in conductivity [S12,S13]. Second, Nafion is normally pretreated by boiling in H$_2$O$_2$ and H$_2$SO$_4$ for several hours [S11-S13]. If the latter procedure was used, our Nafion films indeed increased their conductivity by a factor of 10, reaching the standard values for solution-cast Nafion of $\approx 10$ mS/cm. Unfortunately, this harsh treatment could not be applied to our membrane devices that became destroyed with Nafion films delaminating from SiNx.
Conductance scales quadratically with $D$, that is, linearly with $A$. Inset shows I-V characteristics for devices with different $D$.

For consistency, most of the 2D membranes reported in the main text were made 2 $\mu$m in diameter. However, we also studied many other membranes with diameters ranging from 1 to 50 $\mu$m. We found that their conductance scaled linearly with the aperture area $A$. Figure S4 shows this for 10 monolayer hBN devices with $D$ between 1 and 4 $\mu$m. Within the typical experimental scatter for devices with the same $D$, the conductance increases linearly with the area $A$ of 2D membranes, in agreement with general expectations. The same scaling was also observed for graphene membranes.

Finally, we have reported in the main text that proton conductivity of catalytically-activated monolayer hBN is so high that the series resistance of Nafion becomes the limiting factor in our measurements. This is further evidenced by comparing $T$ dependences of different devices in which Nafion was the limiting factor. Those include ‘bare-hole’ devices (Nafion only), ‘bare-hole’ devices with Pt (Nafion/Pt/Nafion) and monolayer hBN membranes activated with Pt. Figure S5
shows a typical behavior of their conductance as a function of \( T \). Consistent with the small activation energy for proton transport in Nafion (<0.02 eV) \([\textit{S11}]\), we found that temperature effects in all the above devices are small over the entire temperature range (see Fig. S5). The nonmonotonic \( T \) dependence for the devices with Pt layers (Fig. S5) remains to be understood but we note that Nafion often exhibits similar nonmonotonic behavior at higher \( T \), beyond the range of Fig. S5 \([\textit{S14}]\). We speculate that the Pt activation shifts this peak to lower \( T \). Importantly for our experiments, the influence of Pt nanoparticles on local conductivity in the Nafion constriction is approximately the same independently of whether an hBN membrane is present or not. This further indicates that the proton conductivity of Pt-activated hBN is so high that it becomes unmeasurable in our experimental setup, essentially because of the limited size of currently available hBN crystals.

\[ \text{conductivity} (\text{S/cm}^2) \]

\[ \text{temperature} ({}^\circ\text{C}) \]

**Figure S5 | Proton transport limited by Nafion.** Temperature dependences for bare-hole devices, Nafion/Pt/Nafion devices and membrane devices with catalytically-activated monolayer hBN. The nominal conductivity is calculated as the measured conductance \( S \) divided by the aperture area \( A \).
Absence of atomic scale defects in 2D membranes

As described in section 1, visual inspection of membranes in SEM can reliably rule out holes and cracks with sizes down to <10 nm (see Fig. S2b). None of such defects could be found in many membranes we visualized in SEM. Occasional cracks such as in Fig. S2b could only be observed if introduced deliberately or a profound mistake was made during handling procedures. However, SEM cannot resolve nm- or atomic-scale defects, and other techniques are necessary to rule out microscopic holes. As already mentioned in the main text, no such defects have ever been reported for pristine graphene obtained by micromechanical cleavage in numerous SEM and scanning tunneling microscopy studies over many years. To add to this argument for the case of our particular membranes, we have used Raman spectroscopy that is known to be extremely sensitive to atomic-scale defects in graphene. The intensity of the D peak provides a good estimate for a concentration of such defects, which could be not only vacancies or larger holes but also adatoms that do not lead to pinholes. Despite our dedicated efforts, we could not discern any D peak in our graphene membranes. This sets an upper limit on the atomic defect density as \( \sim 10^8 \text{ cm}^{-2} \) or one defect per \( \mu \text{m}^2 \) [S15]. Furthermore, such a low density of defects in graphene is in stark contrast with a high density (\( \sim 10^{13} \text{ cm}^{-2} \)) of sulfur vacancies found in mechanically cleaved MoS\(_2\) [S16]. Notwithstanding, no proton current could be detected through our MoS\(_2\) membranes. If we assume each vacancy to provide a hole of \( \sim 1 \text{ Å} \) in size, the expected \( \sim 10^5 \) vacancies present in our typical MoS\(_2\) membranes would provide an effective opening of \( \sim 30 \text{ nm} \) in diameter. Using the results of Figure S3, this is expected to lead to a conductance of \( \sim 3 \text{ nS} \), that is, \( >100 \) times
larger than the limit set by our measurements on proton conductance through monolayer MoS$_2$. This shows that individual vacancies in fact provide much smaller proton conductivity than their classical diameter suggests.

To strengthen the above arguments further, we tried to rule out even individual vacancies from our proton conductive (graphene and hBN) membranes. The most sensitive technique known to detect pinholes is arguably measurements of gas leakage from small pressurized volumes [S17,S18]. To this end, a microcavity of typically $\sim$1 $\mu$m$^3$ in size is etched in a Si/SiO$_2$ wafer, sealed with graphene or hBN and then pressurized. If the pressure inside the microcavity is higher than outside, the membrane bulges upwards; if it is lower, downwards. Changes in pressure can be monitored by measuring the height of the bulge as a function of time using atomic force microscopy (AFM). If there are no holes in the membrane, the gas leaks slowly through the oxide layer, and it typically takes many hours until the pressure inside and outside the microcavity equalize [S17]. However, the presence of even a single atomic-scale hole through which atoms can effuse allows the pressure to equalize in less than a second [S18].

Following the procedures reported previously [S17,S18], we prepared microcavities in a Si/SiO$_2$ wafer and sealed them with monolayer graphene. The microcavities were placed inside a chamber filled with Ar at 200 kPa for typically 4 days to gradually pressurize them. After taking the devices out, the membranes were found to bulge upwards. Figure S6 shows the deflation of such micro-balloons with time. In agreement with the previous report [S17], the Ar leak rates were found to be $\sim$10$^3$ atoms per second. If an atomic-scale hole is introduced by, for example, ultra-violet
chemical etching, the leak rate increases by many orders of magnitude, leading to practically instantaneous deflation [S18]. Furthermore, we found no difference in the deflation rates for membranes with and without evaporated Pt.

![Graph showing height profiles and time](image)

**Figure S6** | **Deflation of micro-balloons to check for atomic scale defects in graphene membranes.** a, Height profiles for a typical graphene membrane at different times. b, Maximum height as a function of time. The inset shows a typical AFM image of a pressurized graphene microcavity (color scale: 0 to 130 nm). We measured six graphene membranes with all of them showing the same deflation rates, independently of whether Pt was deposited on top or not. Similar behavior was observed for hBN monolayers.

In principle, it could be argued that membranes with pinholes smaller than the kinetic diameter of Ar (0.34 nm) or pinholes blocked with Pt nanoparticles should show no detectable leaks. However, monolayer membranes with subnanometer-sized pinholes are known to be rather unstable mechanically due to a tendency of defects to enlarge under strain [S18], which for the applied pressures reached significant values of ~1%. Our micro-balloons remained stable and could be pressurized many times. This behavior consistent with the previous work [S17,S18] assures that no individual
pinholes were present in graphene and monolayer hBN obtained by mechanical cleavage.

**#4 Detection of proton flow by mass spectrometry**

To show directly that the electric current through our 2D membranes is carried by protons, we used an alternative setup described in the main text and shown in more detail in Fig. S7a. Protons transferring through graphene are collected at a catalyst Pt layer where they recombine to form molecular hydrogen: $2H^+ + 2e^- \rightarrow H_2$. The hydrogen flux is then measured with a mass spectrometer. Because the electric current $I$ is defined by the number of protons passing through the graphene membrane, the hydrogen flow $F$ is directly related to the passing current $I$, with no fitting parameters (see the main text).

![Figure S7](image)

**Figure S7 | Hydrogen flow detection.** a, Schematics of our devices for mass spectroscopy measurements. b, Example of the observed hydrogen flow rates as a function of time and measured current for different negative biases on the graphene membrane, which we applied in steps.
For this particular experiment, the membrane devices were made as large as possible (50 µm in diameter), which was required to increase the hydrogen flux to such values that they could be detectable with our mass spectrometer (Inficon UL200). To collect the electric current at the graphene membrane, a metallic contact (100 nm Au/5 nm Cr) was fabricated next to the SiNx aperture, before transferring graphene on top to cover both aperture and contact (right inset of Fig. 3 in the main text). This side of the Si wafer (with graphene on top) was then decorated with 1-2 nm of Pt to increase the proton flux and allow its easier conversion into hydrogen. The opposite face of the graphene membrane was covered with Nafion and connected to a PdHx electrode in the same way as described in section 1.

The resulting device on the Si wafer was glued with epoxy to a perforated Cu foil that was clamped between two O-rings to separate two chambers: one filled with a gas and the other connected to the mass spectrometer (Fig. S7a). First, we always checked the setup by filling the gas chamber with helium at the atmospheric pressure. No He leak could be detectable above background readings of the spectrometer at ~10^-8 bar cm^3/s. Then, the chamber was filled with our standard gas mixture (10% H2 in argon at 1 bar and at 100% humidity). No hydrogen flux could be detected without applying negative bias to graphene. However, by applying such a bias a controllable flow of H2 at a level of ~10^-5 bar cm^3/s was readily detected (Fig. S7b). This figure shows the hydrogen flow rates F as a function of time for one of our devices using negative biases from 0 to 20 V. When cycling back from 20 to 0 V, the curves retraced themselves, indicating that the membrane was undamaged during the measurements.
Atomic hydrogen is highly unstable with respect to its molecular form, and it is most likely that the conversion into molecular hydrogen takes places at the surface of Pt rather than in the vacuum chamber. Accordingly, the Pt layer has to be discontinuous to let hydrogen escape. For continuous coverage (>5 nm of Pt), we observed formation of small hydrogen bubbles that grew with increasing the amount of electric charge passed through the circuit. Largest bubbles eventually erupted. It is also instructive to mention the case of continuous Au films evaporated on top of the above devices (already containing a discontinuous Pt layer). We found that a bias applied across such devices again resulted in the formation of bubbles at the interface between graphene and the metal film. The bubbles could burst and sometimes even damaged the membrane. This disallowed the use of continuous metal films for the mass spectrometry experiment. The same bubbling effect was observed for hBN membranes covered with a Pt film that provided the continuity of the electrical circuit for insulating hBN. These observations serve as yet another indication of proton transfer through graphene and hBN membranes. On the other hand, no bubbles could be observed for thicker 2D crystals that again shows their impermeability to protons. Note that, although thin Pd films were more transparent for atomic hydrogen (see the main text), large currents and hydrogen fluxes needed for mass spectrometry also led to hydrogen bubbles, which prevented the use of hBN with Pd in the mass spectrometry experiments.

#5 Theoretical analysis of proton transport through 2D crystals
As discussed in the main text, it is possible to understand our results qualitatively by considering the electron clouds created by different 2D crystals. These clouds impede
the passage of protons through 2D membranes. In addition to the plots of the electron density for graphene and hBN monolayers in Fig. 1b of the main text, Figure S8 shows similar plots of these clouds with superimposed positions of C, B and N atoms using the ball-and-stick model of graphene and hBN crystal lattices. In addition, Figure S8 plots the electron density for monolayer MoS$_2$. One can immediately see that the latter cloud is much denser than those of monolayer hBN and graphene, which explains the absence of proton transport through MoS$_2$ monolayers.

For quantitative analysis, we first note that proton permeation through graphene has previously been studied using both ab initio molecular dynamics simulations (AIMD) and the climbing image nudged elastic band method (CI-NEB) [S19-S21]. These studies have provided estimates for the proton transport barrier $E$ in graphene ranging from $\approx 1.17$ eV to 2.21 eV [S19-S21]. We reproduced those results for the case of graphene and extended them onto monolayer hBN.

![Graphene, hBN, MoS$_2$](image)

**Figure S8 | Electron clouds of 2D crystals.** Integrated charge densities for graphene, monolayer hBN (nitrogen is indicated by blue balls; boron in pink) and monolayer MoS$_2$ (S is in yellow, Mo in brown).

All our simulations were performed using the CP2K package [S22] with the Pade exchange-correlation functional form [S23]. The energy cutoff of plane-wave
expansions was 380 Ry, and we used the double-\(\zeta\) valence basis with one set of polarization functions [S24] and the Goedecker-Teter-Hutter pseudopotentials [S23]. In the first approach, the bombardment of graphene and monolayer hBN with protons of varying kinetic energy was simulated using AIMD in the NVE ensemble (that is, Number of atoms, Volume and Energy are assumed constant). The barrier was estimated as the minimum kinetic energy necessary for proton transfer. The AIMD simulations have yielded graphene’s \(E\) between 1.30 eV and 1.40 eV, in agreement with results of refs S19,S20.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{CI-NEB simulations. Energy profiles as a function of the proton distance to the center of the hexagonal ring in graphene and hBN (a and b, respectively). Carbon atoms are shown as cyan-colored spheres, nitrogen in blue, boron in pink and protons (H\(^+\)) in white.}
\end{figure}

In the second (CI-NEB) approach, we calculated the energy for various configurations (usually referred to as ‘images’), which correspond to different distances between a proton and a 2D membrane [S25]. This provided a series of images for a proton approaching the membrane. The energy was then minimized over obtained images and plotted as a function of distance to 2D crystals. The barrier \(E\) was estimated using the differential height of energy profiles. Figure S9 shows
examples of such energy profiles for graphene and monolayer hBN. From the CI-NEB calculations, we have estimated the proton barrier as 1.26 eV and 0.68 eV for graphene and monolayer hBN, respectively, in agreement with the AIMD results. Finally, to model the effect of Pt on proton transport, we again used AIMD simulations. To this end, 4 Pt atoms were placed at a fixed distance (4 Å) from the graphene membrane and the bombardment with protons was simulated as described above. The addition of the Pt atoms resulted in a significant reduction of the barrier to ≈0.6 eV; that is, by a factor of 2. The absolute value of the reduction in the barrier height is in good agreement with the experimental observations.

Figure S10 | AIMD simulations for the proton barrier in graphene with Pt. Carbon atoms are shown in cyan, Pt in ochre, H$^+$ in white. a, Experimental situation is mimicked by placing 4 Pt atoms at a distance of 4 Å from the graphene sheet. b, Figure shows the trajectory of protons with initial kinetic energy $E = 0.7$ eV (the other two Pt atoms cannot be seen due to the perspective). The bended trajectories indicate that the decreased barrier is due to the interaction of protons with Pt.
#6 Proton transport through 2D crystals in liquids
Although Nafion was the material of choice in this work due to its stability and convenience of handling, in order to show the generality of our results, we have also investigated proton conductivity of 2D crystals when they were immersed in water solutions. For these experiments, devices were fabricated in the same way as described previously but instead of covering 2D crystals with Nafion, they separated two reservoirs containing liquid electrolytes. A polydimethylsiloxane seal was used to minimize leakage along the 2D crystal/substrate interface (Fig. S11 inset; yellow) [S9]. Ag/AgCl electrodes were placed in each reservoir to apply a bias across the membranes and measure ionic currents (Fig. S11). Devices for this experiment were usually more fragile than Nafion devices due to the lack of mechanical support but robust enough to measure them several times.

Figure S11 | Proton transport through 2D crystals in liquids. a, Examples of I-V characteristics for mono-, bi- and tri-layer hBN covering an aperture of 2 µm in diameter. The inset shows schematics of the liquid cell (0.1M HCl solution on each side). In the case of trilayer hBN, the current is within the range given by a parasitic parallel resistance. Each point in the figure is the stable current obtained from chronoamperometry. Sweeping to negative voltage biases showed the same current response. b, Histograms for the 2D crystals
that exhibited clear proton current in the liquid cell setup. Each bar represents a different sample with a 2 μm diameter membrane. The shaded area shows the detection limit set by leakage currents.

Typical I-V profiles of single-, bi-, and tri-layer hBN are presented in Fig. S11a; the current response was symmetric with respect to bias voltage. This behavior was highly reproducible as evidenced by the statistics in Fig. S11b. For devices prepared in the same manner but without a 2D crystal, the conductivity $S$ was $>10^4$ times higher than in the presence of monolayer hBN, which ensured that the 2D crystals limited the proton current. As in the case of Nafion, we found a parasitic parallel conductance but it was somewhat higher (~20 pS) for the liquid cell setup. Within this accuracy, we could not detect any proton current through monolayer MoS$_2$, bilayer graphene, trilayer hBN or any thicker 2D crystals. Most importantly, the measured proton conductivities using electrolytes agree extremely well with the values found using Nafion as the proton conducting medium (cf. Fig. 1b and Fig. S11b).

**Supplementary references**


Our proton transport experiments have established that monolayers of hexagonal boron nitride (hBN) and graphene are highly permeable to thermal protons. Furthermore, the transport mechanism was established as an Arrhenius activated process with activation energies much lower than predicted by the existing theory. However, the transport mechanism was not completely understood. Does the surrounding medium play a role in the transport mechanism?

Traditionally, to gain further insight into proton transport mechanisms, hydrogen is substituted by its heavy isotope deuterium. Because their electronic configurations are the same, both isotopes form bonds with the same force constants. However, their difference in mass does affect their vibrational frequencies within that bond. Therefore, the reactivity of that bond is influenced by isotopic substitution. And indeed, this effect has long been used to separate hydrogen from its heavier isotopes deuterium and tritium, mostly for nuclear energy applications [66]–[69], [71], [72], [103], [104].

The main finding of this work is that protons and deuterons transfer across 2D crystals at different rates; deuterons find it harder to cross the barrier posed by the crystals. The reason for that is that the medium surrounding the protons plays a crucial role in the transport mechanism. Protons and deuterons in water oscillate with respect to the oxygen atom with a quantized frequency dictated by the reduced mass of the atoms and the bond
strength. Crucially, this frequency will be quantized with different zero point energies for protons and deuterons. Then, because of this difference in zero point energy, the isotopes will face different effective energy barriers. Indeed, our mass spectrometry and conductivity measurements have established that deuterons face an effective energy barrier $\approx 60$ meV higher than protons. This energy difference translates into a separation factor of $\approx 10$ for a hydrogen-deuterium electrolyte and $\approx 30$ for hydrogen-tritium.

Our results provide fresh insight into the transport mechanism of hydrogen nuclei through atomically thin electron clouds and, furthermore, establish monolayers of graphene and hBN as promising materials for isotope separation and enrichment technologies.

The work presented in this section has been submitted for publication. My contribution to this work was to fabricate devices (with help from Sheng), measure the devices, analyze the data, develop the theory to explain our results and help in the design of the experiments. A. K. Geim directed the project, O. Marshall performed IR spectroscopy measurements. A. K. Geim, I.V. Grigorieva and myself wrote the manuscript.
Sieving Hydrogen Isotopes through Two Dimensional Crystals


One-atom-thick crystals are impermeable to all atoms and molecules but hydrogen ions (thermal protons) penetrate relatively easily through them. Here we show that membranes made from graphene and monolayer boron nitride can be used to separate hydrogen isotopes. Using electrical measurements and mass spectrometry, we have found that deuterons permeate through these crystals much slower than protons. The isotope effect is attributed to the difference of \( \approx 60 \) meV between zero point energies of the O-H and O-D bonds, which represent initial states of hydrons in their thermally activated transmission through the membranes. In addition to providing insight into the proton transport mechanism, the found isotope separation factor of \( \approx 10 \) at room temperature offers a highly competitive and scalable way for hydrogen isotope enrichment.

Unlike conventional membranes used for sieving atomic and molecular species, graphene and monolayer hexagonal boron nitride (hBN) exhibit subatomic selectivity (1-5). They are permeable to thermal protons (5) – and, of course, electrons (6) – but
impermeable to larger, atomic species (1-5,7-9). Investigating whether deuterons – nuclei of the heavier hydrogen isotope, deuterium (D) – can pass through these two-dimensional (2D) crystals is interesting for both exploring the potential of the subatomic selectivity and elucidating its mechanism (5,9). Indeed, the role of proton transfer in chemical reactions is conventionally probed by substituting protium (H) with deuterium (10-15). Because their electronic configurations are exactly the same, both hydrons form chemical bonds with the same force constant. Yet, because of the mass difference, their vibrational energies are different. If proton transfer limits the rate of a chemical reaction, its activation energy may notably change upon substitution of H with D. This phenomenon usually referred to as the kinetic isotope effect (10,11,16-18) is routinely exploited to enrich mixtures of H and D and, for example, produce heavy water (10,19,20).

We have studied hydron transport through monocrystalline membranes made from mono- and few-layer graphene and hBN using the technique developed previously (5,21). In brief, graphene and hBN crystals were mechanically exfoliated and suspended over micrometer-sized holes etched in silicon nitride wafers (fig. S1). Both sides of the resulting membranes were coated with a proton conducting polymer – Nafion (22) – and electrically contacted using Pd electrodes that convert electron into hydron flow (23) (inset of Fig. 1A). The electrical conductivity measurements were performed in either H\textsubscript{2}-Ar/H\textsubscript{2}O or D\textsubscript{2}-Ar/D\textsubscript{2}O atmosphere in 100 % humidity at room temperature (T). The different atmospheres turned Nafion into proton (H-Nafion) or deuteron (D-Nafion) (24) conductors with little presence of the other isotope (fig. S2). We refer to these two setups as H- and D- devices. As a reference, we also fabricated similar samples but without 2D
membranes. They were used to measure hydron conductivities of H- and D- Nafion (21). Those were found to be indistinguishable and sufficiently high (∼1 mS cm⁻¹) to avoid any noticeable series contribution to the measured electrical resistance of H- and D-devices (21). For both types of devices, the current I varied linearly with applied bias (Fig. 1A). Different 2D membranes showed widely different areal conductivities σ (Fig. 1B). For the purpose of this report, we focus on the most conductive crystals. Monolayer hBN exhibited the highest proton σ, followed by bilayer hBN and monolayer graphene (Fig. 1B), in agreement with the previous work (5).

Our main finding is that σ was markedly smaller (∼10 times) for D-devices compared to their H-Nafion counterparts, independent of the tested 2D crystal and its σ (Fig. 1B). Moreover, we carried out similar measurements for Pt-activated membranes (2D crystals covered with a discontinuous layer of Pt to enhance hydron transport) (21) and, again, the conductivity for deuterons σ_D was an order of magnitude lower than that for protons σ_H (fig. S3). To understand this universal difference in transfer rates for protons and deuterons, we point out that hydron permeation through 2D crystals is a thermally activated process (5) and, although hydron barriers and conductivities may vary strongly, the ratio σ_H/σ_D is determined only by the difference ΔE between proton and deuteron activation energies rather than the energies themselves. Therefore, neglecting small differences in attempt rates (21) we can write σ_H/σ_D = exp(ΔE/k_BT) where k_BT is the thermal energy. Statistical analysis of our results in Fig. 1B yields σ_H/σ_D ≈ 10 ±0.8, which translates into ΔE ≈ 60±2 meV.
Fig. 1. Hydron conductivities of 2D crystals. (A) Examples of I-V characteristics for proton and deuteron transport through monolayers of hBN and graphene. Top inset: Schematics of the experimental setup. Pd electrodes supply protons (h) or deuterons (d) into H- or D-Nafion; 2D crystals serve as barriers for hydrions. (B) Proton and deuteron conductivities (shaded and solid bars, respectively) for the most hydron conductive crystals. Each bar corresponds to a different device (nearly thirty are shown). The dotted lines mark the average conductivities, and the shaded areas around them show the standard errors.

In our second set of experiments, we measured proton and deuteron flows directly, using mass spectrometry (fig. S4). Following ref. 5, we used monolayer graphene membranes (up to 50 µm in diameter) to separate two chambers referred to as input and output (Fig. 2). On the input side, graphene was coated with a thin Nafion layer and faced a reservoir containing a proton-deuteron electrolyte (HCl in H2O mixed with DCl in D2O). The atomic fraction of protons (h) and deuterons (d) in this mixture ([h]:[d], where [h]+[d] = 100%) could be changed as required. The other side of graphene was decorated with Pt nanoparticles and contacted using a microfabricated wire. This side faced a vacuum chamber of the mass spectrometer (21). The use of graphene rather than hBN allowed us to make much larger membranes, and the decoration with Pt significantly reduced the
proton barrier (5). This combination was essential to achieve gas flows sufficient for detection by mass spectrometry. We also had to apply much larger (>10 times) currents than those used in the above electrical conductivity measurements.

**Fig. 2. Isotope effect measured by mass spectrometry.** (A) D₂ flow detected using Pt-activated graphene membranes (orange symbols) and porous carbon (brown) with only deuterons at the input. Inset: Same for 100% proton input. (B) D₂ flow versus electric current for various proton-deuteron fractions at the input electrolyte. Inset: Schematic of the experimental setup. The shown data are for membranes of 50 μm in diameter. All the dashed lines are guides to the eye.

In the mass-spectrometry setup (see Fig. 2B), a voltage bias applied between the electrolyte and 2D membrane drove hydrons across graphene and onto the Pt catalyst where they evolved into three possible molecular species: protium (H₂), protium deuteride (HD) or deuterium (D₂). By simultaneously measuring I and the output gas flow F, we found that F varied linearly with I for any [h]:[d] input but the proportionality coefficients depended strongly on the electrolyte composition. For an input containing only protons, only H₂ could be detected by the spectrometer, as
expected, and the flow was described well (within ≈20% scatter for different devices) by the mass-charge relation (5,21)

\[ F = k e T(I / 2e) \]  

where \( e \) is the elementary charge. This equation means that each hydron transferring through graphene leads to an electron flowing through the external electric circuit (21). The same relation was observed for our reference devices that used porous carbon cloth instead of graphene (fig. S4). For 100% deuterons at the input, again only \( \text{D}_2 \) could be detected at the output. However, the \( \text{D}_2 \) flow was ~10 times smaller than that expected from Eq. 1 (Fig. 2A). Crucially, the tenfold drop in \( \text{D}_2 \) flow could be attributed only to the presence of graphene because substituting it with porous carbon resulted in the full recovery of the above mass-charge relation (inset of Fig. 2A). These observations indicate that, unlike porous carbon, graphene membranes respond differently to the presence of protons and deuterons, in qualitative agreement with our electrical conductivity measurements. We attribute the breakdown of Eq. 1 for the case of deuterons to the fact that a large fraction (∼90%) of deuterons did not cross graphene but instead evolved into \( \text{D}_2 \) at the input side. This was clearly evidenced by the formation of microbubbles between Nafion and the graphene membrane (fig. S5).

For intermediate [h]:[d] mixtures, all the three gases (\( \text{H}_2 \), HD and \( \text{D}_2 \)) could be detected exhibiting the following trends. First, as the fraction of protons at the input was increased, the combined gas flow also increased, gradually approaching the one prescribed by Eq. 1 (fig. S5). Second, the proportionality coefficient between \( F \) and \( I \) measured for different gases was very sensitive to the input proton concentration \([h]\) (fig. S6). For example, if \([h]\) increased from zero (deuterons only) to 35%, the \( \text{D}_2 \) flow
decreased by more than an order of magnitude (Fig. 2B). To quantify these observations, we measured the flow of all three gases using various [h]:[d] inputs. Fig. 3A shows mole fractions for the output gases as a function of [h]. One can see that the fraction of D₂ was significant only for large concentrations of deuterons (≥90%). At [d] = 90%, most of the deuterons crossing graphene membranes already evolved into HD. Further increase in [h] resulted in the output being dominated by protium and, for [h] = [d], H₂ accounted for ≈85% of all molecules in the output gas whereas the rest was HD (Fig. 3A). It is straightforward to convert these data into the percentage of H and D atoms in the output gas (21). As seen in Fig. 3B, the output fraction of atomic protium [H] was disproportionally high with respect to the input fraction of protons [h]. For example, for equal amounts of protons and deuterons at the input, protium accounted for ≈95% of all atoms passing through the graphene membrane. This behavior represents highly efficient hydron sieving. Indeed, the sieving quality of membranes is usually characterized by their separation factor α. Our experiments yield α ≈10 (21), which compares favorably with all other existing methods for hydrogen isotope separation (19-21, 25-27).

The mass-spectrometry results in Fig. 3B can be described quantitatively by the difference ΔE = 60 meV between activation energies for protons and deuterons, which was reported above for the electrical measurements. As shown in (21), the protium output is given by

\[
[H] = \frac{[h]}{[h] + \exp(-\Delta E/k_B T)[d]}
\]  

(2).

This dependence is plotted in Fig. 3B and shows excellent agreement with the experiment. For our reference devices with porous carbon electrodes, we measured [H]
≈ [h] (that is, no selectivity) as expected from Eq. 2 for membranes with no barrier for hydrons (fig. S7).

Fig. 3. Hydron selectivity of graphene membranes. (A) Relative fractions of H₂, HD and D₂ in the output flow for eight different compositions of the input electrolyte ([h] + [d] = 100%). (B) Fraction of protium atoms at the output for different [h] inputs. The solid red curve shows [H] calculated using Eq. (2) without fitting parameters. Inset: Schematic of the energy barrier presented by a 2D crystal for proton and deuteron transfer. The initial state in the process is a hydron-oxygen bond. The solid blue and red lines indicate its zero point states for protons and deuterons, respectively.

To understand the physics mechanism behind the observed sieving properties of 2D crystals, we point out that all the studied membranes (graphene, mono- and bi- layer hBN and all their Pt-activated counterparts) exhibited the same ∆E ≈60 meV within our experimental accuracy (21). This strongly suggests that the difference between proton and deuteron transport lies not in the 2D crystals themselves but somewhere else. To this end, we recall that hydrons in Nafion move along oxygen bonds provided by water molecules and sulfonate groups (22). Vibrational energies of both O-H and O-D bonds
are quantized with a large zero point energy reaching ≈0.2 eV for protons. It is ≈60 meV lower for deuterons because they are twice heavier (inset of Fig. 3B). These values are documented in literature (10,28,29) but we also measured them for our Nafion films (fig. S2). As illustrated in the inset of Fig. 3B, quantum oscillations increase the initial-state energy (with respect to vacuum) during hydron transfer through a 2D crystal and this reduces the overall activation barrier. Because deuterons have a 60 meV lower zero point energy than protons (inset of Fig. 3B), 2D crystals provide higher electrical and mass-flow resistances for deuterons compared to protons.

The reported isotope effect allows several important observations about proton transport through 2D crystals. First, zero point oscillations in Nafion reduce the activation barrier by as much as ≈0.2 eV compared to theory values (5,8,30). We speculate that the remaining difference between experiment and theory (5,9) may be accounted for by considering other effects of the surroundings (for example, two-body processes involving a distortion of electron clouds (5) by protons at the Nafion-graphene interface). Second, the experiments confirm that chemisorption is not the limiting step in proton transfer through 2D crystals because, otherwise, the isotope effect would be sensitive to their chemical composition. Third, it is quite remarkable that zero point oscillations, a purely quantum effect, can still dominate room-T transport properties of particles 4000 times heavier than electrons.

Finally, in the described proof-of-concept experiments we used exfoliated 2D membranes because of their high crystal quality (5) but a similar separation factor α was also achieved for cm-sized graphene grown by chemical vapor deposition (21). The highly competitive α combined with the simple and robust underlying mechanism, the
straightforward setup and the realistic possibility of its industrial scale-up can make 2D crystals attractive enough to be incorporated into hydrogen-isotope separation technologies such as, for example, production of heavy water or tritium recovery. In the latter case, the found sieving mechanism implies even higher $\alpha \approx 30$ (21).

References

21. See supplementary material on Science Online.
1. Electrical conductivity measurements

Devices for the study of hydron transport using electrical measurements were fabricated by suspending mechanically exfoliated 2D crystals over apertures that were etched in 500 nm thick silicon-nitride membranes. Graphite and hBN crystals were purchased from *NGS Naturgraphit* and *HQ Graphene*, respectively. The high sensitivity of electrical measurements allowed us to use relatively small holes (2 to 10 μm in diameter), and this provided an opportunity to study not only graphene but also mono- and bi-layer hBN. This is because available hBN crystals cannot be exfoliated to monolayers with sizes similar to those achievable for graphene. Both sides of the suspended graphene and hBN membranes were coated with a thin Nafion layer, and either PdH$_x$ or PdD$_x$ electrodes (31) were mechanically attached to Nafion (see fig. S1). We refer to section Methods of ref. 5 for more details on fabrication of such hydron transport devices.

![Fig. S1. Devices for electrical measurements of hydron conductivity. (A) 2D crystal is suspended over a hole etched into a free standing silicon-nitride (SiNx) membrane. Both sides](image-url)
are coated with Nafion, and Pd electrodes are attached mechanically. (B) Optical photo of the final device.

For electrical measurements, the assembled devices were placed in a chamber with a controlled atmosphere of either 10% H\textsubscript{2} in Ar at 100% H\textsubscript{2}O relative humidity or, alternatively, 10% D\textsubscript{2} in Ar at 100% D\textsubscript{2}O humidity. The reported I-V characteristics were measured with Keithley’s SourceMeter 2636A at voltages typically varying between ±200 mV and using sweep rates <0.1 V min\textsuperscript{-1}. Importantly, the employed small biases allowed us to completely avoid bubble formation for any [h]:[d] input.

We first characterized our setup in terms of leakage currents and found parasitic parallel conductance of ~5 pS due to leakage along the silicon-nitride surface under the humid conditions. In further control experiments, we measured the conductivity of D- and H-Nafion films using devices of the same design but without 2D crystal membranes. No difference could be found between Nafion enriched with the different isotopes, and its bulk conductivity remained ~ 1 mS cm\textsuperscript{-1}, in agreement with the values reported previously for H-Nafion films prepared in the same manner (5).

2. Remnant protium content in D-Nafion

The vibrational modes of protons attached to water molecules have been extensively studied using infrared spectroscopy (28,29,32-34). In our work, we employed this technique to estimate the amount of O-H bonds remaining in the D-Nafion films after their long exposure to D\textsubscript{2}O. To this end, a Nafion solution was drop-cast onto cadmium fluoride windows to form thin films (~1 μm thick). The windows were then integrated
into an environmental chamber where the Nafion films were exposed to either 100% H\textsubscript{2} + H\textsubscript{2}O or 100% D\textsubscript{2} + D\textsubscript{2}O atmosphere. The measurements were carried out with a Bruker Vertex 80 FTIR spectrometer, and fig. S2 shows examples of the obtained spectra.

H-Nafion exhibited a strong absorbance peak at ≈3,500 cm\textsuperscript{-1} (≈0.4 eV), which corresponds to the stretching mode of the OH oscillator, ν\textsubscript{s}(O-H). For D-Nafion, the corresponding mode is shifted by ≈1,000 cm\textsuperscript{-1} to the frequency of the OD oscillator, ν\textsubscript{s}(O-D). This shift can be translated into the difference between zero point vibrational energies of the two oscillators, which yields ΔE = \( \left( \frac{1}{2} \right) hc [ν\textsubscript{s}(O-H) − ν\textsubscript{s}(O-D)] \) ≈60 meV, in agreement with literature values (see the inset of Fig. 3B of the main text). Importantly, only a very weak OH peak could be detected in D-Nafion (inset of fig. S2). By comparing its integrated intensity with the OH and OD peaks, we estimate that, after changing the atmosphere from light to heavy water, the residual atomic fraction of H in D-Nafion was less than ≈1 %.
Figure S2. Infrared spectroscopy of H- and D- Nafion. IR spectra of Nafion films exposed to light and heavy water. Inset: Magnified D-Nafion spectrum shows a small OH peak at 3,500 cm⁻¹ due to remnant protium.

It is instructive to estimate a possible effect of the remnant protium found in our D-Nafion on the measured deuteron conductivity of the membranes. Their total conductivity $\sigma_D$ is given by conductivities of the individual isotope channels, that is, $\sigma_D = 0.99\sigma_D^* + 0.01\sigma_H^*$ where the star refers to the actual rather than measured conductivities for hydron transport, and we assume the maximum amount of 1% for protium. Because deuterium concentration in H-Nafion is negligible (that is, $\sigma_H \equiv \sigma_H^*$) and the electrical measurements reported in the main text yielded $\sigma_H/\sigma_D \approx 10$, one can easily find that $\sigma_H^*/\sigma_D^* \approx 11$. Therefore, the correction due to protium contamination of D-Nafion is relatively minor and within the statistical error of our transport measurements shown in Fig. 1B of the main text.

3. Pt decorated membranes

We also studied electrical conductivity of Pt-activated graphene and monolayer hBN. To prepare the membranes, Pt nanoparticles were deposited onto them by evaporating a discontinuous layer of Pt (nominally, 2 nm). Figure S3 shows examples of I-V responses for an hBN membrane prepared in this way. As with non-decorated 2D crystals, we observed a tenfold increase in the areal conductivity $\sigma$. Similar results were also obtained for bilayer hBN and monolayer graphene (not shown here for brevity).
Fig. S3. I-V responses for Pt-decorated monolayer hBN.

Note that the measurements in fig. S3 allow us to determine room-$T$ proton conductivity for Pt-decorated monolayer hBN, which exhibits the highest $\sigma$ among all the studied 2D crystal membranes. Previously (5), the proton conductivity of this hBN membranes was found too high to be determined experimentally because H-devices with or without the membranes showed the same conductivity limited by Nafion contact regions. The deuteron transport measurements circumvent this problem. Because the conductivities of H- and D- Nafion are the same, the found deuteron conductivity for Pt-activated monolayer hBN in fig. S3 allows an estimate of its proton conductivity as $\approx 3$ S cm$^{-2}$. This is comparable with the conductivity of commercially available Nafion membranes (35).

4. Mass transport measurements

Graphene devices used in our mass spectrometry experiments are shown in fig. S4. They were also fabricated by suspending monolayers of mechanically exfoliated graphene over apertures etched into silicon-nitride membranes (fig. S4A). The apertures were 10 to
50 μm in diameter. To achieve proton/deuteron flows sufficient for mass spectrometry
detection, we catalytically activated graphene with Pt as described above, which
significantly reduced the barrier for hydron permeation (5). The Pt layer covered the
output (vacuum) side of the graphene membranes, which faced our mass spectrometer
(Inficon UL200). Their opposite (input) side was coated with a Nafion film (5% solution; 1100 EW) and, then, the assembly was annealed in a humid atmosphere at
130°C to crosslink the polymer for better hydron conductance. For further details on
microfabrication procedures, we refer to ref. 5. Note that the measurements could also
be carried out without the Nafion layer. However, its use significantly improved
reliability of our devices due to mechanical support (otherwise, atomically-thin
membranes were exposed to a differential pressure of 1 bar between the input chamber
and vacuum). As reference devices, we used the same assembly (fig. S4A) but graphene
was substituted with a carbon cloth containing Pt nanoparticles, referred to in the main
text as porous carbon (purchased from FuelCellsEtc).

The proton-deuteron electrolyte was obtained by mixing 0.15M HCl in H₂O with a D-
electrolyte in different proportions. The latter consisted of 0.15M DCl (99% D atom
purity) in D₂O (99.9% D atom purity). Isotope fractions in the resulting electrolyte were
prepared with an accuracy of ± 0.5%. A Pt wire was placed inside a chosen [h]:[d]
electrolyte, and a dc voltage applied between this electrode and the Au microelectrode
evaporated on graphene (see fig. S4B). A Keithley 2636A was used for both applying
voltage and measuring current I. The gas flow and electric current were measured
simultaneously. For HD and D₂ (masses 3 and 4, respectively), background fluctuations
in our spectrometer were small enough to allow us to resolve flows of the order of 10⁻¹⁰
bar cm$^3$ s$^{-1}$. For H$_2$ (mass 2) the accuracy was \( \sim 10^{-8} \) bar cm$^3$ s$^{-1} \) because of the background vacuum. Because of this lower resolution, in the latter case we used only 50-µm membranes to achieve higher H$_2$ flows. Figure S4C shows typical measurements for protium deuteride, and examples of similar measurements for the case of H$_2$ can be found in ref. 5.

Fig. S4. Gas flow devices and measurements. (A) Schematic of graphene membranes. For control experiments, a carbon cloth was used instead of graphene. (B) Optical image of one of our devices (view from the output side). A graphene monolayer (its position is outlined by the dashed lines) covers a circular aperture that is etched in a silicon-nitride membrane visible as a yellowish square. Graphene is electrically contacted using a gold electrode. Scale bar, 100 µm. The bottom area seen as beige is an adjacent multilayer graphene flake. (C) Typical data-acquisition run used in measurements of hydron transport. The particular example is for a flow of HD (atomic mass 3) through graphene using a \([10\% \text{ h}]:[90\% \text{ d}]\) mixture at the input. The flow was controlled by applying voltage to the gold electrode.
5. Relation between charge and mass flows

Our mass spectrometer measured the flow $F_G$ in units of bar cm$^{-3}$ s$^{-1}$, that is, $p_G V / t$ where $p_G$ is the partial pressure of a selected gas, $V$ the detector’s volume and $t$ the time. Here we use subscript $G$ to refer to different gases: H$_2$, HD and D$_2$. The number of molecules $N_G$ entering the mass spectrometer can then be calculated by using the ideal gas law $p_G V = N_G k_B T$ where $k_B$ is the Boltzmann constant and $T$ the temperature (room temperature in our case). Therefore, $F_G = N_G k_B T / t$. On the other hand, the electrical current $I_G$ associated with the flow of charged nuclei is given by $I_G = 2eN_G / t$. The factor 2 takes into account that two hydrons, each carrying the elementary charge $e$, are required to create one gas molecule detected at the output. If all hydrons are successfully transferred through the graphene membrane, the mass and charge flows are related by the simple equation

$$F_G = I_G (k_B T / 2e)$$

This equation agrees well with our experimental results if a [100% h] electrolyte was used at the input (also, see ref. 5). However, the mass-charge correspondence was found to break down in the presence of deuterium. As shown in the main text, for [100% d], the detected gas flow was an order of magnitude smaller than expected from the measured values of $I$. As mentioned in the main text, we attribute this disagreement to conversion of deuterons into deuterium atoms at the input side of graphene membranes. This process led to the formation of gas bubbles that were easily observed if large currents were applied (see figs S5A,B). Similar bubbles were previously reported for
proton transfer (5) but only if a continuous metal (Pt or Au) layer covered the output side of a graphene membrane. No bubbles were observed for a [100% h] electrolyte and using a discontinuous Pt layer in either the present work or ref. 5. We do not fully understand the origin of such a strong difference between hydrogen and deuterium but note that the observed 10 times slower permeation rate for deuterons results in them spending more time at the input side of the graphene membrane where they can be converted into gaseous D₂. At small currents, the growth of microscopic bubbles can probably be compensated by their dissolution. However, formation of large bubbles leads to mechanical detachment of the Nafion film, which - once started - is an irreversible process.

For completeness, fig. S5 shows the observed relation between charge and mass flows for intermediate concentrations of protons in the input. Here, to quantify our observations, we have introduced transfer coefficients $\gamma_G \in [0,1]$ which define the slopes of the $F$-$I$ curves found by mass spectrometry for each gas (see Fig. 2 of the main text) so that $F_G = \gamma_G I (k_B T/2e)$. By adding $F_G$ for D₂, HD and H₂ using the same input electrolyte, we can determine the total gas flow $F = \sum \gamma_G I (k_B T/2e) = \Gamma I (k_B T/2e)$ where $I$ is the total electric current and $\Gamma = \gamma_{D_2} + \gamma_{HD} + \gamma_{H_2} \in [0,1]$. If $\Gamma = 1$, all the electric current translates into mass flow. If $\Gamma < 1$, some of the hydrons reaching the graphene membrane accept electrons from it but do not pass through. Figure S4B shows $\Gamma$ found for different [h]:[d] inputs.
Fig. S5. Bubble formation and charge-to-mass transfer. (A) Schematics of the bubble formation. (B) Optical image of a device that during its final run was measured at high currents and using a [100% d] electrolyte. The top view is from the input side covered with a Nafion film. It is optically transparent and the green fringes appear due to Nafion areas of different thicknesses. (C) Transfer coefficient $\Gamma$ for different proton concentrations [h] in the input electrolyte. The red curve is a guide to the eye.

6. Reproducibility of gas flow measurements

*Figure S6* shows our measurements using (A) the same device but different [h]:[d] electrolytes and (B) the same [h]:[d] inputs but different devices. One can see that the results are highly reproducible whereas the data scatter allows one to judge systematic errors in our mass flow experiment. Importantly, the measurements were little affected by gas bubbles at the graphene-Nafion interface. This is somewhat counterintuitive because the bubble formation is a random process. To understand this apparent contradiction, one needs to appreciate that such bubbles reduce the effective area available for hydron transfer but this does not affect the relation between $F$ and $I$ which is independent of the area. Indeed, regions where Nafion detached from the graphene...
membrane became inactive reducing both the charge and mass flows proportionally to the detachment area. The rest of the 2D membrane is expected to maintain the original $F$-$I$ characteristics. However, bubbles led to a gradual degradation of our devices. The confinement of the electric current into an increasingly smaller area led to higher voltages required to maintain the same $I$. This aging effect was observed for deuteron-containing electrolytes if currents larger than $\sim 3 \, \mu A$ were used. In this regime, after a gradual increase in resistance, our devices were suddenly destroyed at a certain voltage. Neither current nor gas flow could be detected after this, and one large bubble appeared over the whole membrane as seen in fig. S5B. To avoid the bubble formation, we avoided large $I$, except for the case of [100% h] where no bubbles appeared.

Fig. S6. Reproducibility of mass spectrometry measurements. (A) Four different runs for the same device (each data-acquisition run looked similar to that shown in fig. S4C). Squares and circles represent different runs for the same [h]:[d]. (B) Two different devices (squares and circles) using same [h]:[d] inputs.
7. Hydron permeation analysis

As discussed in Supplementary Section 5, the slopes of $F-I$ characteristics can be fully described by transfer coefficients $\gamma_G$. We used the experimentally found $\gamma_G$ to determine the mole fractions of each constituent gas in the output as:

$$[G] = \frac{\gamma_G}{\gamma_{H_2} + \gamma_{HD} + \gamma_{D_2}}$$

where $G$ refers to $H_2$, HD or $D_2$. From the mole fractions, atomic fractions $[H]$ and $[D]$ in the output flow can be readily calculated. Because each $D_2$ molecule consists of two D atoms, HD of one H atom and one D atom and $H_2$ of two H atoms, the fraction of protium atoms in the output gas flow is

$$[H] = \frac{\frac{1}{2} [HD] + [H_2]}{[D_2] + [HD] + [H_2]}$$

Similarly, the deuterium fraction at the output is given by

$$[D] = \frac{\frac{1}{2} [HD] + [D_2]}{[D_2] + [HD] + [H_2]}$$

To relate the input proton $[h]$ and deuteron $[d]$ fractions to the output atomic fractions of different hydrons, we write

$$[H] = \frac{[h] P_h}{[h] P_h + [d] P_d}$$

(S1)
where \( P_h \) and \( P_d \) are the probabilities for protons and deuterons to cross the membrane, respectively. The above equations obviously satisfy the necessary condition, \([H] + [D] = 100\%\) for both input and output.

Both protons and deuterons can be expected to exhibit thermally activated (Arrhenius) permeation through graphene crystals as observed previously (5) but with different activation energies \( E_h \) and \( E_d \), respectively, so that

\[
P_{h,d} \propto \exp(-E_{h,d}/k_B T)
\]

Therefore, equation (S1) takes the form

\[
[H] = \frac{[h]}{[h] + \exp(-\Delta E/k_B T) [d]}
\]

This equation is used in the main text to analyze the measured input-output fractions. The fact that \( \Delta E \approx 60 \text{ meV} \) (refs 28,29) is smaller than even \( E_h \approx 250 \text{ meV} \) (found in ref. 5 for Pt-activated graphene) justifies the use of the Arrhenius dependence for deuterons, too.

In deriving equation (S3), we ignored for simplicity the fact that attempt rates for protons and deuterons crossing the barrier could be different. Indeed, the frequency of zero point oscillations for protons is \( \sqrt{2} \) times higher than for deuterons because the latter are twice heavier. In the simple model shown in the inset of Fig. 3B of the main text, this should translate into the same ratio between their attempt rates. If so, equation (S3) should be modified with a pre-factor \( 1/\sqrt{2} \) in front of the exponent in the denominator. However, in our analysis given in the main text, we have chosen to neglect
possible differences in attempt rates because it is known that they depend not only on zero point frequencies but often involve slower movements of neighboring atoms and, therefore, the attempt rates for hydrons are usually smaller and differ less than the simple model suggests (29). Moreover, even if we assume that the attempt rates differ by as much as $\sqrt{2}$, the consequences for our conclusions would be minor. Indeed, we found that the theory curve in Fig. 2B of the main text would then bend slightly stronger but still remain within the error bars of the experiment. The good agreement between the experiment and theory in Fig. 2B probably indicates similar attempt rates for both hydrons (that is, the difference is less than $\sqrt{2}$), in agreement with the previous studies (29).

8. Control measurements with porous carbon

Figure S7 shows that, if a porous electrode (carbon cloth) was used instead of a graphene membrane, no difference in permeation rates for protons and deuterons could be detected. Nevertheless, it is worth mentioning that in principle a finite difference in production of protium over deuterium can occur even in the case of equal permeation through a barrier film. This may be due to different gas evolution rates for different hydrons at the electrodes (36-41). It is hardly surprising that no such difference was detected in our experiments. First, the isotope effect reported for electrolysis using polymer electrolytes such as Nafion is small, exhibiting a separation factor $\alpha \approx 3$ even under optimum conditions (37). Such $\alpha$ would lead to differences in output [H] fractions within the error bars of fig. S7B. Second, electrolysis is sensitive to applied voltages and
current densities and requires fine tuning and cleaning of electrodes in order to achieve the above modest separation factor (36-41). In our experiments, no special preparation of electrodes was necessary, and currents and voltages could be significantly different for different devices and experimental runs. This comparison with the existing hydron separation method also emphasizes the fact that, in addition to the large separation factor of ≈10, graphene membranes provide a very robust isotope effect.

![Graph showing gas flow with a reference electrode (porous carbon). (A) Gas fractions for different [h]:[d] inputs. (B) Atomic output versus input calculated using the data in (A). The blue line shows the behavior expected for the case of no selectivity: [H] ≈ [h].](image)

**9. Isotope separation factor**

The efficiency of isotope separation techniques is characterized by a separation factor (20)

\[
\alpha = \frac{[H]/[D]}{[h]/[d]}
\]
which is the ratio of relative concentrations of protons and deuterons at the input and output sides of a separation device. If the concentration of one of the isotopes is low, it is straightforward to show that equation (S3) leads to

\[ \alpha = \exp(\Delta E / k_B T) \]  

(S4).

Using the isotopic shift energy \( \Delta E \approx 60 \text{ meV} \) for the hydron-oxygen bond, equation (S4) yields \( \alpha \approx 10 \) at room \( T \). Note that exactly the same exponent defines the ratio of hydron conductivities, \( \sigma_H / \sigma_D \), in charge transport measurements as follows from equation (S2). The experimentally found value, \( \sigma_H / \sigma_D = 10 \pm 0.8 \) (Fig. 1B of the main text) agrees well with the above value of \( \Delta E \).

10. Potential applications

Hydrogen isotopes are important for various analytical and tracing technologies, and heavy water is used in large quantities at nuclear fission plants. Accordingly, there have been a large number of methods developed for separation of hydrogen isotopes (12,19,20,26,27,40-42). These methods include liquid H2O distillation (\( \alpha \approx 1.05 \)), electrolysis (\( \alpha \approx 2 \) to 10), ammonia-hydrogen exchange (\( \alpha \approx 3 \) to 6), liquid H2 distillation (\( \alpha \approx 1.5 \)), water-hydrogen exchange (\( \alpha \approx 2.8 \) to 6), aminomethane hydrogen exchange (\( \alpha \approx 3.5 \) to 7), water hydrogen sulphide exchange (\( \alpha \approx 1.8 \) to 3) and multi-photon laser separation (\( \alpha >20,000 \)). All these methods, except for the multi-photon laser separation that is deemed impracticable (19), are or were used in industrial-scale heavy water production. Our report shows that graphene and hBN membranes offer a highly competitive separation factor, \( \alpha \approx 10 \). This comes on top of the fundamentally
simple and robust sieving mechanism, potentially straightforward setups and only water at the input without the use of chemical compounds (19). Similar considerations apply for separation of tritium and its removal from heavy water (19,20). Using the proton-triton energy shift $\Delta E \approx 88$ meV (ref. 43), equation (S4) yields $\alpha \approx 30$ and $\approx 3$ for protium-tritium and deuterium-tritium separation, respectively.

As for applications, mechanical exfoliation of 2D membranes is obviously a non-scalable technology. We used it only to prove the concept, explore the hydron permeation mechanism and avoid crystal defects and pinholes (5,9). Nonetheless, we also repeated some of the separation experiments using 50 µm membranes made from graphene grown by chemical vapor deposition (CVD) (44,45) and achieved the same $\alpha \approx 10$. Furthermore, we made square-cm membranes of Pt-activated CVD graphene placed on Nafion films and used them in our mass spectroscopy setup (Fig. 2B of the main text). Again, we found practically the same separation factor. This observation may seem surprising because, unlike exfoliated crystals, CVD graphene contains many defects. However, atomic-scale defects are not expected to result in any reduction of the separation efficiency that is determined only by $\Delta E$ rather than the overall barrier height. In addition, a certain but relatively small amount of macroscopic cracks and pinholes is present in CVD graphene (9). These areas provide no selectivity (similar to the case of porous carbon in fig. S7) but their contribution is minor (proportional to the damaged area) because the hydron flow occurs mostly through the electrically contacted areas.

Because of the increasing availability of CVD-grown graphene, there is a realistic prospect of scaling up the described devices from micron and cm sizes to those required for mass separation of hydrogen isotopes. Indeed, it is now possible to grow meter-large
graphene sheets and transfer them onto a supporting film (45), which again can be Nafion. Manufacturing of CVD graphene in square km quantities no longer sounds futuristic because much larger production volumes have been considered for touchscreen devices based on graphene (45). Also, note that, according to the Fenske equation, the large $\alpha$ implies only several stages of enrichment for cascade plants to obtain 99% pure heavy water and strongly tritiated one.

Furthermore, it is instructive to estimate possible energy costs associated with the described isotope separation method. For Pt-activated graphene, its proton conductivity $\sigma$ is $\approx 100$ mS/cm$^2$. Using low voltages $V \approx 0.1$ V to avoid bubble formation at the Nafion-graphene interface, we can easily achieve proton currents $I = \sigma V \approx 100$ A per m$^2$. This translates into the $\text{H}_2$ production rate $R = I/2N_Ae \approx 2$ moles per hour per square meter (where $N_A$ is the Avogadro number) and yields the energy costs $IV/R = 2N_AeV \approx 5$ Wh per mole or $\approx 0.3$ kWh per kg of feed water. This compares favorably with higher energy costs in the existing enrichment processes (19). In principle, much higher throughputs (100 times) can be achieved using Pt-activated hBN with $\sigma \approx 1$ mS/cm$^2$ but its CVD growth in industrial quantities has not been demonstrated yet.

Supplementary references

32. Okumura, M., Yeh, L. I., Myers, J. D. & Lee, Y. T. Infrared spectra of the solvated hydronium ion: Vibrational predissociation spectroscopy of mass-selected $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_n\cdot(\text{H}_2)n$. *J. Phys. Chem.* 94, 3416–3427 (1990).
8 Concluding Remarks

Membranes are physical barriers between two interfaces that allow for selective transport of species between them. From living cells to desalination technologies, membranes are classified according to the size and selectivity of their pores. In that sense, we have demonstrated that monolayers of graphene and hBN push this definition to the limit: they are subatomically selective membranes. These crystals reject all atoms but allow protons through; allow electrons to tunnel, but selectively sieve particles differing by only one neutron. This is a completely new phenomenon. No other group of materials exhibits selectivity with subatomic resolution. In this context, one cannot help speculating on whether one day crystals will be tailored to display selectivity to a particular atom or group of particles. Is there a limit to what can be separated using a membrane?

But back to the present, there is probably much to be learned from these crystals. For example, can we use them to enhance the performance of photoelectrolysis cells? Much effort has been dedicated to the development of technologies that can harness the energy from the Sun. One of them is splitting water using solar energy to obtain hydrogen and oxygen. This process is especially attractive as a way of storing energy. Indeed, that’s the challenge of most renewable energy technologies; storing the excess energy produced in times of plenty to release it continuously into the energy grid.
Another interesting line of research is to exploit the proton and electron conducting properties of these crystals to create new energy harvesting devices. A natural first step is to incorporate these crystals into the existing fuel cell technologies. But the completely new properties of these crystals may one day lead to the development of new energy harvesting technologies. New materials tend to be the starting point of new technological developments.

But perhaps, for now, some of the most exciting properties of these crystals will be found when studying their behavior as barriers between two interfaces. Thinking about it, many interesting phenomena take place between interfaces. Cells use proton gradients through membranes to harness the energy from sunlight or glucose; electrons tunnel across thin barriers separating two conducting materials; batteries work because ions in electrolytes can interact with metal surfaces; friction is established due to long range interactions between two surfaces; the list is endless. And now, 2D crystals allow us to separate interfaces by barriers just one atom thick with relative ease. The study of these crystals properties is a new research field and it has just begun. What we’ll find, only time will tell.
9 References


References


