

New avenues for the large-scale harvesting of blue energy

Alessandro Siria¹, Marie-Laure Bocquet² and Lydéric Bocquet¹

Abstract | Salinity gradients have been identified as promising clean, renewable and non-intermittent sources of energy — so-called blue energy. However, the low efficiency of current harvesting technologies is a major limitation for large-scale viability and is mostly due to the low performances of the membrane processes currently in use. Advances in materials fabrication with dedicated chemical properties can resolve this bottleneck and lead to a new class of membranes for blue-energy conversion. In this Perspective, we briefly present current technologies for the conversion of blue energy, describe their performances and note their limitations. We then discuss new avenues for the development of a new class of membranes, combining considerations in nanoscale fluid dynamics and surface chemistry. Finally, we discuss how new functionalities originating from the exotic behaviour of fluids in the nanoscale regime can further boost energy conversion, making osmotic energy a tangible, clean alternative.

Access to sustainable, abundant and inexpensive sources of energy is one of the key challenges faced by our modern society. Since the beginning of the industrial revolution, fossil fuels (in the form of coal, oil or gas) have been our primary source of energy¹. However, the high environmental impact of burning fossil fuels has led to widespread eco-friendly sentiments in the past decade². Several sources of clean energy (associated with low post-production carbon emissions) have been identified, including solar, wind and water power^{1–4}; however, to date, none of these power sources can replace fossil fuels, mainly because of the limited efficiency of generating and storing electrical power, their moderate availability, their intermittency and the prohibitive cost associated with energy conversion.

The salinity difference between sea water and river water has recently been identified as an additional source of clean energy, known as blue or osmotic energy. The cost of a large-scale facility is less prohibitive than that of solar or wind farms¹, and the facility can be installed ideally wherever a river streams into the sea. Based on the entropy change associated with saltwater mixing, it is estimated that 0.8 kWh m^{-3} (equivalent

to 3 kJ per litre of water) can be produced at the sea–river interface⁵. Although this energy density is typically 4–5 orders of magnitude lower than that available by burning fossil fuels, the abundance of fresh and salty water makes this energy source very appealing. For example, the transfer of non-salty water from the Amazon River alone into the Atlantic sea translates to a power of $\sim 1 \text{ TW}$; this is equivalent to 1,000 nuclear reactors and is constantly wasted. Most of this blue energy cannot be easily recovered, but estimates suggest that more than 1 TW can be harvested worldwide, corresponding to an available energy of $\sim 8,500 \text{ TWh}$ (REF. 4). To better appreciate the potential of osmotic power, this value is twice as large as the total hydroelectric energy consumption in 2016, and 10 and 25 times larger than the total wind and solar energy consumption, respectively⁶.

Wastewater and brines, such as those extracted from oil drilling or generated by desalination plants, can be seen as additional energy reservoirs^{6,7}. Therefore, harnessing osmotic energy from such sources may also benefit the challenging disposal of complex industrial wastewaters, such as those from the oil and gas industries^{8–10}.

Currently, several approaches have been proposed to harvest energy from a salinity gradient, most of which are based on separation processes that make use of membranes^{11–14}. The two main methodologies currently used to extract and convert osmotic energy are pressure retarded osmosis (PRO) and reverse electrodialysis (RED). Both approaches involve the use of partially permeable membranes with sub-nanoscale pores to separate two reservoirs filled with fresh and salty water (FIG. 1). In PRO (FIG. 1a), water moves through a semipermeable membrane, driven by the large osmotic pressure due to the salinity difference between the two sides of the membrane. At the sea–river interface, the osmotic pressure drop can be as large as 30 bars and is even larger in the presence of brines or wastewaters. Water flows from the low-salinity reservoir to the high-salinity reservoir, and this flux is then used to move a turbine connected with the latter reservoir, thereby generating electrical power. PRO has been tested for large-scale energy production by a pilot plant developed by Statkraft in Norway and by the Mega-ton Water System project in Japan. The Norwegian plant generates an average of less than 1 W m^{-2} of the separating membrane, which is substantially lower than the target power density of 5 W m^{-2} needed to make PRO economically profitable^{15–17}, and Statkraft has recently suspended the project. In RED, ions are driven across a stack of alternating cation-selective and anion-selective membranes under a salt concentration gradient (FIG. 1b). The salinity gradient thus allows the separation of anion and cation fluxes across the membranes, generating a net electric transport that can be collected using suitable electrodes. One of the main advantages of the RED approach is that the charge separation driven by osmotic pressure is directly converted into electrical energy. Recent advances have enabled power outputs in the range of several watts per square metre⁴. In model configurations using silica nanochannels, this power can even reach larger values of $\sim 8 \text{ W m}^{-2}$ (REF. 18). The company REDStack in the Netherlands is currently exploring this approach on a large scale, with a prototype plant built over the

dam in Afsluitdijk. A conversion efficiency in the range of several watts per square metre of membrane has been achieved, which is close to the commercial goal. These results show that the RED approach has large-scale viability. It also encourages current researchers to find more efficient ways to harvest and store osmotic energy, for example, by using new and promising capacitive electrodes¹⁹.

The major hindrance of state-of-the-art approaches for osmotic energy conversion is their poor energy efficiency²⁰, which is still too low to provide a widely viable source of energy⁴. However, there is no fundamental reason for such low efficiency. The inherent limitations of PRO and RED stem from the osmotic transport processes occurring within the membranes. Accordingly, understanding and harnessing fluid and ionic transport in the nanoscale regime is of key importance for the optimization of the membrane processes and for overall technological advancement of this area.

Several studies have demonstrated that the combination of a new class of materials for membranes with tailored surface chemistry may boost the conversion efficiency by several orders of magnitude^{21–23}; this potentially provides an additional approach to making osmotic energy viable for large-scale applications. Blue energy is still an emerging and mostly unexplored topic at the interface between membrane science, materials chemistry and nanoscale fluid dynamics. Fundamental exploration is required to understand, optimize and scale up this energy-conversion process.

In this Perspective, we discuss the physical and chemical phenomena involved in the conversion of the osmotic power, as well as several possible approaches to further improve blue-energy harvesting.

Harvesting osmotic power

Current approaches for harvesting osmotic power rely on the separation of molecular species — ions from water in PRO and cations from anions in RED — which can be considered the main cause of the low energetic efficiency. Molecular separation involves membranes with sub-nanometre porosity, which strongly limits energy conversion. For example, in the case of PRO, the driving force is the large osmotic pressure difference, $\Delta\pi$, between sea water and fresh water ($\Delta\pi \approx 30$ bars, equivalent to a 300 m high dam), but the water flow (Q) is highly impeded by the sub-nanometre pores of the semipermeable membrane. The harvested power, which is the product of the osmotic pressure and the water flow ($P = \Delta\pi \times Q$), is accordingly very small. Similar arguments apply to RED. Improving the conversion efficiency of these approaches seems like squaring a circle. Most of the efforts so far have been devoted to optimizing the engineering of PRO and RED plants, but surprisingly little has been done over the past few decades to optimize nanoscale phenomena occurring at the membrane.

Several recent experiments have shown that molecular separation is not a prerequisite for osmotic flow^{21–23} and that phenomena occurring within the membrane in the nanoscale regime should be considered in order to circumvent many of the limitations of PRO and RED. One of these phenomena is the so-called diffusio-osmotic transport, which was introduced in the pioneering works of Derjaguin in the 1940s but was largely overlooked until recently^{24–28}. Diffusio-osmosis is a surface mechanism driven by an osmotic pressure gradient occurring within the first few nanometres from the surface of the membrane pores (FIG. 2a). It does not require the use of semipermeable channels to develop osmotic flow because it results from specific interactions between the solute (in this case, a salt) and the surface. The concentration gradient along the surface gives rise to an (ionic) electric current, known as the diffusio-osmotic current, as the ions move under the interfacial osmotic pressure gradient. Diffusio-osmosis is therefore an intermediate process between PRO and RED, and as this process occurs at the surface, increasing the surface area of the nanoporous membranes is an advantage in this case.

Diffusio-osmosis transport originates from the electrostatic interaction of the ions with the surface of the nanopores within the nanometric Debye layer (λ_D) close to the surface²⁶. The salt concentration gradient in the bulk induces an interfacial osmotic pressure gradient within the Debye layer. This generates a water flux that exhibits a plug-like profile. The velocity of the diffusio-osmotic flow (V_{DO}) results from the balance between the water viscous stress and the osmotic pressure gradient and can be estimated as follows:

$$V_{DO} \approx \frac{k_B T}{8\pi l_B \eta} \frac{\Delta \log C}{L} \quad (1)$$

where $\Delta \log C$ is the difference in the logarithm of the salt concentration (C) between the reservoirs, L is the pore length, η is the water viscosity and $l_B = 0.7$ nm is the Bjerrum length. If the surface of the nanopore exhibits a net surface charge (Σ), the excess ion flux is carried by this flow, thus generating an osmotic electrical current (I_{osm}):

$$I_{osm} \approx N \times 2\pi R \Sigma V_{DO} \quad (2)$$

for a membrane with N pores of radius R and length L . This simple estimate is in qualitative agreement with a more accurate formulation involving the detailed description of ionic transport within the electric double layer. It should be noted that I_{osm} scales linearly with respect to Σ only in the case of highly charged surfaces. In the limit of low surface charge, a considerably smaller diffusio-osmotic current is expected, which scales with respect to Σ as $I_{osm} \approx \Sigma^3$ (see the Supplementary information within REF. 21).

The membrane therefore acts as an ionic current generator (FIG. 2a), and the generated electric power is collected by connecting electrodes in the reservoir to an external load resistance. Using the equivalent electric circuit, the maximum extractable power is found to scale as follows^{21,22}:

$$P_{MAX} = \frac{R_M I_{osm}^2}{4} \quad (3)$$

where R_M is the ionic internal resistance of the membrane.

This mechanism has been studied in membranes made of boron nitride (BN) nanotubes²⁹ (FIG. 2b) and has been shown to provide particularly efficient osmotic power conversion²¹. In this case, nanotubes with a radius in the range of tens of nanometres showed an osmotic energy conversion

Glossary

Bjerrum length

The distance at which the magnitude of the electrostatic interaction between two charged particles is comparable to their thermal energy.

Plug-like profile

The velocity profile of a fluid flowing in a pipe under interfacially driven flows (for example, electro-osmosis or diffusio-osmosis). A plug flow is characterized by a constant flux velocity across any cross section of the pipe perpendicular to the direction of the flow, except within the first few nanometres from the surface.

Shockley diode

A semiconductor device based on several layers of p-doped and n-doped regions. In the original realization, the diode is a p–n diode.

Zeta potential

The electric potential at the interfacial double layer, usually defined at the location of the slipping plane (typically within a molecular distance from the bare surface). The zeta potential is measured by electro-osmotic or streaming current measurements.

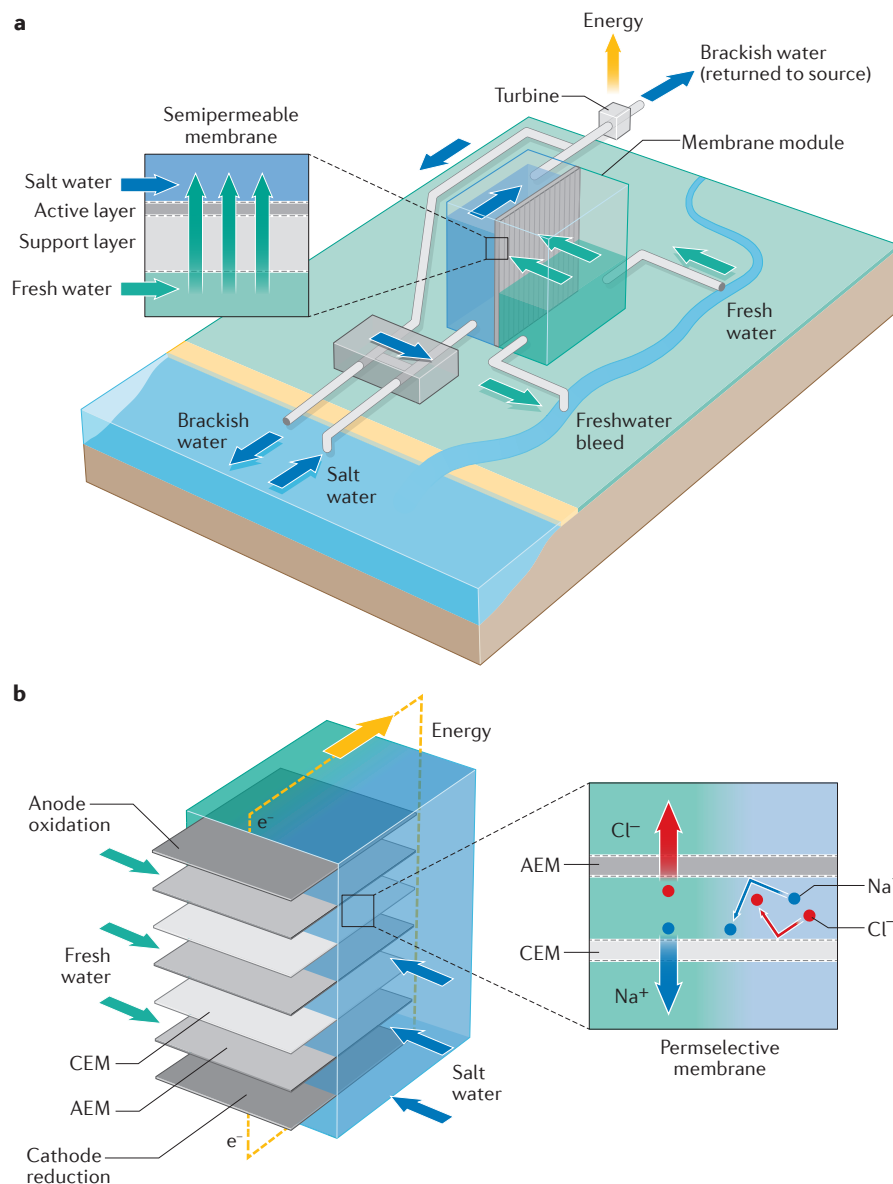


Figure 1 | Osmotic energy conversion power plant. a | Schematic of a pressure retarded osmosis (PRO) power plant. Here, salty and fresh water are separated by a semipermeable membrane (inset). The difference in salinity generates a large osmotic pressure that pushes the fresh water (low salinity) through the membrane into the salty water reservoir. This osmotic-generated flux moves a turbine connected with the salty water reservoir, which generates electricity. **b** | The schematic of the reverse electrodialysis (RED) power plant is similar to that of the PRO plant, but the processes at the membranes are different. In this case, a stack of ion-selective membranes separates the salty and fresh water, and the salinity gradient drives the ions across the membranes. The anion and cation fluxes are therefore separated, generating a net electric transport that can be collected using suitable electrodes. AEM, anion-exchange membrane; CEM, cation-exchange membrane. Adapted with permission from REF. 4, Macmillan Publishers Limited.

density of several kilowatts per square metre. This result is three orders of magnitude larger than the energy conversion density typically obtained with PRO or RED processes. Furthermore, a recent study showed that the use of atomically thin MoS_2 membranes with nanopores in the range of a few nanometres in diameter can lead to an outstanding power density of 10^6 W m^{-2}

(REF. 22). A power density in the range of 700 W m^{-2} has also been reported for the case of atomically thin membranes based on hexagonal BN (h-BN) and graphene with larger pores in the range of a few tens of nanometres in diameter²³. These promising results demonstrate that the successful and efficient generation of osmotic power is indeed possible.

Membranes for blue-energy conversion

The remarkable conversion efficiencies observed in the case of nanoporous BN or MoS_2 membranes can be explained by analysing the diffusio-osmotic phenomenon in detail^{21,22}. First, diffusio-osmosis does not require any molecular separation to generate electric current; therefore, in both cases, nanopores do not need to be selective for water (as in PRO) or any specific ion (as in RED). Another favourable parameter is the small length of the nanochannels. The power is expected to scale inversely with the membrane thickness L ; therefore, the molecular thickness of the nanoporous BN or MoS_2 membranes (FIG. 2c) further increases the power density.

The main cause of the large generated currents, however, is the large surface charge exhibited by the BN and MoS_2 nanopores. Depending on the pH, in both cases, a surface charge up to $\sim 1 \text{ C m}^{-2}$ has been measured, which is two orders of magnitude larger than that of other conventional materials, such as silica, which has a surface charge in the range of tens of millicoulombs per square metre (REF. 26).

Based on the discussion above, thin membranes with nanoscale pores and materials with high surface charge (which generate diffusio-osmotic ionic currents) should be considered in order to boost the osmotic power and provide increased energy-conversion efficiencies. Last but not least, the large-scale production of membranes amenable to large-scale energy production should remain of central concern.

Screening 2D membranes. In the context of osmotic energy conversion, recently developed nanomaterials are an obvious choice. The molecular thickness of 2D materials such as graphene, h-BN or dichalcogenide sheets can strongly increase the ion-concentration gradient (FIG. 2), as demonstrated by the large power densities achieved by using these materials^{22,23}. Furthermore, these materials can now be fabricated at large scales, and nanopores can be generated by ion beams^{30–32}. From a fundamental point of view, several aspects need to be understood and addressed, such as the effects of the entrance of ionic and water flows into the nanopores and the electric charging of the nanopores in molecularly thin materials²³.

Graphene oxide (GO) is another interesting material for the production of membranes for osmotic power conversion³³. GO membranes are made of stacked layers of graphene flakes with a ‘millefeuille’

geometry, similar to that reported in REF. 34 (FIG. 2d). This material combines some of the properties of graphene, resulting from the molecular interspacing induced by staking of the different layers, with the possibility of facile, large-scale production.

The promise of carbon nanomaterials.

Carbon materials are outliers in the field of nanofluidics and are worth specific discussion in the context of blue energy. Several exotic phenomena in terms of fluid transport within carbon materials have been reported in the literature^{26,35}. From a materials perspective, carbon exhibits a large number of allotropic forms and a wide range of physical and chemical properties. Fluid transport across carbon structures has been investigated recently, particularly when confined in carbon nanotubes (CNTs) and between graphene sheets^{23,35}. Notably, water transport through CNTs has been observed to be strongly enhanced — by up to four orders of magnitude in the smallest nanotubes — than that predicted by classical hydrodynamics²⁶. Theoretical studies to understand the origins of enhanced flow in nanotubes found an ultra-low wall–fluid friction coefficient at the water–nanotube interface, which is much smaller than that at any other interface^{26,35}.

The enhanced water flow across CNTs — first observed in macroscopic membranes with a very large number of tubes³⁵ and also in individual nanotubes³⁶ — has triggered considerable interest in carbon materials for nanofluidic applications. Applications towards osmotic energy conversion have been less explored, although such distinctive properties have great potential. It was recently shown that low surface friction may considerably enhance the osmotic flow and thus the generated electric power³⁷. The combination of the large water permeability of the nanotubes with a relatively high molecular selectivity would boost the energy-conversion efficiency, which is particularly appealing in the context of PRO but would also be advantageous in water-desalination processes. Furthermore, tuning the chemical properties of the water–solid interface will also have an important role for the development of a new class of efficient membranes.

The large-scale production of CNT membranes has long been one of the main hindrances to their use in large-scale applications. However, the development of 2D graphene materials and their stacked forms, such as GO, holds great promise, because these materials retain many key advantages

of carbon materials with a less prohibitive technical cost in terms of fabrication.

Nanofluidic experiments and *ab initio* modelling for materials screening.

Maximizing the osmotic power requires that the nanoporous material under consideration exhibits a high surface charge. Thus, predicting whether a material supports a large surface charge when it is in contact with a solution is an important step for the design of new membranes. BN nanotubes were

found to exhibit a surface charge of 1 C m^{-2} , corresponding to 1–5 electrons per square nanometre, which is crucial for efficient osmotic power generation. This value is considerably higher than that measured for other materials generally used in micro- and nanofluidics, such as SiO_2 , with typical surface charges in the range of a few tens of millicoulombs per square metre, which is insufficient for osmotic power applications. The origin of the considerable reactivity of BN, and therefore the high surface charge,

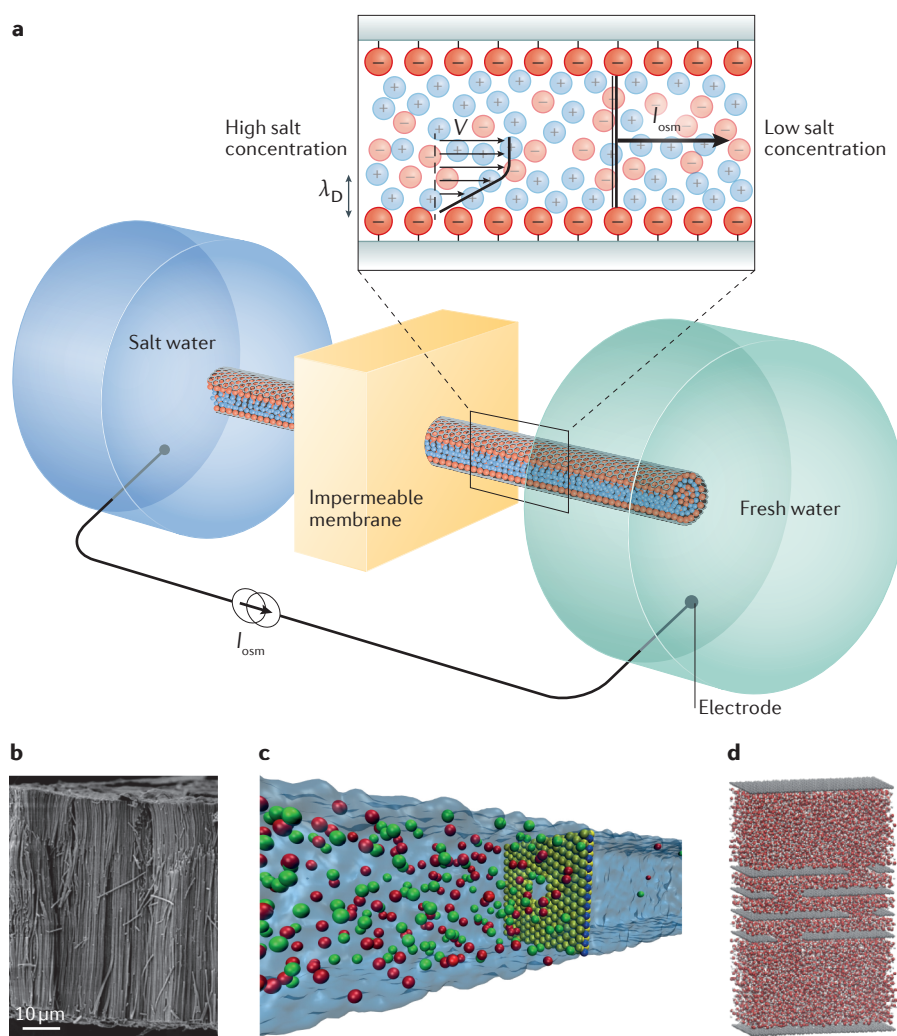


Figure 2 | Diffusio-osmotic process for osmotic energy conversion. Diffusio-osmotic transport was demonstrated in charged nanochannels used as nanofluidic membranes for salinity-gradient energy conversion (part a). Diffusio-osmosis is a surface-driven mechanism that originates from an osmotic pressure gradient occurring within the first few nanometres from the surface (inset). This generates a plug-like water flow profile (arrows), which carries the excess surface charge²². Examples of the membranes include nanotube-based membranes²⁹ (part b); drilled 2D materials, for example, MoS_2 , as described in REF. 22 (part c); and multilayer carbon structures akin to graphene oxide membranes³⁴ (part d). λ_D , nanometric Debye layer; I_{osc} , osmotic electrical current; V , voltage. Part a (top) is adapted with permission from REF. 21, Macmillan Publishers Limited. Part a (bottom) is adapted from REF. 61, courtesy of Bruno Bourgeois, b2infographie, France. Part b is reproduced with permission from REF. 29, American Chemical Society. Part c is reproduced with permission from REF. 22, Macmillan Publishers Limited. Part d is reproduced with permission from REF. 34, American Institute of Physics.

has remained elusive for some time, but recent *ab initio* calculations have highlighted the considerable — and quite unexpected — chemisorption of anionic hydroxide on the BN surface³⁸.

Overall, the most-active materials are typically those featuring more ionic bonds (such as BN, MoS₂ or TiO₂), whereas less-active materials have more covalent bonds (for example, SiO₂, graphene or Si₃N₄) (FIG. 3); however, further insight into the mechanisms of surface charging on these layered materials is needed. For example, it is important to elucidate the detailed charging mechanism of the materials at the interface with water, the role of its ionicity and the effect of the surface structure of the material (for example, honeycomb-like patterns or amorphous materials of the same chemical nature) on the arrangement of solvated ions. Also, the role of hydrophilicity versus hydrophobicity and its consequence on interfacial transport need to be explored³⁹. For example, the hydrophobic material AgI has shown an important and counter-intuitive charging capacity at its surface, despite having a relatively low zeta potential³⁹. An efficient strategy to answer these questions and identify eligible materials with high surface reactivity requires combined inputs from controlled nanofluidic experiments and *ab initio* modelling.

Experimental measurements of the ionic conductance of nanopores (drilled across a material under investigation) provide insight into the surface chemical reactivity of the material. The ionic conductance reflects the number of mobile charge carriers, so that a measured excess of the conductance, as compared to its bulk value, can be interpreted in terms of the contribution from the surface^{21,22,26,36}. Therefore, measuring the surface conductivity represents an efficient way to estimate the surface charge and chemical reactivity. In addition, the possibility of measuring the conductance even for single pores in nanoporous materials under various physico-chemical conditions (for example, through changing pH or the nature of the ions) makes this approach amenable for quantitative analyses, in contrast with surface zeta potential measurements, which remain difficult to interpret quantitatively. A broad variety of materials can be studied with this approach. For example, single nanopore conductance measurements can be performed to probe surface coatings obtained from the atomic layer deposition of BN or TiO₂, both in their crystalline and amorphous phases. Functionalized surfaces with dedicated chemical coatings can also

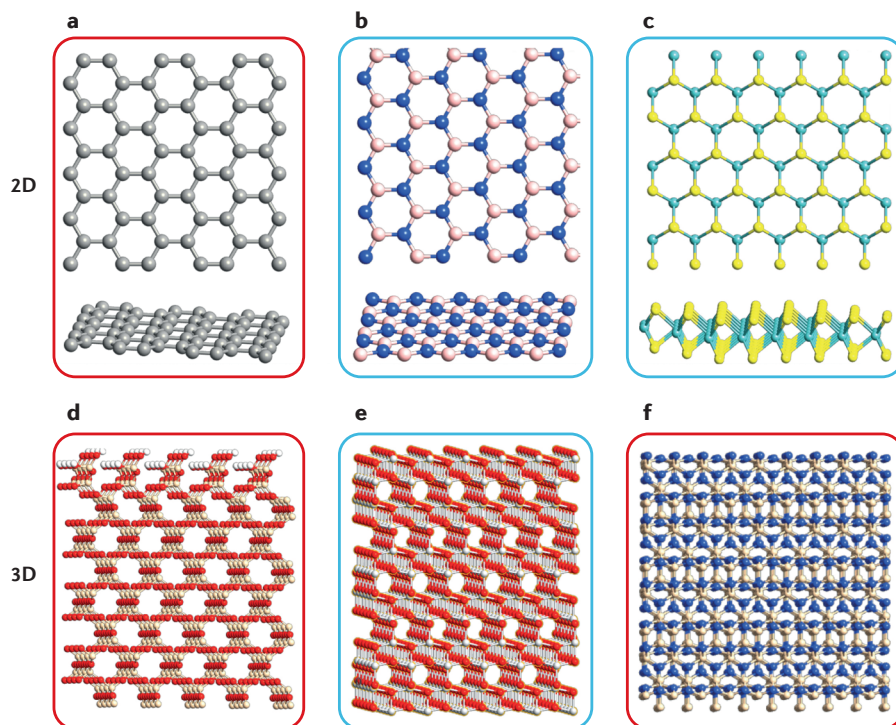


Figure 3 | Material structures for new membranes. In the top row, the top and perspective views of prototypical 2D materials are shown: graphene (part **a**), hexagonal BN (part **b**) and trilayer MoS₂ (part **c**). C, B, N, Mo and S atoms are represented in grey, pink, blue, green and yellow, respectively. The bottom row shows the side view of eligible 3D crystalline materials: the cristobalite phase of SiO₂(001) (part **d**), the anatase phase of TiO₂(001) (part **e**) and silicon nitride, Si₃N₄(001) (part **f**). Si, O, Ti and N atoms are represented in beige, red, light grey and blue, respectively. Materials highlighted in blue are characterized by ionic bonds and exhibit higher surface charges than the materials featuring covalent bonds, highlighted in red. The structures were designed with Virtual NanoLab atomistic software version 2016.1.

be studied^{40–41}. It was recently demonstrated that surfaces coated with polydopamine exhibit high surface charges⁴². Similar studies have identified track-etched polyimide⁴³ and polyelectrolyte multilayers⁴⁴ as promising materials for efficient membranes. Although these routes to chemically modify nanoporous surfaces can be advantageously used in the context of osmotic power, their full potential in this respect remains to be explored.

Atomistic simulations on model systems enable the rationalization and further screening of the surface properties of various materials. The chemical reactivity between water and substrates remains challenging to predict. Semi-empirical approximations, such as those used in classical molecular dynamics, are not sufficient to accurately predict the chemical reactivity of a material, and more computationally expensive *ab initio* approaches are needed. Periodic density functional theory (DFT) has become the standard method widely used in the community of *in silico* surface scientists to model surface processes and surface

properties⁴⁵. The inclusion of water as a solvent in the vicinity of a surface, however, remains one of the biggest challenges in atomistic simulations. It is possible to explicitly take into account water molecules and their dynamics in an all-atom quantum simulation by using specific functionalities implemented in one of the most commonly used DFT codes, CP2K⁴⁶. This approach, however, is extremely costly in terms of computational time. A less costly alternative would make use of an implicit solvation model in which water is effectively taken into account in terms of a space-dependent dielectric permeability⁴⁷, as is now implemented in VASP^{48–51}, another popular DFT code. The implicit solvent scheme represents the first approach to capture the solvent effect at interfaces. This approach has been successfully applied to explore the chemical reactivity of a h-BN layer³⁸. A key finding is the highly favourable adsorption of OH[−] ions on a BN layer with *sp*³ re-hybridization of the B anchoring site, which results in a negative charging of the single-layer material. The covalent bond

between OH^- and B has been found to be stable in an implicit water model, and a $\text{p}K_{\text{a}}$ of 6 was computed after the inclusion of DFT-based thermodynamic corrections, in excellent agreement with the value extracted from the analysis of nanofluidic measurements²¹.

The computational method can be easily extended to enable a thorough screening of various materials. Important questions need to be answered; for example, how do the performances of crystalline and amorphous isomers compare, what is the effect of the molecular confinement and what is the reactivity of the edge states of nanopores in 2D materials? Although computational studies require massive supercomputers, the computational resources and theoretical approximations currently available make an exhaustive computational screening of these systems valuable and feasible.

Scaling-up requirements. Although the results obtained from BN and MoS_2 highlight the unforeseen and considerable potential of these materials in the context of osmotic energy, it remains to be demonstrated how such results can be scaled up to large membranes. This is a crucial condition for the large-scale viability of blue-energy conversion.

Once good materials are identified, a number of supplementary tests are needed to assess the reliability of the processes under real-life conditions, such as in the presence of salts and at the relevant pH. In this context, it is of great importance to test the fouling resistance of these new materials and membranes. Fouling is already known to be a major limiting factor for the efficiency of membranes in aqueous environments. Membranes with pore sizes in the nanometre and sub-nanometre range, as in the case of PRO and RED applications, greatly suffer from clogging owing to the presence of biological pollutants, heavy metals and/or large organochlorides and organosulfates under real-life conditions. Therefore, costly and energy-consuming water pretreatment and membrane regeneration

processes are unavoidable. Furthermore, the efficiency of membranes with ion-selective nanopores is affected by charge polarization, which influences ion transport and eventually the energy-conversion efficiency. In contrast to simple osmotic transport, diffusio-osmotic transport is expected to be free of these effects. Diffusio-osmotic transport does not require membrane semipermeability or full ionic selectivity and allows the use of much larger pores — as demonstrated by the high conversion measured for BN nanotubes with diameters in the range of tens of nanometres²² — reducing the extent of membrane fouling. In addition, materials suitable for diffusio-osmotic transport present very large surface charges, which have biocidal properties, making these materials useful for the removal of biological pollutants from solutions. The use of large pores also limits the effect of charge polarization and ion selectivity.

Altogether, diffusio-osmosis seems to overcome several limitations affecting standard osmotic transport, resulting in a higher energy-conversion efficiency, and has the potential to be successfully applied to large-scale applications (TABLE 1).

Membranes for nonlinear nanofluidics

Up to now, we have focused our discussion on material aspects that can increase osmotic power. Indeed, existing design principles for membranes used in this process are usually quite simple, as they are mostly related to nanopores traversing a thin membrane layer. Additional geometric and chemical characteristics of the membrane are then adapted depending on the process considered: PRO, RED or diffusio-osmotic currents. However, there are some interesting leads to explore using more advanced membrane designs, such as asymmetric membranes made of two different structures and materials (FIG. 4a). For example, Zhang and co-workers produced a two-layer membrane by assembling a block copolymer with a porous polyethylene terephthalate membrane exhibiting conical pores⁵². They measured an output power of up to

0.35 W m^{-2} ; this is promising considering that this value corresponds to a pore density of 10^7 cm^{-2} , which is much lower than the typical values of 10^9 – 10^{10} cm^{-2} (for example, those obtained for ion-track-etched pores). They attribute this good performance to the suppression of the polarization phenomenon existing in traditional RED due to ionic diode effects occurring in the asymmetric bipolar membranes.

The interesting results obtained by Zhang and co-workers, however, deserve further exploration. We argue that this result connects the generation of osmotic power to advanced transport phenomena that occur in fluid transport at the nanoscale^{26,53–58}. In particular, these phenomena involve the possibility to depart from the classical linear response regime, in which fluxes (for example, electric current) linearly depend on the thermodynamic forces — in this case, the chemical potential gradient. These exotic properties can be exploited to further boost the osmotic energy conversion. Below, we highlight the potential of dedicated membrane designs involving composite structures.

Ionic diodes. One of the most remarkable effects recently observed in nanofluidic experiments is the formation of ionic diodes^{26,53–58}. An asymmetric nanochannel with asymmetric surface charge density can be considered as the fluidic analogue of the more common p–n junction⁵⁹. Interestingly, the surface charge on the nanopore acts as a doping agent, delivering additional charge carriers, with negative charge corresponding to donors (n-doped) and positive charge to acceptors (p-doped). In nanofluidics, the presence of an electric charge on the pore surface leads to an uneven distribution of ions with opposite charge, which gives rise to an electric potential. This is known as the Donnan potential and is equivalent to a shift in the Fermi level energy at a p–n junction. This situation typically occurs when Debye layers close to the opposite surfaces of the pore overlap^{26,60}. The condition for the emergence of a Donnan

Table 1 | Comparison of current approaches to blue-energy harvesting

	Pressure retarded osmosis (PRO)	Reverse electrodialysis (RED)	Nanotube diffusio-osmosis	2D nanopore diffusio-osmosis
Membrane pore size (nm)	<1 (REF. 4)	~1 (REF. 4)	5–100 (REF. 21)	~1 (REF. 22)
Laboratory-generated power density (W m^{-2})	7–8 (REF. 11)	~8 (REF. 18)	10^3 – 10^4 (REF. 21)	~ 10^6 (REF. 22)
Large-scale generated power density (W m^{-2})	1–2.7 (REF. 4)	1.2–2.2 (REF. 4)	None	None

potential, however, is less restrictive, as it mainly requires that the surface charge exceeds the number of bulk charge carriers in the nanopore. Experimentally, an ionic diode can be realized either in the presence of a disymmetric surface charge⁵⁵ or a disymmetric channel size^{52,56,57}.

Similar to semiconducting systems, an ionic diode is characterized by a strongly nonlinear electric response; the dependence of the ionic current on the voltage drop is asymmetric, showing high conductance for a positive voltage drop and low conductance for a negative voltage drop. The ionic transport is accordingly rectified, and ions move preferentially through the device in one direction. Ion transport in nanoscale channels obeys the same equations as electrons and holes in semiconducting materials^{26,59}, and similar to the case of a Shockley diode⁵⁴, the resulting ionic current (I) can be expressed as

$$I = I_s \left(\frac{eV}{\exp(k_B T)} - 1 \right) \quad (4)$$

where I_s is the so-called saturation current and is a function of the donor and acceptor density, eV is the voltage, k_B is the Boltzmann constant and T is the temperature⁵². Such a nonlinear response extends to other transport phenomena, as shown recently⁵⁸: asymmetric nanopores also lead to a rectification of the water flux under salinity gradients, resulting in an asymmetric effective osmotic pressure and, consequently, an osmotic diode. Altogether, the water flux also exhibits a rectified response in terms of salinity contrast, coupled to a strong nonlinear dependence on the imposed voltage⁵⁸.

Nonlinear ionic transport is fundamentally appealing as it can be of considerable practical value for blue-energy applications. We next highlight how this type of transport can be used to strongly improve the osmotic energy conversion.

Asymmetric membranes to boost energy conversion. To understand how nonlinear transport affects energy conversion, it is worth recalling how the maximum extractable power, P_{MAX} , originates. P_{MAX} depends on the intrinsic characteristics of the membrane, such as the membrane resistance (R_M) and the electric current (I_{osm}) that is generated by the membrane under a salinity gradient, as reported in equation 3.

When the membrane is in contact with a load resistance (R_L) associated with the device used to extract the generated power (FIG. 4b), two regimes can be obtained for the

equivalent electrical circuit. For low R_L , the generated osmotic current I_{osm} mainly flows and dissipates through the load resistance, and the power that can be extracted scales as $P_{osm} \approx R_L I_{osm}^2$. For high R_L , the generated current mainly circulates in a loop within the membrane, and the extractable power reduces to $P_{osm} \approx R_M^2 I_{osm}^2 / R_L$. Altogether the extractable power versus R_L exhibits a maximum for $R_L = R_M$, leading to the maximum osmotic power, P_{MAX} . This suggests that for high R_L , most of the osmotic power is lost within the membrane itself, dissipating the osmotic energy as Joule heating in the nanopores.

For a membrane exhibiting an ionic diode behaviour, its resistance acts as a Shockley diode⁵⁸. Under reverse bias, the diode blocks the back current, avoiding power dissipation in the nanochannel, and the membrane behaves as an ideal current generator. Accordingly, for an ideal diode membrane with an equivalent infinite resistance in the reverse-bias configuration, the osmotic power is expected to scale linearly with the load resistance, $P_{osm} \approx R_L I_{osm}^2$. Of course, some limitations are expected because this ideal case can occur only if the diode stays in its 'blocking' regime, that is, with no electrical current flowing through the membrane. For a large membrane voltage and consequently large loading resistance, the diode will switch back to exhibiting a linear behaviour, thus limiting the achievable extractable power. The above argument clearly shows that nonlinear and exotic behaviours resulting from complex nanofluidic devices can be harnessed to circumvent the limitations of osmotic power.

The elements discussed so far direct towards the design of asymmetric membrane systems, which can generate diode-like, strongly rectified, fluid transport, corresponding with what was reported in REF. 52. In that specific case, the asymmetric membrane was obtained by assembling two materials, one of which exhibited conical pores, and was expected to yield a diode-like response. Alternatively, composite membranes with asymmetric materials will lead to surface charge gradients along the nanopores, thus creating the required condition for asymmetric doping and diode fluidic response. Two-dimensional heterostructures, such as h-BN on graphene or an equivalent material (FIG. 4c), are good candidates and are expected to respond according to the ionic diode behaviour. Alternatively, membranes with asymmetric chemical coatings can also be considered to obtain differential charge on the surface of nanopores within the membrane.

Considering the vast range of materials suitable for osmotic energy conversion, the number of possible combinations and configurations is not far from being limitless.

Conclusions

In this Perspective, we have discussed technologies for the conversion of the energy originating from the mixing of solutions with different salinities. Although the potential of this new source of clean and renewable energy is huge, its large-scale exploitation is still prohibited because of the low efficiency of current conversion schemes. Commercial viability is expected to be achieved for an extracted power of approximately 5 W m^{-2} of membrane used, but the actual value obtained with standard approaches (PRO and RED) is lower than a few watts per square metre.

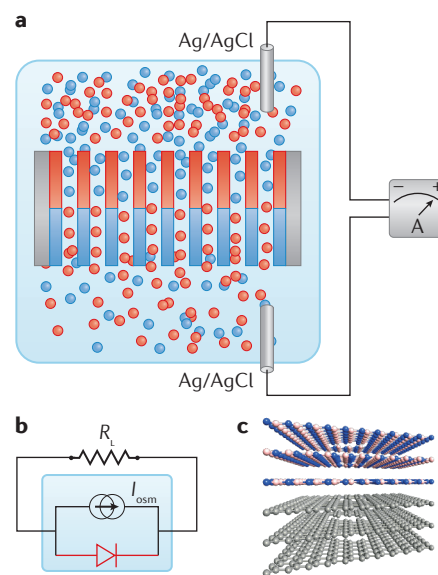


Figure 4 | Asymmetric membranes. Asymmetric membranes can be designed to boost energy conversion through the ionic diode effect. **a** | Sketch of charge asymmetry in a nanoporous membrane, leading to an ionic diode response under a salinity gradient⁵⁸. The blue and red colours indicate positive and negative charge states, respectively, for the ions and membrane coating. The membrane pore size is not fully selective for ions and allows the transport of both charges. The asymmetry in the charge coating of the membrane affects ion transport, creating an asymmetric ionic diode. **b** | Equivalent electrical circuit for the asymmetric membrane. The membrane generates a current I_{osm} in parallel with a diode (in red). The membrane is connected to a load resistance R_L to extract the generated power. **c** | Illustration of an asymmetric membrane. Charge asymmetry can be achieved by using multiple layers of nanoporous 2D materials, composed of weakly charged carbon layers on top of highly charged h-BN layers.

Recent findings of extremely high osmotic power densities using new materials as membrane supports have revived the field. These results indicate new avenues for the development of dedicated membranes based on highly reactive materials. It is now necessary to further explore the class of materials that matches the conditions for a scalable osmotic power production. We also noted the high potential of nonlinear transport to further boost energy conversion, suggesting the design of asymmetric membranes. The roadmap towards this objective is quite clear.

Blue-energy conversion is an emerging field at the interface between chemistry, materials science and nanofluidic transport. It is a rich playground in which fundamental science can be directly applied to boost the blue-energy harvesting performance. There is hope that this renewable, clean and democratic source of energy can reach a level where it becomes viable at a large-scale. This is definitely an exciting time.

A. Siria and L. Bocquet are at the Laboratoire de Physique Statistique–Paris Sciences et Lettres (PSL) Research University, École Normale Supérieure, Unités Mixtes de Recherche (UMR) Centre National de la Recherche Scientifique (CNRS) 8550, 24 rue Lhomond, 75005 Paris, France.
alessandro.siria@lps.ens.fr
lyderic.bocquet@lps.ens.fr

M.-L. Bocquet is at the École Normale Supérieure–Paris Sciences et Lettres (PSL) Research University, Département de Chimie, Sorbonne Universités–University Pierre et Marie CURIE (UPMC), Paris 06, Centre National de la Recherche Scientifique (CNRS) Unités Mixtes de Recherche (UMR) 8640 PASTEUR, 24 rue Lhomond, 75005 Paris, France.
marie-laure.bocquet@ens.fr

doi:10.1038/s41570-017-0091

Published online 8 Nov 2017

- Chu, S. & Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* **488**, 294–303 (2012).
- Daw, R., Finkelstein, J. & Helmer, M. Chemistry and energy. *Nature* **488**, 293 (2012).
- Graetzel, M., Janssen, R. A., Mitzi, D. B. & Sargent, E. H. Materials interface engineering for solution-processed photovoltaics. *Nature* **488**, 304–312 (2012).
- Logan, B. E. & Elimelech, M. Membrane-based processes for sustainable power generation using water. *Nature* **488**, 313–319 (2012).
- Yip, N. Y. & Elimelech, M. Thermodynamic and energy efficiency analysis of power generation from natural salinity gradients by pressure retarded osmosis. *Environ. Sci. Technol.* **46**, 5230–5239 (2012).
- British Petroleum. Statistical review of world energy. *British Petroleum* https://www.bp.com/content/dam/bp-country/de_de/PDFs/brochures/statistical_review_of_world_energy_full_report_2011.pdf (2011).
- Wang, X. *et al.* Probabilistic evaluation of integrating resource recovery into wastewater treatment to improve environmental sustainability. *Proc. Natl Acad. Sci. USA* **112**, 1630–1635 (2015).
- Vidic, R. D., Brantley, S. L., Vandenbossche, J. M., Yoxheimer, D. & Abad, J. D. Impact of shale gas development on regional water quality. *Science* **340**, 1235009 (2013).
- Shaffer, D. L. *et al.* Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions. *Environ. Sci. Technol.* **47**, 9569–9583 (2013).
- Gregory, K. B., Vidic, R. D. & Dzombak, D. A. Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements* **7**, 181–186 (2011).
- Chou, S. *et al.* Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density. *J. Membr. Sci.* **389**, 25–33 (2012).
- Lee, K. P., Arnot, T. C. & Mattia, D. A review of reverse osmosis membrane materials for desalination — development to date and future potential. *J. Membr. Sci.* **370**, 1–22 (2011).
- Post, J. W., Hamelers, H. V. & Buisman, C. J. Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system. *Environ. Sci. Technol.* **42**, 5785–5790 (2008).
- Veerman, J., Saakes, M., Metz, S. J. & Harmsen, G. J. Electrical power from sea and river water by reverse electrodialysis: a first step from the laboratory to a real power plant. *Environ. Sci. Technol.* **44**, 9207–9212 (2010).
- Nijmeijer, K. & Metz, S. in *Sustainability Science and Engineering* Vol. 2 Ch. 5 (eds Escobar, I. C. & Schafer, A. I.) (Elsevier, 2010).
- Gerstandt, K., Peinemann, K. V., Skilhagen, S. E., Thorsen, T. & Holt, T. Membrane processes in energy supply for an osmotic power plant. *Desalination* **224**, 64–70 (2008).
- Skilhagen, S. E. Osmotic power — a new, renewable energy source. *Desalin. Water Treat.* **15**, 271–278 (2010).
- Kim, D., Duan, C., Chen, Y. & Majumdar, A. Power generation from concentration gradient by reverse electrodialysis in ion-selective nanochannels. *Microfluid. Nanofluid.* **9**, 1215–1224 (2010).
- Porada, S. *et al.* Carbon flow electrodes for continuous operation of capacitive deionization and capacitive mixing energy generation. *J. Mater. Chem. A* **24**, 9313–9321 (2014).
- Straub, A. P., Deshmukh, A. & Elimelech, M. Pressure-retarded osmosis for power generation from salinity gradients: is it viable? *Energy Environ. Sci.* **9**, 31–48 (2016).
- Siria, A. *et al.* Giant osmotic energy conversion measure in individual transmembrane boron nitride nanotubes. *Nature* **494**, 455–458 (2013).
- Feng, J. *et al.* Single-layer MoS₂ nanopores as nanopower generators. *Nature* **536**, 197–200 (2016).
- Walker, M. I. Extrinsic cation selectivity of 2D membranes. *ACS Nano* **11**, 1340–1346 (2017).
- Fair, J. C. & Osterle, J. F. Reverse electrodialysis in charged capillary membranes. *J. Chem. Phys.* **54**, 3307–3316 (1971).
- Anderson, J. L. Colloid transport by interfacial forces. *Annu. Rev. Fluid Mech.* **21**, 61–99 (1989).
- Bocquet, L. & Charlaix, E. Nanofluidics, from bulk to interfaces. *Chem. Soc. Rev.* **39**, 1073–1095 (2010).
- Ajdari, A. & Bocquet, L. Giant amplification of interfacially driven transport by hydrodynamic slip: diffusio-osmosis and beyond. *Phys. Rev. Lett.* **96**, 186102 (2006).
- Lee, C. *et al.* Osmotic flow through fully permeable nanochannels. *Phys. Rev. Lett.* **112**, 244501 (2014).
- Bechelany, M. *et al.* Synthesis of boron nitride nanotubes by a template-assisted polymer thermolysis process. *J. Phys. Chem. C* **111**, 13378–13384 (2007).
- Celebi, K. *et al.* Ultimate permeation across atomically thin porous graphene. *Science* **344**, 289–292 (2014).
- O'Hern, S. C. *et al.* Selective ionic transport through tunable subnanometer pores in single-layer graphene membranes. *Nano Lett.* **14**, 1234–1241 (2014).
- Surwade, S. P. *et al.* Water desalination using nanoporous single-layer graphene. *Nat. Nanotechnol.* **10**, 459–464 (2015).
- Joshi, R. K. *et al.* Precise and ultrafast molecular sieving through graphene oxide membranes. *Science* **343**, 752–754 (2014).
- Yoshida, H. & Bocquet, L. Labyrinthine water flow across multilayer graphene-based membranes: molecular dynamics versus continuum predictions. *J. Chem. Phys.* **144**, 234701 (2016).
- Majumdar, M., Siria, A. & Bocquet, L. Flows in one-dimensional and two-dimensional carbon nanochannels: fast and curious. *MRS Bull.* **42**, 278–282 (2017).
- Secchi, E. *et al.* Massive radius-dependent flow slippage in single carbon nanotubes. *Nature* **537**, 210–213 (2016).
- Rankin, D. J. & Huang, D. M. The effect of hydrodynamic slip on membrane-based salinity-gradient-driven energy harvesting. *Langmuir* **32**, 3420–3432 (2016).
- Grosjean, B. *et al.* Chemisorption of hydroxide on 2D materials from DFT calculations: graphene versus hexagonal boron nitride. *J. Phys. Chem. Lett.* **7**, 4695–4700 (2016).
- Bonthuis, D. & Netz, R. R. Unraveling the combined effects of dielectric and viscosity profiles on surface capacitance, electro-osmotic mobility, and electric surface conductivity. *Langmuir* **28**, 16049–16059 (2012).
- Prakash, S. & Karacor, M. B. & Banerjee, S. Surface modification in microsystems and nanosystems. *Surf. Sci. Rep.* **64**, 233–254 (2009).
- Fuest, M., Rangharajan, K. K., Boone, C., Conlisk, A. T. & Prakash, S. Cation dependent surface charge regulation in gated nanofluidic devices. *Anal. Chem.* **89**, 1593–1601 (2017).
- Lee, H., Dellatore, S. M., Miller, W. M. & Messersmith, P. B. Mussel-inspired surface chemistry for multifunctional coatings. *Science* **318**, 426–430 (2007).
- Guo, W. *et al.* Energy harvesting with single-ion-selective nanopores: a concentration-gradient-driven nanofluidic power source. *Adv. Funct. Mater.* **20**, 1339–1344 (2010).
- Costa, R. R. & Mano, J. F. Polyelectrolyte multilayered assemblies in biomedical technologies. *Chem. Soc. Rev.* **43**, 3453–3479 (2014).
- Tocci, G., Joly, L. & Michaelides, A. Friction of water on graphene and hexagonal boron nitride from *ab initio* methods: very different slippage despite very similar interface structures. *Nano Lett.* **14**, 6872–6877 (2014).
- Sulpizi, M. & Sprik, M. Acidity constants from vertical energy gaps: density functional theory based molecular dynamics implementation. *Phys. Chem. Chem. Phys.* **10**, 5238–5249 (2008).
- Mathew, K., Sundararaman, R., Letchworth-Weaver, K., Arias, T. A. & Hennig, R. G. Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. *J. Chem. Phys.* **140**, 084106 (2014).
- Kresse, G. & Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B* **47**, 558–561 (1993).
- Kresse, G. & Hafner, J. *Ab initio* molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium. *Phys. Rev. B* **49**, 14251–14269 (1994).
- Kresse, G. & Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
- Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
- Zhang, Z. *et al.* Engineered asymmetric heterogeneous membrane: a concentration-gradient-driven energy harvesting device. *J. Am. Chem. Soc.* **137**, 14765–14772 (2015).
- Schasfoort, R. B., Schlautmann, S., Hendrikse, J. & van den Berg, A. Field-effect flow control for microfabricated fluidic networks. *Science* **286**, 942–945 (1999).
- Karnik, R. *et al.* Electrostatic control of ions and molecules in nanofluidic transistors. *Nano Lett.* **5**, 943–948 (2005).
- Karnik, R. *et al.* Rectification of ionic current in a nanofluidic diode. *Nano Lett.* **7**, 547–551 (2007).
- Siwy, Z. & Fulinski, A. Fabrication of a synthetic nanopore ion pump. *Phys. Rev. Lett.* **89**, 198103 (2002).
- Siwy, Z., Kosinski, I. D., Fulinski, A. & Martin, C. R. Asymmetric diffusion through synthetic nanopores. *Phys. Rev. Lett.* **94**, 048102 (2005).
- Piccolo, C. B., Gravelle, S., Joly, L., Charlaix, E. & Bocquet, L. Nanofluidic osmotic diodes: theory and molecular dynamics simulations. *Phys. Rev. Lett.* **111**, 244501 (2013).
- Kittel, C. *Introduction to Solid State Physics* 5th edn (Wiley, 1976).
- Andelman, D. in *Handbook of Biological Physics* Vol. 1 Ch. 12 (eds Lipowsky, R. & Sackmann, E.) (Elsevier, 1995).
- Biance, A.-L. & Bocquet, L. Une Energie en osmose avec l'avenir. *La Recherche Magazine* (Dec 2013).

Acknowledgements

A.S. acknowledges funding from the European Union's Horizon 2020 Framework Programme/European Research Council (ERC) Starting Grant agreement number 637748 — NanoSOFT. L.B. acknowledges support from the European Union's FP7 Framework Programme/ERC Advanced Grant Micromegas and funding from a Paris Sciences et Lettres (PSL) chair of excellence. All authors acknowledge funding from the Agence Nationale de la Recherche (ANR) project BlueEnergy.

Author contributions

All authors contributed equally to the preparation of this manuscript.

Competing interests statement

The authors declare no competing interests.

Publisher's note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

How to cite this article

Siria, A., Bocquet, M.-L. & Bocquet, L., New avenues for the large-scale harvesting of blue energy. *Nat. Rev. Chem.* **1**, 0091 (2017).

FURTHER INFORMATION

CP2K: <https://www.cp2k.org/about>

VASP: <https://cms.mpi.univie.ac.at/vasp/vasp/vasp.html>

Subject categories

Physical sciences / Chemistry / Energy

[URI /639/638/675]

Physical sciences / Materials science / Materials for energy and catalysis

[URI /639/301/299]

ToC blurb**000 New avenues for the large-scale harvesting of blue energy.***Allesandro Siria, Marie-Laure Bocquet and
Lydéric Bocquet*

Blue energy can be cleanly and renewably harvested from a salinity gradient. The large-scale viability of this non-intermittent source is restricted by certain challenges, including the inefficiency of present harvesting technologies. This Perspective describes how nanofluidics can afford membranes better able to convert chemical potentials to electrical potentials.

Figure permissions:

Figure 1: Adapted **with permission from** REF. 4, Macmillan Publishers Limited.

Figure 2: Part **a (top)** is adapted **with permission from** REF. 21, Macmillan Publishers Limited. Part **a (bottom)** is adapted from REF. 61, courtesy of Bruno Bourgeois, b2infographie, France. Part **b** is reproduced with permission from REF. 29, American Chemical Society. Part **c** is reproduced with permission from REF. 22, Macmillan Publishers Limited. Part **d** is reproduced with permission from REF. 34, American Institute of Physics.

