Angewandte Highlights

Energy Harvesting

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Nanofluidics for Giant Power Harvesting**

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When a reservoir of fresh water is in contact with a reservoir of sea water through a membrane, so-called osmotic power can be generated from the resulting salinity gradient. In theory, there is a global potential of about 2 terawatts that can be generated where the rivers flow into the sea—this is equivalent to the world's electricity consumption in 2008. This renewable energy based on the natural phenomenon of osmosis is a source of sustainable power, and its production does not release carbon dioxide or other pollutants.

Currently, there are two membrane-based approaches to extract such energy, namely pressure-retarded osmosis and reverse electrodialysis.[1] Pressure-retarded osmosis uses a special kind of semipermeable membrane through which only fresh water can pass. The resulting osmotic pressure difference between fresh water and sea water can drive a mechanical turbine to generate electricity. Alternatively, reverse electrodialysis uses a semipermeable membrane that only allows the transport of ions while electricity is generated directly from the flow of ions due to the salinity gradient. Unfortunately, however, the power obtained from these technologies extracting osmotic energy is relatively low, with only 1–3 watts generated per square meter of membrane.[1] In addition, the potential of their widespread adoption is limited by process efficiency, cost, and fouling and lifetime of the membranes. Because of these limitations, the sustainable benefits of this form of energy remain a largely untapped resource.

The recent development in nanofluidics—the study and application of the phenomena involving the confinement of fluid motion at the nanoscale in which one or more dimensions are less than 100 nm[2,3]—may provide a solution for harvesting such salinity-gradient energy. In this case, the nanochannels have characteristic dimensions comparable to the Debye length (λ_D), the length scale over which charge carriers screen out electric fields. The Debye length is inversely proportional to the square root of the ionic concentration. Hence, for a solution of a monovalent electrolyte in the 0.1 M to 1 mM concentration range, λ_D varies from 1 to 10 nm. As a result, electrolytes confined in such nanochannels show emergent transport models (e.g. electroosmotic flow) deviating from that of their bulk counterparts, where the energy conversion efficiency is expected to be higher.[4,5] Although the theoretical possibility of generating electrical energy based on the phenomena that a streaming current and a streaming potential are created by solvent flow through a nanochannel was explored in the 1960s,[6,7] it has been attracting increasing attention recently in line with advances in nanotechnology. The development of synthesis techniques in inorganic one-dimensional nanomaterials makes it possible to control pore sizes on the nanometer scale, making it possible to synthesize various types of nanopores and nanochannels.[8] For example, power generation in individual nanofluidic devices by the pressure-driven transport of ions has been demonstrated in silica nanotubes and nanochannels,[4,9] whose geometries remain well-defined right down to the region where the Debye length is on the order of the height of a nanofluidic channel (rectangular cross-section). Under such conditions, a pressure-gradient-driven flow can be used to generate electric power because of streaming currents, but the energy conversion efficiency is still quite low at about 3%. Thus, a key challenge of building distinctive and well-controlled nanochannels (e.g. surface chemistry) for nanofluidic devices still exists, although a number of theoretical analyses, such as Poisson–Boltzmann theory for the ion double layers and Navier–Stokes equations for fluid flow,[10] have been applied to estimate the mass and ion dynamics within the nanochannels.

Recently, the team lead by L. Bocquet developed an elegant and efficient nanofluidic device, whose unique design features and choice of materials endow it with the distinct ability to harvest energy from the salinity gradient.[11] They fabricated a new class of hierarchical nanofluidic devices consisting of a single boron nitride nanotube (BNNT) connecting two reservoirs across an impermeable and electrically insulating silicon nitride (SiN) membrane (Figure 1 a). The rationale behind choosing BN as a confining material is that the crystallographic structure of BNNTs is similar to that of carbon nanotubes, and the transport of water in such carbon-based nanochannels has been demonstrated to be nearly frictionless.[12] In addition, the electronic properties of BNNTs are radically different from those of carbon materials; the chemical reactivity of the BNNT surfaces is a function of pH because of the chemical equilibrium in Equation (1),

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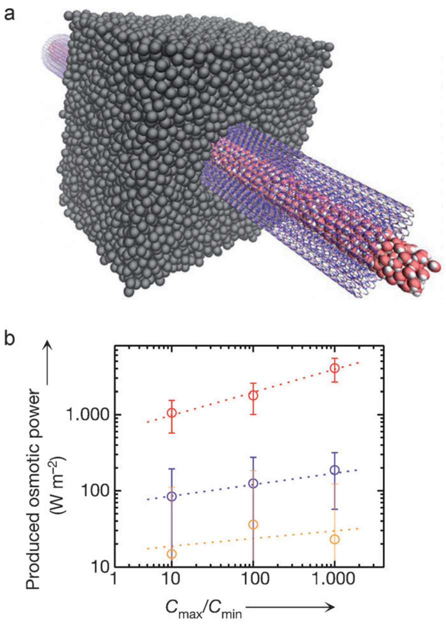

Figure 1. a) Sketch of the transmembrane BNNT for nanofluidic measurements. b) Plot of osmotic power generation (per unit surface of the BNNT) versus the concentration difference under salinity gradients for the BNNT with an inner radius of 40 nm and a length of 1250 nm for the three pH values (yellow: 5.5; purple: 9.5; and red: 11). The dotted lines serve as a guide for the eye. In this graph, the minimum concentration is fixed at $C_{min} = 10^{-3}$ м. Reprinted from Ref. [11] with permission.

where the ideal stoichiometry formula, BN_3, is used to represent the materials of boron nitride.

$$\text{“}BN_3\text{”} + H_2O \rightleftharpoons BN_3{-}OH^- + H^+ \tag{1}$$

In order to fabricate the device, Bocquet et al. first drilled a nanopore with a diameter of 100 to 200 nm in a SiN membrane using a focused ion beam and subsequently used a nanomanipulator located in a scanning electron microscope to insert a nanotube with an inner radius of 15–40 nm into it. Once the tube was in place, the hole was sealed with naphthalene using local electron-beam-induced deposition. Finally, the membrane traversed by the BNNT was connected to two macroscopic fluid reservoirs containing potassium chloride (KCl) solutions; two Ag/AgCl electrodes were immersed in the fluids on either side of the nanotube to measure the electric current passing through the BNNT. This device configuration allowed the researchers to characterize the fluid transport in a single nanochannel under electric, chemical, and pressure forcings, and combinations thereof.

With this highly novel experimental device, they were able to study the electrical transport induced by the salinity gradient in individual BNNTs, known as diffusio-osmosis, for the first time. Diffusio-osmosis occurs due to the attraction of potassium chloride to the wall of the nanotube, which causes a locally high potassium chloride concentration, which in turn generates an osmotic pressure gradient at the channel wall in the same direction as the salinity gradient.[2] The Bocquet group first demonstrated the presence of a very large, pH-sensitive surface charge carried by the inner walls of BNNTs due to the water dissociation at the BNNT surface (as described in the chemical equation above). The giant surface charge density (as high as 1 C m^{-2}) played a key impact on the osmotic transport through the nanotube, whereby an electric current is generated by a difference in salt concentration. When they used different KCl concentrations (in the range of 10^{-3} м to 1 м) in the two reservoirs, they found that a very large, osmotically driven current was achieved in the nanoampere range, whereas the pressure-driven streaming current was in the picoampere range. They excluded the possibility of the current being produced by reverse electrodialysis, which is based on an ion-selective mechanism to convert the salinity gradient into electric energy, because the Debye layer did not overlap in their nanotube configuration. Rather, they suggested that this osmotic current was a result of the diffusio-osmotic flux induced by the difference in salt concentration at the inner interface of the BNNT. This in turn arises from the strong negative surface charge characteristic of BNNTs, which attracts the potassium cations contained in the salt water. Based on their measurement and calculation, a single BNNT can reach a maximum power density of 4 kW m^{-2} (Figure 1 b). Extrapolating this result to a 1 m^2 BNNT membrane indicates that it would have a power density of about 4 kW, which is three orders of magnitude higher than the performance of the current prototype osmotic power plants.

In summary, Bocquet et al. have fabricated a hierarchical nanofluidic device to harness osmotic energy with 1000 times the efficiency of current prototype systems, and it may represent a new avenue in the exploration of novel sources of renewable energy. This extremely efficient and giant power generation from the salinity gradient is possible because of the unique quality of BN as the confining material: its tremendous surface charge generates much larger osmotic current than alternative materials do. In addition, the mechanism behind this device may have potential impact in ultrafiltration, desalination, and even bio-analysis.

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[1] B. E. Logan, M. Elimelech, *Nature* **2012**, *488*, 313.
[2] W. Sparreboom, A. van den Berg, J. C. T. Eijkel, *Nat. Nanotechnol.* **2009**, *4*, 713.
[3] H. Daiguji, *Chem. Soc. Rev.* **2010**, *39*, 901.
[4] H. Daiguji, P. Yang, A. Majumdar, *Nano Lett.* **2004**, *4*, 134.
[5] F. H. J. van der Heyden, D. J. Bonthuis, D. Stein, C. Meyer, C. Dekker, *Nano Lett.* **2006**, *6*, 2232.
[6] J. F. Osterle, *Appl. Sci. Res. Sect. A* **1964**, *12*, 425.
[7] D. Burgreen, F. R. Nakache, *J. Appl. Mech.* **1965**, *32*, 675.
[8] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353.
[9] F. H. J. van der Heyden, D. J. Bonthuis, D. Stein, C. Meyer, C. Dekker, *Nano Lett.* **2007**, *7*, 1022.
[10] D. Gillespie, *Nano Lett.* **2012**, *12*, 1410.
[11] A. Siria, P. Poncharal, A.-L. Biance, R. Fulcrand, X. Blase, S. T. Purcell, L. Bocquet, *Nature* **2013**, *494*, 455.
[12] K. Falk, F. Sedlmeier, L. Joly, R. R. Netz, L. Bocquet, *Nano Lett.* **2010**, *10*, 4067.