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1 Introduction

The energy of saline gradients resulting from the mixing of solutions with different concentrations such as seawater and freshwater, also called blue energy, is a renewable, non-intermittent, non-carbonated energy source, whose potential is recognized as considerable,^{1,2} but remains essentially not exploited. Similarly, energy storage in the form of salt gradients is not considered, although it offers an energy density ten times higher than hydraulic gravity storage and a much smaller ecological footprint than battery technologies.

The harvesting of saline gradient energy using membranes with ionic selectivity was investigated as early as in the 70s.^{3,4}

The two main technologies are the pressure retarded osmosis (PRO), whereby semi-permeable membranes produce mechanical energy, and reverse electro-dialysis (RED), in which ion-selective membranes produce electrical current.

A nanofluidic exchanger for harvesting saline gradient energy[†]

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The energy of saline gradients is a very promising source of non-intermittent renewable energy, the exploitation of which is hampered by the lack of viable technology. The most investigated harvesting methods rely on selective transport of ions or water molecules through semi-permeable or ion-selective membranes, which demonstrate limited power densities of the order of a few W m^{-2} . While in the last decade, single nanofluidic objects such as nanopores of nanotubes have opened up very promising prospects with power density capabilities in the order of kW or even MW m⁻², scale-up efforts face serious issues, as concentration polarization phenomena result in a massive loss of performance. We propose here a concept of a nanofluidic exchanger for power generation from saline gradients, focused on designing a nanoscale flow able to harvest the power at the output of the nanopores. We study analytically and numerically a simple exchanger made of a selective nanoslit fed by a nanofluidic assembly. One specific feature of such an exchanger relies on the non-linear ion fluxes through the nanoslit analytically expressed from the integration of the Poisson-Nernst-Planck equations. Such an elemental brick could be massively parallelized in stackable electricity-generating layers using standard technologies of the semi-conductor industry. We demonstrate here a scheme for rationalizing the choice of the exchanger parameters, taking into account the transport properties at all scales. The full numerical resolution of the three-dimensional device shows that net power densities of 300 W m⁻² and more can be achieved.

> But the low power density of membrane-based processes, still today of the order of a few Watts per square meter, is considered as a major obstacle for their economic viability.⁵⁻⁷ In the last ten years, investigations at the scale of single nanopores have raised new perspectives, demonstrating the possible harvesting of saline gradient energy with power density as high as kW m⁻² and even MW m⁻².⁸⁻¹¹ This was obtained with materials developing large surface charges of the order of C m⁻² in solution, in particular in basic environments, such as for instance boron nitride nanotubes (BNNTs),8 molybdenum disulfide,9 and titanium oxide twodimensional materials.¹¹ These findings triggered renewed interest for the harvesting of saline gradient energy based on exploiting the properties of nanopores, the so-called nanopore-based power generation from saline gradients (NPG).^{12,13}

> However besides the scale-up difficulties, an intrinsic limitation is the interaction between nanopores, whereby nanopores assembled in a 2D membrane tend to lose their power density capabilities with respect to their nominal performances as single objects.¹⁴⁻¹⁶ This effect is due to the phenomenon of concentration polarization (CP) which refers to the adverse concentration gradient built in reservoirs under the high ionic throughput of the membrane or

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nanopores.¹⁷⁻¹⁹ CP depends strongly on the topological dimensions of the ion source/well and of the reservoir. CP is negligible for a single nanopore, (a 0D source feeding a 3D volume), as the so-called "tip effect" produces diffusive flux of very high intensity in the vicinity of the pore inlet/outlet.²⁰ In contrast, a 2D source feeding a 3D volume produces a diffusion layer of the size of the macroscopic system, or of the hydrodynamic boundary layer in the presence of a transverse flow. CP is so serious that it was argued that the best nanopores available today, assembled in a 2D membrane and operated with a typical boundary layer of 25 um, would suffer from a colossal loss in power generation as high as 10⁵ with respect to the individual nanopore capabilities.¹⁹ As a result, CP limits the power density of the best possible nanopore-based membranes to 10 W m⁻², raising a major issue on the viability of NPG.¹⁹

Clearly, the viability of harvesting energy from saline gradients is not only a question of membrane materials, but also of process.²¹ Here, we want to address the question: for a given capability of nanopores, how much can one improve the power density of a harvesting device by tailoring the flows and boundary layers so as to minimize the detrimental effect of concentration polarization? For this purpose, we explore here a new concept of nanopore power generation, focused on the optimization of the micro- and sub-micrometric scale flow in ducts communicating through selective elements. A simple device that could be realized with standard semiconductor machining is described in section 2. We base our optimization on a multi-scale analysis of the ion transport. At the level of the selective element, we solve analytically the non-linear Poisson-Nernst-Planck equations and express the selectivity and ion fluxes as a function of the local boundary

conditions in chemical and potential gradients. At the level of the ducts, a first hypothesis of perfect mixing in the section allows us to identify the Sherwood number as the relevant non-dimensional number and to find a master law for the output power from which the net power density is optimized. Finally, a 3-dimensional numerical resolution shows that with the best today available materials for the selective element,^{8,9,11} a net power density as large as 300 W m⁻² can be achieved per global unit area of the device, exceeding by more than 30 times what could be obtained by assembling nanopores of similar quality in a membrane.¹⁹ The actual capabilities of the device could be even larger by further optimizing a differential flow in the ducts and by taking into account the effect of osmotic flows.

2 A nanofluidic exchanger of osmotic energy

2.1 Principle

We study here a simple fluidic exchanger able to implement submicrometric boundary layers at the inlet/outlet of ion selective elements. The core pattern is made of two nanoducts separated by a nanoslit (Fig. 1). Such a microfluidic design has already been proposed in the field of continuous water purification,²² in membraneless redox flow cells for electrochemical energy conversion,^{23,24} or even for studying ion concentration polarization.^{25,26} For the sake of simplicity, we focus here on a geometry that can be achieved by available technologies from the semiconductor industry such as direct bonding, 3D assembly, and silicon on insulator,^{27,28} allowing a multi-scale flow design to be implemented and to possibly stack it in the 3D dimension.



Fig. 1 Left: Elemental exchanger made of two half-nanoducts of width *b* and height 2*a*, carrying high (indigo) and low (turquoise) concentration liquids in the *z* direction. Nanoducts are connected by a cation selective nanoslit of height *H* and width *W*, whose walls bear a surface charge σ . The nanoslit allows ion fluxes per unit length J^+ and J^- in the *x* direction from the high concentration to the low concentration nanoducts. Electrodes (grey bottom face) maintain a constant potential in the nanoducts. Center: Sectional view of the system. Right: Top view of a parallelized setup with elemental exchangers placed side-to-side. The nanoducts are fed from the bottom plane through inlet and outlet ports (rectangles with dots or crosses) by underlying larger ducts running in the transverse direction (not sketched). The solutions flow in the nanoducts through a length *L*. Long arrows indicate the liquid flow in the nanoducts, whereas transverse short arrows indicate the nanoslit fluxes.

However other possibilities, embedding for instance portions of membranes, could be as well designed.

Nanoslits are the ion-selective part of the device, they are coated with charge-active materials thanks to the library of coatings available in the semi-conductor industry (such as BN, Mo, TiO₂) and develop a surface charge σ in solution. The width W of the nanoslits is analogous to a membrane thickness, determining the amplitude of the saline gradient from the electrolytes running in the nanoducts. It can be made as small as 50 nm within the current precision of 3D-assembly²⁹ without requiring additional mechanical support. The height H of the nanoslits is tuned by appropriate spacers carved on the top of the walls before assembly. The minimum value lies in the subnanometer range and corresponds to the directly bonded surfaces.³⁰ It is presently established that water and, to some extent, ions diffuse through the gap between directly assembled silicon surfaces without dramatic slowing down of their kinetics as compared to macroscopic properties.^{31,32} The role of the nanoducts is to replenish the electrolyte concentration feeding the nanoslits and to collect/furnish the associated ion fluxes. For this purpose, they are coated with electrodes prior to assembly. A fluid circulation is maintained by connecting the nanoducts to a network of underlying feeding ducts of a larger scale running in the transverse direction, using ports drilled at the bottom of the nanoducts (ports of length as small as a few nanometers can be achieved with the silicon-oninsulator techniques).

2.2 The elemental nanofluidic exchanger

We study hereafter the power generated by the elementary brick of the above periodic device: the elemental exchanger made of two half-nanoducts of width b, height 2a, and length L along the z-axis, communicating along their length through a nanoslit. In each nanoduct, the nanoslit is located at (x, y) = (0, 0) and the transverse x-axis is oriented toward the center of the duct so that the section is defined as $x \in (0, b)$ and $y \in (-a, a)$. In the assembly sketched in Fig. 1, nanoducts operate over half of their length under counter-flow conditions. Having studied separately the co-flow and counter-flow situations, we have found that although slightly better, the counter-flow conditions do not produce a very significant change in the power generation, therefore we focus here only on the coflow situation where the average velocity in both nanoducts is U. In this first approach, we neglect the osmotic volume flux through the nanoslit with respect to the forced volume flux in the ducts. Also, we do not consider the issue of feeding the nanoducts by the underlying larger duct network, which could be achieved in a hierarchical manner using a constructal design in order to minimize the additional pressure drop.33,34

Hereafter, the power per unit area will refer to the device area (2b + W)L. This choice of the scaling area is different

from the case of membranes or single nanopores/nanotubes, which chose as the reference area the area normal to the ion flux. But our choice is consistent with the usual scaling considerations, because for a given design of the nanoducts and nanoslit, the total power output and cost of the device will be proportional to its area. Numerical estimations will assume power generation from seawater/freshwater feeding. The sodium chloride concentrations in mol L^{-1} fed at the entrance of the high (respectively low) concentration nanoduct are noted $C_{\rm H} = c_{\rm H} / (10^3 \, \mathcal{N}_{\rm A}) = 600 \, \rm mM$ and $C_{\rm L} = c_{\rm L} /$ $(10^3 \ \mathcal{N}_A) = 1 \ \text{mM}$, where c_H and c_L are the numeric concentrations in m⁻³. The surface charge of the nanoslit walls is equivalent to the one of NPG reported in the litterature:¹⁹ it is assumed to arise from the dissociation law $\sigma = -eN/(1 + 10^{pK_a-pH})$ of functional groups in number density $N = 4 \text{ nm}^{-2}$, having a dissociation constant $pK_a = 4$ and operated at pH = 7.¹⁹ The numerical value $\sigma = -0.6$ C m⁻² is similar to what has been observed in experiments on single nanotubes or nanopores under basic pH conditions.^{8,9}

3 Non-linear selective transport in the nanoslit

3.1 Analytical solution for the Poisson-Nernst-Planck equation

The transport of ions in the nanoslit, that is in the *x*-direction, is modelled with the Poisson–Nernst–Planck equation averaged over the thickness *H*. The thickness average is expected to be a good approximation when the Dukhin numbers $\text{Du} = |\sigma|/ecH$ are larger than unity, therefore we restrict our approach to $\text{Du}_{\text{L}} > \text{Du}_{\text{H}} \ge 1$, that is $H \le 11$ nm for the above chemical conditions. In this first approach, we neglect the osmotic flux, the consequence of which is discussed later. Without loss of generality, we consider $\sigma < 0$. We also assume that anions and cations have the same diffusion coefficient *D* (general case in the ESI†). Under these conditions, the fluxes $J^+(z)$ and $J^-(z)$ of ions at coordinate *z* per unit width dz of the nanoslit, oriented along the *x*-axis starting at the high salinity nanoduct (x = 0) and ending at the low salinity nanoduct (x = W), are written as:

$$J^{+} = -DH\left(\frac{\mathrm{d}c^{+}}{\mathrm{d}x} + \frac{c^{+}e}{k_{\mathrm{B}}T}\frac{\mathrm{d}V}{\mathrm{d}x}\right)$$
(1a)

$$J^{-} = -DH\left(\frac{\mathrm{d}c^{-}}{\mathrm{d}x} + \frac{c^{-}e}{k_{\mathrm{B}}T}\frac{\mathrm{d}V}{\mathrm{d}x}\right)$$
(1b)

$$c^+ - c^- = -2\sigma/eH \tag{1c}$$

Introducing the reduced coordinates $\tilde{x} = x/W$, reduced potential $\psi = eV/k_{\rm B}T$, reduced concentrations $\tilde{c}^{\pm} = c^{\pm}eH/|\sigma|$, and average concentration $\tilde{c} = (\tilde{c}^+ + \tilde{c}^-)/2$, the 1D-PNP equations become:

$$\frac{eW}{D|\sigma|}\left(J^{+}+J^{-}\right) = K^{+}+K^{-} = -2\left(\frac{\mathrm{d}\tilde{c}}{\mathrm{d}\tilde{x}}+\frac{\mathrm{d}\psi}{\mathrm{d}\tilde{x}}\right)$$
(2a)

$$\frac{eW}{D|\sigma|}\left(J^{+}+J^{-}\right) = K^{+}-K^{-} = -\left(2\tilde{c}\frac{\mathrm{d}\psi}{\mathrm{d}\tilde{x}}\right) \tag{2b}$$

In the permanent regime, the ion conservation is written as div $J^+ = \text{div } J^- = 0$, therefore the fluxes J^+ and J^- are uniform along *x*. Introducing the selectivity $t = (J^+ - J^-)/(J^+ + J^-)$, these equations integrate as:

$$\tilde{c} + t \ln(\tilde{c} - t) + \frac{K^+ + K^-}{2}\tilde{x} = \operatorname{cst}_1$$
(3a)

$$\psi + \tilde{c} + \frac{K^+ + K^-}{2}\tilde{x} = \operatorname{cst}_2 \tag{3b}$$

As boundary conditions, we assume the continuity of the electro-chemical potential of the ions at x = 0 and W. In the high salinity channel $\tilde{x} = 0^-$, the potential is $\psi_h = 0$ and the local concentration at the level of the nanoslit is $c_{ho}(z)$, whereas in the low salinity channel $\tilde{x} = 1^+$, these quantities are respectively $\Delta \psi$ and $c_{lo}(z)$. The continuity of the electrochemical potential $\ln \tilde{c}^{\pm} \pm \psi$ determines the internal boundary salinities $\mathscr{C}_h = \tilde{c}(0^+)$, $\mathscr{C}_\ell = \tilde{c}(1^-)$ and the potential difference acting in the nanoslit (see ref. 35 and the ESI† for detailed derivation):

$$\mathscr{C}_{h,\ell} = \left(1 + \tilde{c}_{h,\ell\sigma}^2\right)^{1/2} = \left[1 + \left(c_{h,\ell\sigma}eH/\sigma\right)^2\right]^{1/2}$$
(4a)

$$\psi(1^{-}) - \psi(0^{+}) = \Delta \psi + \ln \frac{c_{\ell o}(1 + \mathscr{C}_{h})}{c_{h o}(1 + \mathscr{C}_{\ell})}$$
(4b)

Together with eqn (3), these boundary conditions give an implicit equation for the selectivity:

$$t \ln \frac{\mathscr{C}_h - t}{\mathscr{C}_\ell - t} + \mathscr{C}_h - \mathscr{C}_\ell = -\Delta \psi + \mathscr{E}$$
(5a)

$$\mathscr{E} = \ln \frac{C_{ho}}{C_{\ell o}} + \mathscr{C}_h - \mathscr{C}_\ell - \ln \frac{\mathscr{C}_h + 1}{\mathscr{C}_\ell + 1}$$
(5b)

from which we obtain the ion fluxes and the current intensity dI per unit length dz of the nanoslit:

$$J^{\pm} = \frac{D|\sigma|}{eW} (1 \pm t) (-\Delta \psi + \mathcal{E})$$
(6a)

$$dI = \frac{2D|\sigma|}{W}t(-\Delta\psi + \mathcal{E})$$
(6b)

At an optimum value $\Delta \psi_{\text{opt}}$, the harvested electrical power $P = (k_{\text{B}}T\Delta\psi_{\text{opt}}/e) \times \int_{0}^{L} dI$ reaches a maximum value, giving the power density per device area:

$$\mathscr{P}_{\text{elec}} = \frac{2Dk_{\text{B}}T|\sigma|}{eW(2b+W)} \times f \tag{7}$$

where the non-dimensional power factor *f* is:

$$f = \max_{\Delta \Psi} \left\{ \frac{\Delta \Psi}{L} \int_{0}^{L} t(z) (-\Delta \Psi + \mathscr{E}(z)) dz \right\}$$
(8)

Eqn (4)–(6) correspond to the full non-linear solution of the PNP equations in the selective nanoslit. In order to close the problem and calculate the harvested electrical power (8),

these equations have to be coupled to the transport equations in the nanoducts in order to calculate the boundary conditions $c_{lo,ho}(z)$, which are further developed in section 4.

3.2 Approximation of perfect selectivity

When the exchanger is operated at infinite velocity, the boundary conditions at the outlet of the nanoslit correspond to uniform concentrations along the *z*-direction, which are the nominal injected concentrations. Under these conditions, the nanoslit selectivity does not vary with *z* and the factor *f* is reduced to:

$$\mathscr{F}(\mathrm{Du}_{\mathrm{H}},\mathrm{Du}_{\mathrm{L}})\max_{\Delta\Psi}\left\{t\Delta\Psi(-\Delta\Psi+\mathscr{E})\right\}$$
(9)

Fig. 2 left compares the numerical value of \mathscr{F} to the approximation $\mathscr{F} \approx (\mathscr{E})^2/4 \approx (\ln c_{\rm H}/c_{\rm L})^2/4$ obtained for a perfect selectivity t = 1. The approximation is very robust if either Du_H > 3 or $c_{\rm H}/c_{\rm L} > 4$. Under these conditions, the nanoslit is almost ideally selective for an applied potential $\Delta \psi \simeq (\ln c_{\rm H}/c_{\rm L})/2$. The maximum electrical power harvested, plotted in Fig. 2 right, is then

$$P_{\rm max} \simeq \frac{G_{\rm slit}}{4} \left(\frac{k_{\rm B}T}{e} \ln \frac{c_{\rm H}}{c_{\rm L}} \right)^2 \tag{10}$$

where $G_{\text{slit}} = (2|\sigma|eDL/Wk_{\text{B}}T)$ is the surface conductance of the nanoslit. With the above conditions for saline concentrations and surface charge, a diffusion coefficient $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, nanoslit length W = 50 nm and microchannel size $2b = 1 \mu m$, the maximum power density $P_{\text{max}}/(2b + W)L$ of the elemental exchanger is 6.3 kW m⁻². For comparison with the state of the art in single nanopore-based power generation, if we take the nanoslit section HL as the reference area, the power density under these conditions of infinite velocity is 640 kW m^{-2} (with H = 10 nm), which is the order of magnitude experimentally found in MoS₂ single nanopores.⁹ More generally, our definition of the power density gives values smaller by a factor H/2b than those which would be obtained by taking the sectional area of the nanoslits as the reference area, because the fluidic circulation occupies most of the area of our exchanger. We show hereafter that although our device presents a geometrical loss in power density because of the fluidic circulation, this loss is more than compensated by a better recovery of the saline gradient power, due to the reduction in concentration polarization enabled by this circulation.

3.3 Selectivity profile t(z)

The approximation of perfect selectivity cannot be used to calculate the power delivered by the elemental exchanger at finite velocity. This is because the salinity ratio c_{ho}/c_{to} decreases downstream of the injection port, and as $\Delta \psi$ is constant along *z*, it cannot be tuned to realize the ideal conditions $t \simeq 1$ all along the length of the nanoducts. As shown in Fig. 3-left, for a constant $\Delta \psi$, the selectivity decreases with the salinity contrast. As a consequence, at



Fig. 2 Left: Maximum value \mathscr{F} of the power factor f (eqn (9)) divided by $(\ln(c_H/c_L))^2/4$, plotted as a function of the injected salinity ratio c_H/c_L . Note that this maximum value is obtained only at infinite velocity when the membrane operates at all points under the same conditions c_H and c_L . The number drawn on each curve is the value of $Du_H = \sigma/eHc_H$. Right: Maximum power density of the elemental exchanger operated at infinite velocity $\mathscr{P}_{max} = Dk_B T |\sigma|/(eWb) \mathscr{F}$ as a function of c_H/c_L , for different values of the dimensional prefactor. Orange curve: $Dk_B T |\sigma|/(eWb) = 600$ W m⁻² obtained with $D = 10^{-9}$ m² s⁻¹, $\sigma = -0.64$ C m⁻², W = 50 nm, and $2b = 1 \mu$ m. Purple curve: 100 W m⁻², blue curve: 10 W m⁻². The salinity ratio $c_H/c_L = 600$ corresponds to seawater/freshwater. The curves essentially do not depend on the value of H in the limit $H < |\sigma|/ec_H$.

finite velocity a decreasing selectivity profile t(z) is observed along the length of the nanoducts, as the concentration contrast decreases downstream of the injection point (see Fig. 3-right). At very low velocity, the concentrations in the nanoducts eventually reach a plateau value and do not evolve anymore at large z. This dynamic equilibrium corresponds to the state t = -1 ($J^+ = 0$), in which only anions migrate through the nanoslit. As the anions are produced/consumed at the electrodes, the resulting concentration flux exchanged by the nanoducts vanishes, and the concentrations stabilize. Accordingly, the region t < -1 is shaded in Fig. 3-left. When the exchanger is operated at finite velocity, the potential $\Delta \psi$ has to be optimized taking into account the selectivity profile, and for these reason the full solutions (5), (4) and (8) of the PNP-equations have to be used to calculate the harvested power.

4 Power output of the elemental exchanger

4.1 Diffusion-convective transport in the nanoducts

The elemental converter is operated by forcing a flow in the nanoducts. Hereafter, we neglect the osmotic flow rate through the nanoslit with respect to the forced flow in the nanoducts (see section 4.4), therefore the velocity profile in the nanoducts is along the *z*-coordinate and invariant along *z*. We consider an equal velocity in both nanoducts of average value *U*. Due to the size difference between the height of the nanoslit and the



Fig. 3 Left: Selectivity *t* plotted as a function of the electromotive force $\ln(c_H/c_L) - \Delta \psi$ for three values of Du_H indicated in the curves. Plain lines correspond to $c_H/c_L = 10$ and dashed lines to $c_H/c_L = 2$. Right: Selectivity $t(\tilde{z})$ versus the dimensionless position along the nanoduct \tilde{z} for four different liquid velocities corresponding to Sh = [1, 2, 5, 100] (from the lower to the upper curve), Du_H = 1, $c_H/c_L = 10$ and $c_H/c_L - \Delta \Psi = 2$.

section of the ducts, the ion flux from the nanoslit is treated as a line source/sink whose amplitude is coupled to the local concentrations according to eqn (4)–(6). The electrodes are assumed to extend up to the level of the nanoslit and maintain the electroneutrality of the ion flux from the nanoslit as well as a uniform electrical potential in the nanoducts. Under these circumstances, the concentration flux per unit length dzdelivered by the nanoslit is equal to the cation flux $J_c(z) = J^+(z)$ given in eqn (6). The ions are transported in the nanoducts by a diffusion–convection equation:

$$\nabla \cdot \left(-\overrightarrow{\nabla} \tilde{c}_h + \tilde{c}_h \frac{u(x, y)}{D} \vec{e}_z \right) = -\delta(x, y) \frac{H}{W} (1+t) (-\Delta \psi + \mathscr{E}) \quad (11a)$$

$$\nabla \cdot \left(-\overrightarrow{\nabla} \tilde{c}_{\ell} + \tilde{c}_{\ell} \frac{u(x, y)}{D} \vec{e}_z \right) = \delta(x, y) \frac{H}{W} (1 + t) (-\Delta \psi + \mathscr{E}) \qquad (11b)$$

where the origin of the *x*, *y* coordinates in each nanoduct lies at the level of the nanoslit, the normalized concentrations $\tilde{c}_{h,\ell} = \frac{c_{h,\ell}eH}{|\sigma|}$ have been used, and *t* and \mathcal{E} are functions of $\tilde{c}_{ho} = \tilde{c}_{h}(0, 0, z)$ and $\tilde{c}_{\ell o} = \tilde{c}_{\ell}(0, 0, z)$ given by eqn (5).

4.2 The thin section approximation: scaling and optimization

For the sake of clarity, we first discuss a one-dimensional approximation of the transport equations whereby the concentrations $c_h(z)$ and $c_l(z)$ are assumed to be uniform in the section of the nanoducts. Using the non-dimensional variable $\tilde{z} = z/L$, the Peclet number $Pe = \frac{UL}{D}$, and the exchange parameter $J_e = \frac{HL^2}{2abW}$, the diffusion-convection equation is written as:

$$-\frac{\partial^2 \tilde{c}_{h,\ell}}{\partial \tilde{z}^2} + \operatorname{Pe} \frac{\partial \tilde{c}_{h,\ell}}{\partial \tilde{z}} = \mp J_{\mathrm{e}}(1+t)(-\Delta \Psi + \mathscr{E})$$
(12)

The parameter J_e is a purely geometrical parameter equal to the ratio of the geometrical conductances HL/W of the nanoslit and 2ab/L of the half-nanoducts. The inlet boundary condition (z = 0) corresponds to the flux prescribed by the feeding ports: $[-\partial_z \tilde{c}_{h,\ell} + \text{Pe} \tilde{c}_{h,\ell}](0) = \text{Pe}/\text{Du}_{H,L}$, while the outlet is left free: $\partial_z \tilde{c}_{h,\ell}(L) = 0$. Eqn(12) is a classical 1D-exchanger equation met for instance in heat exchangers, except that the exchange term (r.h.s) is non-linear. From eqn (8), the maximum power density collected is:

$$\mathscr{P}_{\text{elec}} = \frac{2Dk_{\text{B}}T|\sigma|}{eW(2b+W)} f\left(\text{Pe}, J_{\text{e}}, \text{Du}_{\text{H}}, \text{Cr} = \frac{\text{Du}_{\text{L}}}{\text{Du}_{\text{H}}}\right)$$
(13)

The power factor f is fully determined by the Peclet and exchanger parameters Pe and J_{e} , and the chemical parameters Du_{H} and Du_{L} , which are the entrance Dukhin numbers in the nanoducts.

By solving eqn (12), we find that the influence of Pe and J_e on the power factor f is essentially described by the single ratio Pe/ J_e which is analogous to a Sherwood number²² and fis essentially a function of 3 parameters only: Sh = Pe/ J_e , Du_H and Cr = Du_L/Du_H = c_H/c_L . As shown in Fig. 4-left, when f is plotted as a function of Sh, we find that the exchange parameter J_e has a very small influence. For Du_H = 1 and $J_e \in$ $[10^{-2}, 10^3]$, f varies at most by 20% in an intermediate Sh region. For Du_H \geq 3, f is essentially independent of J_e at J_e \geq 1.

At very low Sherwood, we find that $f \simeq \text{Sh}^2/8$ for all values of J_e and inlet conditions Du_H and Du_L (see the ESI† for the analytical derivation). In this low Sherwood limit, the



Fig. 4 Left: Dimensionless power factor $f(Sh, J_e, Du_H, Du_L)$ calculated from eqn (12) and (13), plotted as a function of the Sherwood number for the inlet concentration ratio $C_H/C_L = 1000$. Black lines: $Du_H = 1$, $J_e = \{10^{-2}, 10^{-1}, 1, 10, 100\}$. Red symbols: $J_e = 1$, $Du_H = \{3(), 10(), 30(), 100()$, 100()



Fig. 5 Net extractable power density \mathcal{P}_{net} calculated from eqn (12), (13) and (15) plotted as a function of the flow velocity U in the nanoducts. The diffusion coefficient is $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, the solution viscosity is $\eta = 1 \text{ mPa s}$, unless otherwise specified, the surface charge is $|\sigma| = 0.64 \text{ Cm}^{-2}$, and nanoducts have a square section of width 2b and a length L = 20b. Left: $C_H = 600 \text{ mM}$, $C_L = 1 \text{ mM}$, W = 50 nm and H = 1 nm. The value of b is shown on each curve. Center: $C_H = 600 \text{ mM}$, $C_L = 1 \text{ mM}$, $b = b_{opt}$. Continuous lines: W = 50 nm, $b_{opt} = 300 \text{ nm}$, $H = \{1, 3, 10\} \text{ nm}$. Dashed line: W = 100 nm ($b_{opt} = 200 \text{ nm}$) and H = 10 nm. Right: W = 50 nm, H = 1 nm, various chemical conditions with $C_H/C_L = 600$, $b = b_{opt}$. Continuous lines: $|\sigma| = 0.64 \text{ Cm}^{-2}$ and $C_H = \{0.6 \text{ M}, 1.8 \text{ M}, 6 \text{ M}\}$, associated with $b_{opt} = \{300, 100, 50\} \text{ nm}$. Dashed line: $|\sigma| = 64 \text{ mC} \text{ m}^{-2}$ and $C_H = 0.6 \text{ M}$ ($b_{opt} = 100 \text{ nm}$).

harvested power is limited by the device feeding and this regime is not of interest for power recovery. At high Sherwood, *f* follows the asymptotic trends $f \simeq W_0(e^2 \text{Sh/Du}_H) (W_0(e^2 \text{Sh/Du}_H) - 2)/4$, where W_0 is the principal branch of the Lambert function and *e* is the exponential basis, up to the maximum value $\mathscr{F}(c_H, c_L)$ discussed above (see the ESI† for derivation). In this asymptotic regimes, *f* also does not depend at all on J_e . We find empirically that the power factor *f* is well described for all Sherwood, inlet Dukhin Du_H and salinity ratio C_r by a master law:

$$f \simeq \frac{1}{4} W_0 (\chi e^2) \left[W_0 ((\chi + 2)e^2) - 2 \right]$$
(14a)

$$\chi = \frac{\text{Sh}}{\text{Du}_{\text{H}}} \left[\frac{\text{Sh}/\text{Du}_{\text{H}} + 3/e^2}{\text{Sh}/\text{Du}_{\text{H}} + 2/\text{Du}_{\text{H}}^2} \right]^{1/2}$$
(14b)

which describes adequately the envelope of the $f(Sh, Du_H, Cr)$ curves over all the Sherwood range up to their saturation value $\mathscr{F}(Cr)$ (see Fig. 4). It is worth mentioning that the intermediate Sherwood range is a rather large region, which extends on several decades in Sherwood values. This is characteristic of the non-linearity of the fluxes in the nanoslit.

4.3 Net power output: rational optimization

The master law (14) allows us to carry out a first rationalization of the geometric parameters of the exchanger in order to maximize the extractable net power density:

$$\mathscr{P}_{\rm net} = \frac{Dk_{\rm B}T|\sigma|}{ebW}f - \frac{K\eta D^2 H^2 L^2}{b^4 W^2 (2b+W)} {\rm Sh}^2$$
(15)

The hydraulic power dissipated per wafer unit surface, $\mathscr{P}_{hydr} = \Delta P \times U4ab/(2b + W)L$ where $\Delta P = K(a/b)\eta UL/b^2$ is the pressure drop applied to the nanoducts, scales as Sh². At high Sherwood (Sh/Du_H > 2), the factor *f* is essentially a function

of Sh/Du_H, and the same property holds for the hydraulic power density as soon as chemical conditions $C_{\rm H}$, $C_{\rm L}$ and σ are prescribed. Enforcing further the aspect ratios a = b (*i.e.* K = 7.11) and $L/b = \lambda$, we find (see the ESI†) that a maximum net power

$$\mathcal{P}_{\mathrm{max,net}} = 0.021 \frac{k_{\mathrm{B}} T c_{\mathrm{H}}}{\lambda} \sqrt{\frac{k_{\mathrm{B}} T D |\sigma|}{e W \eta}}$$
 (16)

can be extracted from the exchanger for an optimum width $b_{\rm opt}$ of the nanoducts:

$$b_{\rm opt} = 41.8 \frac{\lambda}{c_{\rm H}} \sqrt{\frac{D|\sigma|\eta}{k_{\rm B} T e W}}$$
 (17)

Under the above-mentioned chemical conditions $(C_{\rm H}/C_{\rm L})$ = 600 mM/1 mM, $\sigma = -0.64$ C m⁻²), an optimum section size $b_{\rm opt}$ = 300 nm is found for W = 50 nm and λ = 20, corresponding to square nanoducts of side 600 nm and length $L = 6 \mu m$. These values illustrate the full use of all available length scales, from nanometers to tens of micrometers, for sculpting efficiently the fluid circulation and maximizing the power generated. The maximum net power density given by eqn (15) under these conditions reaches 1 kW m⁻² (Fig. 5). This value exceeds widely the theoretical predictions of 10 W m⁻² for the maximum output of membranes made of nanopores of the same surface charge as the nanoslit considered here, operated with the same salinities.¹⁹ It is worth noting that the net power density of the optimized exchanger is about 10 times less than its maximum power density calculated without subtracting hydraulic losses (or in other words, ignoring CP). However this loss of a factor 10 is much lower than the losses induced by the concentration polarization effects in 2D membranes, estimated to be as large as 105.19 As a result, even if the geometrical arrangement of the selective pores in the

nanofluidic exchanger is less efficient than in 2D membranes, because they occupy only a small fraction of the available area, they lead to a more favorable power recovery due to the nanofluidic circulation.

Another feature is that for ratios $\text{Cr} \geq 10$, the optimum Sherwood for operating the exchanger is in a region where the power factor *f* does not depend on Cr, therefore the maximum net power does not depend on Du_L. Finally, a quite remarkable feature is that once the exchanger is designed with $a = b = b_{\text{opt}}$, the pressure head needed to operate the device at the maximum net power depends only on the osmotic pressure of the high salinity fluid and has the value $\Delta P = 0.032k_{\text{B}}Tc_{\text{H}}$ (see the ESI†). For seawater of concentration 600 mM, the optimum pressure head is found to be equal to 5×10^4 Pa = 0.5 atm, a value which does not raise specific operational problems for nanofluidic systems.

4.4 Numerical study of the three-dimensional transport

The above results obtained in the 1D approximation of the elemental exchanger neglect the formation of a boundary layer inside the nanoducts, and one should expect that the actual 3D situation harvests smaller power densities. For comparison, we study numerically the full 3D coupled-convection-diffusion eqn (11) with the *COMSOL* software (implementation described in the ESI†). The net power density is presented in Fig. 6.

For comparable conditions, the net harvested power is lower than in the 1D approximation, but not by orders of magnitude, and a significant power density of 300 W m⁻² is obtained with a square nanoduct section of size 2b = 500 nm. Clearly the forced convection is less efficient than in the 1D case to increase the harvested power, which is due to the formation of concentration polarization layers in the channels at the level of the nanoslit. As a result, the size b =300 nm is no longer an optimum nanoduct section and the net power density increases with decreasing nanoduct size. However the optimum velocity is found to be the same as in the 1D simplification, with a value of $0.03-0.04 \text{ m s}^{-1}$ for the chemical conditions investigated, therefore the operating pressure is comparable. We also note two significant features of the full 3D solution, different from the 1D approximation. The first one is that the net power density depends weakly on the width W of the nanoslit, decreased by only 66% when the latter is increased from 20 to 200 nm. This property is a consequence of the remaining concentration polarization and could ease the nanofabrication of the device. The second feature is that the concentration profile at the level of the nanoslit varies much more in the low concentration nanoduct, increased by a factor 100, in comparison with the high concentration nanoduct where the relative variation is only 20% (Fig. 6 left). This situation is not ideal, as it is the logarithm of the high/low concentration ratio which drives the energy conversion. Therefore, we could expect a significantly higher net power density by using asymmetrical nanoducts or flows. We have not studied further the optimization of an asymmetrical exchanger, as other patterns for the selective nanoslit could also be of interest (assembly of vertical nanoslits, etc.).

Finally it is important to keep in mind that the 3D transport equations solved here neglect the osmotic volume flux coming from the nanoslit, and thereby underestimate the extractable power. Any volume flux from the nanoslit should result in additional transverse convection in the nanoducts, able to enhance the mixing across their section and thereby limit further the residual concentration polarization. Indeed, the osmotic volume flux is expected to occur from the high concentration toward the low



Fig. 6 Net extractable power density \mathscr{P}_{net} calculated from the 3D transport eqn (11), (8) and (15), plotted as a function of the average flow velocity U in the nanoducts. The diffusion coefficient is $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, the solution viscosity $\eta = 1 \text{ mPa s}$, inlet concentrations are $C_H = 600 \text{ mM}$ and $C_L = 1 \text{ mM}$. The nanoslit height is H = 1 nm and its surface charge $|\sigma| = 0.64 \text{ Cm}^{-2}$. Nanoducts have a square section of size 2b and a length L = 20b. Left: Nanoslit width W = 50 nm, nanoduct section $2b = \{0.3, 0.5, 1.0\} \mu \text{m}$. Center: Nanoduct section 2b = 500 nm, nanoslit width $W = \{20, 40, 60, 100, 200\} \text{ nm}$. Right: Value of the electrolyte concentration in the high-concentration nanoduct C_h and the low-concentration nanoduct C_L . The size of the square section is 2b = 500 nm and the velocity $U = 0.03 \text{ m s}^{-1}$.

concentration, in the same direction as the concentration flux. Taking into account the thickness-averaged Stokes equation in the nanoslit, the expected osmotic volume flux per unit length *z* of the nanoslit is of magnitude $H^2 |\sigma| k_{\rm B} T / W \eta e.^{36,37}$ The latter quantity has the dimension of a diffusion coefficient and represents in the unit of *D* a contribution ranging from 0.7 (H = 1 nm) to 70 (H = 10 nm) under the above conditions of operation. This effect could contribute to wash away the remaining CP and enhance significantly the net harvested power density. Further work is under progress to quantify fully the effect of the osmotic volume flux and of the diffusion–osmotic current in the elemental exchanger.

5 Conclusions

In conclusion, we show here that tailoring the flow at all intermediate length scales between the nanoslit and the macroscopic scale is a promising route for taking full advantage of the capabilities of nanopores for power generation from salinity gradients. The elemental exchanger studied here demonstrates the possibility of power densities of the order of kW m⁻², not only much larger than the current PRO and RED systems, but also a hundred times larger than the theoretical predictions for the maximum output of membranes made of the best available nanopores.

In this first approach, we have made a number of simplifications, such as neglecting the osmotic flow through the nanoslit, or neglecting charge-regulation effects due to variations in electrolyte concentration and pH. These effects can quantitatively modify our results on power density, but should not alter the qualitative trend that is highlighted here. Confrontation with experimental work will be necessary to guide the modelling and take into account the relevant physical effects.

Silicon-based nanofabrication techniques are particularly well appropriate for tailoring accurately a wide range of length scales from the subnanometric gap size offered by the direct bonding assemblies up to the macroscopic wafer size. The simple exchanger studied here is only one of the many possible arrangements, and other geometries based on different directions of flow circulation such as those used in hollow fiber systems³⁸ could be realized. Taking advantage of three-dimensional piling of integrated fluidic circuits is a straightforward extension which could lead to high power volume densities. Further work is needed to study the direct bonding of materials able to develop high surface charge, such as boron nitride, titanium or molybdenum oxides, and to understand ion transport in these highly confined bonded interfaces.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Saranath Sripriya: investigation, software, data curation, and writing of the initial draft. Cyril Picard: supervision, conceptualization, investigation, formal analysis, visualisation and writing – review & editing. Vincent Larrey: conceptualization. Frank Fournel: conceptualization. Elisabeth Charlaix: project administration, supervision, conceptualization, investigation, formal analysis, writing – review & editing and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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