

## Single-layer MoS<sub>2</sub> nanopores as nanopower generators

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### Osmotic power and energy conversion efficiency

Analytical model for osmotic potential and power has been previously derived by *Kim et al*<sup>1</sup>. Briefly, in that analytical model, the osmotic potential is given by equation 1 of the main text. The current can be obtained as<sup>2</sup>,

$$I_{os} \propto \frac{2\pi RS(\Sigma) k_B T}{L \eta \lambda_B} \ln \left[ \frac{a_{KCl}^{cis}}{a_{KCl}^{trans}} \right] \quad (1)$$

The power generation from the nanopore is given as,

$$P = V_{os} I_{os} \quad (2)$$

Furthermore, the power generation is maximized when the output voltage is half of the maximum voltage produced by the pore/nanochannel and is given by<sup>1</sup>

$$P_{max} = \frac{1}{4} \frac{V_{os}^2}{R_{pore}} \quad (3)$$

The energy conversion efficiency can be calculated using the ratio of output power/*Gibbs* free energy of mixing,

$$\eta_{max} = \frac{f(\Sigma)^2}{2} \quad (4)$$

For typical concentrations of 1 M KCl (*cis*) and 1 mM KCl (*trans*) in single-layer MoS<sub>2</sub> nanopores, we obtain conversion efficiency of 0.2 which is much higher than conversion efficiency reported for in BNNTs<sup>2</sup>(0.08) or in nanochannels<sup>3</sup>(0.03). This difference is mainly due to the smaller pore size of single-layer MoS<sub>2</sub> nanopores.

### Chemical potential gradient driven diffusion voltage

In addition to characterizing the system with a standard salt gradient system, it is possible to generate the chemical potential gradient-driven diffusion current generation by using different type of liquids.

A large chemical potential gradient can be created at the junction of two different liquids, For example, we can further improve the efficiency of power conversion by using a combination of pure room-temperature ionic liquids BminPF<sub>6</sub> and zinc chloride solution. We measured the power consumption on a variable load resistor and found the maximum output around 18 nW from the pore when the load resistance equals the internal resistance of the nanopore ( $R_{pore} = (9.4 \pm 2.1) \text{ M } \Omega$ ). Such values are much higher than the KCl concentration gradient system. We could attribute the observed power generation to the large Gibbs mixing energy due to chemical potential difference between two liquids. However, we would also like to mention the direct measurement of output in **Extended data Fig. 8d** and the transistor-powering demonstration cannot exclude the electrode contribution.

In order to show the general applicability of osmotic power generation, here, we discuss a general process of the power generation in liquid-liquid junction system by considering the *Gibbs* energy change of the system.

The cost of *Gibbs* mixing energy is used to generate the electric work, given as,

$$-zFE = \Delta_{mix} G \quad (1)$$

where  $z$  is the charge number,  $F$  is *Faraday* constant;  $E$  is the potential difference and  $\Delta_{mix}G$  is the change of *Gibbs* mixing energy respectively.

Taking into account the ion selectivity, the current is composed of cation and anion currents. This equation should then be written as,

$$-zFE = (2t_m - 1)\Delta_{mix}G \quad (2)$$

Where  $t_m$  is the transport number of the selective ions.

This simple model highlights three important factors for liquid junction potential: *Gibbs* mixing energy including both enthalpy and entropy contributions, ion selectivity which relates to surface charge of the pore material properties and  $z$ , the number of electrons of the charge carriers. Therefore, the larger power might be attributed to the giant *Gibbs* mixing energy of pure ionic liquid BminPF<sub>6</sub> and saturated ZnCl<sub>2</sub> solution.

### Computational nanofluidics model

**SI Table 1.** The Lennard-Jones parameters and charges.

Interaction	$\sigma$ [Å]	$\epsilon$ [kcal mol <sup>-1</sup> ]	Charge [e]
C-C <sup>4</sup>	3.3900	0.0692	0.0000
Mo-Mo <sup>5</sup>	4.2000	0.0135	0.6000
S-S <sup>5</sup>	3.1300	0.4612	-0.3000
O-O <sup>4</sup>	3.1656	0.1554	-0.8476
H-H <sup>4</sup>	0.0000	0.0000	0.4238
Mo-O	3.9960	0.0581	-----
S-O	3.4150	0.2824	-----
K-K <sup>6</sup>	2.8400	0.4300	1.0000
Cl-Cl <sup>6</sup>	4.8305	0.0128	-1.0000
C-O <sup>7</sup>	3.4360	0.0850	-----
C-H <sup>7</sup>	2.6900	0.0383	-----
Rest	Obtained by Lorentz-Berthelot rule.		

Using MD, we applied different ionic concentration ratios across a single-layer MoS<sub>2</sub> membrane. The KCl concentration in the *cis* reservoir is always kept at 1 M while changing the concentration in the *trans* reservoir (0.1, 0.01, 0.002 and 0.001 M) to achieve different salinity ratios of 10, 100, 500 and 1,000. The current is plotted for different applied electric fields as shown in **Extended data Fig. 4b**. As discussed in the main text, the possible explanation for the experimentally observed non-monotonic short-circuit current is due to the competition between the diffusion process (dominant exchange process) and the migration of ions owing to the induced Donnan potential near the interfaces of the nanopore. The potential is induced owing to the cation selectivity of the pore. The potassium selectivity coefficient is defined as  $\frac{J_{K^+} - J_{Cl^-}}{J_{K^+} + J_{Cl^-}}$  where  $J_{K^+}$

and  $J_{Cl^-}$  are the flux of potassium and chloride ions, respectively. The flux of each ion type depends on its concentration and velocity inside the pore. Now, using MD simulations, we confirmed the cation selectivity of the negatively charged pore by analyzing the concentration of

each ion type (potassium and chloride) as a function of the radial distance from the center of the pore (**Extended data Fig. 4c**). As expected, the potassium ions (counter-ions) are attracted to the charged surface of the pore, while the chloride ions (co-ions) are repelled from the surface. This results in an electrical double layer with a higher concentration of the counter-ions. The selectivity of the pore as well as the individual ionic flux is tabulated for different ratios in **SI Table 2**. The selectivity of the pore decreases with increase in the saline concentration ratio due to an increase in the co-ion concentration inside the pore as shown in **Extended data Fig. 4c**.

**SI Table 2.** The individual contribution of ions to the current and the potassium selectivity coefficient of the pore.

Concentration ratio	$J_{K^+}$ [#/ns]	$J_{Cl^-}$ [#/ns]	Potassium selectivity coefficient
10	2.34	0.34	0.7462
100	15.34	2.67	0.7034
500	12.67	2.34	0.6882
1000	10.34	2.00	0.6758

We also investigated the effect of osmotic flow of water on the currents by computing the area-averaged velocity ( $\hat{v}_{water}$ ) of water inside the pore.  $\hat{v}_{water}$  ranges from 0.05 to 0.1 m s<sup>-1</sup> which is 1 to 2 orders of magnitude smaller than the averaged velocity of ions (total averaged velocity of ions -  $\hat{v}_{water}$ ) inside the pore resulting in an insignificant contribution to current due the osmotic flow of water.

The short-circuit current and open-circuit electric field are plotted for different ratios in **Extended data Fig. 4d** and **Extended data Fig. 4e**, respectively. The non-monotonic short circuit current and monotonic increase in open circuit electric field with concentration ratio are qualitatively consistent with the experimental observations (main **Fig. 3**). To understand the mechanism behind the non-monotonic current characteristics, a continuum based analysis is carried out. **Extended data Fig 5a** shows the variation of short-circuit current with different salinity gradient ratios. A non-monotonic variation in the short-circuit current is also captured from the continuum model. However, the continuum based PNP equations only qualitatively predicts the MD observations. This is because, in continuum calculations, we have assumed a constant mobility for each ion in the entire system while in MD the mobility increases (for a single-layer MoS<sub>2</sub>) inside the pore (discussed later in the text) resulting in a higher drift velocity of ions and, in turn, a higher migration and diffusive ionic current for MD.

To explain the mechanism, we calculate each component of flux inside the nanopore and understand the dominant exchange process. We have neglected the convective current contribution due to the fluid flow as the velocity of water is 1 to 2 orders of magnitude smaller than the velocity of ions from our MD calculations. Inside the nanopore, owing to the salinity concentration ratio of the reservoirs and the cation-selectivity of the pore, we observe dominant contribution of diffusive flux of potassium ions (counter-ions) in comparison to the diffusive flux of chloride ions. Furthermore, due to the nanopore cation-selectivity and predominant diffusion of potassium ions, we observe a build up of positive potential (Donnan potential) near the interface of nanopore and low concentration reservoir. Also, a negative potential is build up at the interface of nanopore and high concentration reservoir, as the chloride ions are blocked from entering into the pore. The net potential difference across the nanopore interface results in an induced electric field directed from low concentration interface region to high concentration interface region. This results in a migration of potassium ions (counter-ions) from low concentration nanopore interface to high concentration nanopore interface and the chlorine ions (co-ions) in the opposite direction. We observe that the dominant exchange process inside the nanopore is always diffusion, however the contribution of migrational potassium flux (countering the diffusive flux of potassium ions) increases at high salinity concentration ratios. It is due to the competition of these two countering fluxes of potassium ions, we observe a non-monotonic short-circuit current in MoS<sub>2</sub> nanopores.

We also considered the effect of membrane thickness on the power generation in our MD simulations. Different membranes of MoS<sub>2</sub> (single-layer, two-layer, three-layer, four-layer, six-layer and twelve-layer MoS<sub>2</sub>) were created to first characterize the thickness effect on the conductance of the nanopores. For all the membranes, a symmetric concentration of 1M KCl is applied. Also, we fixed the length of the reservoir, ( $L_{reservoir} = 4 \text{ nm}$ ). With different layers of MoS<sub>2</sub>, the overall length of the system ( $L$ ) changes ( $L = 2L_{reservoir} + L_{pore}$ ), so to have a consistent bias ( $\Delta V$ ) across all the systems we adjust the applied electric field ( $E$ ) using  $E = \frac{\Delta V}{L}$ . Note, in molecular dynamics, the applied electric field is uniform in the entire system while in experiments, the electric field is mostly felt at the membrane. The I-V curves for all the membranes are plotted in **Extended data Fig. 6a**. From theory, conductance scales inversely with the thickness of the membrane; therefore, the conductance is plotted as a function of the reciprocal thickness ( $t^{-1}$ ) in **Extended data Fig. 6b**. The variation of conductance with inverse thickness is not linear as predicted by the classical theory. In addition to the thickness, ionic mobility also influences the conductance. **Extended data Fig. 6c** shows how the average mobility (averaged over the cross-section) of each ion inside the pore changes with the increase in the number of MoS<sub>2</sub> layers. There is a very sharp reduction in the mobility of potassium ions inside the pore of a multilayer MoS<sub>2</sub> compared to that of the single-layer membrane.

The abrupt reduction of mobility is due to the fact that the counter-ions (potassium) are strongly adsorbed to the charged surface of the multilayer pores. **Extended data Fig. 7a** shows the concentration of ions inside the pores for all the membranes. The concentration of potassium ions increases significantly in the double layer ( $\lambda$ ) near the wall. Based on the classical theory, the double layer ( $\lambda = \sqrt{\frac{\epsilon_0 \epsilon_r RT}{2F^2 z^2 c_0}}$ ) for a symmetric monovalent electrolyte ( $z_K = z_{Cl} = z = 1$ ) is calculated to be 0.308 nm assuming  $c_0 \sim 1M$  concentration observed at the center of the pore. Because of the adsorption, the mobility of ions decreases sharply within the  $\lambda$  layer. This reduction is also evident by looking at the residence time of potassium ions inside the  $\lambda$  layer (**SI Table 3**). The residence time increases for multilayer membranes compared to that of the single-layer membrane. In **Extended data Fig. 7b**, the mobility of ions is plotted as a function of the number of layers of MoS<sub>2</sub>. Within  $\lambda$  the mobility decreases sharply from a single layer to two layer and three layer MoS<sub>2</sub>. Beyond that the mobility remains constant at a much lower value compared to that of the single layer MoS<sub>2</sub>. Outside  $\lambda$ , the mobility decrease is not as sharp, but the mobility in a single-layer is higher compared to multilayer MoS<sub>2</sub>.

**SI Table 3.** The residence time of potassium ions inside the  $\lambda$  layer at 1 V.

Number of MoS <sub>2</sub> layers	Residence time of K <sup>+</sup> within $\lambda$ [ns]
1	0.08
2	1.52
3	3.46
4	5.53
6	7.26
12	$\geq 15$

The effect of having multilayer membranes of MoS<sub>2</sub> on the power generated by these membranes was also studied by performing MD simulations. A concentration gradient of 1000 ( $C_{max} = 1M$  and  $C_{min} = 1mM$ ) is used across the multilayer membranes to obtain the open-circuit voltage as the maximum power is proportional to both the conductance and the square of open-circuit voltage. **Extended data Fig. 7c** shows the open-circuit electric field ( $E_{oc}$ ) as a function of the number of layers in MoS<sub>2</sub>. Once the open-circuit voltage ( $V_{oc} = E_{oc} \cdot L$ ) and the conductance dependence on thickness are known, the power generated is estimated for multilayer MoS<sub>2</sub> membranes as a ratio of  $P_{max}^n$  to  $P_{max}^1$  ( $n$  denotes number of layers) in **Extended data Fig. 7d**. A multilayer MoS<sub>2</sub> reduces the osmotic power substantially. For instance, the power for a twelve-layer MoS<sub>2</sub> is predicted to be only about 3% of that of the single-layer membrane.

Using our continuum model, we also investigate the effect of pore size on the short-circuit current. **Extended data Fig. 5b** shows the variation of short-circuit current with pore diameter. We observe a non-monotonic variation in the short-circuit current consistent with the experimental predictions. To understand this result, consider the extreme limits of the pore diameter, i.e.,  $D_{pore} \rightarrow 0$  and  $D_{pore} \rightarrow D_{reservoir}$  (no membrane). In the lower limit, ( $D_{pore} \rightarrow 0$ ), we block the ions passing through the interface and hence, there is negligible diffusion of ions as the membrane diameter is zero and the induced electric field at the nanopore interface is small. This results in a no short-circuit current. In the upper limit ( $D_{pore} \rightarrow D_{reservoir}$ ), the selectivity of the pore is lost and hence, the concentration of the ions inside the pore is almost equal to the bulk concentration and the system will equilibrate quickly, resulting in almost an equal and opposite diffusive flux of potassium and chloride ions. Further, the induced electric field at the nanopore interface is small owing to loss of ion selectivity. This results in a weak migrational flux of both the ions. Hence, the resulting short-circuit current is small. For other diameters between these extreme limits, we observe higher diffusive flux of potassium ions compared to chloride ions (owing to pore selectivity) and a small contribution of migrational flux (opposite to diffusive flux) for potassium ions. Hence, we observe a higher current at all diameters in between the extreme limits. Henceforth, we observe a non-monotonic characteristic in the short-circuit current. Our calculations reveal that continuum based numerical model provides a sufficient proof to explain the mechanism behind the current characteristics observed in the experiments.

## References

- 1 Kim, D.-K., Duan, C., Chen, Y.-F. & Majumdar, A. Power generation from concentration gradient by reverse electrodialysis in ion-selective nanochannels. *Microfluid. Nanofluid.* **9**, 1215-1224 (2010).
- 2 Siria, A. *et al.* Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube. *Nature* **494**, 455-458 (2013).
- 3 Van der Heyden, F. H., Stein, D., Besteman, K., Lemay, S. G. & Dekker, C. Charge inversion at high ionic strength studied by streaming currents. *Phys. Rev. Lett.* **96**, 224502 (2006).
- 4 Barati Farimani, A. & Aluru, N. Spatial diffusion of water in carbon nanotubes: From fickian to ballistic motion. *The Journal of Physical Chemistry B* **115**, 12145-12149 (2011).
- 5 Liang, T., Phillpot, S. R. & Sinnott, S. B. Parametrization of a reactive many-body potential for mo-s systems. *Phys. Rev. B* **79**, 245110 (2009).
- 6 Joung, I. S. & Cheatham III, T. E. Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations. *The Journal of Physical Chemistry B* **112**, 9020-9041 (2008).
- 7 Wu, Y. & Aluru, N. Graphitic carbon-water nonbonded interaction parameters. *The Journal of Physical Chemistry B* **117**, 8802-8813 (2013).