A Theoretical Investigation On MoS₂ Nanopore Power Generators

Zhuo Huang[1]*, Makusu Tsutsui[2], Yan Zhang[1], Yuhui He[1], Xiang Shui Miao[1], Masateru Taniguchi[2]

[1]School of Optical & Electronic Information, Huazhong University of Science & Technology, Wuhan, China
* Email: huangzhuo1949@hust.edu.cn
[2]Institute of Scientific & Industrial Research, Osaka University, Osaka, Japan

Abstract
Ultra-thin nanopore devices have attracted a broad scope of scientific and technological interests, with potential applications such as molecule detection, ionic diodes, sea water desalination and DNA Translocation. Recently large amplitudes of osmotic currents have been induced in one-atom thick layer MoS₂ nanopore systems by imposing a salt concentration bias [1]. It highlights the prospect of utilizing ultrathin nanopores as nanopower generators. In this work we pioneer a new electrokinetic analysis by outlining the significance of MoS₂ membrane surface charges on the ionic transport. Comparing to the conventional models where only those surface charges within the nanopore wall were considered [2], our results show satisfactory agreements with the experiments. The presented work indicates the crucial role of the MoS2 membrane surface charges in nanopore transport, and thus provides a very useful method for evaluating all ultrathin nanopore devices.

1. Introduction

In the past few years, nanopore systems have emerged as a new device architecture in probing single molecules, DNA sequencing, genetics and medical diagnostics. Advances in nanofabrication allow production of synthetic nanopores in suspended membranes (such as silicon nitride thin films and graphene) with controllable pore diameters down to the molecular scale. The fabricated ultrathin nanopores based on two-dimensional (2D) material have shown enhanced performance compared to the traditional thick nanopores in many aspects (such as DNA sequencing and energy harvest) owing to the atomic thickness.

Tremendous progresses have been made in the past decades on exploring the ion transport properties in nanopores and nanochannels. The MoS₂ nanopores are regarded to be negatively charged upon contacting with water[3] as shown in the schematic diagram Fig.1. In order to screen the presence of surface charges on the MoS₂, a layer of counterions (cations) is induced adjacent to the wall while the coions (anions) are repelled from the wall. This complex system is the so-called electrical double layers (EDL) and the thickness of EDL depends on the salt concentration of the imposed electrolyte. Moreover, when a salt concentration bias is imposed at two reservoirs of a single-layer MoS₂ system, the EDL become thicker and thicker around the high concentration end (C_{max}) than those at the low one (C_{min}). In the open-circuit condition, the diffusion of those extra cations in EDL and the different mobilities between K^+ and Cl^- would together result in an electrical potential V_{open}.

However, a crucial difference between this ultrathin nanopore system and the previously discussed ones is the role of those charges on the membrane surface. In our previous discussions only the effect of charges on the inner walls of nanopores or nanochannels was considered, while that of those on the membrane surfaces was neglected. (characterized by σ_w and σ_m in Fig.1 respectively). Here the rationale is that the traditional nanopores or nanochannels were enough thick or long and thus the effect of σ_m on the transport within the channel was trivial. However, this approximation no long stands for the ultrathin MoS₂ nanopores.

In this work we first demonstrate our analysis by considering the MoS₂ membrane surface charges, and then we analyze the dependence of surface charge density (σ_m shown Fig1) on the surface chemistry. In this manner the tuning of σ_m by solution salt concentration has also been studied. We show that our results agree excellently with the experimental observations [1].

2. Theoretical modelling

The ion transport properties in both inner nanopore and the outside regions can be described by the Teorell-Meyer-Sievers model [4] or by the space-charge model [5]. Here we separate the atomically thin MoS₂ system to two parts: inner nanopore; outside of nanopore. Due to the restriction of paper space, we present only the analysis of membrane surface charge effect, while neglect the discussion on σ_w since it can be found in conventional models.
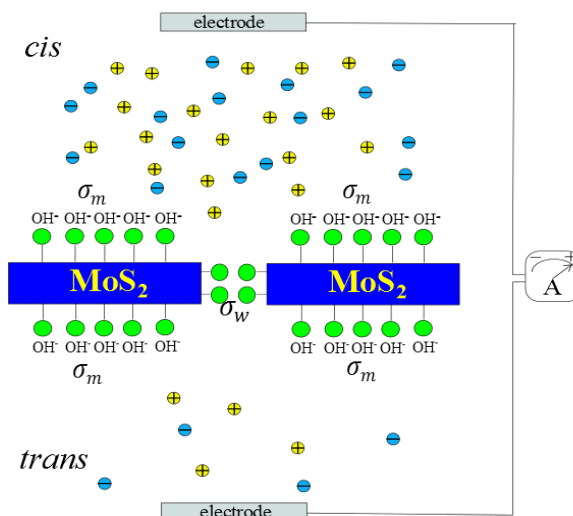

Fig1 schematic of MoS₂ nanopore system：σ_w and σ_m respectively are the surface charges on the inner walls of nanopores and those on the membrane.

As shown in Fig1, we view the outside of nanopore as a particular conical nanochannel in which the cone angle is $\pi/2$. In Space-charge model, the potential in conical nanopore is divided into two components: the electromotive and electrostatic ones due to the axial symmetry:

$$V(r,\theta) = V_0(r) + \phi(r,\theta) \qquad (1)$$

The electrical potential $\phi(r,\theta)$ is then deduced via the Poisson-Boltzmann equation describing the K^+ and Cl^- ions in the angular direction:

$$\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\bar\phi(r,\theta)}{\partial\theta}\right) = \frac{\sinh(\bar\phi(r,\theta))}{\lambda_D^2(r)} \qquad (2)$$

With boundary condition

$$\begin{cases} \left.\dfrac{\partial\bar\phi(r,\theta)}{\partial\theta}\right|_{\theta=0} = 0 \\ \left.\dfrac{\partial\bar\phi(r,\theta)}{r\partial\theta}\right|_{\theta=\theta_m} = \dfrac{e\sigma_m}{\varepsilon kT} \end{cases} \qquad (3)$$

In the above $\bar\phi = e\phi/K_B T$ is the nondimensionalized potential, σ_m is the density of surface charges on the membrane surfaces, and $\lambda_D = \sqrt{\varepsilon_f K_B T/2C_0 e^2}$ is the Debye length which characterizes the thickness of EDL. In our approach the concentration along the pore axis, $C_0(r)$, is estimated by using COMSOL.

On the other hand, under the open-circuit situation the electrical current along channel axis is written as follows

$$\left(-\mu_+\frac{\partial V_0}{\partial r}\Lambda_+ - D_+\frac{\partial\Lambda_+}{\partial r}\right) - \left(\mu_-\frac{\partial V_0}{\partial r}\Lambda_- - D_-\frac{\partial\Lambda_-}{\partial r}\right) = 0 \qquad (4)$$

Where $\Lambda_\pm(r)$ is the line density of monovalent cations/anions along the conical nanopore axis direction:

$$\Lambda_\pm(r) = 2\pi r^2 C_0(r)\int_0^{\theta_m}\exp[\mp\bar\phi(r,\theta)]\sin\theta d\theta \qquad (5)$$

The open-circuit voltage ΔV_{op} is then attained from Eq.4:

$$\frac{\partial V_{op}}{\partial r} = -\frac{D_+\Lambda_+ - D_-\Lambda_-}{D_+\Lambda_+ + D_-\Lambda_-}\frac{kT}{e}\frac{\partial\ln C_0}{\partial r} \qquad (6)$$

We have demonstrated that the circuit model of nanopore power generator is equivalent to a voltage source and a resistor in series $V_{out} = \Delta V_{op} - I_z R_{ch}$. With respect to Eq.3, we arrive at the expression for the resistance in nanopore :

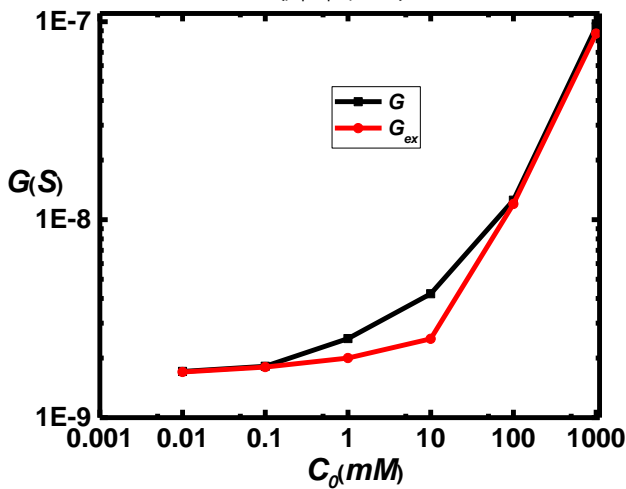$$R_{ch} = \int_0^R \frac{1}{e(\mu_+\Lambda_+ + \mu_-\Lambda_-)} dr \qquad (7)$$

Fig.2 Calculated electrical conductance **G** by our method (black line) and experimental conductance(red line) of KCl solution in MoS2 nanopore system [1], in which pore size is 6nm, thickness is 0.65nm and the surface charge density on the wall (σ_m and σ_w) is -0.053C/m^2 at PH=5.
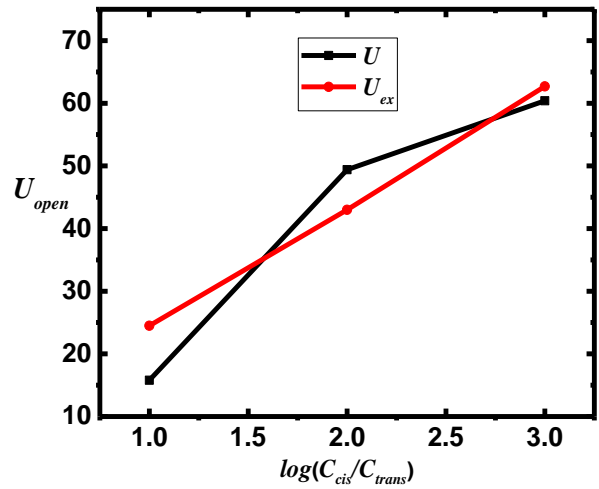

Fig.3 Calculated open-circuit osmotic potential **U** (black line) and experimental generated osmotic potential **U**$_{ex}$ (red line) as a function of the salt gradient imposed to MoS2 nanopore system [1]. C_{cis} is set to be 1M KCl; C_{trans} is tunable from 1mM to 1M KCl. In the system, pore size is 15nm, thickness is 0.65nm and PH=11.

3. Conclusions

We have verified that the existing experimental $I(V)$ results of single-layer MoS2 nanopore system is quantitatively interpreted by our theoretical model and analysis. The role of the charges on the MoS2 membrane surface and the associated surface chemical equilibrium are for the first time evaluated and outlined. Thus our model provides an insight into the physical mechanism and a potential guidance for the future design of nanopower generator by utilizing salt concentration bias across ultrathin nanopores.

References

[1] Feng J, Graf M, Liu K, et al. *Nature*, 2016, 536(7615):197.
[2] He Y, Tsutsui M, Scheicher R H, et al. *ACS Senors* 2016, pp 807–816
[3]Ghuman, Kulbir Kaur, S.Yadav, and C.V. Singh. *Journal of Physical Chemistry C* 119.12(2015):
[4] Meyer, K. H.; Sievers, J.-F.. *Helv. Chim. Acta* 1936, 19, 649 −664
[5] Fair, J. C.; Osterle, J. F. *J. Chem. Phys.* 1971, 54, 3307−3316.