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Enhancing the Efficiency of Energy Harvesting from Salt Gradient with ion-selective Nanochannel

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Abstract: The development of nanofluidic energy harvesting system plays a fundamental role in harvesting osmotic power from Gibbs free energy within salt concentration gradient, which is considered as a future clean and renewable energy source. In this study, a silica-nanochannel based nanofluidic energy harvesting system was fabricated and its output power density could reach 705 W/m² under suitable KCl concentration bias which exceeded—by almost two orders of magnitude—the results obtained by previous work. The enhancement of energy harvesting was mainly ascribed to the appropriate length of nanochannel that makes a good balance between the desirable ion selectivity and the unfavorable large resistance of nanochannel. This high-performance nanofluidic energy devices could be used in a variety of applications, including power biomedical tiny devices or constructing future clean-energy recovery plants.

Keywords: CMOS-compatible nanochannel, Salt Gradient, Channel with optimum length, Energy Harvesting
1. Introduction

Over the past decades, the utilization of Gibbs free energy released during the mixing of river and sea water has boosted a broad spectrum of interests and is widely recognized as a promising renewable-energy source owing to its environmentally friendly, large reserves and easy accessibility.[1-3] The osmotic power can be generated by alternately stacking layers of cation/anion selective membranes which separate different concentrations of salt solutions.[4-6] The ions diffuse spontaneously to the opposite directions due to the chemical potential gradient arises at the interface of these two liquids. The Gibbs free energy of mixing can be continuously converted into electrical energy by means of net diffusion current. The energy conversion process is called reverse electrodialysis (RED).[4-6] Thus far, many advancements have been made to design and explore the membranes for viable energy harvesting.[7, 8] However, the high membrane resistance and to-be-optimized ion selectivity remain the major bottlenecks to obtain high energy conversion efficiency thus impeding their practical applications.[5, 9]

Recently, nanofluidic channel systems have been proposed as new candidate to harness the osmotic energy owing to its high ionic throughput and excellent ion selectivity caused by surface charge effect.[10-12] Concerning the recent reports on nanofluidic/microfluidic RED,[13-24] the harvested power density up to $2.6 \times 10^3 \text{ W/m}^2$ has been obtained by
Guo et al. based on ion-selective track etched nanopore embedded in polyimide membrane.[13] Meanwhile, in order to overcome the swell-and-shrink issue of organic membranes in electrolytes, Kim et al. fabricated CMOS compatible silica nanochannels based on a standard semiconductor manufacturing process to harvest energy by RED.[15] However, the highest power density measured was only 7.7 W/m² under KCl concentration bias, where the channel is 4 nm high ($H$), 40 μm long ($L$) and equivalently 25 μm wide ($W$). For the sake of practical applications, it calls for designing CMOS-compatible nanochannels of appropriate sizes to optimize the osmotic energy converting efficiency. Conventionally, it was regarded that the osmotic current kept increasing with decreased length of the nanochannel ($L$).[25] However, recently Cao et al. found that the generated electric power would decrease by reducing the channel length ($L < 400$ nm).[26] According to our previous research, it was ascribed to the strong short channel effect, particularly at the low-concentration end, which eventually weakens the ion selectivity of the nanochannels.[27, 28] Therefore, to achieve the largest energy harvesting efficiency the optimal nanochannel/nanopore length should be in the range of 400 to 1000 nm.[26]

Here, we demonstrate a silica-nanochannel based nanofluidic energy harvesting system driven by KCl concentration gradient as shown in Fig.1a. Silicon nanochannel with the lengths ~715 nm was fabricated by electron beam lithography as shown in Fig.1d. The power generation and the
efficiency of energy conversion were obtained by measuring short-circuit current ($I_{sc}$) and the open-circuit voltage ($U_{oc}$) under different KCl concentration gradients.[13]

FIG. 1 (a) Schematic diagram for the silica-nanochannel based nanofluidic energy harvesting system. (b) Schematic illustration of the electric field induced by salt gradient in nanochannel. An ion flux driven by chemical potential through the channel is selected by the negatively charged channel, forming a diffusion current composed majorly of positively charged ions, and then leading to the induced electric field. (c) SEM cross section of the micro and nanochannel. (d) A zoom-in image of the nanochannel. The nanochannel height $H = 40$ nm, length $L = 715$ nm and width $W = 350$ nm.

2. Experimental details

2.1 Fabrication of nanochannel

Briefly, nanochannel patterns were delineated by an electron beam lithography (EBL) technique using the resist ZEP-520A on a 10 mm square piece of a (100)-oriented silicon wafer coated with a 300 nm SiO$_2$ layer.
The sample was then immersed in xylene and isopropanol for 70 seconds and 30 seconds, respectively, to peel off the EB resist. In the next step, the sample was subjected to CF$_4$/O$_2$ isotropic reactive ion etching to partially etch away the SiO$_2$ film. Finally, residual EB resist was removed by immersing the substrate in Dimethylformamide (DMF). As a result, a straight fluidic channel (length 715 nm, width 350 nm, and height 40 nm) was created as shown in Fig. 1. The nanochannel heights were measured by an AFM before polydimethylsiloxane (PDMS) bonding and checked again after bonding by measuring ionic conductance of nanochannel with 1.0 M KCl solution.

2.2 Sealing of nanochannel and current-voltage characteristic measurements

To reduce the noise during current measurements, a 500 μm thick polydimethylsiloxane (PDMS) sheet with four 2 mm diameter holes was prepared (two for inserting Ag/AgCl electrodes and the other two for the inlet and outlet of KCl solution) through oxygen plasma treatments to activate the surface and then sealed onto the nanochannel chip. We then set a fixed concentration of 1 M KCl solution in one reservoir, while the KCl concentration in the other reservoir was tuned from 0.1 mM to 1 M KCl. We measured the current and voltage across the channel by using a pair of Ag/AgCl electrodes to characterize the current–voltage ($I$–$V$) response of the nanochannel as shown in Fig.1a. The salinity gradient
across the nanochannel was considered unchanged during the current-voltage (I–V) measurements since the mixed volume through the single nanochannel was negligible compared to the reservoir capacity (~1.6 mL each) during the measurement time. All the experiments were conducted at room temperatures.

3. Results and Discussion

3.1 Ionic current–voltage characteristic

To gain a better insight into the performance of the silica nanochannel power generator, we first characterized the ionic transport properties of silica nanochannel under various KCl concentrations, which can provide information on the surface effect of the nanochannel. The inset of Fig. 2 shows the measured I–V characteristic of silicon nanochannel under various KCl concentrations from $10^{-6}$ to 1 M. The measured conductance depends on the salt concentrations and shows saturation at low salt concentrations as black line shown in Fig. 2. The saturation is mainly due to the presence of surface charges on the nanochannel.[30, 31]

The predicted channel conductance (red line), taking into account the contribution of the surface charge density ($\sigma_w$), is given by the space-charge model as demonstrated in our previous works:[32]

$$R_{ch} = \int_0^L \frac{1}{e(\mu_+\Lambda_+ + \mu_-\Lambda_-)}dz$$
Where $L$ is the channel length, $\mu_\pm$ is the mobility of cations/anions, $\Lambda_\pm$ is the line density of cations/anions along the nanochannel axis direction:

$$\Lambda_\pm = 2\pi C_0(z) \int_0^R \exp \left( \mp \frac{e\varphi}{k_BT} \right) r dr , \varphi \text{ is potential in the channel that mainly depends on the salt concentration } C_0 \text{ and the surface charge density } \sigma_w. \text{ In the simulation, } \sigma_w \text{ is set as } -53 \text{ mC/m}^2 \text{ which is typical for SiO}_2 \text{ surface.}[33-35] \text{ Under high KCl concentration conditions, } \Lambda_\pm \text{ mostly depends on the salt concentration } C_0. \text{ In this situation, the surface charges contribute little to the net ionic current and the bulk effect dominates the conductance of the channel. However, the wall surface charges play a prominent role in a low salt concentration condition and lead to the saturation of the conductance.}[36-38]. \text{ The differences between simulation results and experimental values at low concentrations are ascribed to the over-estimated surface charge density of nanochannel. In the experiments the top side of nanochannel is made by PDMS with surface charge density } \sigma_w \approx -5.5 \times 10^{-4} \text{ mC/m}^2, \text{ while in the simulation it is assumed as cylindrical channel made by SiO}_2 \text{ with } \sigma_w \approx -53 \text{ mC/m}^2[39, 40].
FIG. 2. Electrical conductance as a function of the concentration of KCl imposed to the SiO$_2$ nanochannel system. The black line with square symbols stands for experimental conductance, while the red line with round symbols for calculated electrical conductance. In the system, the channel length, width, and height is 715 nm, 350 nm, and 40 nm, respectively, and the surface charge of the channel, $\sigma_w$, is $-0.053 \frac{C}{m^2}$. Current–voltage response of SiO$_2$ nanochannel under different KCl concentrations is plotted in inset.

3.2 Energy harvesting characteristics

To evaluate the energy harvesting characteristics of silica-based nanofluidic device, the open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$) and output power density were investigated under a series of KCl concentration gradients.

The energy harvesting system is driven by the salt concentration gradient as shown in Fig. 1b. The highly negatively charged surface selectively allows the counterions (in this case potassium ions) to pass through, resulting in a net positive current. By measuring the $I$–$V$ response of the channel in the concentration gradient system, we can measure the
short-circuit current \((I_{sc})\) corresponding to zero external bias, while the open-circuit voltage \((V_{oc})\) generated across the nanochannel can be obtained from the voltage measured from a source meter \((V_{\text{measure}})\). The pure open-circuit voltage \((V_{oc})\) generated in the nanochannel can then be obtained by subtracting the contribution from the electrode-solution interface at different concentrations \((V_{\text{measure}} - V_{\text{redox}})\), which follows the Nernst equation.\(^{[15, 41]}\) The open-circuit voltage \(V_{oc}\) can be described as:\(^{[15]}\)

\[
V_{oc} = S(\Sigma) \frac{RT}{F} \ln \frac{r_{C_H} C_H}{r_{C_L} C_L}
\]

Here the \(S(\Sigma)_{is}\) denotes the ion selectivity\(^{[42]}\) for the SiO\(_2\) nanochannel (and equals 1 for the ideal cation-selective case, and 0 for the non-selective case), which is defined as \(S(\Sigma)_{is} = t_+ - t_-\), with \(t_+\) and \(t_-\) as the transference numbers for cations and anions respectively. \(F, R, T\) and \(r\) are the Faraday constant, the universal gas constant, the temperature and the mean activity coefficient, respectively. By fitting the experimental data presented in Fig. 3a to the above equation, we find the mean ion-selectivity coefficient \(S(\Sigma)_{is}\) is to be 0.78, suggesting high selectivity of cations.
FIG. 3 (a) Dependence of the open circuit voltage $V_{oc}$ on the concentration gradient of the SiO$_2$ nanochannel. $C_{trans}$ is set to be $C_{max}$. 1 M KCl, and $C_{cis}$ is tunable from 1 M to 0.1 mM KCl. The black line with square symbols stands for the measured zero current potential, $V_{measure}$, the red line with round symbols for redox potential, $E_{redox}$, which is produced by the unequal voltage drops at the electrode–solution interface in different KCl concentrations, and the blue line with triangle symbol for the open circuit voltage, $V_{oc}$. (b) Dependence of the short circuit current $I_{sc}$ (red line) and the measured maximum power output density (blue line) on the concentration gradient of the SiO$_2$ nanochannel.

We systematically measured the dependence of $I_{sc}$ and $V_{oc}$ on the concentration gradient. The high concentration at cis reservoir ($C_{cis}$) was fixed at 1 M, while the low concentration at trans reservoir ($C_{trans}$) was gradually increased from 0.1 mM to 1 M, with the concentration gradient ratio defined as $C_{cis}/C_{trans}$. As shown in Fig. 4, when $C_{cis}/C_{trans}$ increased from 1 to 10000-fold, $V_{oc}$ experienced a peak value at medium
concentration gradient of about 1000-fold (blue line in Fig. 3a), while \( I_{sc} \)
gradually increased from zero to about 280 pA and then decreased (red line
in Fig. 3b). Since the ion diffusion is driven by the concentration gradient,
a higher concentration gradient should result in higher \( V_{oc} \) and \( I_{sc} \).
However, the surface charge density decreases due to the decrease of \( C_{trans} \)
leading to the decreased ion selectivity by surface effect, eventually result
in the decrease of \( V_{oc} \) when the concentration gradient reached 1000-
fold.[32, 33, 35, 43] Meanwhile, the resistance of the nanochannel \( R_{ch} \)
kept increasing with the decreasing of \( C_{trans} \), leading to the earlier decrease
of \( I_{sc} \) (\( C_{cis}/C_{trans} = 100 \)).

The blue line in Fig. 4b shows the maximum output power density of
the nanochannel, \( P_{out} \), as a function of \( C_{cis}/C_{trans} \); \( P_{out} \) is defined by
\[
P_{out} = \frac{1}{W \times H} P_{max},
\]
where \( P_{max} \) is the maximum power and \( W \times H \)
represents the cross-sectional area of the channel. The value of \( P_{max} \) was
calculated by the equivalent circuit model, \( P_{max} = \frac{1}{4} I_{sc} \times V_{oc} \).[32] The
\( P_{out} \) gradually increased and then decreased as the concentration gradient
increases. The maximum power output density attained in the 715 nm-
length nanochannel was 705 W/m², which was about two orders
enhancement compared with the previous experimental results as shown in
table 1.[15] We ascribe it to the optimum length of nanochannel. On one
hand, the electrical resistance of the nanochannel shows an excellent linear
relationship with respect to the channel length. Therefore, the reduced
channel length generally promotes the diffusion current under salt gradient. On the other hand, it will greatly undermines the transmembrane concentration difference across nanochannels when decreasing the channel length and thus reduce the ion selectivity of nanochannel.[26, 28, 44] These two competing factors result in a moderate length (715nm) of nanochannel would make a good balance between in the resistance and the ion selectivity of nanochannel, and then lead to a high output power density.[26]

Table 1 Maximum power density of different energy harvesting systems

<table>
<thead>
<tr>
<th>Authors</th>
<th>Nanochannel/nanopore type</th>
<th>Length/Thickness</th>
<th>Power density(W/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guo et al. (2010)[13]</td>
<td>Track-etched conical nanopore in polyimide membrane</td>
<td>12 μm</td>
<td>20-2600 (C$<em>{max}$/C$</em>{min}$=1000)</td>
</tr>
<tr>
<td>Ouyang et al. (2013)[21]</td>
<td>Silicon nanochannels formed by packed nanoparticles</td>
<td>50 μm</td>
<td>2.820 (C$<em>{max}$/C$</em>{min}$=1000)</td>
</tr>
<tr>
<td>Chang et al. (2016)[18]</td>
<td>Paper based capillary</td>
<td>36 mm</td>
<td>0.003 (C$<em>{max}$/C$</em>{min}$=1000)</td>
</tr>
<tr>
<td>Kim et al. (2013)[45]</td>
<td>Anodic alumina nanopores</td>
<td>60 μm</td>
<td>0.007 (C$<em>{max}$/C$</em>{min}$=10)</td>
</tr>
<tr>
<td>Ji et al. (2016)[46]</td>
<td>Nanochannels in graphene oxide</td>
<td>0.5 - 100 μm</td>
<td>0.770 (C$<em>{max}$/C$</em>{min}$=50)</td>
</tr>
<tr>
<td>Kim et al. (2010)[15]</td>
<td>Silica nanochannels</td>
<td>0.14 mm</td>
<td>7.700 (C$<em>{max}$/C$</em>{min}$=1000)</td>
</tr>
<tr>
<td>Present study</td>
<td>Silica nanochannel</td>
<td>715 nm</td>
<td>705 (C$<em>{max}$/C$</em>{min}$=1000)</td>
</tr>
</tbody>
</table>

4. Conclusion

In summary, we have demonstrated a nanofluidic power generator based on a CMOS compatible nanochannel that can efficiently convert Gibbs free energy to electrical one by exploiting the ion-concentration gradient effect.
The output power density generated in our experiments has reached 705 W/m², which was about 2 orders larger than that obtained with similar nanochannel materials. The substantial enhancement of energy harvesting efficiency has been attributed majorly to the optimized channel length of SiO₂ nanochannel. The physical mechanism has been illustrated as that a long channel results in increased ion selectivity and meanwhile smaller electrical conductance. The former benefits while the latter reduces the energy converting efficiency. A short channel would do the opposite. Thus we have demonstrated through our experiments that nanochannels with appropriate lengths would make the nice trade-off and achieve significantly enhanced energy converting. From a perspective of potential application, our work may provide guidance to the design of high-performance nanofluidic power source supplying energy for micro/nanoscale-sized devices.

Acknowledgments

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