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A method of producing electrokinetic power through forward osmosis

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A power generation method for harvesting renewable energy from salinity gradient is proposed. The principle of the proposed method encompasses forward osmosis (FO) and electrokinetic phenomena. With the salinity difference between draw and feed solutions, FO allows spontaneous water flow across a semi-permeable membrane. The flow of water is then directed through a porous medium where the electric power is generated from the electrokinetic streaming potential. With a glass porous medium and a commercial flat sheet FO membrane in a batch mode configuration, our lab scale experimental system has demonstrated the produced electrokinetic voltages of about several hundreds of milli-volts. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4756903>]

To mitigate energy shortage and environment related issues has prompted demands for the production of electricity from renewable sources. Harvesting of electrokinetic (EK) energy has drawn much attention because its conversion process does not produce any carbon dioxide.¹ Numerous studies have focused on generating electrokinetic currents by forcing water to flow through porous materials.^{2,3} Others have concentrated on electrokinetic properties of single well-defined channels.⁴ Due to the low thermodynamic efficiency, the main effort of the research in the field is to improve the energy conversion efficiency both theoretically⁵ and experimentally.⁶ As the electricity in terms of streaming potential is produced from a hydrostatic pressure driven fluidic system via electrokinetic phenomena,⁷ a question naturally arises—where does such hydrostatic pressure source come from? Furthermore, hitherto both theoretical and experimental studies have reported that efficient energy conversion may be achieved in the electric double layer (EDL) overlap regime which usually occurs in the context of submicro- and nano-fluidic systems. However, to drive water flow in such submicro- and nano-fluidic channels, high external pressure source will be expected. To address these issues, here we present a method to produce electrokinetic power by using salinity gradient driven forward osmotic flow. To demonstrate the proposed power generation method, an experimental system was developed. Specifically, we investigated the characteristics of the forward osmosis (FO) induced water flux, the generated EK streaming potential, and the power density. Without need of any physical external pressure source, the system was able to produce the electrokinetic voltage of about several hundreds of milli-volts at very low flow rates of merely several millilitres per minute. The flow induced streaming potential has the same order of magnitude as the open-circuit voltage produced by a single unit of fuel cell. In analogy to fuel cell technology, we thus would coin the proposed method, an electrokinetic-forward osmosis cell (EKFOC) technique.⁸

A schematic diagram of the EKFOC power generation within a single micro-channel is presented in Figure 1. EK power generation only needs micro-channel, electrolyte solution, and pressure gradient to work. The physics behind is that when an electrolyte is in contact with micro-channel, charge separation occurs at the proximity of the channel wall surface and causes redistribution of ions, leading to the formation of an EDL.⁹ EDL comprises an immobile inner layer (stern layer) and a mobile outer layer (diffuse layer). Ions in the stern layer are strongly attracted to the charged channel wall surface, while those in the diffuse layer are free to move. When coupled with hydrodynamic pressure driven flow, net amount of counter ions will be streamed towards lower pressure end of the channel. Consequently, accumulation of the counter ions at the lower pressure end of the channel will lead to the generation of a potential known as the streaming potential, and the corresponding flow of ions will generate an electric current known as the streaming current. With both streaming potential and current, electrokinetic power is produced. Albeit the low thermodynamic efficiency is recognized as major hurdle in EK power generation, yet the implementation of FO for generating pressure source to drive electrolyte across the micro-channel could address this

FIG. 1. Schematic illustration of the proposed electrokinetic-forward osmosis cell method for power generation within a single micro-channel. Forward osmosis driven flow is utilized to produce streaming potential due to the accumulation of net amount of counter ions at the downstream end of the channel, and the streaming potential is detected by a pair of electrodes.

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lack and also offset much of the energy requirement. On the other hand, FO is a natural phenomenon where water can be spontaneously transported from a dilute feed solution towards a concentrated draw solution separated by a semi-permeable FO membrane. Herein, the osmotic pressure gradient generated by the concentration difference is the driving force for such water transport. Based on the afore-described concepts, a lab scale experimental system in a batch mode configuration with integration of the EK and FO parts was constructed for demonstrating the proposed power generation method (see Section S1 in the supplementary material¹⁰). The readily available glass based porous medium was employed in the EK part, and it can be treated as an array of micro-channels connected in parallel. The utilization of such porous medium not only can avoid the complex and costly sophisticated micro-fabrication processes but also can reduce total resistance and thus obtain much larger electrical current (see Section S2 in the supplementary material¹⁰). In addition, the EK part is arranged in direct connection with the feed side of the FO part to take advantage of the water transport mechanism generated by FO. A commercial membrane made of cellulose triacetate was employed in the FO part. A pair of Ag/AgCl electrodes (in meshed type) was placed at both sides of the porous medium as a current collector and also as a mean to characterize the power performance. In our experiments, the feed solution is DI water, and the draw solutions are NaCl solutions with molar concentration from 0.5 M (as seawater) to 4 M. Such a wide range of draw concentrations was chosen in order to examine the osmotic pressure effect on the performance of power generation.

In the EK part, an analytical formula based on the capillary model provides a relationship among the total volumetric flow rate Q , the pressure difference ΔP across the porous medium, and the streaming potential $\Delta\phi$ as follows:

$$Q = \frac{\varphi}{\tau} \left\{ \frac{A_{pm} a^2}{8\mu L} (\Delta P) - \frac{A_{pm} \varepsilon \zeta}{\mu L} \left[1 - \frac{2 I_1(\kappa a)}{\kappa a I_0(\kappa a)} \right] (\Delta\phi) \right\}, \quad (1)$$

where a is the average pore size, A_{pm} is the surface area of porous medium, ε is the solution permittivity, μ is the electrolyte viscosity, L is the length of the porous pore channel (or the thickness of the porous medium), I_0 and I_1 are the modified Bessel functions of the first kind of zeroth and first order, respectively, ζ is the pore zeta potential that characterizes the strength of EDL, and κ is the inverse of EDL thickness. In addition, Eq. (1) includes structural properties of the porous medium in terms of the porosity φ and tortuosity τ . These two characteristic parameters determine (i) the number of equivalent pore channels per unit area of porous medium and (ii) the effective flow path across the porous medium, respectively. In Eq. (1), the first term on the right-hand side represents the pressure driven flow derived from FO, and the second term is due to the streaming potential induced electro-osmotic flow¹¹ in the opposite direction to the pressure driven flow. Meanwhile, the streaming potential at the steady state is related to the pressure difference by³

$$\Delta\phi = \frac{\varepsilon \zeta}{\mu \lambda_f} \Delta P, \quad (2)$$

where λ_f is the electrolyte conductivity. In the experiments, we used only the DI water [$1 \mu\text{S}/\text{cm}$] as the electrolyte flowing across the porous medium since it is connected to the feed side of the FO part. The surface charging condition of the porous medium plays a crucial role in the power generation performance of the EKFOC. With a higher zeta potential, a larger net amount of counter ions migrate towards the downstream end of the channel, thereby resulting in a higher streaming potential.¹¹

In the FO part, a semi-empirical model is used for describing the water flux across a FO membrane with consideration of the concentration polarization effect (shown in the exponential terms of the numerator for modifying the osmotic pressures in bulk phases) and the reverse draw solute permeation effect¹² (shown in the denominator). The model is expressed as¹³

$$J_w = A \left(\frac{\pi_{d,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{f,b} \exp\left(\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} [\exp\left(\frac{J_w S}{D}\right) - 1]} - \Delta P \right), \quad (3)$$

where k denotes the mass transfer coefficient (which is related to the concentration distribution at the membrane-solution interface), D is the diffusivity of solute ions, A and B are, respectively, the water and salt permeability constants, S is the structural parameter of the membrane known as the membrane effective thickness, π is the osmotic pressure (which can be estimated by van't Hoff theorem as $\pi = 2RTc$,¹⁴ where R is the gas constant, T is the absolute temperature, and c is the solution concentration) with subscripts d, f, and b representing the draw solution, feed solution, and bulk phase, respectively, and ΔP is the pressure difference induced by FO due to the flow resistance across the porous medium. Furthermore, the water flow rate across the porous medium is equal to that across the semi-permeable membrane, and thus we have

$$Q = J_w A_m, \quad (4)$$

where A_m is the surface area of the semi-permeable membrane. Evidently, Eqs. (1)–(4) form a closed formulation of our EKFOC. With given bulk osmotic pressures in draw and feed sides, i.e., $\pi_{d,b}$ and $\pi_{f,b}$ (equivalent to bulk salt concentrations), one can readily obtain four unknowns (ΔP , $\Delta\phi$, Q , J_w) from the model.

Figure 2(a) shows the results of water flux and flow rate produced by various concentration differences and osmotic pressure differences. In the figure, the water fluxes generated by FO without inclusion of the EK part (i.e., the porous medium) are provided as baseline fluxes for comparison. It is obvious that the fluxes with the presence of the porous medium are much lower compared to the baseline fluxes. The reduction in fluxes is attributed to the building up of pressure gradient for driving water to flow across the porous medium. Another noticeable observation is that the experimental flux does not linearly vary with the concentration difference or osmotic pressure difference $\Delta\pi$. This scenario can be attributed to the concentration polarization effects¹⁵ which lead to significant reduction in the effective osmotic pressure difference across the FO membrane. More specifically, the concentration polarization effects result from two reasons: (i)

FIG. 2. (a) FO induced water flux and flow rate versus concentration difference and osmotic pressure difference between draw solution and feed solution. (b) Streaming potential as a function of FO induced pressure difference and flow rate. (c) Power density of EKFOC as a function of FO induced pressure difference and flow rate (LMH = liter/m² h. In calculation $A = 2.2 \times 10^{-12}$ m/Pa s, $B = 1 \times 10^{-7}$ m/s, $S = 625$ μm , $R_{\text{int}} = 0.5$ M Ω , $a = 6.5$ μm , $\phi/\tau = 0.03$, $A_m/A_{pm} = 58$, $\zeta = -100$ mV, and k is a function of concentration difference determined by experimental flux).

draw solution in contact with the membrane layer is gradually diluted by the permeated water flux from the feed side, giving rise to a decrease in the osmotic pressure of draw side; (ii) leakage of salt from the draw side to the feed side can increase the osmotic pressure of feed side. Overall, the modeling results are able to predict the experimental results reasonably.

Figure 2(b) shows the experimental results of the streaming potential against the FO flow induced pressure difference and equivalent volumetric flow rate. The experimental results indicate a linear relationship between the streaming potential and the induced pressure difference (or the equivalent volumetric flow rate), which also favorably agrees with the model prediction as shown in Eq. (2). The results have shown that our system can produce electrical voltages within the same order of magnitude as those produced by one unit of typical fuel cell (several hundreds of milli-volts), and much higher than those generated by flowing water through carbon nano-tubes¹⁶ and over graphene¹⁷ (several tens of milli-volts).

An estimation of the power density versus FO flow induced pressure difference and equivalent flow rate is presented in Figure 2(c). The maximum power generated in EKFOC is equal to the square of streaming potential over total resistance (see Eq. (S4) in the supplementary material¹⁰). Since the pore channels in the porous medium are considered to be connected in parallel, the total resistance is inversely proportional to the number of channels (see Eq. (S7) in the supplementary material¹⁰). For every unit area of the porous medium, the total resistance is estimated to be in the order of $10^1 \Omega$. Since the streaming potential is linearly related to the FO flow induced pressure difference or flow rate, a quadratic relationship between power density and FO flow induced pressure difference (or flow rate) is expected. This figure also indicates that the EKFOC performs better under the condition of higher water flux which requires FO membrane to have both good water permeability and superior solute selectivity. In this respect, tackling concentration polarization and salt leakage effects as mentioned earlier can lead to better power performance. Besides, the power performance can be further enhanced if an optimized EK porous medium is incorporated with both geometric structure and surface properties. Hence, apart from identifying a suitable semi-permeable FO membrane there is also imperative need to search for better materials of porous medium to improve the power performance.

In conclusion, we have demonstrated our proposed method of electrokinetic power production with utilization of the forward osmotic flow induced by salinity gradients. With our experimental system, we have obtained the electrical voltages in the same order of magnitude as those produced by one unit of typical fuel cell and much higher than those generated when water flows through carbon nano-tubes and over graphene. Having features of working in extremely low pressure environment, simple and compact configuration with no mechanical moving parts, and no involvement of sophisticated auxiliary equipments, this method could potentially be utilized as a feasible and sustainable mean to harvest enormous amount of renewable energy from salinity gradient. Other than abundant natural sources (e.g., sea water), salinity gradients can also be readily available from industrial sources, such as brackish water and concentrated brine discharged from desalination plants (disposal of these usually poses environmental problems). Hence this proposed method can be further extended to alleviate environmental problems associated with the desalination waste.

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