Electrokinetic power generation driven by forward osmosis

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Electrokinetic Power Generation Driven By Forward Osmosis

By

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Abstract

In this project, an unprecedented technique by leveraging the synergy of forward osmosis (FO) and electrokinetic (EK) phenomena for generating direct electricity (or power interchangeably) is developed and thoroughly studied. The source of the energy comes from the chemical potential difference between a pair of solutions of different concentration. To harvest the enormous source from nature, salinity gradient presented between fresh river and seawater is identified as the targeted source which leads to conceiving the concept of FO-EK energy harvesting technique from salinity gradient. In this concept of power generation, direct electricity is electrokinetically generated in the forms of streaming potential and streaming current with the much required hydrodynamic flows generated by the FO process. Both EK and FO are classified as interfacial phenomena and do not contain any mechanical moving parts in the system. In addition, the extra pumping requirement is excluded and replaced by FO process to avoid involvement of sophisticated machineries. Apparently, the entire power generation process is emission free without any pollution to the environment i.e. a sustainable technology.

Comprehensive and extensive experimental studies are carried out to demonstrate the proposed technique and the functionality of the proposed FO-EK energy harvesting method. A specially designed prototype system is fabricated for this purpose which includes two separate units of *FO flow generator* and *EK power generator* in modular form. In conjunction, a theoretical framework on the basis of Onsager reciprocal relationship and osmotic transport across semi-permeable membrane with consideration of concentration polarization effects is developed to aid in the modelling of the FO-EK processes. With this model, the theoretical interrelationship that

connects FO and EK is established. Overall, the model predictions can fit the experimental measurements reasonably well.

It is identified from the experimental studies that FO semi-permeable membrane (for the FO flow generator) and the porous media (for the EK power generator) are critical components for determining the overall power performance of the FO-EK system. Nonetheless, membranes are generally susceptible to concentration polarization effects. Therefore, two methods are proposed to mitigate this aspect by physical and chemical means. First, piezoelectric zirconate titanate (PZT) attachment is adopted to generate physical vibration on the membrane-solution interface to enhance mixing and break down polarization layer. Second, surface additive treatment is used by zwitterionic additive dimethylethylammoniumpropane sulfonate (DMAPS) to introduce hydrophilic moieties onto membrane surface to provide better wetting for facilitating water transport across the membrane. Both methods are successful in achieving positive results in terms of better water flux performance at certain optimum conditions in comparison with the baseline flux.

On the other hand, it is identified that the porous media incorporated should possess the characteristics of high zeta potentials as well as surface charge density. In addition, slip with hydrophobic surface would also enhance the transport of ions/charges across the microchannel for generating higher specific power (power per unit pressure). Slip enables the reduction in pressure resistance created by FO and leads to the improvement of overall energy conversion efficiency. Similarly, surfactant additive treatment method is employed to modify the channel surface to attain these characteristics by using anionic additive sodium dodecyl sulphate (SDS).

Results obtained are consistent with the proposed mechanism and the increments in performance are substantial. Uniquely in this project, the EK power generators are stacked up according to the analogy of electrical circuit where multiple units of EK power generators are connected in series and in parallel electrically. Multi-fold of streaming potential and streaming current are achieved over a single unit EK power generator where the induced pressure difference is kept at minimal. With this unparalleled scalability, the power generating capacity is scalable which can be regulated and sized accordingly depending on the actual power demand. Furthermore, an economic assessment of a large scale power plant (in the order of MW) is also performed. It is found that the energy cost produced by FO-EK technique is competitive with other renewable resources. It is foreseen that this technique could potentially lead to the realization and development into commercial applications with the modular design configuration.

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“Success is a journey, not a destination. The doing is often more important than the outcome”

-Arthur Ashe

Nomenclature

a	Microchannel/capillary radius	(m)
A	Water permeability constant	(m/s.Pa)
A_c	Cross-sectional area of channel	(m ²)
A_e	Effective area of the porous medium	(m ²)
B	Salt permeability constant	(m/s)
C	Molar concentration of salt	(M)
d_h	Hydraulic diameter	(m)
D	Solute Diffusion coefficient	(m ² /s)
e	Elementary charge	(Coulombs)
F	Faraday constant	(C V ⁻¹)
G	Hydrodynamic conductance	
I_c	Conduction current	(Ampere)
I_s	Streaming current	(Ampere)
I_0	Zero-order modified Bessel function	
I_1	First-order modified Bessel function	
J_w	Water flux	(m/s)
J_s	Salt flux	(kg/m ² s)
k_B	Boltzmann constant, (J K ⁻¹)	
k	Mass transfer coefficient	(m/s)
K_c	Mean mass transfer coefficient	(m/s)
K	Solute resistivity for diffusion	(s/m)
L	Length of the capillary/Channel	(m)

L_e	Effective length of the equivalent capillary of the porous glass disk (m)	
m	Ionic mobility	
M	Streaming conductance (electro-osmotic flow)	
n	Ionic number concentration	(1/m ³)
N	Total number of the equivalent capillaries/microchannels in a porous medium	
M	Molarity	(mol/m ³)
P	Hydraulic perimeter	(m)
ΔP	Hydrostatic pressure difference	(Pa)
q	Flow rate across a single unit channel	(m ³ s ⁻¹)
Q	Total volumetric flow rate	(m ³ s ⁻¹)
R	Universal gas constant	(J K ⁻¹ mol ⁻¹)
R_T	Channel total resistance	(Ohm)
R_e	Reynolds number	
Sh	Sherwood Number	
Sc	Schmidt Number	
S	Structure factor (m)/Electrical Conductance	
t	Thickness	(m)
T	Temperature	(K)
$\forall$	Total volume of the porous glass media	(m ³)
$\forall_e$	Void volume of the porous glass media	(m ³)
z	Cation/anion charge or valence	
Z	Figure of merit	

Greek symbols

π	Osmotic pressure	(Pa)
i	Van't Hoff factor	
ε_m	Porosity of membrane	
ε_0	Permittivity of vacuum or free space	(C m ⁻¹ V ⁻¹)
ε_r	Relative permittivity or dielectric constant	
ζ	Zeta potential	(V)
μ	Fluid viscosity	(kg m ⁻¹ s ⁻¹) or (Pa.s)
κ	Debye-Huckel parameter or inverse of the EDL thickness (m ⁻¹)	
λ	Debye length or EDL thickness or $\frac{1}{\kappa}$	(m)
λ_f	Fluid or bulk conductivity	(S m ⁻¹)
λ_s	Surface or Stern layer conductivity	(S)
ρ_e	Free or net charge density	(C m ⁻³)
η	Electrokinetic energy conversion efficiency	
σ	Membrane Reflection coefficient	
σ_{sc}	Surface charge density	
τ	Tortuosity	
φ	Porosity	
ψ_s	Surface potential	(V)
$\Delta\phi$	Streaming potential	(V)
$\Delta\phi_{over}$	Over-potential	(V)

Subscripts

<i>a</i>	Anions
<i>b</i>	Solution in the bulk
<i>c</i>	Cations
<i>d</i>	Draw solution
<i>f</i>	Feed solution
<i>g</i>	Porous glass disk
<i>i</i>	Ionic species
<i>l</i>	Parameters related to the solvent of the solution
<i>m</i>	Membrane
<i>w</i>	membrane wall
<i>s</i>	Parameters related to the solute of the solution

Chapter 1 Introduction

Heavy reliance on energy produced from traditional fossil fuels has aggravated environmental problems due to the inevitable and voluminous emission of greenhouse gases such as CO₂, SO₂ and NO_x with high level of particulate matters. Together with the accelerated global development, these problems have been exacerbating in recent years. To alleviate this critical issue, rigorous research has been initiated to develop new ways to produce energy in a more environmental friendly and sustainable manner. This includes technologies developed for harvesting energy from renewable energy sources such as wind, solar and tidal wave. However, one type of renewable energy source remains largely unexploited is from the mixing of fresh and seawater. According to the Gibbs free energy of mixing theory^[1], 2.2kJ of energy is released when a liter of fresh water is flowing into the sea. This translates to an enormous amount of energy with its potential capacity estimated of about trillion watts (TW)^[2-4] which is approximately half of the current hydropower supply^[5]. Hence, the salinity gradient represents yet another promising source of renewable energy and can be harvested all year round.

At present, several methods have been established specifically for harvesting this form of clean and renewable energy through salinity gradient. Among them, two membrane based methods, reversed electrodialysis (RED)^[4, 6-8] and pressure retarded osmosis (PRO)^[5, 9-11] are regarded as the most practical and viable options due to the recent advancement as well as commercial availability of cation (anion) selective and semi-permeable membranes. Other than these two membrane based methods, other methods have been developed for harvesting energy from salinity gradient, such as the reversed capacitive deionization method^[12-14] and a similar method known as mixing entropy batteries^[15].

In RED, two specific types of membranes are required, and they are cationic exchange membrane (CEM) and anionic exchange membrane (AEM). The former is selectively permeable to cations while the latter is permeable to anions. The separation of ions produces an electrical potential between two membranes and thus can be directly applied as electrical energy. However in RED, heavy ions would be trapped and accumulated in the ion exchange membrane. At the end, not only the membrane must be treated as chemical waste but extra effort and expenses are needed for the disposal. Besides, RED requires external pumping to pump the flow over tiny channels between the pair of ion exchange membrane. Hence, this also requires some mechanical strength for the membrane and causes loss in pumping energy due to the resistance within the tiny channels. Thus, to make RED be self-sustainable, the energy produced must be sufficient for counter-balance the pumping work and other losses.

Whilst in PRO, two solutions of different salinities are separated by a semi-permeable membrane which only allows the spontaneous transport of water (but selectively retains solutes) from the low salinity side (feed solution) towards the pressurized high salinity side (draw solution). Although the draw solution is hydraulically pressurized, the osmotic pressure gradient is still high enough to drive water to transport across the membrane. However, the flow is retarded and considerably reduced due to building up of a hydraulic pressure gradient which is against the osmotic pressure gradient. The hydraulic pressure can be further built up at the draw solution side to its maximum which exactly counterbalances the osmotic pressure to stop the water transport. Subsequently, the draw solution side is then depressurized through a hydro turbine to generate power in the same fashion as a hydroelectric plant.

Essentially, PRO is a variant of osmosis or forward osmosis (FO), but FO involves zero or no externally applied pressure. Therefore, there are much less stringent requirements on membrane mechanical strength for FO process than for PRO process, because the latter requires membranes of high mechanical strength to withstand highly pressurized environment. With less pressurized environment, FO would generate higher water flux, and the issue of membrane fouling can be greatly minimized. Albeit the development of thin film composite membrane^[16, 17] that comes with substantially higher water flux and reasonable ruggedness to withstand higher operating pressure, the performance of PRO is still far from the targeted value^[18]. In addition, PRO requires sophisticate auxiliary machineries such as turbine, pressure exchanger (energy recovery device) and high pressure pumps to complement energy conversion process. All these additional requirements would then incur high capital expenditure on infrastructure and thus impede the widespread application of PRO energy harvesting from salinity gradient. In view of these inherent drawbacks of PRO, it is therefore preferably to utilize FO alone as the primary mechanism for generating power.

In addition, electrokinetic (EK) power^[19] resulted from flow induced streaming potential and streaming current has drawn much attention with its power generating capability that does not produce any carbon dioxide^[20] and comprises no mechanical moving parts. The electrokinetic power is generated simply by forcing water to flow through some form of dielectric channels in micro or nano meter range. Numerous studies have attempted on generating electrokinetic power using porous materials^[21-23] while others have concentrated on studying the electrokinetic properties of single well-defined channels^[24-26]. Nonetheless, due to the inherent low thermodynamic energy conversion efficiency from hydrodynamic pressure driven flow into

electrokinetic power, the primary focus of the research in this field is still very much on the improvement of the energy conversion efficiency both theoretically^[27-30] and experimentally^[31-34]. Furthermore, 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 channel in submicro- and nano-order. However, this becomes another major drawback as even higher external pressure source is expected to meet this requirement.

To bridge this gap, a method to produce electrokinetic (EK) power driven by forward osmosis (FO) flow generated by salinity gradient is proposed in this work. This concept represents the first time a synergy combination of FO and EK phenomena for direct power generation. In practical, river or fresh water and seawater can be modeled as the feed and the draw solution, respectively. The salinity gradient can then be converted into water flow from a dilute feed solution towards a concentrated draw solution via FO processes. Then such water flow is directed to pass through microchannels where electrical power is generated due to the EK phenomena^[26, 28, 35-39]. Hence, the efficiency of this method would be high as no other form of energy input is necessary to generate power.

The primary objective of the project is to realize this concept and to prove its functionality. Hence, a bench scale prototype system consists of a FO flow generator and an EK power generator will be constructed and tested experimentally in terms of the power generating capability. For the FO flow generator, proprietary membrane made of CTA (cellulose triacetate)

developed by Hydration Technologies Innovation (HTI)^[40] will be used throughout this project. This is the first and the only commercial FO membrane currently available. It is selected specifically for this project as it achieves better flux and good salt rejection as reported in the experiments carried out by various research groups.^[41-43] Besides, EK power generator will incorporate dielectric porous media, which represent an array of microchannels, of glass and polymer polyethylene types. NaCl salt solution and DI water will be employed to simulate as the seawater and fresh river water, respectively. Characterization studies will be carried out to identify the various dominating parameters that determine power performance of this proposed method. To understand further the interrelationship between FO and EK, a theoretical model on the basis of Onsager relationship and osmotic flow process will be used to establish the theoretical connection between them. Hence this would permit to gain insights of the importance of each parameter to the contributions of actual experimental results

Apart from the above mentioned works, it is found that substantial reduction of water flux due to the severe concentration polarization^[44-46], has limited the usage of FO. In a more complicated situation, it may worsen the membrane performance further through fouling. Therefore, it is crucial to come out with innovative approach for improving the FO water flux performance which in turn will be beneficial for the EK power performance. Besides, the inherent low energy conversion efficiency of EK^[47] is also another important aspect need to be addressed.

As such, the objectives of the second part of this project would focus on devising practical methods to further enhance and optimize the overall power performance. Both chemical and physical means will be studied to examine on the FO membranes (flow generator) and the porous media (power generator) separately to meet these objectives. The proposed methods include:

1. Enhancement of water transport across membrane by piezoelectric zirconate titanate (PZT) induced surface vibration
2. Modification of membrane surface properties with zwitterionic surfactant additives - Dimethylethylammoniumpropane sulfonate (DMAPS)
3. Modification of porous media channel surface properties with anionic surfactant additives – Sodium Dodecyl Sulfate (SDS)

PZT is a ceramic perovskite material that composes of the chemical elements lead and zirconium and the chemical compound titanate; these inorganic chemicals are combined under extremely high temperatures. In this project, *reverse piezoelectric effect* will be employed where stress and strain are generated when an electric field is applied under oscillating frequency. As such, PZT will undergo a shape change that forms vibrating mechanism. Physically, vibrating signal with frequencies ranging from the order of 100Hz to kHz is applicable to PZT element. With the vibrating feature integrated onto membrane surface, it could potentially reduce the concentration polarization effects.

Relevant studies ^[48-50] have employed the idea of mechanical vibration to reduce fouling. It works as an added component or feature onto a membrane surface without complex surface treatment or chemical process. As such it is possible to apply this method on all kinds of flat sheet membranes at a convenience way. This method is expected to generate shear flow near the membrane-solution interface and thus to break down the external concentration polarization barrier potentially. Similarly, in the porous support layer of asymmetric membrane, solutes or ions may be adsorbed to the inner wall or block the pores, leading to declination in permeation flux. Hence, with the vibrating oscillation at relatively high speed, solute particles may shake off from the pore wall and therefore mitigate the pore blocking effect. Furthermore, it may enhance mass transfer of water molecule across membranes and consequently improve water flux transport. Determination of optimum frequency, size, and number units of PZT shall be carried out to maximize its performance.

Chemically, this project utilizes an additive of a special class of *zwitterionic* surfactant known as DMAPS ^[51]. DMAPS is polar and highly soluble in water even at high molarity. It can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the solvent or buffer. It is also compatible with all other classes of surfactants and is easily soluble even in the presence of concentrated electrolytes, acids and alkalis ^[52]. Therefore, zwitterionic is compatible with the electrolytes NaCl draw solution that would be employed throughout the FO experiments in this project.

Uniquely in this project, zwitterionic additive is mixed with DI water to form the treatment solution. Membranes are then treated with the zwitterionic solution. With surface treatment process taken place, it could potentially improve hydrophilicity and wetting of membranes. Thus far, no report has been documented on the effect of zwitterionic additive surface treatment or coating on FO membranes. By comparison, zwitterionic especially that containing phosphorylcholine and sulfobetaine groups have been used extensively as a surface modifying agent copolymer in ultrafiltration (UF) membranes. The zwitterionic copolymer membranes are blended with common polymeric materials, such as polyethersulfone, polyacrylonitrile, cellulose acetate etc. by the common *phase inversion method* in a water bath. Such surface graft polymerization improves membrane hydrophilicity and anti-fouling capability^[53-59]. Hence, the direct addition of zwitterionic additive eliminates the complexity of casting new membranes and avoids complicated chemical processes. This significantly reduces the time consumption and is a relatively simple method to implement. In anticipation, hydrophilicity (in relation to surface charges or zeta potential) may be altered under the influence of the additive. Thus, study of the effect of zwitterionic additive shall be carried out systematically to determine its influence on the water flux performance of FO.

For ease of implementation, the direct chemical treatment method with anionic additive sodium dodecyl sulfate (SDS) is extended to modify the surface properties of porous media. SDS surfactant is chosen for this study as it has been used previously for modifying silica^[60] as well as ceramic surface^[61] which is coherent to the dielectric type porous media employed in this study. Moreover, it was found that application of SDS can modify the zeta potential of a particle

suspension^[62] . This has shown the potential of applying SDS for enhancing the EK power performance. The detailed studies on the effects of PZT attachment, zwitterionic DMAPS and anionic SDS additive will provide insightful information of the respective mechanisms influencing the overall EK power performance driven by FO.

Chapter 2 Literature Review

This chapter consists of two parts to review distinct subjects of Forward Osmosis (FO) and Electrokinetic (EK). The basic principles and development of respective phenomenon are introduced. Technological research studies associated with these principles are discussed and presented in the following sections. Subsequently an intriguing niche area is identified by hybridizing between these two principles, leading to a novel state of the art technique for energy harvesting from salinity gradient.

Part A: Forward Osmosis (FO)

This section reviews past and current research works on Forward Osmosis (FO). An introduction on FO and other closely related processes such as pressure retarded osmosis (PRO) and reverse osmosis (RO) are elaborated and discussed. Next, the basic components i.e. draw and feed solutions, semi-permeable membrane, that make up of a functional FO processes are presented. Subsequently, the main bottleneck in the development of FO i.e. concentration polarization is reviewed through investigations carried out by various research groups. A summary of the current major obstacles in FO is presented. Niche areas for FO are identified to address the major obstacles. Then, it is followed by a review of the related studies that have been carried out in this area. Finally, based on the literature review, the major framework is identified, that is to focus on the enhancement of water flux performance in FO.

2.1 Basic Principle of Forward Osmosis (FO)

In general, FO refers to the transport of water molecules through a selectively permeable membrane driven by osmotic pressure gradient across the membrane. In another words, water moves from a region of higher water chemical potential (low concentration) to a region of lower water chemical potential (high concentration). Primarily, the driving force is the difference in solute concentrations across the membrane that allows passage of water, but rejects most solute and ions. Essentially, FO is also regarded as direct osmosis.

Physically, osmotic pressure (π) can be described as the pressure which, if applied to the more concentrated solution on one side of the membrane, would prevent transport of water across the membrane. Through van't Hoff theorem^[63], the osmotic pressure (in atm) can be estimated by equation below as:

$$\pi = iMRT \quad 2.1$$

where i is known as van't Hoff factor, M is the molarity, R is the gas constant ($0.0836 \text{ L.atm/mol.K}$), and T is the temperature in Kelvin.

FO uses the osmotic pressure differential (solely chemical gradient) across the membrane rather than hydraulic pressure differential as in reverse osmosis (RO), as the principle driving force for the transport of water through membrane (Refer to the schematic diagram as shown in Figure 2.1) low concentration solution (or feed solution) and high concentration solution (or draw solution)

are separated by a semi-permeable membrane. The concentration difference of the solution can produce an osmotic pressure difference that will draw water from the feed solution side to the draw solution side of the membrane. It is a simple and direct process driven purely by concentration difference across the membrane. If an increasing pressure is applied to the draw solution side, the magnitude of water flow will decrease until no flow occurs such that the exerted pressure will be equivalent to the osmotic pressure difference across the membrane.

Figure 2.1 Schematic diagram of osmosis processes^[46].

There are two closely related processes which are pressure retarded osmosis (PRO) and reverse osmosis (RO). In PRO, it can be viewed as an intermediate process between FO and RO, where a hydraulic pressure is applied in opposite direction of the osmotic pressure gradient. However, the main disparity is that the applied pressure shall not be greater than the osmotic pressure difference to be deemed as PRO. Distinctly, PRO is also different from RO as the net water flux is still in the direction towards the concentrated draw solution as in FO.

Figure 2.2 Direction and magnitude of flux as a function of applied pressure in forward osmosis (FO), pressure retarded osmosis (PRO) and reverse osmosis (RO). Figure adopted from^[11]

Whereas in RO, the hydraulic pressure applied to the draw solution is greater than the osmotic pressure difference across the membrane. In this case, there is net flow of water from the draw side to the feed side of the membrane. Figure 2.2 shows the relationship and direction of water flow among the three different osmotic processes.

Overall, the water flux transport in FO, RO and PRO regimes is described by

$$J_w = A\sigma(\Delta\pi - \Delta P) \quad 2.2$$

where A is the water permeability constant. σ is the reflection coefficient which is also known as the Staverman reflection coefficient^[64]. It can be referred to as the ratio of the effective

osmotic pressure to the actual osmotic pressure when $J_w = 0$. Hence, in practical FO process, reflection coefficient is always less than unity as there is leakage of solutes from one side of the membrane to the other that causes the osmotic pressure to vary. $\Delta\pi$ and ΔP are the osmotic pressure difference and the applied hydraulic pressure difference, respectively.

2.2 Draw Solutions

It is the source of the driving force in FO processes. Different terms are employed in the literature to name this solution that includes draw solution, osmotic agent, osmotic media, driving solution, osmotic engine, sample solution etc.. However, draw solution is the most widely used term as it is more appropriate to describe the osmosis phenomenon where apparently water is drawn from the feed to the draw side. An effective draw solution should be of high osmotic pressure so that higher driving force can be generated and thus eventually higher water flux. Referred to Equation 2.1, the osmotic pressure of draw solution is proportional to the van't Hoff factor i , molarity M and temperature T . Hence, by increasing these factors, higher osmotic pressure could be generated.

Literature reviewed shows that seawater, Dead Sea water and Salt Lake water^[65-67] have all been used or considered as the source for draw solutions in various investigations associated with FO and PRO. Various other chemicals have also been suggested and tested as solutes for draw solutions. For example, sulphur dioxide was suggested by Batchelder^[68] in FO desalination of seawater. Glew^[69] also suggested using mixture of water and another gas (e.g. sulphur dioxide)

or liquid (e.g. aliphatic alcohols) as draw solution. Significantly, Glew was also the first researcher who proposed the recycling of draw solution in conjunction with FO. Frank^[70] used aluminum sulfate solution. Kravath and Davis^[71] used a glucose solution. Kessler and Moody^[72] used mixed solution of glucose and fructose for seawater desalination. Stache^[73] used a fructose concentrated solution to create a nutritious drink during FO of seawater. McGinnis^[74] suggested solutions of potassium nitrate and sulphur dioxide as draw solutions for seawater desalination. Significantly, McCutcheon et al^[41, 75] demonstrated a novel method which combines ammonia and carbon dioxide gases in a specific ratio to create highly concentrated draw solution. Furthermore, it can easily be thermally decomposed into gases form and to be recycled at merely 60°C. The osmotic pressure was claimed to be in excess of 250atm which allows high recoveries of potable water and substantial reduction in concentrated brine discharges. In turns, this could potentially overcome environmental issues associated with discharged brines from conventional thermal seawater desalination plants. However, it was found that this draw solution is unstable as it is decomposed even before its temperature reaches 60°C^[42]. Thus, rigorous research effort is then required to develop a viable draw solution for wide spread application of FO especially in the context of seawater desalination. Nonetheless, an ideal draw solution should possess the following characteristics:

- 1) High osmotic efficiency i.e. highly soluble with low molecular weight that would allow for generating higher osmotic pressure;
- 2) Non-toxic ;
- 3) Amiable and compatible with membrane so that it will not degrade or deteriorate the membrane due to chemical incompatibility ; and
- 4) Easy and economic separation and recycling of draw solutes.

Intriguingly, with the advance of nanotechnology, naturally non-toxic magnetoferritin^[76-78] has been tested as a potential candidate for draw solute which can be rapidly separated from aqueous stream by applying a magnetic field. This provides an alternative to conventional separation methods such as thermal evaporation, precipitation and adsorption methods.

2.3 Membranes in FO

Generally, membranes can be categorized into two types, (1) symmetrical or isotropic membranes, and (2) asymmetrical or anisotropic membranes. Asymmetrical membranes have heterogeneous morphology which means they are made up of two or more materials in composite form. Whereas symmetrical membranes are made from single material and have homogeneous morphology. Physically, asymmetrical membranes consist of an extremely thin surface layer backed by a thicker porous support layer or substructure. The effective separation is controlled by the surface layer, where the substructure functions as a mechanical support. Figure 2.3 illustrates the morphology difference between a symmetrical or isotropic and an asymmetrical or anisotropic membrane.

2.3.1 Isotropic Membrane

Generally for isotropic membrane, it includes two types namely the microporous and nonporous dense type membrane. Structurally, the microporous membrane has a rigid, highly voided, randomly distributed and interconnected pores. The pore size is in the order of 0.01 to 10 μm in diameter. Particles are being rejected by the membrane depending on the pore size of the membrane. Practically, the separation of particles or solutes by microporous membranes is

mainly a function of particle molecular size and pore size distribution. In general, only molecules that differ considerably in size can be separated effectively by microporous membranes, and it can be classified into ultrafiltration and microfiltration range depends on membrane pore size. As for nonporous dense membrane, it consists of a single layer homogenous dense selective film through which permeants are transported by diffusion under the driving force such as pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material.

2.3.2 Anisotropic Membrane

Practically, membrane should be as thin as possible for achieving good transport rate. However, conventional film fabrication technology limits manufacture of mechanically strong, defect-free films to only about 20 μm thickness. Thus, recent development and advancement in novel membrane fabrication techniques has resulted in producing anisotropic membrane structures. This is considered one of the major breakthroughs of membrane technology during the past 30 years. Anisotropic membranes consist of an extremely thin surface layer supported on a much thicker, porous substructure. The surface layer and its substructure may be formed in a single operation or separately. In composite membranes, the layers are usually made from different polymers. The separation properties and permeation rates of the membrane is determined exclusively by the surface selective layer; the substructure functions as a mechanical support. The advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial processes use such membranes.

Figure 2.3 Schematic of general types of membranes^[46] with a) symmetrical or isotropic and b) asymmetrical or anisotropic morphology.

Semi-permeable membranes, made up of any dense non-porous selectively permeable material, could be used for FO. FO membranes employed a solution-diffusion model ^[46, 79, 80] in which permeants dissolve in the membrane material and then diffuse through membrane along a concentration gradient. The permeants are separated because of the difference in solubility of the materials in the membrane and the difference in the rates at which the permeants diffuse through the membrane. It is different from the pore-flow model (filtration model) in which permeants is transported by pressure driven convective flow through tiny pores. Separation is achieved as permeants are excluded by difference in size. These transport mechanisms are illustrated in Figure 2.4.

Figure 2.4 Illustration of molecular transport through a membrane by (a) pore-flow model and (b) solution-diffusion model^[46].

Early researchers had experimented various type of membrane materials for instances bladders of pigs, cattle, collodion, rubber, porcelain, goldbeaters' skin^[81] etc.. It was until 1960, Loeb and Sourirajan revolutionized the membrane technology by establishing the well-known Loeb-Sourirajan process^[82] to produce the first defect free, high flux, anisotropic RO membrane. This development also facilitated the progression of membrane separation technology from laboratory scale to industry level.

Various configurations of membranes are available nowadays, such as flat sheet, spiral wound, tubular (capillary or hollow fiber) as well as bag type. In most cases, flat sheet and hollow fiber membranes are commonly employed for studies due to their relatively ease of implementation.

In 1970s, researchers used mainly RO membranes in their FO studies. Votta et al.^[81] used commercially available RO membranes in wastewater treatment. Kravath and Davis^[71] used both flat sheet and hollow fiber RO membranes for desalination of seawater. Goosens and Van-Haute^[83] used cellulose acetate (CA) membrane reinforced with mineral fillers to evaluate membrane performance through FO testing. Mehta and Loeb^[84] experimented with aromatic polyamide (PA) RO membrane for their PRO study. However, much lower flux was obtained in their studies as RO membranes are not meant and suitable for FO processes. Generally, RO membranes comprise thick support layer to withstand highly pressurized environment. Hence, this sub layer could strongly reduce the water flux performance due to concentration polarization effect where water transport is restricted. Further details of concentration polarization will be elaborated in the following Section 2.4.

At present, there is only one commercial entity, known as Hydration Technologies Innovation (HTI – previously known as Osmotek Inc), has developed the commercial FO membrane. Despite this FO membrane is also asymmetrical type yet it is much thinner than conventional RO membrane with thickness measurement ranging from 50µm to 400 µm. It consist of a very fine dense selective layer of merely 1µm. Figure 2.5 shows a cross-sectional SEM image of such FO membrane. This proprietary membrane has been used successfully in commercial applications such as water purification for military, emergency relief and recreational purposes ^[40, 85, 86] .

Nonetheless, it was also used and tested by various research groups ^[81, 87-89] in different applications and studies of FO processes. By far, it generates the best performance and much superior to RO membranes in FO processes. The major contributing factors are due to:

1. It is made up of cellulose triacetate which is hydrophilic in nature.
2. It comprises of a thin support layer which has less resistance to water transport.
3. Overall thickness of the membrane is much less than that of RO membranes. It doesn't have thick porous backing as compared to RO membranes, and therefore has less severe concentration polarization effects.

**Published US Patents of the HTI proprietary FO membrane^[90] could also be found online.*

Figure 2.5 SEM pictures (taken in-house) of cross-sectional view of FO (cartridge type) membrane by HTI.

Generally, most researchers used polymeric asymmetric membranes in their studies. Common polymeric materials which have been reported in literature include cellulose acetate (CA),

cellulose triacetate (CTA), polyamide (PA), polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) etc..

Recently, Wang et al.^[91] have developed a single-layer asymmetric polybenzimidazole (PBI) nanofiltration hollow fiber membrane for FO processes. It is claimed that PBI has characteristics of unique nanofiltration properties, robust mechanical strength and excellent chemical as well as thermal stability. Furthermore, PBI membranes have also been employed in RO^[92] and utilized as an ion exchange membrane in fuel cell^[93]. Investigation on this membrane has shown high selectivity of divalent ions as its mean effective pore size is around 0.32nm in radius which is comparable to RO membrane pore size. Although this membrane shows high salt selectivity of close to 97% of NaCl, the recorded water flux was merely 3.84LMH when the osmotic pressure difference was maintained at 100atm. This is much lower flux compared to the flux produced by commercial FO membranes^[94]. Nevertheless, it is claimed as a potential candidate for FO process; however, the membrane should be further improved and optimized.

Subsequently, Yang et al.^[95] have developed an improved dual layer hollow fiber that comprises of polybenzimidazole (PBI) and polyethersulfone (PES) layers in their FO studies. Structurally, the membrane consists of an ultra-thin selective layer of 1.5μm formed by PBI and a fully porous water channels underneath a micro porous sponge like support structure of PES. Therefore, water can rapidly diffuse through this ultra-thin layer by osmotic pressure gradient. As such, this membrane can produce much better flux than its predecessor^[91] and is comparable to the water

flux produced by commercial FO membrane. Water flux of 33.8 LMH was recorded using 5M MgCl_2 as a draw solution at room temperature of 23°C and limited salt leakage of less than 1gMH. In terms of chemical stability, PBI and PES based membrane could be operated in harsh chemical environment due to its superior chemical resistance. In contrast, it was reported that commercial FO membrane which is made of cellulose triacetate (CTA) was not stable and would degrade in alkaline solutions at pH 9 ^[96]. Thus, there is still lack of a feasible FO membrane that is both chemically stable and able to produce sufficient permeation flux.

In Summary, the desirable characteristics of FO membrane would have to fulfill the following criteria:

1. Highly dense selective layer for high solute rejection and good selectivity
2. Thin membrane support layer with minimum porosity for low reduce internal concentration polarization (*ICP)
3. Hydrophilic for high water flux and low membrane fouling
4. Robust mechanical strength for sustainability and durability
5. Good chemical stability in draw and feed solutions

**To be discussed in the Section 2.4*

2.4 Concentration Polarization

In the case of FO, where no hydraulic pressure is applied, Equation 2.2 can be reduced to $J_w = A\sigma(\Delta\pi)$ (where $\Delta\pi$ denotes the bulk osmotic pressure difference between the draw

solution and the feed solution). However, various studies ^[75, 82, 84, 97] reported in the literature have found that much lower water flux was obtained than the prediction of this formula. This implies that there is a counteracting effect which reduces the bulk osmotic pressure difference considerably, and giving rise adverse effect on the net or effective osmotic pressure difference $\Delta\pi_{eff}$ that governs the water transport across the active layer of a FO membrane. Primarily, such adverse effect on water flux is attributed to the concentration polarization effects which can be divided into two categories namely:

1. External concentration polarization (ECP)
2. Internal concentration polarization (ICP).

2.4.1 External Concentration Polarization

During osmotic process, water flux is transported from the feed side to the draw side by osmotic pressure difference. When feed solution flows through the selective dense layer, solutes are retained and accumulated near the membrane wall layer. This building up of solutes at the active layer will increase the concentration as well as the osmotic pressure at the effective feed site. As such, the net osmotic pressure difference is reduced and this phenomenon is known as concentrative ECP.

Simultaneously, when water flux permeates through the dense selective layer, draw solution in contact with the dense layer is first diluted by the permeated water and reduces the draw solution concentration at this layer. Therefore, the osmotic pressure is reduced at the interface compared

to the bulk osmotic pressure. This reduction in osmotic pressure is known as dilutive ECP. Figure 2.6 (a) illustrates the effect of both concentrative and dilutive ECP across a dense selective membrane.

2.4.2 Internal Concentration Polarization

In a more common scenario, where an actual asymmetric FO membrane is employed, a more complex concentration polarization phenomenon would occur. It is known that an asymmetric membrane comprises composites of a dense selective layer and a porous support backing layer. Therefore, the orientation of the membrane i.e. dense layer facing (SL-D) draw or feed (SL-F) plays an important part in determining the type ICP that will be explained in the following.

If the dense selective layer is facing the draw solution (SL-D), also known as a PRO mode, a polarized layer will be established within the porous support backing layer as water flux flows from the feed side to the draw side. This flow brings the solute across and is confined in the pore of the porous layer. Hence, similar to concentrative ECP, concentration is built up within this porous layer and it is referred to as concentrative ICP (see Figure 2.6 (b)). Furthermore, if the dense layer is facing the feed solution (SL-F) is denoted as a FO mode, the draw solution will be in direct contact with the porous support layer of the membrane. Thus, as water permeates the selective layer, the draw solution (restricted within the porous substructure) is diluted. This is referred to as dilutive ICP and is illustrated in Figure 2.6(c).

Referred to Figure 2.6, the bulk osmotic pressure difference is relatively higher than the actual osmotic pressure difference or is denoted by effective osmotic pressure gradient $\Delta\pi_{eff}$, across the effective site of dense selective layer. As such, osmotic driving force is reduced significantly by CP effects that result in much lower water flux compared with what the basic formula has predicted. In addition, it is obvious to visualize a more severe impact from ICP, as it is inherently influenced by the membrane morphology and internal structure which can't be mitigated easily by physical mean.

Figure 2.6 Illustration of osmotic pressure profiles under different membrane configurations and orientations with consideration of both internal and external concentration polarization effects^[94] with

- (a) Symmetric dense membrane subjected to dilutive and concentrative ECP effects
- (b) Asymmetric membrane with dense selective layer facing draw solution (SL-D or PRO mode) subjected to dilutive ECP and concentrative ICP

- (c) Asymmetric membrane with dense selective layer facing feed solution (SL-F or FO normal mode) subjected to dilutive ICP and concentrative ECP.

$\pi_{d,b}$ is the bulk draw osmotic pressure, $\pi_{d,m}$ is the membrane effective osmotic pressure on the draw side, $\pi_{f,b}$ is the bulk feed osmotic pressure, and $\pi_{f,m}$ is the membrane effective osmotic pressure on the feed side.

However, from literature ^[75, 94, 98], ECP plays a minor role and thus it's not the main contribution for water flux reduction in FO process. ECP can be minimized by using counter-current flow method or cross-flow (CCF) method. Counter-current flow means that feed and draw solution flowing tangential to the membrane but in opposite direction, and it was first proposed by Loeb and Bloch^[99]. Counter-current flow method could provide constant trans-membrane pressure, thereby making the process more efficient. However, ICP cannot be mitigated by the counter-current flow method because it takes place within porous layer of a membrane. As such, solutes confined within the pores are restricted with contact to the applied hydrodynamic flow. Hence, the contribution of ICP effect to flux reduction is much more severe than that of ECP effect.

To account for the CP effects, hydrodynamic modifying factors also known as the modifying *moduli* (exponential terms) are employed in the flux equation. Hence, in PRO mode, where dilutive ECP and concentrative ICP are present, Equation 2.2 becomes

$$J_w = A[\pi_{d,b} \exp(-\frac{J_w}{k}) - \pi_{f,b} \exp(\frac{J_w S}{D}) - \Delta P] \quad 2.3$$

and similarly in FO mode, where concentrative ECP and dilutive ICP are present, Equation 2.2 becomes

$$J_w = A[\pi_{d,b} \exp(-\frac{J_w S}{D}) - \pi_{f,b} \exp(\frac{J_w}{k}) - \Delta P] \quad 2.4$$

In these exponential terms, k is the mass transfer coefficient of solute ions and is depend on the hydrodynamic conditions at both sides of the membrane-solution interface. S is the structural parameter of the porous support layer, and D is the diffusion coefficient of solutes. The structural parameter is defined as $S = t_m \tau_m / \varepsilon_m$, where t_m , τ_m and ε_m are the thickness, tortuosity and porosity of the membrane support layer, respectively. Hence, much lower flux is expected due to the polarization losses that substantially reduce the effective osmotic driving pressure across the membrane.

2.5 Niche Areas for FO

Major hurdles currently encountered by FO technologies are summarized as below:

1. Lack of specific designed FO membranes which should have the following specific features:
 - a. high water flux performance
 - b. superior rejection property
 - c. low fouling, low concentration polarization propensity
 - d. robust mechanical strength and good chemical stability

2. Lack of desirable draw solutions for which the draw solutes could be easily removed and recycled for continual process. Moreover, FO processes should consume minimal amount of energy for the recovery and separation processes.

Through review of the various studies, niche areas for FO have been identified in this project to address the major hurdles as specified above. Instead of developing better membranes and making new draw solutions, it is also possible to apply physical and chemical methods to enhance FO performance in the following aspects:

- Enhance membrane layer hydrophilicity for better water flux transport, i.e. to achieve higher mass transfer coefficient k and the solution diffusion coefficient D
- Reduce concentration polarization effects by either mechanical or chemical means

By targeting these two aspects, FO water flux performance could be enhanced so as to maximize the performance and widen the applications of FO technology.

Specifically, substances such as surfactants have been used in various studies to investigate their influence on membrane performance. Surfactants are amphiphilic substance that contain of hydrophilic as well as hydrophobic domains. Usually, a surfactant molecule consists of a hydrophilic head group to which alkyl chain of a hydrophobic hydrocarbon tail is connected. It is categorized into four groups depending on the charge of the head-group: nonionic (zero-charged), anionic (negative charged), cationic (positive charged) and zwitterionic (neutral charged). Characteristically, it tends to adsorb onto surface or assemble at interfaces so it is often

coined as surface active agent or simply surfactant. Besides, surfactant can accumulate to form large micelles at specific concentration known as the critical micelle concentration (CMC)^[52].

From literature, significant improvement in water flux was reported with membrane pre-treated with surfactants through simple contacting procedures^[100-102] such as immersing the membrane in a surfactant solution. There was also an evidence that cleaning of membrane with surfactants added in the cleaning solution produces positive effects on membrane performance as it could modify the membrane surface temporary^[103]. It was found that this membrane pre-treated with surfactant achieved enhanced water flux of 20% over untreated membrane. The surface of the treated membrane was also known to be more hydrophilic and appeared smoother. The hydrophilicity of the membrane, discussed herein, was determined by water contact angle measurement method.

However, surfactants may also adversely affect the membrane performance as they could be adsorbed in the membrane pores to increase concentration polarization^[104] and membrane resistance especially at the critical micelle concentration (CMC) of the surfactants. Jönsson and Jönsson^[101] investigated the influences of anionic, cationic and nonionic surfactants on ultrafiltration membranes. It was found that adsorption of surfactants occurred severely near the CMC point where water flux was reduced substantially. Hence the competing effect of adding surfactant to treat membrane required an optimum concentration for best performance.

For FO experiments, McCutcheon and Elimelech^[94] also added an anionic surfactant sodium dodecyl sulfate (SDS) directly into feed solutions, and the membrane support layers was orientated in a PRO mode. The concentration of SDS was kept at 1mM because at this particular concentration, surface tension of water can be reduced from 70.9 to 53.9mN/m (determined by using a Wilhelmy plate tensiometer). Sharp increase in water flux was observed upon addition of SDS in the feed solutions. It was claimed that the surfactant could provide better wetting of the support layer which subsequently improves the continuity of water across the support layer and thus facilitates water flow. The addition of SDS anionic surfactant also improved the hydrophobicity (becomes more hydrophilic) of the membrane support layer. However, flux was declined over longer period as the SDS may be retained by the active layer and accumulated at the porous support layer, which eventually block the pores and suffered internal concentration polarization (ICP). This is because further increase of SDS concentration at the interface layer may reach its CMC point where the ICP effect was exacerbated. The deterioration of water flux was due to the formation of large micelles at CMC to hinder water flow through the porous layer.

Recently, Sun et al.^[56] successfully fabricated a PAN (polyacrylonitrile)-based zwitterionic (DMMSA^{*}) blended membrane that could reduce membrane fouling, specifically protein adsorption significantly. This zwitterionic material consists of a sulfobetaine group $[-N^+(CH_2)_nSO_3^-, n = 1,2,3,4]$, which has received increasing attention as it is more effective in resisting protein adsorption than other hydrophilic groups. Contact angle measurement also showed improved hydrophilicity of the zwitterionic blended membrane compared to the original unmodified PAN membrane. Generally, membranes which are more

hydrophilic possess better fouling resistance ability. Hence the introduction of the *zwitterionic* compound can hydrophilize the PAN membrane so that less protein would be adsorbed on the membrane surface and rendered the membrane less easily fouled and easier to be cleaned. According to the experiments, water flux was able to maintain at 92% to the initial flux even after gone through three cycles of filtration process. In this manner, the lifespan of the membrane is lengthened and the membrane can be reused after many work cycles. Similarly, Wang et al^[57] fabricated a polyethersulfone(PES)-based membrane that was also blended with the zwitterionic sulfobetaine DMMSA(*N,N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl)). The membrane also performed much better in terms of flux permeation and antifouling ability. The ultrafiltration experiments showed that the flux recovery rate could reach as high as 82.8% after four cycles of filtration process.

All these examples reported in literature have shown that additives like surfactants could potentially enhance water flux performance by improving the hydrophilicity of a membrane. Despite above examples, no detailed studies have ever been reported for treating FO membranes except for a FO study reported by Arena et al.^[105] on thin film composite (TFC) RO membrane using polydopamine. Their results showed substantial improvement of water flux performance which enables it to be utilized in other engineered osmotic processes such as FO.

Thus, it is intriguing to study the effect of surfactants treatment on FO membranes to tune the water flux performance. Beside the anionic, cationic and non-ionic surfactants as mentioned

from the literature, *zwitterionic* surfactant has not been examined on FO. Based on the results obtained by Sun et al.^[56] and Wang et al.^[57], *zwitterionic* surfactants may be a promising candidate to enhance water flux performance in FO membranes.

On the other aspect, the idea of mechanical vibration was reported in several studies^[48-50] to tackle fouling issue. This idea is possible to be implemented in FO processes to reduce concentration polarization effect. In terms of ECP, the vibration generated near membrane-solution interface could agitate and also probably break down the ECP layer. This will enhance water flux transport. It also helps to homogenize the concentration near the interface that works similarly to a laboratory ultra-sonicator. Thus the effective osmotic pressure can be maintained across the membrane selective layer. When oscillating at certain frequencies, it could potentially reduce ICP as solutes or particles that are trapped within the porous media could be shaken off from the pore surfaces, thereby mitigating pore blocking problems and reducing concentration polarization effect. Furthermore, it may enhance mass transfer, diffusion and convection of water molecule across membrane and contribute to the improvement of water flux transport.

Although it is impossible to have mass application of FO without having economical membrane and adequate draw solution, it is crucial to understand the major problems encountered by FO so that solutions could be devised effectively. It is understood that concentration polarization is a critical issue associated with osmotic driven process as it reduces water flux performance tremendously compared with theoretical ideal water flux. Therefore, it is on top of the priority

and paramount important to tackle this problem. Essentially, enhancing the water flux in FO may also imply the reduction in concentration polarization effects simultaneously.

2.6 Osmotic Power Generation By Membrane Based Technology

Two existing techniques exist for harnessing salinity gradient energy in the context of membrane based technology. They are i) pressure retarded osmosis (PRO) and ii) reversed electrodialysis (RED). Both are actually the theoretical opposite version of reverse osmosis (RO) and electrodialysis (ED) respectively. The fundamental principles of these two technologies and their current state-of-the-art will be presented in the following sections.

2.6.1 Pressure Retarded Osmosis (PRO)

In PRO, two solutions of different salinities are separated by a semi-permeable membrane to only allow the spontaneous transport of water (but selectively retain solutes) from the low salinity side (feed solution) towards the pressurized high salinity side (draw solution). Although the draw solution is hydraulically pressurized, the osmotic pressure gradient is still high enough to drive water to transport across the membrane. However, the flow is retarded and considerably reduced due to building up of hydraulic pressure gradient which is against the osmotic pressure gradient. The hydraulic pressure can be further built up at the draw solution side to its maximum which exactly counterbalances the osmotic pressure to stop the water transport. Then the draw solution side is then depressurized through a hydro turbine to generate power in the same fashion

as hydroelectric plant. Equation 2.2 can be readily applied to describe this process. A schematic diagram PRO energy harvesting method is illustrated in Figure 2.7.

Currently, intensive research has been carried out to study power generation using PRO. To have a rough gauge of how much power is generated using PRO, about 5W/m^2 is obtained when 1M NaCl draw solution and 970 kPa of hydraulic pressure are provided at the draw side ^[11, 106]. In a generic model of PRO electric generator, solvent is water and solute is mainly sodium chloride. The existing osmotic concentration gradient between them causes solvent to diffuse from a less concentrated region to a more concentrated region across a semi permeable membrane. This osmotic process increases the relative energy density of the draw solution. Thus, intense osmotic pressure is created in it. This pressure, calculated based on the concentration gradient of fresh water and sea water, can go up to 25 bars. Power is then generated by depressurizing the pressure within the draw solution chamber through a turbine. At the moment, PRO is considered a relatively new technology in renewable power generation technology and is expected to have a great future. This method is being intensively studied by the Norwegian utility Statkraft, and they have estimated that up to 25TWhr/yr would be available from this process in Norway alone.

Figure 2.7 Schematic diagram of a PRO energy harnessing process.^[18]

2.6.2 Reversed Electrodialysis (RED)

This concept was first proposed by Pattle^[107]. In RED, two specific types of membranes, a cationic exchange membrane (CEM) and an anionic exchange membrane (AEM), are utilized and stacked between a pair of cathode and anode electrodes. The former is selectively permeable to cations and the latter is permeable for anions. Hence, when streams of seawater and freshwater are passed through the compartments in between the membrane pair, ions will be transported across each type of membrane driven by chemical gradient or concentration difference. In the case of seawater, the cation is the sodium ion whereas the anion is the chloride ion. Therefore, sodium ions permeate through the cationic exchange membrane towards the cathode, and the chloride ions permeate through the anionic exchange membrane towards the anode. The salinity gradient results in a potential difference (e.g. 80mV for seawater and river water) over each membrane that is the so-called membrane potential. The separation of ions produces an electrical potential between the outer compartments of the membrane stack is the sum of the potential

differences over each membrane. Furthermore, electroneutrality of the solution in the anode and cathode is maintained via oxidation and reduction at the anode and cathode surface respectively. Hence, electron can be transferred from the anode to the cathode via an external electric circuit. This electrical current and the potential difference over the electrodes can then be used to generate electrical power across an external load connected to the circuit. The concept of a RED power generator is described in Figure 2.8^[4].

Figure 2.8 Conceptual illustration of an energy conversion scheme using reverse electrodialysis; A and C represent anion and cation exchange membrane, respectively. I is the electrical current or transported charge (A), N is the number of cell pairs (in this case $N= 3$), $N \Delta V_1$ denotes the potential difference over the applied external load (V), whereas the power generated is $I (N \Delta V)$ (W).^[4]

Part B: Electrokinetic (EK) Phenomena

Electrokinetic phenomena are founded on the basis of electric doubly layer theory. It was first proposed by Helmholtz in 1879. After that, several scientists such as Stern and Debye have made further great contributions to the theory. An overview of this development was presented by Hunter^[108]. In this part of the literature review, emphasis will be put specifically on *flow induced streaming potential* and *streaming current* phenomena. It is an unique and unconventional way of energy conversion method for converting water energy into usable form of electrical energy. A development history of energy conversion in micro- and nano-channel is presented, and factors affecting the *efficiency* are discussed. In the later part, an innovative idea was conceived by feasibly synergize EK and FO principles for harvesting energy from salinity gradient.

2.1 Electric Double Layer (EDL) – Charge Separation/distribution at Solid-liquid Interface

It is well known that majority of substances can be charged immediately once immersed in an aqueous medium through electrochemical mechanisms of ^[108]

1. Adsorption of the charged species
2. Dissociation of the ionisable groups (ion dissolution)
3. Surface ionization

For instance, a dielectric channel of glass capillary could get negatively charged once in contact with electrolyte solution with a suitable pH condition, temperature and conductivity. The charged surface is due to the dissociation of silanol groups^[109] as following electrochemical process:

The negatively charged surface attracts positive counter ions and repels negative co-ions, causing the redistribution of ions adjacent to the capillary surface and thus leading to the formation of an *electric double layer* (EDL). Most widely accepted model for EDL is based on Stern's model as illustrated Figure 2.9, where the EDL is separated into two layers, i) an immobile inner layer, known as Stern layer (dominated by the electrostatic force) and a mobile outer layer, known as the diffuse layer (dominated by the thermal Brownian motion) ^[110].

The centers of any ions “attached” to the charged surface, i.e., ions in the Stern layer, comprise the Stern plane. Beyond the Stern plane, ions whose centers are located away from it form the diffuse mobile part of the EDL. This plane, consisting of the centers of the ions one or two radii away from the surface, is defined as the shear plane, where the no-slip fluid flow boundary condition is assumed. The potential at the shear plane is referred to as zeta potential (ζ), which is slightly different in magnitude from the Stern potential ψ_d ^[111].

Figure 2.9 Schematic illustration of an EDL of a negatively charged (SiO^-) dielectric surface (e.g. glass capillary) according to the Stern model. A potential distribution profile near the wall surface is shown with the Debye length (EDL Thickness) λ or $1/\kappa$, zeta potential ζ , surface potential ψ_s and stern potential ψ_d .

Zeta potential characterizes the strength of an EDL and is a determining factor for the ionic distribution in the diffuse layer of the EDL. Zeta potential is a property of *surface material* and is influenced by a number of factors, such as:

- Electrolyte concentration
- pH value of the solution
- Level of surface adsorption

Since it is an important factor in EK phenomena and a primary parameter to be considered, with According to Rice and Whitehead and Tropp et al. ^[112, 113], Smoluchowski gave an approximation for the zeta potential as:

$$\zeta = \frac{\sigma \delta}{\epsilon_0 \epsilon_r} \quad 2.6$$

In this expression, derived from a capacitor model for the electrostatic field in an EDL, herein σ is surface charge and δ is the characteristic thickness or the so called Debye length of the double layer. The thickness of the EDL, i.e., the Debye length λ , can be estimated by considering a balance of electrical potential energy and thermal energy ^[114], which is given by:

$$\lambda = \left(\frac{\epsilon_0 \epsilon_r k_B T}{\sum e^2 z_i^2 n_i} \right)^{1/2} \quad 2.7$$

Typically, the Debye length represents a characteristic distance from the Stern plane to a plane where the electric potential decays to approximately 33% of the surface potential^[111]. EDL thickness can also be represented as $1/\kappa$ where κ is the Debye-Huckel parameter which for a mono-valence electrolyte is described as

$$\kappa = \sqrt{\frac{2n_b z^2 e^2}{\epsilon_0 \epsilon_r k_B T}} \quad 2.8$$

κ is also the inverse of Debye length as $1/\lambda$.

Furthermore, zeta potential for silica surfaces (e.g. glass capillary) in an electrolyte can be readily determined using the Stern Model developed by Behrens and Grier obtained from Wang et al. ^[115, 116] as

$$\zeta(\sigma_{sc}) = \frac{kT}{e} \ln \frac{-\sigma_{sc}}{e\Gamma + \sigma_{sc}} - (pH - pK) \frac{kT \ln 10}{e} - \frac{\sigma_{sc}}{C} \quad 2.9$$

where pK is the logarithmic dissociation constant, Γ is the surface density of chargeable sites and C is the Stern layer's phenomenological capacity. While the surface charge density can be found by Grahame equation which for monovalent electrolyte solution ^[117-119], it can be estimated by

$$\sigma_{sc}(\zeta) = \frac{2\varepsilon_0\varepsilon_r kT\kappa}{e} \sinh\left(\frac{e\zeta}{2kT}\right) \quad 2.10$$

Solving equations 2.9 and 2.10 simultaneously could lead to determination of the electrostatic boundary conditions of a channel wall surface.

A log-log plot of EDL thickness for an symmetrical (1:1) monovalent electrolyte solution, such as NaCl or KCl solution with $z_1 = z_2 = 1$, calculated from the Equation 2.7, is shown in Figure 2.10. It can be seen from this plot that EDL thickness is inversely proportional to the electrolyte concentration in the order from nano to micro meter range.

Figure 2.10 Log-log plot of EDL thickness for a symmetrical (1:1) monovalent electrolyte solution with various concentrations.

2.2 Basic Principle of Electrokinetic (EK) Phenomena in Micro-channels

The term electrokinetic (EK) is associated with the relative motion between two charged phases, namely i) the charged solid surface and ii) the induced charged fluids. Generally, EK phenomena are the consequences of interactions between an EDL and certain applied fields, such as electric field, magnetic field, pressure field, gravitational field or centrifugal field.

EK techniques provide some of the most popular small-scale, non-mechanical strategies for manipulating particles and fluids. In general, four types of EK phenomena are more commonly encountered, namely, electro-osmosis (EO), flow induced streaming potential and streaming

current (FISP/SC), electrophoresis (EP) and sedimentation potential (SP). In the following section, these forms of EK phenomena will be described.

2.2.1 Electro-osmosis (EO)

Figure 2.11 Schematic diagram of electro-osmosis (EO) in a micro-channel with negatively charged walls.

EO is the induced motion of a liquid driven by an applied electric field across a stationary charged capillary tube, porous media or membrane. When a negatively charged micro-channel is subjected to an applied electric field, the excess cations in EDL experience a Coulomb force and draw the liquid towards the cathode terminal due to viscous interactions. EO phenomenon can be utilized to pump liquid through porous media, capillaries or some other kinds of micro-channels of different geometries and materials ^[120-123].

2.2.2 Flow Induced Streaming Potential (FISP)

Figure 2.12 Schematic diagram of flow induced streaming potential and streaming current in a micro-channel with negatively charged channel walls.

FISP is resulted from interaction between pressure field and EDL, which is considered as a reciprocal phenomenon of electro-osmosis. When an aqueous medium is driven by a pressure gradient passing through a micro-channel, counter-ions in EDL with respect to the channel surface charge are induced to flow towards the downstream end. The flow of ions is commonly named as convection current or streaming current. In order to counterbalance the convection current, conduction current in the opposite direction is simultaneously generated, which is essentially caused by potential difference or electric field due to the accumulation of the excess of counter-ions at the downstream end of the micro-channel. Such electric field strength corresponding to the induced potential is defined as streaming potential. Obviously, such EK process directly converts the mechanical energy (pressure form) into electrical energy. In some practical aspects, the phenomena of flow induced streaming potential and streaming current are

exploited to characterize various EK parameters, such as zeta potential ζ ^[124]. One fundamental equation relating the measured streaming potential to the zeta potential is given by the well-known Helmholtz-Smoluchowski equation ^[125] (extended expression to Eqn 2.6) as follow

$$\zeta = \frac{\Delta\phi}{\Delta P} \cdot \frac{\mu}{\varepsilon} \cdot \left(\lambda_f + \frac{2\lambda_s}{a} \right) \quad 2.11$$

where $\Delta\phi$ is the streaming potential, ΔP the hydrodynamic pressure difference along the capillary channel, μ the liquid viscosity, λ_f the bulk liquid conductivity, ε the liquid permittivity, λ_s the surface conductivity and a the capillary radius.

2.2.3 Electrophoresis (EP)

Figure 2.13 Schematic diagram of electrophoresis on a negatively charged particle subjected to an electric field.

Similar to EO, electrophoresis (EP) is the motion of charged matters, such as ions/molecules or charged particles, relative to a stationary liquid ^[126]. When a charged particle is placed in a stationary aqueous medium, the counterions relative to the particle's surface charges are attracted and the coions are rejected, generating an EDL around the charged particle. Overall, the region consisting of the charged particle and the surrounding ionic cloud appears to be neutral. Once the charged particle is subjected to an electric field, it is driven to move due to the Coulomb force along the electric field line; while the surrounding mobile counter-ions in the EDL slightly move in the opposite direction but still around the charged particle. At equilibrium state, the forward Coulomb force on the charged particle and the backward viscous force due to the stationary aqueous medium are finally balanced with each other. Such EK phenomenon is usually employed as an approach to measure and characterize the surface potential of charged particles ^[111].

2.2.3 Sedimentation Potential (SP)

Figure 2.14 Schematic diagram of sedimentation potential induced by a negatively charged particle moving in a stationary aqueous electrolyte solution.

Sedimentation potential (SP) is the motion of charged particles relative to the stationary liquid driven by the gravitational or centrifugal field. The motion of the dispersed charged particles disrupts the equilibrium symmetry structure of EDL. The relatively backward viscous flow around the particles drags counterions in the diffuse layer of the EDL away from the particles, resulting in the slight displacement in the relative position between the charged particles and the surrounding EDL. Then the region occupied by the charged particle and the counter-ions in EDL gains polarization with one end dominated by the surface charges of the particle and the other

end dominated by the counter-ions. Consequently, an electric field, usually defined as the sedimentation potential, is generated from this process.

It is evident that, among the four types of the EK phenomena, FISP and SP are the processes of converting the kinetic energy into electric energy, whilst EO and EP are completely opposite processes compared with the former two phenomena. Similarly, the same analogy applied as in the reversed membrane processes of PRO and RED.

2.3 Developments of EK Energy Conversion

Based on earlier classification of the various EK phenomena, it is understood that both EO and EP employ electric field to induce motion, whereas in the contrary, FISP and SP have the opposite electrokinetic coupling effect such that hydrodynamic motion is used to produce an electric field. Nonetheless, the EK phenomena exist on the basis of the EDL, which forms due to the distribution of electric charges near a dielectric charged surface^[88, 127] for instance a glass or polymer based material.

However, there are two modes of energy conversion: i) the generation mode and ii) the pumping mode. Energy conversion in pumping mode indicates a conversion of electrical energy into mechanical energy achieved through electro-osmosis scheme, whereas the generation mode indicates a conversion from mechanical energy into electrical energy achieved through flow

induced streaming potential and streaming current (FISP/SC). Fundamentally, three basic elements are required for electrokinetic energy conversion, there are

- i) Micro to nano sized dielectric channels or capillaries
- ii) Liquid electrolyte that forms the solid-liquid interface or energy carrying medium
- iii) Pressure difference or electric field as the energy source

FISP and EO effects were first observed by Reuss in 1809 and Quincke in 1859, both are associated with EDL formed at the solid-liquid interfaces. EK energy conversion has been studied for nearly 40years^[128, 129]. Osterle 1964^[129] is the pioneer who studied EK energy conversion with achieving an efficiency of 0.392% in DI water.

In recent years, Yang et al^[35, 39] revealed that the streaming potential is applicable to an electrokinetic micro battery consisting of an array of micro-channels. Their results suggested that the driven hydrostatic pressure for a liquid (i.e. DI water) provided by an external energy source, usually a manual hand pump or electrical driven pumps, can be converted into electrical work of order about $\mu\text{W}/\text{cm}^3$, depending on the properties of the electrolyte solution and channel wall. To illustrate the concept, they studied steady-state pressure driven flow through micro-porous glass filter that represents an array of micro-channels. The pressure was derived using a 30cm hydrostatic column. It was concluded that a higher current can be obtained by using a solution with higher conductivity. Thereafter, Olthuis et al.^[130] also conducted similar experiments using a glass plug of 60mm diameter and 3.5mm thick with nominal pore sizes ranging from 1-1.6 μm .

Again, they achieved a power rate of 20nW by applying a pressure difference of 1atm using 1mM KCl solution as the electrolyte.

Hence, it is in reality more practical to employ porous material such as glass filter, porous membrane or even rock and soil as a natural candidate for electrokinetic energy conversion. In addition, the use of natural materials avoids complex micro or nanofabrication processes to produce sophisticate micro-channel arrays with a large surface area to volume ratio. To this end, porous materials having high porosity ratio up to 60% could be readily applied to achieve this aspect.

2.4 EK Energy Conversion in Nano-channel

Albeit using EK phenomenon for energy harvesting is an innovative approach but literature has shown that the main drawback for EK energy conversion is due to the low practical efficiency. Chang and Yang ^[131] provided a good review on the conversion efficiency of the micro-fluidic-based batteries ranging from 0.01~15% which is still far from practical utilization. In view of this, it is suggested to adopt nano-sized ^[28, 132-138] channels in order to enhance the conversion efficiency.

This is because as EDL thickness is in the range of a few to tens of nanometer and streaming current is only generated and confined within this thin layer. Hence, the remaining cross

sectional area of a micro-channel does not contribute to net ionic transport. Therefore, it is opinionated to devise a way to utilize a larger fraction of the cross sectional area, thereby increasing the power performance. In other words, this means reducing the channel size to the same order of magnitude as the EDL i.e. in the nano-meter scale.

However, it also increases the viscous losses due to higher surface to volume ratio. Thus, much higher pressure is required to drive the flow across small channels. Furthermore, a unipolar solution characteristic may form within the channel due to ionic selectivity that restricts the ions transport. This is when the channel diameter is smaller than the Debye length, a unipolar solution of counterions is created within the nanochannel and the coions are electrostatically repelled at the channel inlet. Hence, if bulk concentration is reduced to the critical concentration level, the mass diffusion rate becomes the rate-controlling step and the potential drops rapidly in the higher current density region. However, when the Debye length of the solution is about half of the channel height, maximum efficiency is also predicted.

Although state-of-the-art micro/nano fabrication technique has given us the advantages and allowing studies to be conducted on uniform well defined geometries where double layers may be overlapped, it is expensive and time consuming on making sophisticated channels, and thus render it infeasible for wide spread applications. Therefore, there's remained an urge to develop and employ more economic materials and methods for realistic applications.

In general, for energy harvesting purpose, following aspects have to be met for practical applications, and they are:

- High energy conversion efficiency
- High power output and magnitude.
- Economical material

2.5 Liquid Slip Effect on EK Energy Conversion Process

Recently, power generation based on EK phenomenon has received increasing attentions^[39, 137, 138], especially with the introduction of liquid slip in micro-channels. A review by Pennathur^[28] and Jan Eijkel^[139] on hydrodynamic slip in EK performance can be referred. Results and findings in this area and coupled with recent theoretical investigation have indicated that liquid slip in micro/nano channels may increase the streaming current as well as streaming potential greatly. Hence, liquid slip method is identified as one promising area towards a feasible and viable device.

Theoretical research^[140] puts forth that the slip on hydrophobic surface significantly enhances the electrokinetic performance in nano-channels, and such hydrophobic enhancement was validated with experiments^[141, 142]. It is well known that two main kinds of frictions in micro-fluidics are resulted from interactions between solvent-wall and solute-wall. Consequently, a lower density boundary layer of water molecules occurring in the vicinity of the hydrophobic surface^[143] decreases the interaction between the water molecules (solvent) and the wall. Hence it allows

smoother transport of water at the wall surface, giving rise to non-zero boundary velocities i.e. slip. In contrast with the wetting case where non-slip boundary condition is applied, significant slip of the liquid in the vicinity of solid surfaces was investigated by series of theoretical and experimental researches^[140, 144, 145]. The charges within the Stern layer, conventionally immobile in the case of a hydrophilic surface, acquire movement for a hydrophobic surface due to slip, contributing to the streaming current by a large amount in addition to increment in the mean velocity within the channel. In other words, the relatively high hydrophobicity of a solid surface, i.e., the high slippage, can amplify the electrokinetic effects and render higher conversion efficiency and power output.

To achieve liquid slip in practice, for instance silica micro-channels can be hydrophobized through a standard methylation procedure^[144]. Use of high hydrophobic solid surfaces would give rise to high liquid velocity and thus lower down pressure requirement. Yet this is in contrary with high surface charge density on the hydrophilic channel walls to give higher zeta potential. Moreover, it is known that the more polar the solid molecules are, the more hydrophilic the solid surface is. This means that the surface wettability of a solid is increased by the introduction of higher surface charge density. Hence, the charged solid surfaces are generally wetting or hydrophilic^[146]. As such, it is important for the solid surface to be polarized to acquire relatively high surface charge density. Therefore, on one hand, one tries to reduce the frictions and increase the apparent slippage within the micro-channels; on other hand, one should also try to increase the surface charge density. Some methods have been reported to overcome this problem by adding polymers^[37] or by employing surface modification with surfactants. In fact, the results

cannot meet well simultaneously with the requirements of strong slip and high surface charge density as there exists competing effect between them.

Therefore, in practice, one has to consider the trade off and to balance these two parameters to achieve a better performance hydrodynamically for enhancing EK energy conversion. However, this remained one of the most challenging issues at the moment. Hydrophobic surfaces are prone to bubble formation which adversely affect the electric field generation and continuity. Furthermore, the absence of surface charge will also disrupt the EDL layer and the corresponding effective zeta potential strength. Despite ways to enhance EK energy conversion discussed earlier, there are other aspects that need our attention which will be discussed in the following sections of 2.6 and 2.7.

2.6 Electrode Polarization/Over-potential Issue

Another challenge faced within the EK generator is how to choose and fabricate reliable and durable electrodes (acts as current collector) to maximize efficiency of the EK system. In practice, the conventional electrodes such as Ag/AgCl have imperfection in the lifetime, especially with a large amount of electrical current is passed ^[28, 147] and the inherent ineffectiveness that leads to over-potential issue. By definition, the over-potential is the potential difference between the thermodynamically determined potential and the real potential. Such over-potential is caused by the limited rate of electrochemical reactions on the electrodes such as electron transfer at the electrode surface, chemical reactions preceding or following the electron

transfer, and mass transfer. The over-potential can be calculated by the Tafel equation or the Butler-Volmer equation as ^[148, 149]:

$$\Delta\phi_{over} = \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right) \quad 2.12$$

$$I_c = Ai_0 \left[e^{\frac{\alpha F \Delta\phi_{over}}{RT}} - e^{-\frac{(1-\alpha) F \Delta\phi_{over}}{RT}} \right] \quad 2.13$$

where i , i_0 , α , F , and A are the current density, exchange current density of the electrodes, transfer coefficient, Faraday constant and surface area of the electrode–solution interface, respectively.

2.7 Electro-viscous Effect

Yang and Li ^[150-152] as well as other researchers ^[153, 154] revealed significant electro-viscous effects in microchannels. In more detailed situation, with flow induced streaming potential at the downstream due to accumulation of net counter ions, an electric field is introduced causing another current opposite to the flow direction, namely the conduction current. This current will produce a liquid flow in the opposite direction, due to the flow of ions ^[151, 153-156], to the pressure driven flow. As a result, there is a reduction in flow rate in the pressure drop direction. If the reduced flow rate is compared with the flow rate predicted by the conventional fluid mechanics theory, such as the Poiseuille laminar flow that is without considering the presence of EDL, it

appears that the liquid would have an apparent viscosity higher than the bulk fluid viscosity, and this effect is referred to as the electro-viscous effect ^[108].

Generally, the EDL effects can be neglected for macro-channel flow, as the thickness of EDL is much thinner compared with the characteristic length of channels for instance the channel radius. However, for a dilute electrolyte solution flowing in microchannels, electro-viscous effect will be presented and contribute significantly to the overall transport phenomena. Since the effect is originated from the EDL field, it is dependent on the material and surface of the channel wall, structural geometry of the channel which includes porosity and tortuosity, the electrolyte concentration and dielectric constant.

Electro-viscous effect can be regarded as a barrier to the water flow when water is pumped through the EK power generator. The higher the effect, the lower the flow rate of water. This eventually would lower down the streaming potential being generated and the resultant efficiency is reduced. Conversely, higher streaming potential would also give rise to higher electro-viscous effects. It is the major effect that causes the significantly higher pressure drop across micro-channel where apparent viscosity appears to be higher than the true viscosity, i.e. $\mu_a / \mu \gg 1$. From literature, electro-viscous effect can produce an apparent viscosity from several percent to 18% higher than the true viscosity of the liquid.

2.8 Emergent Applications

Other than the adoption of the idea for energy conversion based on flow induced streaming potential and streaming current, various other practical applications have also been developed based on this principle, including

- Zeta potential characterization on solid-liquid interfaces ^[125, 132, 153, 157-161]
- EK pressure sensor^[162] and flow meter^[163]

Conventionally works in the area of electrokinetic transport phenomena mainly focus on electroosmotic flow. However, it should also be recognized that the flow induced streaming potential has become an emergent technique for surface characterization of materials with solid liquid interfaces specifically to determine the zeta potential ^[153, 158, 159]. One of the most widely used methods to characterize the surface charge under the influence of surrounding medium of a membrane is by flow induced streaming potential method. This method can provide a quantitative approach for determining the zeta potential at various pH conditions. The surface characteristic is one critical aspect for the design and operation of membrane processes. Generally, two different approaches can be performed: by flow through the membrane (trans-membrane streaming potential) or by flow across the top surface of the membrane (tangential streaming potential).

Nonetheless, Kim et al^[162, 163] also demonstrated the concept of a micro pressure sensor and flow meter by calibrating the value against the measured electrokinetic signals of streaming potential and streaming current. The linearity of the measured value was verified experimentally and it

was found that this approach could outperform conventional method significantly in terms of response time and range of linearity.

2.9 Other Similar Approaches for Energy Harvesting

A similar approach based on electric double layer concept was recently developed. This new type of technology behaves like a reversed of capacitive deionization method (R-CDI) and is known as *capacitive double layer expansion* (CLDE) method. Nevertheless, it has been demonstrated successfully capable of generating electrical power by applying sequential flow of fresh and saline water to pass through porous electrodes^[12-14]. The electric double layer formed on the surface of electrodes is strongly dependent on the concentration of the electrolyte solution. Hence, expansion of double layer occurs when stream of fresh water flows through the porous electrode right after the stream of saline or seawater. Therefore, this expansion will spontaneously increase the voltage, and current is reversed to produce direct power.

Yet another similar method was demonstrated by utilizing special developed anionic and cationic electrode pair^[15] which interact with the chloride and sodium ion respectively in the solution. Electrodes are continuously charged and discharged, through which sequential flow of fresh and seawater is applied. The charging and discharging processes are to exchange ions between the electrodes and solution. Although, no additional components needed to convert into electricity, flow process control must be in placed to provide the sequential flow of fresh and seawater, and extra pumping effort is required. Besides, this type of technology necessitates the need for

specific electrode material with high surface area to increase the power output; this increases the system complexity and compromises the stability of the power generating process.

Other similar approaches by flowing water across carbon based material such as i) carbon nanotube (CNT) ^[164] ^[165] ii) graphene^[166] are also able to generate voltage and current which can be translated into energy. However, they aren't associated with the EDL concept as discussed in the context of this research although the physical approach is very much identical.

2.10 Hybridization between FO and EK

Electrokinetic flow induced streaming potential and streaming current is an interesting form of energy conversion technique due to its simplicity. All it needs is just micro-sized channels, water and pressure gradient. However, the much lower conversion efficiency has hindered it from becoming the promising technique for the future until the liquid slip concept is introduced. This has renewed the interest and encouraged further development for making it a useful and practical method. Nonetheless, pressure source is still a must to convert the energy from mechanical into electrical form. Since, FO is a natural spontaneous process where water can be transported by a concentration gradient. Therefore synergy hybridization between FO and EK is conceived to complement the needed water transport mechanism in EK. This in turn has led to an emerging innovative idea for energy harvesting technique specifically from salinity gradient (chemical potential difference). The concept of producing electrokinetic power driven by forward osmosis will be elaborated and discussed in subsequent Chapter 3.

2.11 Chapter Summary

This chapter reviewed and discussed the key aspects of Forward Osmosis (FO) and Electrokinetic (EK) phenomena. The basic principles and variants of the respective phenomenon were detailed and elucidated. From the literature, various research studies had been carried out to address issue encountered specifically the concentration polarization in FO, and the low energy conversion efficiency in EK. A niche was then identified by hybridizing these two phenomena synergistically, and leading to an innovative concept of energy harvesting from salinity gradient.

Chapter 3 Concept of Energy Harvesting from Salinity Gradient Encompasses Forward Osmosis and Electrokinetic Principles

3.1 Forward Osmosis – Electrokinetic (FO-EK) Energy Harvesting Technique

In this chapter, a synergistic hybridization of two principles of forward osmosis (FO) and electrokinetic streaming potential and streaming current forms the basis of the concept of energy harvesting from salinity gradient.

As introduced earlier in the literature review, FO is essentially a natural phenomenon where spontaneous transport of water occurs when two solutions of different salinities are separated by a semi-permeable membrane. The difference in concentration (or chemical gradient) generates an osmotic pressure gradient (Equation 2.2) that drives water transport from a dilute feed solution towards a concentrated draw solution. Through the semi-permeable membrane in FO, contaminant, solutes and ions are retained by the membrane, and only water is allowed to pass through the membrane. Fundamentally any pair of solutions of different salinity or concentration can be employed as the feed and draw solution. By tapping it from nature, river or fresh water can be utilized as the *feed solution* and seawater as the *draw solution* that forms the salinity gradient.

A physical illustration of FO phenomenon is depicted in Figure 3.1. It shows that when water is drawn from the feed side, a hydrostatic head of water column is built up at the draw side. In another perspective, the draw effect or water transport driven by FO would actually create a

suction pressure developed at the feed side. Hence, the salinity gradient can be converted into water flow from a dilute feed solution towards a concentrated draw solution via the FO processes.

Unlike osmotic power generation method by pressure retarded osmosis (PRO), the draw solution is first hydraulically pressurized by an external source. Thus, the flow is retarded and considerably reduced due to the building up of a hydraulic pressure gradient ΔP which is against the osmotic pressure gradient. Subsequently, the draw solution side is then depressurized through a hydro turbine to generate power in the same fashion as a hydroelectric plant. Fundamentally, PRO is a variant of osmosis or forward osmosis (FO) yet FO does not require externally applied pressure. Therefore, less stringent requirements on membrane mechanical strength for FO than for PRO to withstand highly pressurized environment. Furthermore, less pressurized environment is also conducive for FO as it would generate higher water flux, and the issue of membrane fouling can be greatly minimized. Besides, PRO requires sophisticate auxiliary machineries such as turbine, pressure exchanger, energy recovery device and high power pumps (depicted in Figure 2.7) to fulfill the energy conversion process. All these requirements would then incur higher capital expenditure on infrastructure and thus impede the widespread application of PRO for energy harvesting. In view of these inherent drawbacks of PRO, it is therefore preferable to utilize FO as the primary mechanism for generating power. This in turn brings in the electrokinetic (EK) concept to complement the energy conversion (from chemical potential to direct electricity) process.

Figure 3.1 Schematic diagram of a Forward Osmosis process with the left-hand side representing the feed solution and the right-hand side denoting the draw solution

In terms of electrokinetic power generation, Figure 3.2 shows a schematic diagram to illustrate the principle of how direct electricity can be generated electrokinetically when an electrolyte solution is directed to flow across a micro-channel. Hence, in the case when river or fresh water is brought contact with a micro-channel, surface of the channel wall will be negatively charged typically due to surface deprotonation or electrostatic ions adsorption. Then counter-ions (ions with sign opposite to the surface charge on microchannel wall) are electrostatically attracted towards the charged channel wall, leading to the redistribution of ions near the channel wall and then the formation of so-called electric double layer^[118] (EDL, with its thickness denoted by κ^{-1}) which comprises an immobile stern layer and a mobile diffuse layer. In the presence of a hydrodynamic flow, an electrical potential is then formed between the inlet and outlet of the channel due to the migration of net amount of cations and anions in the diffuse layer, and this

potential is known as streaming potential $\Delta\phi$. Meanwhile, the flowing of net amount counter-ions through the channel also produces the streaming current, I_s . Consequently, electric power is produced and collected via an electrode pair.

In conventional EK conversion process, additional physical pressure is required to drive the flow across micro-channel for producing electrical energy. The efficiency of converting pressure energy into electrical energy is low ^[35, 39, 47, 133, 167, 168] as much of the pressure energy is dissipated by overcoming the resistance across the micro-channels. Furthermore, the pressure energy itself is mostly derived from an electrical energy source for instance an electrical pump. Albeit the low thermodynamic efficiency is recognized as major hurdle in EK power generation, yet the innovative implementation of FO for generating free pressure source to drive electrolyte across the micro-channel could address this lack and also offset much of the energy requirement. Apparently, this concept provides a new and promising mean for harnessing energy from salinity gradient with the advantage of virtually no need for extra energy input for generating the much needed hydrodynamic flows in EK energy conversion.

Figure 3.2 Schematic diagram for streaming potential $\Delta\phi$ and streaming current I_s resulted from water flow across a micro-channel with electric double layer (EDL, κ^{-1}).

3.2 Conceptual Design of FO-EK Energy Harvesting Unit

The FO induced pressure is used to transport water through microchannels by the introduction of a porous medium. The electrokinetic streaming potential is generated through such porous column whose pore size can be either at micro or nano-scale level. The porous medium can be made in various dielectric materials such as glass, polymer, and ceramic. As such, the cost can be reduced greatly compared to the situations where the channels are custom made via other intricate means such as micro fabrication technique. Since porous medium can be represented as an array of channels connected in parallel, the streaming current can also be improved noticeably. Besides, higher flow rate would also result in higher streaming potential as more convective transport of charges/ions is possible for achieving better performance and energy output. With the concept introduced earlier, several variant configurations are conceived for energy harvesting purpose, and they are:

1. FO-EK in pumping mode
2. FO-EK in suction mode
3. FO-EK in stacking mode i.e. multiple stacks in parallel and series

Figure 3.3 describes a self-sustainable energy harvesting unit that is designed on the basis of the FO and EK principles in pumping configuration. Herein, the FO unit is regarded as the flow or pressure generator and the EK unit as the power generator or energy converter.

Figure 3.4 shows another configuration utilizing the FO effect in a suction mode. Feed water is drawn across the porous media column, and direct electricity is generated electrokinetically through the EK power generator.

Figure 3.5 shows an individual power generation units connected or stacked in series and in parallel manner. When each power generation unit is connected in series, such multiple-stack of EK power generation is expected to produce higher streaming potential. Whereas when it is stack in parallel manner, larger streaming current is expected. Therefore, with such stacking method shown in Figure 3.5, both the streaming potential and the streaming current can be possibly scaled up towards a usable rating for practical applications.

Figure 3.3 Schematic diagram of a self-sustainable electrokinetic power generation unit utilizing the forward osmosis (FO) effect in a pumping mode. Electrokinetic streaming potential is generated through a porous media column.

Figure 3.4 Schematic diagram of a self-sustainable electrokinetic power generation unit utilizing the forward osmosis (FO) effect in a suction mode. Electrokinetic streaming potential is generated through a porous media column.

Figure 3.5 Multiple stack configuration of electrokinetic (EK) power generation units in series and in parallel and multiple stack configuration with forward osmosis (FO) in parallel configuration.

3.3 Chapter Summary

This chapter introduced and elaborated the new concept for energy harvesting from salinity gradient utilizing two different principles of forward osmosis (FO) and electrokinetic (EK) flow induced streaming potential and streaming current. Subsequently, various conceptual designs were embodied which establish the possible physical connection between these two principles. In general, the concept shows that the energy harvesting can undergo two mode namely the pumping and suction mode, and leads to the multiple stacking mode that enables scalability.

Chapter 4 Analytical Model for Electrokinetic Flow Induced Streaming Potential and Streaming Current (Power) Driven by Forward Osmosis Flow

4.1 Overview:

This chapter presents a holistic approach for deriving a representative analytical model describing the entire system of EK power generation driven by FO. At beginning, reference is made to the Onsager reciprocal relationships to model the EK power generation part. Various phenomenological coefficients are specified with the case of maximum power generation. A unique non-dimensional factor known as the figure of merit Z is obtained that characterizes the interaction between the fluid medium and channel. The respective coefficients are determined by adopting a continuum model with consideration of EDL effects. The continuum model includes Poisson-Boltzmann (PB), Navier-Stokes (NS), and Nerst-Planck (NP) equations which govern the electric, flow, and ionic transport fields respectively. Subsequently, the model is extended from a single uniform channel to the entire porous media or seen as an array of microchannels with consideration of the structural geometries such as porosity, tortuosity etc.. Finally, the theoretical connection between the FO and EK is established with the FO part obtained from readily available equations (Equations 2.3 and 2.4) with consideration of concentration polarization effects. The derived analytical model aids in the design and optimization of the energy conversion process and forms the theoretical framework for future development.

4.2 Onsager Relationship

Onsager reciprocal relationship has been aptly applied for determining the electrokinetic energy conversion in a microchannel. A number of researchers ^[128, 129, 133, 167, 169, 170] have employed this relationship as an analytical approach to investigate the thermo-electro-hydrodynamic behavior of electrokinetic energy conversion in microchannels. This relationship describes the volumetric flow rate Q , electric current I , through a channel of arbitrary geometry^[171] in two separate phenomenological equations as follow,

$$Q = G(\Delta P) + M(\Delta \phi) \quad 4.1$$

$$I = M(\Delta P) + S(\Delta \phi) \quad 4.2$$

where ΔP and $\Delta \phi$ are respectively the pressure difference and the streaming potential difference across the channel. G , M and S are known as phenomenological coefficients that denote the hydrodynamic conductance, streaming conductance and electrical conductance, respectively. Specifically each characterizes the hydrodynamic pressure driven flow, the streaming current and the conduction current. It is noted that the same set of equations is also applicable in the pumping mode, which however is not the focus of this research. In the power generation mode, the power output W and efficiency η are described as

$$W = I\Delta \phi \quad 4.3$$

$$\eta = \frac{I\Delta \phi}{Q(-\Delta P)} \quad 4.4$$

For the case of maximum generation of power, the maximum power output and corresponding efficiency are given as

$$W_{\max W} = \frac{1}{4} ZG(\Delta P)^2 \quad 4.5$$

$$\eta_{\max W} = \frac{Z}{2(2-Z)} \quad 4.6$$

when the streaming potential reaches the maximum as follow

$$\Delta\phi_{\max W} = \frac{M}{2S}(-\Delta P) \quad 4.7$$

which is exactly half of the maximum voltage (open circuit voltage) produced by the generator when the total current is zero. Z is known as the figure of merit ^[128, 129, 167, 169, 172] described as

$$Z = \frac{M^2}{GS} \quad 4.8$$

which is a non-dimensional parameter being a function of fluid and channel properties. In the subsequent section, the respective coefficients will be determined by employing a continuum model with consideration of the EDL effect.

4.3 Finding the Phenomenological Coefficients

Those coefficients introduced in the preceding section can be found through the electrokinetic flow theory for the capillary model for instance a cylindrical tube with length L and radius a (refer to the schematic diagram Figure 3.2). The capillary model was also applied to channels of other cross sectional geometries such as slit, parallel plate or rectangular channel ^[112, 173, 174]. Chun and co-workers^[127] dealt with in depth analyses on microfluidics in a microchannel encompassing electrokinetic streaming potential and streaming current phenomena. They developed the momentum equation for an incompressible fluid by verifying the external body force and the relevant flow induced electric field from the theoretical analyses of the Navier-Stokes (NS) and Poisson-Boltzmann (PB) equations. Both the NS and the PB equations govern the flow field and the electric field, respectively. Furthermore, the basic principle of the net current conservation is faithfully applied in the microchannel by taking into account the Nernst-Planck (NP) equation.

4.3.1 Electric Field in A Charged Microchannel Governed by PB Equation

When an electrolyte is in contact with a charged surface, charge separation near the channel wall leads to the ions distribution and forms the EDL with an electric field established. The generalized form of the PB equation can be utilized to evaluate the potential $\psi(r)$ across the channel as following,

$$\nabla^2 \psi = -\frac{\rho_e}{\varepsilon} \quad 4.9$$

Where ε is the dielectric constant of the medium and ρ_e is the net charge density which is defined as follows

$$\rho_e = \sum z_i e n_i \quad 4.10$$

where z_i and n_i is the valence and ionic concentration (volume densities) of type i-ions respectively, e is the elementary charge. The ionic concentration can be determined using Boltzmann distribution as

$$n_{\pm} = n_b \exp\left(\mp \frac{ze\psi}{k_b T}\right) \quad 4.11$$

Thus for monovalent, symmetric electrolyte solution for instance Sodium Chloride (NaCl), the net charge density becomes

$$\rho_e = ze(n_+ - n_-) = zen_b [\exp(-\Psi) - \exp(\Psi)] = -2zen_b \sinh \Psi \quad 4.12$$

where $\Psi = ze\psi / k_b T$ is the dimensionless electric potential. Substituting Equation 4.12 into Equation 4.9, the PB equation then becomes

$$\nabla^2 \psi = \frac{2Zen_b \sinh \Psi}{\varepsilon_0 \varepsilon_r} \quad 4.13$$

with an assumption of low surface potential $\Psi \ll 1$, the PB equation can be linearized according to the Debye-Huckel Approximation^[118] with $\sinh \Psi \approx \Psi$, such that equation 4.13 becomes

$$\nabla^2 \psi = \frac{2Z^2 e^2 n_b \psi}{\varepsilon k_b T} = \kappa^2 \psi \quad 4.14$$

where κ is the inverse Debye length which has been defined in the literature review section previously. Therefore, in cylindrical coordinates, the linearized PB equation can be expanded as

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = \kappa^2 \psi \quad 4.15$$

Hence solving Equation 4.15 (by using Bessel's modified equation detailed derivation can refer to Appendix C), with appropriate boundary conditions below

$$\psi = \psi_s \quad \text{at} \quad r = a \quad 4.16$$

$$\frac{d\psi}{dr} = 0 \quad \text{at} \quad r = 0 \quad 4.17$$

An analytical solution is then obtained as

$$\psi = \psi_s \frac{I_0(\kappa r)}{I_0(\kappa a)} \quad 4.18$$

where I_0 is the modified Bessel function of the first kind of zeroth order. Thus with Equations 4.9 and 4.18, the net charge density would then be described as

$$\rho_e = -\epsilon \nabla^2 \psi = -\epsilon \kappa^2 \psi_s \frac{I_0(\kappa r)}{I_0(\kappa a)} \quad 4.19$$

4.3.2 Flow Field Coupled with EK Interaction

The equation of motion within a cylindrical microchannel can be described by the NS equation. It governs the flow of incompressible liquid i.e the electrolyte solution, and is given by

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \cdot \nabla) \vec{v} = -\nabla p + \mu \nabla^2 \vec{v} + \vec{F}_z \quad 4.20$$

where ρ and μ are the density and viscosity of the fluid, $\vec{v}$ and p represent the velocity and pressure, and $\vec{F}_z$ is the external body force due to the z-directional flow induced electric field E_z acting on the net charge density ρ_e as ^[152]

$$\vec{F} = \rho_e \vec{E}_z \quad 4.21$$

and if an one-dimensional steady-state is considered, low Reynolds number laminar flow in this study, the Stokes equation is faithfully applied and therefore NS equation is reduced to the following

$$0 = -\nabla p + \mu \nabla^2 \vec{v} + \vec{F}_z \quad 4.22$$

Hence, in cylindrical coordinates, Equation 4.22 can be rewritten as

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dv_z(r)}{dr} \right) = \frac{dp}{dz} - \rho_e E_z \quad 4.23$$

where E_z can be described by the flow induced streaming potential ϕ as

$$E_z = -\frac{d\phi(z)}{dz} \quad 4.24$$

with appropriate boundary conditions for $v_z(r)$ as,

$$v_z(r) = 0 \quad \text{at} \quad r = a \quad 4.25$$

$$\frac{dv_z(r)}{dr} = 0 \quad \text{at} \quad r = 0 \quad 4.26$$

solving equation 4.23 with above boundary conditions and substitute Equations 4.19 and 4.24 for the net charge density ρ_e and electric field E_z , one can obtain an analytical solution for the velocity profile $v_z(r)$ as

$$v_z(r) = \frac{a^2 - r^2}{4\mu} \left(\frac{\Delta P}{L} \right) - \frac{\varepsilon \psi_s}{\mu} \left[1 - \frac{I_0(\kappa r)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{L} \right) \quad 4.27$$

an integral with respect to z from 0 to L and setting $\Delta P = P_0 - P_L$ and $\Delta \phi = \phi_0 - \phi_L$. In addition, the volumetric flow rate q can be found by taking the following integration across the channel radius as

$$q = 2\pi \int_0^a v_z(r) r dr = \frac{\pi a^4}{8\mu} \left(\frac{\Delta P}{L} \right) - \frac{\pi a^2 \varepsilon \psi_s}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{L} \right) \quad 4.28$$

where I_1 is the modified Bessel function of the first kind of first order.

4.3.3 Flow Induced Streaming Potential and Streaming Current

The ionic flux transport J in the microchannel (specifically in the mobile layer of the EDL) can be described by employing the Nernst-Planck Equation as follow

$$J_i = n_i \vec{v} - D_i \nabla n_i - mn_i \nabla \phi \quad 4.29$$

where m is the ionic mobility given as $m = zeD/k_bT$ and D is the electrolyte diffusion coefficient. Herein, the transport of ions in the microchannel comprises three terms, including convection, diffusion and migration terms due to pressure difference flow, concentration gradient and electric potential gradient respectively. Since there is no axial concentration gradient in the present case, the diffusion term can be neglected. Hence, the current density can be rewritten by the streaming current part (the first term) and the conduction current part (the second term) as follow

$$i = e \sum z_i \vec{J}_i = e\vec{v} \sum z_i n_i - em \nabla \phi \sum z_i n_i \quad 4.30$$

The streaming current I_s is due to the transport of net amount of ions in the mobile region of the EDL driven by the pressure difference. In turn, the accumulation of ions sets up an electric field E_z (flow induced streaming potential $\Delta\phi$) that causes the conduction current I_c to flow back in the opposite direction. At steady state, zero net current ^[127, 159, 175, 176] is ensured, giving rise the flowing condition

$$I_T = I_s + I_c = 0 \quad 4.31$$

4.3.4 Finding Streaming Current, Conduction Current and Streaming Potential

Integrating the first term in Equation 4.30, leads to the streaming current expressed as

$$I_s = 2\pi \int_0^a \rho_e(r) v_z(r) r dr \quad 4.32$$

which essentially, is an integration of the product of velocity profile and the net charge density, and taking $\psi_s = \zeta$, where ζ is the zeta potential, yielding streaming current as follow (derivation see appendix C)

$$I_s = -\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{L} \right) - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta \phi}{L} \right) \quad 4.33$$

As for the conduction current, Ohm's Law is applied to be expressed as

$$I_c = \frac{\Delta \phi}{R_T} \quad 4.34$$

where R_T is the total channel resistance which comprises of the surface resistance R_s and the fluid resistance R_f respectively in parallel as

$$R_T = \frac{1}{\left(\frac{1}{R_s} + \frac{1}{R_f} \right)} = \frac{R_s R_f}{R_s + R_f} \quad 4.35$$

The surface resistance and the fluid resistance are defined as^[127]

$$R_s = \frac{L}{2\pi a \lambda_s} \quad 4.36$$

$$R_f = \frac{L}{\pi a^2 \lambda_f} \quad 4.37$$

Where λ_s and λ_f are the surface conductivity and fluid conductivity respectively. Hence, total resistance R_T becomes

$$R_T = \frac{L}{2\pi a \lambda_s + \pi a^2 \lambda_f} \quad 4.38$$

Using the expressions for the streaming current and the conduction current, and invoking condition of zero net current, one can obtain an analytical formula for the streaming potential per unit pressure difference as

$$\frac{\Delta\phi}{\Delta p} = \frac{\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right]}{\frac{L}{R_T} - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right]} \quad 4.39$$

Introducing a new parameter known as the **Dukhin Number**, which is defined as the ratio of surface conductivity to fluid conductivity as

$$Du = \frac{\lambda_s}{a \lambda_f} \quad 4.40$$

Equation 4.39 can be further simplified as

$$\frac{\Delta\phi}{\Delta p} = \frac{\varepsilon \zeta \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right]}{(2Du + 1) \mu \lambda_f - \varepsilon^2 \kappa^2 \zeta^2 \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right]} \quad 4.41$$

The total current $I_T = I_s + I_c$ becomes

$$I_T = -\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{L} \right) - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta \phi}{L} \right) + \pi a^2 \lambda_f (1 + 2Du) \left(\frac{\Delta \phi}{L} \right) \quad 4.42$$

Finally, comparing Equations 4.1 and 4.2 with Equations 4.28 and 4.42, one can determine the respective phenomenological coefficients as

$$G = \frac{\pi a^4}{8\mu L} \quad 4.43$$

$$M = -\frac{\pi a^2 \varepsilon \zeta}{\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \quad 4.44$$

$$S = \frac{\pi a^2 \lambda_f (1 + 2Du)}{L} - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \quad 4.45$$

and the *figure of merit* Z is obtained by substituting above phenomenological coefficients back to Equation 4.8 as

$$Z = \frac{8 \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right]^2}{(\kappa a)^2 \left\{ \frac{D(1 + 2Du)\mu}{\varepsilon \zeta^2} - \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \right\}} \quad 4.46$$

4.4 Analytical Formula for Entire Porous Medium

In the context of this work, dielectric porous medium (which represents an array of microchannels connected in parallel) will be utilized in the subsequent various experiments studies. Hence it is more appropriate to extend the previously derived phenomenological equations into a more holistic model that includes geometries of the channel such as porosity ϕ and tortuosity τ , and the total number of unit microchannels N across each porous medium. Therefore, the total volumetric flow Q rate across the entire porous medium can be described as

$$Q = N \cdot q = N \cdot \left\{ \frac{\pi a^4}{8\mu} \left(\frac{\Delta P}{L_e} \right) - \frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{L_e} \right) \right\} \quad 4.47$$

where L_e is the effective length of the channel. With the following definitions ^[177]

$$N = \frac{A_e}{\pi a^2} = \frac{\phi A}{\sqrt{\tau}} \cdot \frac{1}{\pi a^2} \quad 4.48$$

$$\tau = \left(\frac{L_e}{L} \right)^2 \quad 4.49$$

where A_e is the effective surface area of the porous medium. The total volumetric flow rate Q then becomes

$$Q = \frac{\phi}{\tau} \left\{ \frac{A a^2}{8\mu L} (\Delta P) - \frac{A \varepsilon \zeta}{\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] (\Delta \phi) \right\} \quad 4.50$$

and similarly the total streaming current $I_{s,Total} = N I_s$ for the entire porous medium with account of geometric properties will be

$$I_{s,Total} = -\frac{\varphi}{\tau} \left\{ \frac{A\varepsilon\zeta}{\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] (\Delta P) + \frac{A\varepsilon^2 \kappa^2 \zeta^2}{8\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] (\Delta\phi) \right\} \quad 4.51$$

Since the arrays of channels are connected in parallel, the streaming potential is remained unchanged.

4.5 Theoretical Connection between FO Flow Generator and EK Power Generator

In this study, the semi-permeable membrane was orientated in the PRO mode where the dense selective layer is facing the draw solution. Due to the presence of the dilutive external and the concentrative internal concentration polarization effects, it lowers down the effective osmotic pressure difference across the membrane. In general, water flux in osmotic processes such as FO, PRO and RO with consideration of the concentration polarization effects can be described by adopting Equation 2.3.

Although, by definition FO does not require externally applied pressure, but a self-induced pressure (the pressure difference term in Equation 2.3) could be presented when a restriction is introduced along the flow path of the water transport. In the context of the proposed FO-EK energy harvesting method, this restriction of flow is formed by driving the flow across the porous medium where EK power generation takes place. The flow rate generated by the FO process can be calculated as

$$Q = J_w A_m \quad 4.52$$

where A_m is the surface area of semi-permeable membrane exposing to the draw and feed solutions. This flow rate is also equal to the flow rate across the porous medium as described by Equation 4.50 previously. The corresponding streaming potential under this flow rate can be found by either Equation 4.39 or Equation 4.41.

Apparently, the four equations (Eqs 2.3, 4.39 or 4.41, 4.50, 4.52) can provide an interrelationship that connects the FO flow generator and the EK power generator theoretically. Notably, these four equations govern four unknowns in the system namely $(J_w, Q, \Delta P, \Delta \phi)$. So the entire theoretical formulation is closed, and there is an unique group of solutions $(J_w, Q, \Delta P, \Delta \phi)$ for a given pair of draw and feed solutions with their bulk osmotic pressures denoted as $\pi_{d,b}$ and $\pi_{f,b}$ respectively. The four equations and unknowns are summarized in Table 4.1.

Equation	Expression	Unknowns
Equation 2.3	$J_w = A[\pi_{d,b} \exp(-\frac{J_w}{k}) - \pi_{f,b} \exp(\frac{J_w S}{D}) - \Delta P]$	$J_w, \Delta P$
Equation 4.50	$Q = \frac{\varphi}{\tau} \left\{ \frac{Aa^2}{8\mu L} (\Delta P) - \frac{A\varepsilon\zeta}{\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] (\Delta\phi) \right\}$	$Q, \Delta P, \Delta\phi$
Equation 4.41	$\Delta\phi / \Delta P = \frac{\varepsilon\zeta \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right]}{(2Du + 1)\mu\lambda_f - \varepsilon^2 \kappa^2 \zeta^2 \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right]}$	$\Delta P, \Delta\phi$
Equation 4.52	$Q = J_w A_m$	Q, J_w

Table 4. 1 Summary of the equations to establish the theoretical connections for FO-EK energy harvesting method.

4.6 Interpretation of Theoretical Results

Figure 4.1 shows the overall figure of merit Z (computed by Equation 4.46) and corresponding conversion efficiency at maximum power (computed by Equation 4.6) against the dimensionless channel height κa with a fixed zeta potential of -100mV. From the graph, it is found that the maximum value of Z or conversion efficiency occurs when κa is equal to 2. If unit EDL thickness ($1/\kappa = \lambda$) is considered, this means the channel radius is twice the EDL thickness. For instance, if DI water is used with its EDL thickness of 304nm, the channel radius having the maximum conversion efficiency would be around 600nm.

In this study, the porous media channel has an average channel radius of around $10\mu\text{m}$. The non-dimensional channel height would be in the order of 10^1 . Another important factor that quantifies the figure of merit Z or energy conversion efficiency is the Dukhin number. It is found that the figure of merit Z is inversely proportional to Dukhin Number. According to the definition of Dukhin Number given by Equation 4.40, to achieve a practical energy conversion efficiency of about 30%, the Dukhin Number must be at least 10 or smaller. This suggests that the surface conductivity λ_s must be as small as possible to realize such efficiency. This again implies that the surface conductivity should be in the order of 10^{-9}S or lowered (estimated with channel radius a and fluid conductivity λ_b in the order of 10^{-6}m and 10^{-4} S/m , respectively). Physically, smaller surface conductivity can limit the conduction current which can be regarded as an alternative path for energy dissipation. Hence by reducing surface conductivity, more net streaming current can contribute in generating the effective power.

Figure 4.2 shows the energy conversion efficiency with respect to Dukhin Number by varying the zeta potential from -20mV to -200mV . It highlighted that the overall energy conversion efficiency is proportional to zeta potential and this relationship is not linear. The increment in efficiency becomes smaller when the value of zeta potential goes higher while Dukhin number goes lower. The maximum efficiency is capped at 50% when figure of merit Z is equal to unity, (deduced from Equation 4.6). Another significant point is that the efficiency reaches a plateau when the Dukhin Number is smaller than a threshold value. As inferred from Figure 4.2, this value corresponds to the cases of unit Dukhin Number.

Figure 4.1 Figure of merit Z and corresponding energy conversion efficiency at maximum power against non-dimensional channel height κa for various Dukhin Numbers of 0.1, 1 and 10 with a fixed zeta potential of $\zeta = -100\text{mV}$.

Figure 4.2 Energy conversion efficiency against Dukhin Number for different zeta potential levels of -20mV, -100mV and -200mV with the non-dimensional channel height κa set at 2.

4.7 Chapter Summary

This chapter detailed the approach for deriving a representative analytical model of an EK power generation driven by FO. Onsager reciprocal relationships were adopted to model the EK power generation part and the use of a non-dimensional factor figure of merit Z to characterize the interaction between the fluid medium and channel. Continuum model includes Poisson-Boltzmann (PB), Navier-Stokes (NS), and Nerst-Planck (NP) equations which govern the electric, flow, and ionic transport fields respectively were employed. Subsequently, the model was extended from a single uniform channel to the entire porous media or an array of microchannels with consideration of the structural geometries such as porosity and tortuosity. Eventually, the theoretical connection between the FO and EK was established. This analytical model can aid in the design and optimization of the energy conversion process, and forms the theoretical framework for future development.

Chapter 5 Investigation of the Functionality of EK-FOC Energy Harvesting Technique

5.1 Experiment System

A bench scale prototype experimental system depicted in Figure 5.1 was constructed to demonstrate the proposed concept of FO-EK energy harvesting technique. Batch configuration was adopted for ease of implementation. The prototype system is composed of two main parts i.e. i) the EK the power generator and ii) the FO flow generator. Modular design was incorporated to distinguish between the FO flow generator and the EK power generator. In the EK power generator, a porous medium was placed within a custom designed acrylic holder and was sealed with rubber gasket. On the other hand, the FO flow generator mainly contains two chambers holding the feed and draw solutions. Both chambers are separated by a semi-permeable FO membrane. In this system, the EK power generator and the FO flow generator are connected in series to take advantage of the FO driven water flow. The detailed design of the respective components can be found in Appendix B.

Schematic Diagram of the Experimental Setup
Draw (Seawater) – NaCl Solution from 0.5M to 4M
Feed (Fresh Water) – DI water

Figure 5.1 Schematic diagram of the EK-FO power generating experimental setup. Detailed dimensions of the EK power generator module can refer to Appendix B5 while the FO flow generator dimensions can refer to Appendix B4.

5.1.1 Materials and Methods

The FO membrane employed in experiments was provided complimentary by HTI[®] (Albany, USA). This membrane has been widely utilized in various FO experiments for sea water desalination [75, 94, 178, 179], and it is the only commercial FO membrane available in the market. The membrane is able to generate decent amount of water fluxes ranging from 5 to 20 Liter/m².hr (LMH) depending on the concentration of the draw solution used. This type of membrane is made of cellulose triacetate (CTA) casted onto a non-woven backing which

consists of polyesters fibers individually coated with polyethylene. The average thickness of this membrane is merely 200 μm , and it is significantly reduced as compared to typical RO membranes (a SEM image of the membrane cross section can be referred to Figure A6). The membrane was cut to fit the FO module frame size of 13cm $\times$ 13cm. The FO membrane was orientated in the PRO mode with the dense selective layer facing the draw solution side. In addition, O-ring seals were fixed on both side of the membrane to prevent possible leakage. In the demonstration experiment, NaCl solutions with concentrations ranging from 0.5M to 4M were used as draw solution to simulate as seawater. DI water was used as the feed solution to represent as freshwater. Such a wide range of concentration of draw solution was chosen in order to examine the osmotic pressure gradient effect on the power performance. NaCl of analytical grade (Sigma-Aldrich, SG) was used for preparing the draw solutions. The water flux transport across membrane was measured using the gravimetric method. In this method, either the feed or the draw reservoirs were placed on an electronic balance to record the weight change over a period of time such that the experimental water flux $J_{w,exp}$ can be calculated as

$$J_{w,exp} = \frac{\Delta w}{A_m \rho_w \Delta t} \quad 5.1$$

where A_m is the membrane surface area, and ρ_w is the water density. An over-flow mechanism was designed in the draw solution reservoir so that constant volume of draw solution was maintained to eliminate the possible build-up of back pressure at the draw side. Hence, a steady water flow across the EK power generator was maintained.

For the EK power generator, both glass and polymer based dielectric porous media were tested, and they are borosilicate glass frit (Schott Duran®, Germany) with pore size ranging from 10-16µm and polyethylene (PE) porous plate (Dusemond, Singapore) with an average nominal pore size of 20µm. Both were prepared in circular disc shape with 20 mm in diameter, and 4mm and 8mm in thicknesses for glass and PE discs, respectively. (SEM images of both types of porous medium are shown in Figure A6 of Appendix A)

It is noted that the EK module is connected to the feed solution side of the FO module in the experimental setup with suction pressure difference developed to draw water from the feed side towards the draw side. Therein, a pair of Ag/AgCl electrode meshes is placed at the inlet and outlet of the porous medium. These two electrodes are connected to a source meter (Keithley 2612A) for measuring the flow induced streaming potential and streaming current readily.

5.1.2 Measuring the flow induced streaming potential and streaming current

All results presented here were experimentally determined in order to validate the practicability of this power generation method by salinity gradient. Figure 5.2 shows a typical streaming potential time evolution curve (hereby using Glass porous disc as an example, other results with PE porous media can be found in Appendix A1) over a period of up to 7000s of various concentrations of NaCl draw solutions against DI water as the feed solution. Obviously, it is seen from the figure that the streaming potential is higher with an increase of draw solution concentration.

Since osmotic pressure is proportional to the solution concentration, a higher draw concentration will produce larger osmotic pressure gradient, and thus more water flux is produced. Hence, a higher pressure is induced as more flux (with reference from Equation 2.3) allows for conversion of pressure to generate the streaming potential. Moreover, it is observed that lower concentration of draw solution requires more time to reach a steady plateau of streaming potential as shown from Figure 5.2. This can be attributed to the natural behavior of FO which is a relatively slow process as the flux generated is in the order of $\mu\text{m/s}$. As a result, a lower concentration draw solution would have to take longer time to build up the water flux as compared to a higher concentration draw solution. The gradient of each curve also gives an indication that the initiation of water flux is inversely related to the draw solution concentration.

Figure 5.2 A typical flow induced streaming potential (OCV) time evolution curve of various concentrations of NaCl draw solutions ranging from 0.5M to 4M for a glass porous disc. (Similar results for polyethylene porous discs can be found in Appendix A1).

In addition, it was noted that non-zero streaming potential and fluctuation of results were seen at the beginning of each experiment. Various reasons were accounted for this, firstly, the tautness of the flat sheet membrane was not fully ensured such that uneven pressure may build up at the FO side which may in turn affect the reading of streaming potential since pressure is the main factor determining streaming potential. Secondly, the water level at the draw and feed chambers may not be at the same height and it might constitute extra hydrostatic pressure that can cause non-zero reading at the beginning stage of each run. However, all these fluctuations at the initial stage will not affect the end results as the system will be able to reach its steady state streaming potential (or Open Circuit Voltage OCV) when the water flux becomes steady concurrently. Furthermore, due to the nature of a batch configuration, the feed reservoir volume would be depleted and lowered over-time, however, this does not affect the unsteadiness of the results once steady flux is fully developed by FO process. Hence, with identified the steady plateau of streaming potential, it can be assured that the flow process is solely driven by FO. Furthermore, the streaming potential dips slightly after it reaches the steady plateau which is attributed to the dilution effect. Nonetheless, this deviation is negligible and falls within a very narrow range. Once having reached a steady state, the system will be subjected to a voltage sweep test (up to the measured streaming potential) to measure the output current from the system and to compute its corresponding power performance. An equivalent electronic circuit as shown in Figure 5.3 can be adopted to analyze the EK power generating mechanism for FO-EK system.

Figure 5.3 Equivalent circuit denoting the EK streaming potential and streaming current across a porous medium.

The flow induced streaming potential E_s or $\Delta\phi$ across the array of microchannels of the porous medium can be described as

$$V_{channel} = V_{source} - E_{redox} = E_s - I_T R_T \quad 5.2$$

where V_{source} is the source potential that is supplied from the source meter during the voltage sweep test. E_{redox} is the potential generated from the redox reaction on the electrodes, however, it is negligible as the electrolyte is DI water. E_s is the steady state streaming potential determined earlier from the OCV tests. And I_T and R_T are the total current and resistance respectively which can also be determined from the voltage sweep test. Hence, the channel voltage can be simplified and given as

$$V_{channel} = V_{source} = E_s - I_T R_T \quad 5.3$$

The total resistance, which is the sum of the porous medium resistance and the electrodes resistance, can be found experimentally as

$$R_T = \frac{\Delta\phi - V_{source}}{I_L} \quad 5.4$$

Furthermore, the EK power generator outputs the maximum power when the resistance of external load is equal to that of the EK power generator, and then the maximum power can be evaluated as (referred to Appendix A6 for more details)

$$P_{max} = \frac{(\Delta\phi/2)^2}{R_T} \quad 5.5$$

Figure 5.4 shows a typical current-potential (I-V) and power-potential (P-V) performance curve obtained from the voltage sweeping test. Apparently, the maximum current at zero source voltage is the streaming current (short circuit current) of the system. From the results, it showed that the streaming potential is proportional to the concentration difference as well as water flux. As a result, higher net amount counter ions are transported across the channel i.e. higher current density. Similarly, the streaming potential is also present even when the current is zero. Also shown in Figure 5.4 is the power-potential curve which is proportional to the concentration difference. Nonetheless, the magnitude of the generated power is of a minimal value (nW), but the concept of this technique is verified; that it is capable of generating power.

In a nutshell, all results obtained are trending higher proportionally to the driven force induced by FO. Higher concentration of draw solutions will give larger osmotic pressure, and thus higher osmotic pressure gradient across the membrane would generate higher water flux.

Figure 5.4 Current-potential (I-V) curve (dashed-dotted line) at various concentrations of NaCl draw solutions (Note that the streaming current corresponds to zero potential, whereas the streaming potential corresponds to zero streaming current). Power curve is also illustrated on the graph, corresponding to that the maximum power occurs at half of the streaming potential (OCV) or that the external load resistance is equal to the EK power generator resistance.

5.2 Comparison of Experimental Results with Theoretical Predictions

5.2.1 Performance of FO Flow Generator

Prior to the test of power generation, the water flux across FO semi-permeable membrane was experimentally investigated and the results are shown in Figure 5.5a. Various concentration differences between the draw and feed solutions ranging from 0.5 to 4M were tested to determine the baseline FO water flux. In these tests, the membrane was arranged in a customized cross-flow module (Figure B2) as shown in Figure A3 with constant trans-membrane pressure and the FO water flux when porous media were attached with the setup depicted in Figure 5.1.

It is seen from Figure 5.5a that water fluxes with incorporation of porous medium are reduced as compared to the baseline fluxes. The reduction in fluxes is due to the flow resistance induced by the porous medium. Furthermore, relatively higher water fluxes are generated across the glass porous medium as compared to the PE porous medium. The difference can be attributed to lower flow resistance across the glass porous medium since the thickness of the glass porous medium is only half of that of PE porous medium. Also it is observed that the reduction in fluxes with respect to baseline fluxes increases with an increase of concentration difference. This should be due to the streaming potential induced electroosmotic flow^[151] which partially counteracts the FO-driven flow in the opposite direction or known as electroviscous effect.

A higher concentration difference induces a higher flux on the one hand, but simultaneously exacerbates the concentration polarization effects on the other hand. Ideally, if the pure water is used as the feed solution, there is no salt leakage across the membrane, and only the external concentration polarization (the first exponential term in Eq. 2.3) is only present. The direct

consequence of such effect is to reduce the effective osmotic pressure difference and thus the water flux across the semipermeable membrane. However, the membrane practically is always leaky to salt ions to some extent at higher water fluxes (as determined by Figure A7 in Appendix A), which could result in another adverse effect known as reverse salt permeation^[180]. Then the salt permeation from the draw side would initiate the formation of internal concentration polarization effect (the second exponential term in Equation 2.3) in the support layer. This effect further reduces the effective osmotic difference across the membrane.

For simplification of the theoretical modeling, the internal concentration polarization (second exponential term Eq. 2.3) is assumed to be absent. Such assumption is believed to be reasonable due to two facts: (i) the membrane in the experiments was orientated with the dense selective layer of membrane facing the draw solution in order to minimize the internal concentration polarization effect and (ii) the experimental results of water flux as shown in Figure 5.5a are quite well described by Eq. 2.3 even with only the external concentration polarization. After fitting the experimental fluxes with Equation 2.3, one can estimate the mass diffusion coefficient k to be of order above 10^{-6} m/s for the baseline and 10^{-7} m/s for glass and polyethylene porous media as shown in Figure 5.5(b). These orders of magnitude are in good consistency with those determined directly with the Sherwood number relationship (see Appendix A3). k is a very important parameter for characterizing the external concentration polarization, and will be much needed later for theoretical prediction of EK power generator. Generally, a larger k indicates a lower strength of concentration polarization. So the baseline in the absence of porous medium suffers less from the external concentration polarization, and PE porous medium would introduce the strongest external concentration polarization for the semi-permeable membrane arranged as

in Figure 5.1. Furthermore, it is found that the mass transfer coefficient increases with the applied concentration difference instead of a constant value. This is due to the fact that the increment of concentration difference enhances the water transport (flow rate) and then the Sherwood number^[10, 75] which is linearly proportional to the mass transfer coefficient.

5.2.2 Flow-induced Streaming Potential and Streaming Current

A calibration test was also conducted beforehand to characterize the relationship between the pressure difference across a porous medium and the flow rate (Figure A5 of supporting information). With this relationship, the hydrodynamic pressure difference developed at various flow rates can be readily deduced. Based on the characterized relationship, it is found that a much higher pressure difference is induced by the FO flow generator across the glass porous medium. Additionally, this calibrated relationship can be combined with Equation A4 and A5 from Appendix A5 to estimate the tortuosity and porosity of porous media which are required in the subsequent theoretical predictions of streaming potential and current. It is found that the tortuosity τ and the porosity φ of glass porous medium is 3.77 and 0.207, respectively, and those of PE porous medium are 1.77 and 0.293, respectively.

(a)

(b)

Figure 5.5 Variation of (a) the experimental water flux $J_{w,exp}$ and (b) the mass transfer coefficient k fitted by using Equation 2.3 with the concentration difference (or osmotic pressure difference $\Delta\pi = \pi_{d,b} - \pi_{f,b}$) between the draw and feed solutions. The baseline results were obtained with the semipermeable membrane in a cross-flow configuration without any porous medium. The results for glass and polyethylene porous media were obtained using the setup shown in Figure 5.1. The feed solution is the DI water and the draw solution is the NaCl solution with various concentrations ranging from 0.5M to 4M.

Figure 5.6(a) presents the relationship between the streaming potential and the FO-induced flow rate for both glass and polyethylene porous media. It is shown that the streaming potential is linearly proportional to the FO-induced flow rate. This is expected since both the flow rate and the streaming potential are linearly proportional to the pressure difference as suggested by Equations 4.41 and 4.5. As seen from the experimental results, the streaming potential generated across the glass porous medium is higher than that generated across the PE porous medium. The theoretical results (Eqs. 2.3, 4.41, 4.50, 4.52) with a fitted zeta potential of -40 mV for the glass medium and a fitted zeta potential of -15 mV for the PE porous medium are also included in the plot for comparison purposes. Generally, the theoretical model agrees reasonably with the experimental measurements, with relatively large discrepancies showing up at the higher flow rates. The above fitting with respect to zeta potentials also concludes that in addition to the structural parameters and induced flow rate, surface charging conditions of the porous medium e.g. zeta potential also play an important role in determining the streaming potential. Usually, a higher density of surface charge (equivalent to a higher zeta potential) would induce a larger streaming potential. The discrepancies at high flow rate are probably due to an assumed constant concentration of the feed solution (DI water) in the theoretical model. However, in experiments the concentration of the feed solution increases due to the salt leakage from the draw solution. Such salt leakage is especially stronger at higher flow rates. Therefore, the EDL as well as the zeta potential in porous medium would be suppressed at higher flow rates, reducing the amount of mobile counter ions in the diffuse layer of EDL, which in turn affects the induced streaming potential.

The results of the streaming current are shown in Figure 5.6(b), from which one can identify a linear relationship between the FO-induced flow rate and the streaming current. It should be noted that the streaming current presented here actually is the total current produced from the entire porous media instead of a single micro-channel. It is observed that the theoretical model employed here underestimates the streaming currents from experiments. This also could be attributed to the increased concentration in the bulk feed solution because of possible salt leakage as mentioned earlier, which enhances the bulk conductivity on the feed side and thus the streaming current.

Figure 5.6 Variation of (a) the streaming potential and (b) the streaming current produced from glass and polyethylene porous media with the FO-induced water flow rate. Dash line represents the model prediction with fitted zeta potentials of -40mV and -15mV for glass and polyethylene porous media, respectively. The range of FO-induced water flow rate corresponds to the NaCl draw solution with its molar concentrations ranging from 0.5M to 4M.

The experimentally measured total resistance for each type of porous medium is illustrated in Figure 5.7. Total resistance is experimentally computed from Eq. 5.4. As mentioned previously, the porous medium can be regarded as an array of micro-channels connected in parallel. Consequently, the total resistance is inversely proportional to the total number of channels N (Eq. 4.48 or A7 in Appendix A) for each porous medium. As illustrated in Figure 5.7, the total resistance of the glass porous medium is at least one order smaller than the PE porous medium. Hence, it is expected that more channels are in the glass porous medium than in the PE porous medium despite their equal surface areas. The lower resistance would reduce the internal loss of power source and certainly makes the glass porous medium a better material for EK power generation.

Figure 5.7 Total electrical resistances R_T of glass and polyethylene porous media as a function of the concentration difference between the draw and feed solutions.

5.2.3 Performance of EK-FO Power Generation.

Figure 5.8 shows the variation of maximal power density with FO-induced water flux. The maximal power density is computed by averaging the maximal power that the EK generator can output over the surface area of the porous medium. Generally, the maximal power density increases as the FO-induced water flux increases. Eq. 5.5 indicates that the maximum power generated in the EK power generator is proportional to the square of the streaming potential. Since the FO-induced water flux is linearly proportional to the streaming potential (see Figure 5.6(a)), a quadratic relationship between the maximal power density and the FO-induced flux is also expected (see Figure 5.8). In addition, the model prediction and the experimental show good agreement. This is because the porous medium can be considered as an array of micro-channel connected in parallel, the streaming potential remains unchanged regardless of the surface area of porous medium. However, the resistance of porous medium is greatly reduced when its surface area increases (equivalent to the increase of the numbers of micro-channels in parallel). It is estimated that the order of total resistance is lowered to several tens of Ohms for one square meter of porous medium. Hence, the estimation from Eq. 5.5 suggests that the power generated per unit area of porous medium (power density) can reach up to 10 W.

Figure 5.8 The maximal power density as a function of the FO-induced water flux. The range of FO-induced water flux corresponds to the NaCl draw solution with its molar concentrations ranging from 0.5M to 4M. (LMH =liter/m².hr.)

5.3 Chapter Summary

This chapter investigated the functionality of EK-FOC energy harvesting technique via a bench-scale experiment setup based on the concept introduced earlier. Experimentally obtained results were compared with theoretical model, and good agreement was shown.

Chapter 6 Experimental Studies for Enhancement and Optimization of FO-EK Energy Harvesting Technique

6.1 Overview

This chapter aims at incorporating various methods to further enhance, maximize as well as to optimize the power performance of FO-EK harvesting technique. Both chemical and physical means were experimented and examined on the FO membrane (flow generator) and the porous medium (power generator) separately to meet these objectives.

In terms of chemical approach, both zwitterionic and anionic surfactants, namely DMAPS (dimethylethylammoniumpropane sulfonate) and SDS (Sodium Dodecyl Sulfate) were utilized to modify the surface characteristics such as hydrophobicity (or wetting properties), zeta potentials of membranes and the porous media microchannel walls respectively. Whereas in terms of physical approach, Piezoelectric Zirconate Titanate (PZT) element induced surface mechanical vibration was adhered on the membrane which aims at breaking down the concentration polarization layer on membrane surface. Hence it would assist in generating higher osmotic pressure gradient force, leading to higher water flux across the membrane.

Detailed discussion of the respective methods will be elaborated in the following sections to demonstrate how each method can bring improvement to the overall power performance of FO-EK substantially. In addition, innovative multiple stacking configurations were developed to illustrate the capability of individual modular unit of EK power generator which can be

combined or stacked together and properly scaled to meet any energy demand. This unique scalability represents a state-of-the-art and big leap forward towards the realization of a practical solution for harvesting energy electrokinetically from osmotic gradient (or salinity gradient).

6.2 Enhancement of Water Flux Performance by PZT Induced Surface Wave Propagation.

This study investigates the feasibility for enhancing water flux transport by adhering piezoelectric (PZT) vibrating thin film onto membrane surface. Hence, with using the induced surface vibration by PZT on membrane-solution interface, it aims primarily to reduce concentration polarization effects and enhance mixing so as to augment the water flux transport across the membrane. Detailed discussion of the experimental approach will be carried out in the following sections.

6.2.1 Materials and Methods

Two different sizes of PZT elements were used in the experiments. They are 14mm and 27mm in diameter. Figure 6.1 shows an example of a 27mm PZT. All PZTs were purchased locally from an electronic components shop. The two ends of PZT wires were connected to a function generator (Model DS360, Stanford Research System) subjected to a maximum AC voltage of 40Vpk-pk and varying frequencies ranging from 300Hz to 10kHz. Varying frequencies were applied in order to examine its effectiveness on improving FO water flux.

Figure 6.1 A unit of PZT vibrating element

Batch configuration was adopted in the experiments where draw and feed solutions were not circulated. Characterization of water flux performance with PZT attachment on membrane surface was studied and compared with that obtained without PZT attachment. The testing parameters include frequency, size of PZTs and numbers of unit of PZTs to examine the effect of each parameter on water flux performance.

6.2.1.1 Experimental Setup for PZT Batch Process Experiment

A customized batch module was constructed for carrying out the flux characterization experiments as shown in Figure 6.2. FO membrane is sandwiched in between two identical half of the module which comprises a rectangular pocket/cavity to hold both feed or draw solutions. Seal-tight with an O-ring over the perimeter of the membrane is to prevent possible leakage. Openings on top of each side of the module are catered for electric cable running as well as the measuring column for measuring water flux magnitude. The detailed drawing of the module can be referred to Appendix B3.

Figure 6.2 Schematic diagram of a cross-sectional view of the PZT-experiments batch module. Electrical wires to the PZT and a flux measuring column are connected to the top of the module via plastic fittings. A functional generator is to provide varying frequency AC voltage for PZT element attached onto the feed side of the membrane. The detailed dimension of the parts involved can be referred to Appendix B3.1 drawing of customized batch module and the actual assembly can be referred to Figure B3 in Appendix B3.

6.2.1.2 Experiment Procedures for PZT Batch Process

NaCl draw solutions ranging from 1M to 4M were prepared prior to the experiments with DI water and DI water was used as the feed solution. A FO Membrane was cut into 100mm x 60mm

in dimension. Prior to the experiment, the FO membrane was first soaked in DI water for an hour to displace the glycerin preservative that can prevent the membrane from dry out or become moldy during shipment and storage. On the other hand, this procedure would ensure that the membrane is in wall contact and is fluidized with water. PZT element was then manually attached onto the supporting layer of the membrane by using silicon based adhesive, and the membrane was orientated in PRO mode with the selective layer of the membrane facing the draw solution.

PZT element was wired with the function generator by running through the opening on top of the feed-side. Frequencies ranging from 300Hz-10kHz were tested at an applied voltage of 40V pk-pk. Draw and feed solutions were then injected into the cavities using a syringe. Once both the draw and feed compartment were fully filled, experiments were started right away with PZT activated. Water flux was calculated by measuring the time taken for the water column in the measuring tube to reach a predetermined height. Water flux J_w can then be obtained by the following formula as

$$J_w = \frac{\Delta H_c A_t}{A_m \Delta t} \quad 6.1$$

where ΔH_c is the change in water column height, A_t is the cross-sectional area of the measuring tube, A_m is the area of the membrane and Δt is the time taken for the water column to reach a certain height. At least 30 data points were collected for each concentration difference, and an average water flux with standard deviation could be obtained.

6.2.2 Results and Discussion

6.2.2.1 Effect of Frequency

Experiments were conducted in batch configuration to determine and compare the water flux performance between one with PZT attachment and one without. Results of the comparison under different sizes of PZT and at various applied frequencies were presented in Figure 6.3. Obviously, the PZT attached membrane could produce much better water fluxes than the membrane without PZT (baseline). Improvements were recorded across all experimental frequencies and concentrations difference. Maximum fluxes recorded at 4M NaCl draw solution were 25LMH and 28LMH for the PZT diameter size of 14mm and 27mm, respectively. Hence, it implies that the size of PZT is one main factor that will give rise to better water flux performance.

Enhancement of fluxes reaching peak occurs at frequency window from 1000Hz to 3000Hz across both sizes of PZT tested. The optimum frequency range was bounded by the red dotted line as shown in Figure 6.3. Another graph showing the percentage improvement of water fluxes versus concentration difference is illustrated in Figure 6.4. Both PZTs tested have achieved significant water flux improvement specifically at concentration difference of 2M within the identified optimum frequency window. An exceptional performance was found that with the larger PZT in 27mm diameter a maximal of about 150% of flux improvement is recorded at concentration of 2M. This significant improvement of fluxes shows that size of PZT plays an important factor on water flux performance. Thus, size effect will be examined in the following section. However, the enhancement of water fluxes starts to decline beyond this optimum

frequency range, though the water flux measured is still higher than that of without PZT. Nonetheless, the results show that the PZT induced surface vibration is able to improve water flux performance of in FO process.

Figure 6.4 shows that there exists a sharp spike of percentage improvement of water fluxes at 2M NaCl draw solution throughout all experimented frequencies from 300Hz to 10kHz. However, at a higher concentration of the NaCl draw solution, the percentage enhancement of fluxes is lower after reaching a peak at 2M NaCl draw solution. Generally, a diminishing trend on percentage improvement is shown after concentration difference of 2M. This also implies that concentration difference of 2M would be the optimum condition for the most effective FO water transport to take place or equally the least concentration polarization effect.

Figure 6.3 Water fluxes against applied frequencies on a PZT unit with its diameter of (a) 14mm (b) 27mm while the driving voltage kept at 40V pk-pk. Experiments were carried out in a batch process configuration with FO membrane orientated in PRO mode. DI water was used as the feed solution.

Figure 6.4 Percentage improvement of water fluxes against concentrations difference with PZT of diameter (a) 14mm, (b) 27mm. Frequencies ranging from 1000Hz to 10kHz were tested with an applied voltage kept at 40V pk-pk. Experiments were carried out in a batch process configuration with membrane orientated in PRO mode. DI water was used as the feed solution.

6.2.2.2 Effect of PZT Size

With the determined optimum frequency window, further tests were carried out to determine the size effect of PZT on water flux performance. Two diameters of 14mm and 27mm PZT with an applied frequency of 3kHz were used, and the results of the size effect of PZT are shown in Figure 6.5. Larger diameter 27mm PZT can generate better flux performance at this optimum frequency. Improvements of fluxes are achieved across all concentrations difference. With respect to percentage improvement, fluxes are greatly improved of approximately 55% with the larger diameter PZT of 27mm as depicted in Figure 6.6. Consistently, overall performance of all sizes of PZT attachment shows best at 2M NaCl draw solution. However the percentage enhancement of fluxes is lower beyond 2M NaCl draw solution which shows a similar trend as the previous results under frequency effect. Hence, it is concluded that larger size of PZT attachment can give better flux enhancement. Therefore 27mm PZT diameter was selected to study the effect of number of units of PZT in subsequent section.

Figure 6.5 Effect of PZT size on water fluxes with the baseline as no PZT. Experiments were operated at an optimum frequency of 3000Hz and driving voltage was kept at 40V pk-pk.

Figure 6.6 Percentage improvement of water fluxes of membrane incorporated with PZT diameters of 14mm and 27mm against concentrations difference. Experiments were operated at an optimum frequency of 3000Hz and 40V pk-pk.

6.2.2.3 Effect of Number of PZT Units

It was determined from the previous section that a larger PZT unit would give better enhancement in flux performance. Therefore only the PZT unit with 27mm in diameter was chosen to undergo this investigation. Two units of 27mm PZT were attached onto the backing layer of a membrane. Results of the experiments are presented in Figure 6.7 which shows much higher water flux for all concentration differences tested. Specifically, the maximum water flux of approximately 50LMH corresponds to a concentration difference of 4M. This value is almost double compared to the flux with only single PZT attachment discussed in previous section. In terms of the percentage improvement shown in Figure 6.8, a tremendous improvement of more than two fold was recorded at the optimum frequency window. Despite a down trend observed after the optimum concentration of 2M, the water fluxes still hit above the 100% improvement mark. Again it is shown that water fluxes are improved much better at the optimum concentration difference of 2M. Apparently, more number of PZT unit attachments is able to generate much higher enhancement in water fluxes.

Figure 6.7 Comparison of flux performance against applied frequency. Two units of diameter 27mm PZT were tested. Experiments were carried out in a batch process configuration with the membrane orientated in the PRO mode. DI water was used as the feed solution.

Figure 6.8 Percentage improvement of water fluxes against concentration difference across a membrane incorporated with two PZT units with diameter of 27mm. Experiments were carried out in a batch process configuration with the membrane orientated in the PRO mode. DI water was used as the feed solution.

6.2.2.4 Phenomenon of Flux Improvement with PZT Induced Surface Vibration Effect

Surface vibration is generated by the PZT unit attached onto the membrane surface. With this attachment in place, it aims to impart the vibration energy onto the membrane so as to mitigate the polarization issue. Basically, PZT film can help to induce shear flow through the vibration generated. This in turn can break down the polarization layer by enhancing motion at the membrane-solution interface. Meanwhile, the induced strong vibrating oscillation wave would also help to repel the solutes which may be accumulated in the membrane pores or crevices. Therefore, pore fouling of the water transport channel can be mitigated, and water flux is improved eventually. Furthermore, the PZT induced vibration may also improve diffusion and convection of water molecules across the membrane, and hence elevate the mass transport across membrane. This could be reflected in the change in mass transfer coefficient with enhanced water flux performance.

From the experiments it was shown that flux performance of the membrane could generally be improved through the attachment of PZT units on membrane support layer. Optimum conditions would have to be determined in the first place. These conditions depend on various parameters which were examined earlier such as the frequency, size and number of unit of PZT attachment. For larger scale, the distribution of the PZT elements would also play an important role on the final water flux transport. It is hypothesized that at the optimum frequency, solutes or ions which adsorb on the membrane surface or pores within the substructure or support layer could be repelled more easily. It might be due to the maximum oscillating vibration, that the membrane

occurs at this resonance frequency range. This could more effectively help dislodge the solutes or ions from the membrane surface as maximum repulsive force would have presented to reduce the fouling. In addition to the frequency, the size of PZT unit also plays a part in enhancing flux performance. It was noted that a bigger PZT element could yield better flux results is attributed to stronger vibration on the membrane surface as it covers bigger surface area. Therefore, oscillating vibration could be induced and transmitted to the membrane from the PZT vibrating element more effectively.

Besides, much better fluxes performance was also obtained with increasing number units of PZT attachment. This in fact has multiplied individual PZT effects in terms of flux performance. As with more units of PZT attached, the collective effects would reduce concentration polarization effect, and thus enhance water transport more effectively. Moreover, it was observed that at the optimum concentration of 2M, it gives the best overall flux improvement. This can be mainly due to the tradeoff between optimized water flux rate and minimal concentration polarization effect. It is known that flux itself would have a self-diminishing effect as higher flux would probably exacerbate the concentration polarization effects. Hence it is deduced that polarization effect could be at its minimal at the optimum concentration difference of 2M. In another words, the net water flux at the optimum concentration difference would achieve its best. This explains the lower improvement of flux at a higher draw concentration, which opposes to the normal perception that a higher concentration should yield more flux improvement. Flux improvement rates are lower at higher draw concentration, this is likely due to that PZT generated vibration

could not overcome the increasing effect of concentration polarization with more concentrated draw solution. Consequently, a decline in the net water flux rate is observed.

6.3 Surface Additive Treatment on FO membrane for Water Flux Enhancement

The major limitation in Forward Osmosis for widespread applications is lack of economical membrane with good water flux performance. This shortcoming is associated with the ubiquitous concentration polarization effects, i.e. ICP and ECP that greatly restrict the water flux rate performance. It is the primary obstacle to be overcome in forward osmosis towards practicality.

Various methods have been adopted to improve this aspect in FO membrane. These include i) developing new membranes with more hydrophilic materials, ii) reducing membrane support layer thickness and iii) modifying membrane surface properties by surfactants. The implementations of the first two approaches require sophisticated tools and sound technical skills. Thus, a more feasible third approach as an alternative pre-treatment to condition the FO membrane in order to achieve better water flux performance is employed. It is a non-invasive approach, namely without altering and compromising the structural integrity of the membrane.

In general, surfactants can be categorized into four different types, namely the nonionic, anionic, cationic and zwitterionic. Specifically, zwitterionic is a subclass of polyampholytes which bear

equal amount of positive and negative charges on different non-adjacent atoms. Hence the total net charge of this chemical compound is zero, which renders it electrically neutral and shows no dependence of the charges on the pH or salt concentration^[181]. Besides, it is well-known that the zwitterionic groups are highly hydrophilic^[182, 183], especially one that contains the sulfobetaine group $[-N^+(CH_2)_nSO_3^-, n=1,2,3,4]$. It was also found from the literature that zwitterionic surfactant has been used successfully as a copolymer in ultrafiltration membranes to increase its wetting properties and corresponding anti-fouling ability to protein adsorption^[56, 184]. Nonetheless, it was achieved via a complex polymerization technique which is beyond the scope of present study.

Hence a niche is surface, as till to date none has ever attempted using a zwitterionic surfactant for treating FO membranes. It is the author hypothesis that zwitterionic moieties could be incorporated onto the membranes surface with a unique membrane surface treatment method developed specifically in this study. This method subjects the membrane to a continuous flow of surfactant solution treatment on both top and bottom of the membrane in a counter flow direction. Meanwhile, the membrane is equilibrated within a customized flow module. Systematic experimental studies are carried out to examine the effect of a particular zwitterionic surfactant of sulfobetaine group known as DMAPS on a commercial FO membrane. Various concentrations of the DMAPS surfactant solutions are used to treat the membrane. Subsequently, a comparison of flux rates is made between a non-treated and a treated membrane. Substantial water flux improvement is obtained at an optimal surfactant concentration, whereby the treatment protocol is identified to play a crucial part to achieve the results. In addition, both captive bubble contact

angle measurement^[185] and Raman spectroscopy are performed to substantiate the findings further.

6.3.1 Materials and Methods

FO Membrane -The same cellulose triacetate (CTA) membrane obtained from HTI was employed in this experiment that forms the basis for comparison. The details of which could refer to Chapter 5.

Zwitterionic Additive - Generally, there are three different zwitterionic groups, i.e. phosphorycholine group (PC), sulfobetaine group and carboxybetaine group. A Zwitterionic surfactant known as dimethylethylammoniumpropane sulfonate (*DMAPS*, with molecular weight 195.28g/mol, $C_7H_{17}NO_3S$, purchased from Sigma-Aldrich SG) was chosen in this study as it belongs to the sulfobetaine group which can potentially yield better wetting properties to FO membrane. Various concentrations of DMAPS solutions ranging from 10 μ M to 20mM were experimented.

6.3.1.1 Experimental Set Up and Procedures

The membrane surface treatment and characterization of water flux performance were carried out based on the schematic setup as depicted in Figure 6.9 (or Figure A10 in Appendix A). A flat sheet FO membrane was sandwiched in between two separate half of a custom-made modules

denoted as the top and bottom module respectively. Each module comprises a symmetrical rectangular flow channels with dimension of 18mm x 3mm x 200mm and is machined fabricated. Polyurethane rubber seals were applied around the perimeter of the flow channel on both sides to prevent possible leakage and keep the membrane in position. Detailed drawing of the membrane module can be found in Appendix B.

Two peristaltic pumps (Masterflex L/S model, Cole-parmer, IL) with variable speed drive were incorporated to circulate the additive treatment solution as well as the feed and draw solutions. The same pumps were used for the characterizations of water flux after the surface treatment. Dampeners were installed prior the channel entrance to smoothen the pulsation flow generated by the peristaltic pumps (positive displacement type). Separately, a needle valve was employed after the exit of the draw solution flow channel to build up pressure in the draw solution side to simulate PRO condition for flux characterization purpose. The built up gauge pressure was recorded using a differential pressure sensor with one side open to the atmosphere. Gravimetric method was used to quantify the water flux transport by measuring the weight change continuously on a weighing scale.

Each fresh membrane will be first treated either by DI water or DMAPS additive solutions of a particular concentration ranging from 10^{-5}M to 10^{-3}M . The membrane treatment cum equilibration process was carried out by running the additive solution in counter-current flow manner along the upper and lower rectangular flow channels of the membrane module.

Hypothetically, this allows for transferring the hydrophilic moieties onto the membrane via surface adsorption mechanism. Each equilibration lasted for 30 minutes. The purpose of the equilibration process has two folds, firstly, to purge out any trapped air or vapor within the porous layer of the membrane so that water passage would be in continuity and be undisturbed. By doing so, it could not only homogenize but also fluidize the membrane better to reduce erroneous flux measurements and enhance accuracy at the flux characterization stage. Secondly, it is to ensure that a standardized procedure was incorporated for treating membrane in consistent manner.

Subsequently, water flux characterization test will be performed after the completion of the membrane treatment. If not otherwise stated, membrane is always orientated in PRO mode throughout the experiments where the dense layer is facing the draw solution. The water flux characterization has two stages with the first one to identify the optimum additive concentration with the needle valve at fully opened position. Thereafter, flux characterization is carried out in PRO condition with applied pressure at the draw solution side by regulating the needle valve position. In this manner, qualitative results can be obtained for examining the additive effects. The procedure for carrying out the experiments is outlined in following section.

Control (Benchmarking) Test Procedure:

1. Cut FO membrane into size of 200mm x 18mm and covers the rectangular channel
2. Place FO membrane between the membrane modules and tension it to make sure the tautness. Membrane is orientated in PRO mode.

3. Tighten the locking bolts of membrane modules (top and bottom halve).
4. Connect the membrane module according to the schematic diagram illustrated in Fig 6.1.
5. Surface treatment on FO membrane with DI water for 30mins by circulating DI water without DMAPS additive solution.
6. Prepare 300ml each of DI water as feed solution and 0.5M NaCl as the draw solution.
7. Switch on the weighing scale, pressure sensor and pump concurrently.
8. Circulate feed and draw solutions with the needle valve at fully open position.
9. Run for 30 minutes and capture weight change of the draw solution at every interval of 1s.
10. Drain out both feed and draw solution completely and record their electrical conductivities.
11. Rinse the feed side channel with fresh DI water 4-5 times until its conductivity drops to the initial DI water range $\ll 5\mu\text{S}/\text{cm}$
12. Repeat steps 6-11 at different gauge pressure with voltages 2.8V, 3.5V and 4.5V (corresponding to pressure of 3.6kPa, 13kPa and 27kPa respectively).
13. Compute the water flux rate at different pressure condition.

B. Experiment Test Procedure:

1. Prepare zwitterionic DMAPS additive solution with its concentrations ranging from $10\mu\text{M}$ to 20mM .
2. Repeat the same procedure set out in A except in Step 5, the surface treatment on membrane with zwitterionic additive solution instead of DI water.

**A minimum of three sets of experiment runs were carried out to compute the average results with a standard deviation error.*

Figure 6.9 Schematic experimental setup for membrane surface treatment and characterization of membrane water flux performance. (actual setup can be found in Figure A10 of Appendix A).

6.3.2 Results and Discussion

An assessment on Figure 6.10 clearly indicates that surface additive treatment by DMAPS is indeed capable of enhancing the water flux (compared with the baseline water flux treated with DI water alone). The average baseline water flux was measured at 10.27LMH. Improvement of water fluxes were recorded across the additive concentration range from 10^{-5} to 10^{-3} M and specifically with the highest increment of flux recorded at 3×10^{-5} M of approximately 11LMH.

This is an increase of 7% over the baseline flux, and $3 \times 10^{-5} \text{ M}$ is identified as the optimum additive concentration for achieving the highest water flux performance.

Figure 6.10 Water flux with zwitterionic additive surface treatment against baseline water flux (dotted line) at various additive concentrations ranging from 10^{-5} M to 10^{-3} M .

It is hypothesized that the mechanism for flux increment is due to the formation of a hydration shells^[181]. These hydrated shells are formed due to the interactions between zwitterions and water molecules. Physically, the more electronegative oxygen atoms of the water molecules will move toward the positively charged ions, whereas the negatively charged ions attract the more electropositive hydrogen atoms of water, thereby creating the hydration shells. In the context of the DMAPS additive employed in this study, the anionic sulfonate groups and cationic ammonium groups (belonging to the zwitterionic sulfobetaine functional group) are close to each other, and could counteract the electrostatic hydration. As a result, hydrophilicity moieties could

then be introduced and adsorbed onto the membrane surface. Besides, the zwitterionic modified membrane surface would not disturb much to the hydrogen-bonded network structure of water significantly ^[186, 187]. This would eventually enhance the wetting properties of the membrane, and allow smoother water transport by suppressing the concentration polarization layer due to the accumulation of salt ions. Pictorial illustration of the mechanisms is shown in Figure 6.11.

Figure 6.11 Mechanisms showing the formation of a hydration layer by zwitterionic additive that changes the wetting properties of the membrane surface and suppress the polarization layer.

Nonetheless, results also show that with higher concentrations of DMAPS additive, specifically beyond 10^{-3}M , the performance of water flux rate declines. The deterioration in flux is most likely due to the formation of macromolecules of a certain volume density. This dense formation of macromolecules could possibly occupy and hence block the membrane pores, thereby reducing the available water transporting channel. As a result, water flux rate is adversely affected, and the declining water flux rate is seen beyond this point. In other words, the

concentration polarization effects could have been exacerbated with the introduction of this additive layer.

Subsequently, with the identified optimum additive concentration, more tests were performed to evaluate the water flux subjecting to a pressure of 3.6kPa, 13kPa and 27kPa respectively applied on the draw side. This is to simulate the PRO process condition where the flux rates are supposed to reduce further due to the opposing pressure that could lower down the effective osmotic pressure gradient. On the contrary, the experimental water flux rates are not reduced but increased upward as shown in Figure 6.12. This unusual behaviour provides different perspectives with surface additive treatment. It shows that additive treatment could actually yield much better flux rate at higher operating pressure. One possible reason for the further improvement could be attributed to an increase in compactness of hydration layer that provides a more homogenous wetting surface. Hence, more effective water transport can be achieved through the entire membrane surface. The improvement in flux rates is substantiated by measuring post experiment feed and draw conductivities shown in Figure 6.13. Generally, higher flux rate means more dilution of the draw solution and thus greater salt leakage to the feed side. Apparently, this is reflected by the decrease and increase in draw and feed solution conductivity, respectively.

Figure 6.12 Water flux rates under the PRO mode with applied pressure on the draw solution side.

Figure 6.13 Feed and draw solution conductivity measured at the end of each test versus various applied pressure under the PRO mode.

Other than quantifying the water flux performance experimentally, another two distinct surface characterization methods were utilized to validate the adsorption of hydrophilic zwitterionic moieties on membrane surface. They are i) contact angle measurement by the captive bubble method^[185] and ii) Raman spectroscopy^[187]; the latter is to identify the spectrum or wavenumber of particular functional groups appeared on the membrane. The results from these two methods are presented in Figures 6.14 and 6.15.

Procedures of performing the captive bubble measurements can be found in Appendix A7. Based on the consolidated data, it is found that the contact angles actually increase significantly for both the dense and support layer especially at lower additive concentrations ranging from 10 μ M to 50 μ M. This is consistent with the earlier findings that the flux improvement fell within 10⁻⁵ to 10⁻³ M and particularly in the 10⁻⁵ to 10⁻⁴ M region. This suggests that the absorption of zwitterionic additives is most effective in this region. In particular, the median value of 30 μ M is exactly the optimum additive concentration that was identified previously. It is noted that a higher contact angle means better wetting of the membrane surface as the angle denotes between the air bubble and the membrane surface. This is in contrast with the conventional way of measuring contact angle between a water droplet and a solid substrate. Nonetheless, this method has further confirmed the attachment of hydrophilic moieties onto the membrane surface successfully.

Figure 6.14 Contact angle (measured by the captive bubble method) against DMAPS surfactant concentration ranging from 10 μ M to 50 μ M.

To extent it further, Raman Spectroscopy (Renishaw, Materials Lab 1 NTU) was used to determine the presence of representative functional group at a certain wavenumber or spectrum. Indeed, with the reference from a standard spectrum table^[188], specific peaks are observed at wavenumbers around 1300 and 3000 which correspond to sulfonates and amines groups that are present in the chemical structure of zwitterionic DMAPS additive. It proves that this functional group solely contributed by the additive, but not anything else is found on the cellulose triacetate FO membrane.

Figure 6.15 Raman spectroscopy intensity profile against wavenumber shift with highlighted peaks denoting the functional groups of sulfonates and amines contributed by the DMAPS surfactant on both support and dense layer sides of a FO membrane.

6.4 Surface Additive Treatment on EK Porous Medium for Augmentation of Streaming Potential and Streaming Current

It has been identified earlier in the literature review section that one of the major limitations of EK power generation is its inherent low energy conversion efficiency ^[35, 39, 133, 167, 168, 189], and usually much less than 10% is determined both experimentally and theoretically by other researchers. Hence, to make it become a viable technique, it is paramount important to address this shortcoming by i) developing an economic method or ii) employing a better material for such purpose. However, making sophisticated channels of optimum sizes and geometries as well as material properties remains a great challenge, and it is beyond our reach in the context of this project. Hence, it is more logical to adopt the first approach by employing an economic method. Moreover in this project, despite the novelty of leveraging the osmotic pressure gradient derived from FO transport water across microchannels, yet the output power is still far too low from any practical usage. In view of this, it is needed to develop an appropriate method to address this issue.

Essentially, power generation by EK is an interfacial phenomenon specifically between the charged channel surfaces in contact with an electrolyte solution subjecting to a hydrodynamic pressure driven flow. Therefore, two possible schemes are identified to augment the power performance either by modifying the channel surface properties or altering the solution properties content. Nevertheless, the solution tested in this project is fixed with DI water. Hence, the focus would naturally be placed towards the first scheme whereby employing a method that could possibly modify the channel surface properties to the advantages of EK. One good

approach is to borrow the same concept used in previous section by using surfactants treatment to vary the channel surface wetting properties or hydrophobicity. By doing so, it could potentially affect the surface charge density on the channel surface, and probably leading to hydrophobic slip. Eventually, it could improve the overall energy conversion efficiency, which coincides to the niche areas identified earlier for developing an economic method.

Therefore the objective of this section is to examine the functionality of employing surface additive treatment method to enhance the power performance of EK power generator experimentally. Anionic surfactant Sodium dodecyl Sulfate (SDS) is employed for this purpose as it has been used previously to treat membranes of porous nature similar to porous media used in this project which gain positive results. Furthermore, it aims targeted at varying the surface properties of the channel specifically the channel wall surface hydrophobicity (to influence the effective viscosity μ) and zeta potential ζ (to alter the EDL thickness). Direct treatment method is employed by pumping surfactant additive solution across porous media at an appropriate flow rate. Thus, certain amount of surfactant molecules could adhere to the channel surface and form the so called self-assembly layer (SAM). Parametric studies are carried out in terms of channel geometry and structural properties including channel size, porosity and tortuosity, channel material types and additive concentrations at various applied flow rate. The characterization is done by measuring the specific streaming potential and streaming current (per unit pressure), and a comparison is made against the baseline results i.e. without any treatment.

6.4.1 Materials and Methods

Surfactant - Anionic surfactant sodium dodecyl sulfate (SDS with MW 288.38 g/mol and chemical formula as $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, purchased from Sigma Aldrich, SG) was employed. Additive concentrations ranging from 10^{-5}M to 10^{-2}M were prepared using DI water as the solvent.

Porous Media - Parametric studies were carried out using two different types of dielectric porous media made of glass and polyethylene based material with various sizes as tabulated below:

Type of Porous Medium	Geometry	Thickness (mm)	Nominal Pore Size (μm)	Abbreviation
Porous Glass Grade 2	Round Disc	3	40-100	PG2
Porous Glass Grade 4	Round Disc	4	10-16	PG4
Polyethylene	Round Disc (Laser Cut)	8	20	PE8

6.4.1.1 Experimental Setup and Procedures

Figure 6.16 A schematic experimental setup for surfactant treatment on porous media and characterization of EK power performance. Actual setup is shown pictorially in Figure A11 of Appendix A.

The experiments framework was designed based on the schematic set up illustrated above for both the surfactant treatment and the characterization of EK power performance. The above set up mainly consists of a peristaltic pump (VSD), an EK power generator (or EK module) that hold the porous media and an electrode pair which was connected to a source meter for measuring the streaming potential and streaming current, a hot plate or weighing scale to heat up the surfactant solution (for better affinity to the channel wall) and allow for quantifying the flow rate experimentally. Pressure sensor (differential type with one end exposed to the atmosphere) and a pulsation dampener were placed in between the pump and EK power generator. Both

function to record the pressure difference (ΔP) and to smoothen the flow across the EK module respectively. The dampener could reduce the fluctuation in reading when measured the streaming current and streaming potential as they are sensitive to the pressure or flow changes. Basically, both are flow induced and depend very much on the flow characteristic.

Direct treatment method was employed; the surfactant solutions were directed across porous media. In this study, during the treatment, the surfactant solutions were constantly subjected to mild heating (around 50C) by the hot plate to enhance the surfactants adsorptivity. Prior to the treatment, the surfactant solutions were subjected to sonication (agitation by ultrasound) process of an hour to enhance its dissolution in the DI water solvent. The treatment solutions were then circulated through the porous medium for at least an hour to ensure that surfactants could be coated or adhered onto the surface of the pores of the porous medium effectively. Subsequently, characterization of specific streaming potential and streaming current was then carried out. While for the baseline results, the treatment was done by using DI water alone for the same period of one hour. *(For each surfactant concentration, at least 3 sets of results were obtained, and each set was tested with applied flow rates ranging from 5ml/min to 30ml/min)*

6.4.2 Results and Discussion

The consolidated experimental results of the specific streaming potential and streaming current (defined as per unit applied pressure in this study) are plotted against the logarithmic surfactant concentration in Figures 6.17 and 6.18. Based on the graphs, it clearly shows that overall results are substantially improved, particularly at the lower surfactant concentration region of 10^{-5}M to

10^{-4} M. More than 100% increase in the specific streaming potential for the glass types porous medium is registered, namely from 0.25mV/Pa to 0.52mV/Pa for PG2 and from 0.14 mV/Pa to 0.3 mV/Pa for PG4. While there is merely 7% (at most) increment for the polyethylene type porous medium PE8, namely from 0.396 to 0.422 mV/Pa. Similarly for the specific streaming current, the glass type porous medium has also achieved good improvement with 64% (from 0.36 to 0.59 nA/Pa) and 63% (from 0.16 to 0.26 nA/Pa) for PG2 and PG4, respectively. On the contrary, much higher improvement for PE8 of 76% from 0.122 to 0.21 nA/Pa is obtained. However above the surfactant concentration of 10^{-4} M, the performance goes down and sometimes even below the baseline result is observed. Apparently, this particular concentration region is identified as the optimum range of surfactant concentration for achieving effective treatment.

Generally, the surfactant treatment on inorganic glass (silica surface) is more prominent than on organic polyethylene material in terms of specific streaming potential. This is in fact, strongly related to the higher zeta potential on silica surface than on polyethylene surface which is estimated to be -40mV and -15mV (determined earlier) for glass and polyethylene, respectively. This is because the silica surface is more polarizable and is in direct relation with the surface charge density ρ_e . Furthermore, higher surface charge density also means the silica surface has better wetting properties and more hydrophilic than the polyethylene surface. As a result, more net charges could be brought downstream, thus forming higher streaming potential. On the other hand, polyethylene has achieved better in terms of specific streaming current as its surface

charge is more mobile with relatively hydrophobic surface. More detailed discussion will be provided next.

Figure 6.17 Overall specific streaming potential of respective types of porous media produced at SDS concentration ranging from 10^{-5}M to 10^{-2}M against baseline result (dotted line). The streaming potential is an average value obtained at various applied flow rate, whereas the baseline is without SDS additive treatment.

Figure 6.18 Overall specific streaming current of respective types of porous media produced at SDS concentration ranging from 10^{-5} M to 10^{-2} M against baseline result (dotted line). The streaming current is an average value obtained at various applied flow rate, whereas the baseline is without SDS additive treatment.

Nonetheless, the improvement in both specific streaming potential and streaming current after the surfactant treatment suggests the possible presence of slip effect. It is hypothesized that surfactant molecules can be adsorbed onto the charge channel surface, and are arranged in such manner that the hydrophobic tail is attached to the channel wall, with the hydrophilic charge head exposing to the bulk electrolyte solution in a structured arrangement known as self-assembled monolayer (SAM) as depicted in Figure 6.19. Hence, the channel surface properties are modified as well as the corresponding interfacial interaction with the electrolyte solution.

Physically, charges within the Stern layer, conventionally immobile in the case of hydrophilic or non-slip boundary condition, may acquire movement with a hydrophobic surface due to slip specifically in tail part of the surfactant SAM. This contributes to the augmentation in streaming current and then translates to higher mean velocity within the channel. As a result, the fluid flow within the channel is enhanced with a lower pressure requirement. Simultaneously, the charged surfactant also increases the overall net charge density in the electric double layer. This gives rise to much higher apparent zeta potential ^[139, 190]. This relationship can be described by Helmholtz-Smoluchowski equation ^[125] (also see Equation 2.11 in the literature review) as follow,

$$\zeta = \frac{\Delta\phi}{\Delta P} \frac{\mu}{\varepsilon} \left(\lambda_f + \frac{2\lambda_s}{a} \right) \quad 6.1$$

where $\Delta\phi$ is the streaming potential, ΔP the hydrodynamic pressure difference along the capillary channel, μ the liquid viscosity, λ_f the bulk liquid conductivity, ε the liquid permittivity, λ_s the surface conductivity and a the capillary radius. Since the charges in the Stern layer have gained mobility, and this will definitely have direct influence on the surface conductivity and causing it to trend higher. It is foresee a tradeoff between the increases in charge transport while at the same time; another pathway for dissipating the power is also presented when the surface charge density becomes larger. Hence, the power performance of EK will be adversely affected. Therefore, we have to be careful in applying the right optimum concentration for achieving positive results.

In addition, the slip length b can then be estimated according to Joly et al.^[190] as

$$\zeta = \zeta_0(1 + \kappa b) \quad 6.2$$

where ζ_0 is the original zeta potential without any treatment, and κ is the Debye-Huckel parameter. Hence the advantages of using surfactants to modify channel surface are demonstrated. Previous studies show difficulty in achieving hydrodynamic slip and high surface charge density concurrently due to the inherent competing effect between these two properties. Through surfactant modification approach, it has not only successfully introduced slip for higher charged density surface but also increase its charge density within the EDL. In conclusion, the hydrodynamic slip due to relatively high hydrophobicity and charge density of the channel surface with surfactant modification could amplify the electrokinetic effects and render higher conversion efficiency and power output.

Figure 6.19 Hypothesized self-assembled monolayer (SAM) of SDS anionic surfactant on channel wall.

6.5 Stacking Effect with EK Power Generator Connected in Parallel and Series Electrically for Multiple Increment of Streaming Potential and Streaming Potential

The EK power generator developed in this project is analogous to a battery. However, the main difference is that EK power generator does not store energy (in chemical form), and is able to generate direct electricity electrokinetically when water flow through an array of microchannels in the form of porous media. These channels are considered to be connected in parallel such that the overall streaming current is the sum of streaming current produced by individual channel with the same voltage or streaming potential. This can be described analytically with an equivalent circuit. The concept of equivalent circuit can be further extended on EK power generator (as a whole) by connecting multiple units in parallel or series configuration for achieving multiplication effect in current and voltage respectively. Hence the objective in this section is to assess the effectiveness of such concept experimentally. By doing so, the overall power generating capability of EK-FOC technique can be greatly enhance. It can pave way for possible large scale production.

6.5.1 Materials and Methods

EK Power Generator consists of PG2 and PG4 porous media, which are chosen in this study due to their yielding of higher power output as confirmed by the previous tests. An equivalent circuit of a single unit EK power generator is depicted in Figure 6.20.

Figure 6.20 An equivalent circuit for an EK power generator with an internal resistance R_{internal} and electrode pair denoted by two ends.

6.5.1.1 Experimental Setup and Procedures

With the setup described by Figure 6.16, tests were carried out to determine the baseline magnitude of streaming potential and streaming current for a single unit EK power generator. Once the baseline was established, it was then transferred to a stacking configuration setup depicted by the schematic diagram below for determining the multiplication effects of streaming potential and streaming current connected in series and parallel. In Figure 6.21, multiple units of EK power generator can be stacked together with a manifold. A peristaltic pump was utilized here to drive and vary water flow. However, in actual EK-FO energy harvesting technique, each of the EK power generators can be driven by an individual FO flow generator. The configuration depicted herein is to simulate the FO flow condition. Thus practically the induced pressure difference across each EK power generator should be identical if the same flow rate is applied.

To minimize the water flow fluctuation, a pulsation dampener was employed after the pump. Furthermore in the experiments, the physical electrical connection of the EK modules in parallel and series was done by connecting wires onto the electrodes with the help of crocodile clips (see Figure 6.22). The overall circuit is delineated and built on the basis of a single EK power generator equivalent circuit as shown. At least 3 sets of results were obtained, and each set was tested with various flow rates ranging from 5ml/min to 30ml/min.

Figure 6.21 Schematic diagram of stacking configuration of EK power generators and connected in parallel electrically. (The actual setup can be referred to Figure A12 in Appendix A)

Figure 6.22 Equivalent circuit connection of EK power generators in a) parallel and b) series electrically. With such connection, the flow rate and pressure difference across each EK power generator module would be equal to a single unit.

6.5.2 Results and Discussion

The results of the stacking effect in series and parallel (up to 4 units of EK power generators) are presented in Figures 6.23 and 6.24 respectively. Inferred from the results, it can be seen that the streaming potential and streaming current are almost linearly proportional to the applied flow rate as well as the number of units of EK generators. For instance, the streaming potential of 1 unit of EK power generator of PG2 at 30ml/min is approximately 0.08V. The corresponding streaming potential for 2 , 3 and 4 units connected in series are 0.18V, 0.28V and 0.39V respectively. Whereas, the streaming currents remained largely unchanged, while showing the same linear relationship against the applied flow rate and independent of number of units of EK power generator. Similarly, with EK power generators connected in parallel, the streaming potential converged and follow a linear relationship against applied flow rate. While the streaming current is the multiple of the unit of EK power generator in connect. Based on the

results, it shows the effectiveness of the stacking approach with augmentation of the potential and the current by connecting multiple EK power generators in series and parallel respectively. The results are consistent with the idea proposed and follow exactly with the general circuit law. With this approach, the power generating capacity can then be regulated and sized accordingly with respect to the actual power demand. In fact, this unique scalability characteristic with the current modular design by stacking configuration is considered a big leap forward in the development of EK-FOC energy harvesting technique, and it paves way for future commercialization.

Figure 6.23 Consolidated results of the streaming potential and streaming current against applied flow rate of EK power generators connected in Series. (a) Streaming potential for PG2 (b) Streaming potential for PG4 (c) Streaming current for PG2 and (d) Streaming current of PG4.

Figure 6.24 Consolidated results of the streaming potential and streaming current against applied flow rate of EK power generators connected in parallel. (a) Streaming potential for PG2 (b) Streaming potential for PG4 (c) Streaming current for PG2 and (d) Streaming current of PG4.

6.6 Chapter Summary

This chapter attempted various methods targeted at enhancing, maximizing, and optimizing the power performance of FO-EK energy harvesting technique. Both chemical and physical approaches were experimented and examined on the FO membrane (flow generator) and the porous medium (power generator), respectively. Experimental results had shown that these methods could largely meet the objective for enhancing the overall energy conversion efficiency.

Chapter 7 Transforming Bench-scale Test to Potential Real Applications

The concept of EK-FOC energy harvesting technique from salinity gradient has been proved, and the technique has been studied by carrying out extensive experimental investigation. To produce desirable electrical power output, it is necessary to grab not only the know-how of combining FO and EK synergistically but also the correct engineering design for stacking them effectively. In spite of both the FO membrane and the dielectric porous medium are obtained readily off the shelves. Besides, together with the modular designed scheme adopted, this provides extra versatility and enables large scale production to facilitate the sizing up of the system subsequently. All are important aspects and crucial for the development of future commercial applications such as a small standalone power generating device (in kW) or a large scale power plant (in MW).

In this chapter, a bench-scale modular system was developed with an intention to showcase the power generating capability of an EK power generator. Specifically, the system was used to show actual power to be generated for lighting up a LED. This allows to visualize the functionality of the system and to relate it for real applications.

Furthermore, a simple economic assessment was provided on the viability of the EK-FOC harvesting technique on a large scale power plant basis. The estimation was carried out with reference to a large scale PRO plant^[9] by using those parameters such as membrane flux rate, zeta potential, surface conductivity, channel resistance etc., determined from the previous FO and EK experiments. The estimation suggests good potential value for commercialization with

indicative price of the power generated at less than 0.15S\$/kWhr which is competitive to other renewable energy costs such as wind or solar power. It should be noted that the figures obtained was based on a conservative estimation method and there is lots of rooms for further improvement as an emerging technology. Hence, it is valid to call for the transformation from benchscale tests toward real applications.

7.1 Bench scale demonstration of EK-FOC power generation

In spite of the various experiments carried out to characterize the performance of EK power generator in terms of streaming potential and streaming current, it hasn't been utilized to powering up an actual device. Hence, an attempt was made for demonstrating its power generating capability by lighting up a LED. A bench scale setup as depicted by the equivalent circuit diagram in Figure 7.1a was employed. The circuit was conveniently prepared on a bread board with components included in the following

1. An EK power generator module comprises a PG4 porous media
2. A 100 μ F capacitor
3. A 3-way toggle switch
4. A Light emitting diode (LED)
5. A standard 100 Ω resistor

The flow across the EK power generator module was driven by a peristaltic pump separately at a flow rate of 50ml/min. In addition, a multi-meter was connected in parallel to monitor charging process. During the charging phase, the 3 way switch was toggled at position 1 while the

capacitor was being charged. By estimation, it would take about 4x of the time constant τ (where $\tau=RC$) or approximately 400s for the capacitor to be fully charged as the internal resistance is of about $10^6\Omega$ as determined experimentally earlier. Once the charging voltage reached the magnitude of streaming potential (or Open Circuit Voltage), the switch was then toggled to position 2 and LED was lighted up through the discharging of the capacitor with a current loading estimated in a range of mA. The indirect powering up of a LED by capacitor discharge was applied to overcome the limitation of direct current produced by EK generator because such direct current is in the order of μA . Obviously it is not sufficient for powering up such LED, which requires at least a current in mA level. Nonetheless, this simple experiment has proved that actual power is indeed produced electrokinetically.

Figure 7.1 a) An equivalent circuit depicting the bench scale setup for demonstrating the power generating capability of an EK power generator through lighting up a LED and b) the actual setup with a multi-meter showing the charging process with increasing voltage generated.

7.2 Assessment on economic viability of EK-FO energy harvesting technique from salinity gradient

An approach, similar to cost (\$/kWhr) estimation of a large scale PRO plant^[9], was adopted to assess the economic aspects for developing an EK-FO power plant. The estimated figures were determined based on the parameters of glass type porous media (PG4) and commercial CTA FO membrane which were obtained commercially. The calculation was distinguished into two parts, namely the technical and costing parts as follow:

7.2.1 Part A: Calculation on Technical Aspects

1. FO membrane flux with fresh river water and seawater (0.5M) as the osmotic pair: 7 L/m²hr (0.36 m³/day)
2. Total membrane area assumed: 1 x 10⁶ m²
3. Total volumetric flow rate (permeate rate) generated: 7 x 10⁶ L/hr
(Equivalent to 1.68x 10⁵ m³/day or 117 x 10⁶ mL/min)
4. Induced streaming potential with a flow rate of 50ml/min in a EK unit 12V
Streaming Potential vs Flow rate relationship of 0.24Vmin/ml (See Figure 7.1)
5. Total units of porous medium (3.14x 10⁻⁴ m² per unit porous medium of Ø20mm) 2.33 x 10⁶ units or 734m²
(determined by using Item 3 divided by a unit flow rate of 50ml/min)
6. Total number of channels per m² of porous medium 1 x 10¹²
7. Overall total number of channels 7.34 x 10¹⁴
8. Total resistance by assuming all connected in parallel 1.36 x 10⁻⁵ Ω

$$R_T = \frac{R_c}{N} \quad (\text{Resistance per channel } 1 \times 10^{10} \Omega)$$

9. Total power generated 10566 kW

$$P = \frac{V^2}{R_T}$$

10. Membrane area power	585.78 kWhr/m ²
(Assumed a lifespan of 10 year for the membrane and an operation schedule of 24hrs/day and 330days/year)	
11. Porous medium area power	7.98 x 10 ⁵ kWhr/m ²
(Assumed a lifespan of 10 year for the membrane and an operation schedule of 24hrs/day and 330days/year)	

7.2.2 Part B: Cost Estimation

1. Plant capital cost:	S\$33.6 x 10 ⁶
Assuming 1/5 capital cost of a large RO plant: S\$200day/m ³	
2. Annual amortization of plant cost	S\$ 2.24 x 10 ⁶ /year
Assume 3% and 20years with Equation 7.1 for calculating the amortization annually	

Cost breakdown in terms of dollar per kilowatt hour

1. Plant cost per kilowatt hour	S\$0.027/kWhr
(Assuming operation at 330days/year and 24hrs/day)	
2. Membrane replacement cost at S\$12/m ² (based on RO membrane)	S\$0.020/kWhr
3. Porous medium replacement cost at 10\$/m ²	negligible
4. Labor cost @ S\$2 x 10 ⁶ /year	S\$0.024/kWhr
5. Operation and maintenance cost @ 5% of capital cost	S\$0.020/kWhr
6. Others, e.g. pretreatment/chemical backwash etc. (10% of total cost)	S\$0.040/kWhr
<hr/>	
Total energy cost	S\$0.131/kWhr
<hr/>	

Through the calculation, the energy cost estimated is S\$0.131/kWhr which is comparable to other renewable energy sources such as wind or solar power. These figures, however, are just indicative only and have much room for improvement specifically by enhancing the specific

streaming potential and ultimately leading to higher energy conversion efficiency, namely from chemical potential into direct electricity. The thorough experiments carried out in Chapter 6 were actually targeted to improve this aspect in FO and EK parts separately. More studies are needed to reduce the energy cost both technically and commercially for making the proposed technique a sustainable technology.

Figure 7.2 A model prediction of the variation of flow induced streaming potential through a glass porous medium with respect to permeate flow rate and hydrodynamic pressure difference induced by FO. A value of the zeta potential of -120mV is used in the model. For an induced FO flow rate of 50ml/min, the streaming potential generated and corresponding pressure difference are estimated to be 12V and 30kPa, respectively.

Amortization Calculation

The formula for calculating amortization for a certain number of periods is shown below:

$$A = P \frac{r(1+r)^n}{(1+r)^n - 1} \quad 7.1$$

where A is the payment amount per period, P is the initial Principal (loan amount), r is the interest rate per period, and n is the number of payments or periods.

7.3 Chapter Summary

In this chapter, a bench-scale modular EK power generator system was developed to demonstrate the actual power generating capability by lighting up a LED. In addition, an economic assessment was also provided to which the EK-FOC harvesting technique were extended into a large scale power plant. The estimation had suggested that this technique has good potential value for commercialization and competitive to other renewable energy such as wind or solar.

Chapter 8 Conclusions and Future Studies

8.1 Conclusions

As indicated in the literature, enormous amount of salinity-gradient energy estimated in the order of trillion Watts from river water and sea water remains largely unexploited so far. Therefore, in this work an innovative method based on the principles of forward osmosis (FO) and electrokinetic phenomena (EK) is developed to harvest this form of energy and coined it as FO-EK energy harvesting technique. Specifically, the energy (or power produced) is derived from the electrokinetic flow induced streaming potential and streaming current with the flow driven by FO.

The proposed technique was demonstrated successfully by constructing a modular prototype system based on the proposed method. A series of experimental studies were conducted to verify its functionality and to characterize its power performance. It was found that the measured power density of the prototype system which is in the order of 10^1W/m^2 , is comparable to the existing more established technologies of PRO and RED. This finding has proven the feasibility of this technique and provided yet another alternative and promising new technology for harvesting energy from salinity gradient.

In parallel, a theoretical framework based on Onsager relationship and osmotic flow process across semi-permeable membrane was developed to model the power generation of the prototype system. The model has provided insights of the connection of the two FO and EK phenomena. It has shown that the model could reasonably explain the experimental results. The correlations

between theoretical and experimental results have paved a way of providing optimal design and good control of the FO-EK technology based systems. The following summaries can be made:

For the FO flow part, the membrane employed should possess the following characteristics,

1. High water permeability and low concentration polarization effects
2. Good surface wetting properties or hydrophilicity to smoothen water transport
3. Good membrane selectivity with minimal salt leakage so as to maintain the osmotic gradient for more effective water transport

All these factors will have direct impact on the EK power generating part. The main emphasis is to maintain sufficient water flux rate across porous media in order to yield stronger flow induced streaming potential and streaming current or the eventual power produced. Besides, the porous medium should also possess the following characteristics:

1. High surface charge density or zeta potential to yield high flow induced streaming potential (more net amount of charges can be brought downstream)
2. Hydrophobic channel wall with certain degree of slip to achieve higher mean flow velocity across the channel. This gives rise to larger streaming current and also reduces the hydrodynamic pressure requirement
3. Low surface conductivity to limit the current dissipation through this conductive path
4. High surface to volume ratio determined by its structural and geometry properties including the channel size, tortuosity and porosity. The most optimum channel size should be two times of the EDL thickness.

It has shown that no additional physical pressure input is required to drive the water flow across porous media. This is considered as one of the most unique features in the proposed FO-EK energy harvesting technique. Other features such as no mechanical moving parts, no involvement of sophisticated equipments and emission free have further justified the FO-EK technology as a sustainable mean for harvesting energy from salinity gradient of the future.

Hence, to overcome the inherent low energy conversion efficiency, namely from FO hydrodynamic pressure driven water flow to EK power. Several physical and chemical methods have been attempted to address this limitation, and they are

1. PZT induced surface vibration on FO membrane
2. Surfactant treatment of FO membrane by DMAPS zwitterionic additive
3. Surfactant treatment of EK porous media by SDS anionic additive

These proposed methods have led to positive improvement results in terms of water flux rate and specific power performance (streaming current and streaming potential per unit pressure or applied flow rate). These improvements are resulted from 1) the PZT vibration induced mixing enhancement and reduction of concentration polarization effects, and 2) surfactant treatment induced modification of the surface properties of FO membrane and porous media.

On the other hand, an advance stacking-up configuration by connecting multiple units of EK power generators in series or in parallel electrically has been devised to augment the streaming potential and streaming current proportionally without increasing the pressure difference. This approach is innovative, and it indicates that EK technique can be scaled up readily according to

the specified power requirements. Therefore, it is foreseen that this state-of-art technology could have a good commercial prospect. However, the power generation of the prototype system was performed in a batch scheme where the draw and feed solutions are not circulated. This is far from practical application, and thus there is a need to develop a system operating in a continuous scheme with constant supply of new feed and draw solutions to maintain the power generation process.

In summary, the recognized three major hurdles are:

1. Low conversion efficiency from FO pressure driven flow to EK power generation
2. Lack of specific membrane and porous media to yield optimum performance
3. Short of a system that could function in a continuous flow scheme

These shortcomings shall be addressed in the following recommendations for future studies section.

8.2 Recommendations for Future Studies

To propel the technology ahead, the future studies fall into two respective directions namely i) to continue research for refining and enhancing the power performance of FO-EK technique and ii) to develop continuous flow systems and new applications. Detailed discussion of the proposed future studies are elaborated as following.

8.2.1 Research on Refining and Enhancing Power Performance of FO-EK technique

8.2.1.1 Study of Fouling Issues on FO Membrane

One of the key problems encountered in membrane based processes is the fouling issue which has not been examined in the present study. Fouling happens due to the accumulation of undesirable deposits on the membrane surface. The deposits can be colloidal particles, chemical and biological species, dissolved organic compounds etc.. which are retained on the membrane surface when feed water permeates through a membrane. The accumulation of these deposits could compromise the membrane performance which reduces the membrane water permeation rate and rejection capability, and more importantly exacerbates the concentration polarization effects. Consequently, this would translate to lower energy conversion efficiency and greatly shortened the life span of the membrane.

Intuitively, it is known that flux performance is directly related to degree of fouling where higher flux normally implies better anti-fouling capability of the membrane and provides longer lifespan. In the present work, even though much higher water flux performance has been achieved with DMAPS additive treatment as well as PZT induced surface vibration at membrane-solution interface, the fouling tendency of the treated membrane has not been studied. Hence, investigation on fouling issues shall be performed as one of the key future studies for enhancing the power performance.

8.2.1.2 Study of Multi-Stage Configuration FO Flow Generator

Figure 8.1 shows a conceptual illustration of a multi-stage configuration of FO flow generator that can break down into intermediate draw and feed solution pair of varying concentration difference. In this configuration, the feed solution of one pair will be the draw solution for the adjointed pair. By doing so, the concentration difference between each pair of solution is lowered so that the concentration polarization effect can be reduced. This is to limit the self-diminishing effect of concentration polarization as higher flux rate means greater polarization effect and possibly more fouling.

Figure 8.1 Conceptual illustration of a multi-stage FO configuration with varying concentrations difference solution pair

8.2.1.3 Study of Electrodes Over-Potential and Polarization Issues

Another key component in the FO-EK system that is overlooked in the main context is the current collector or electrodes. Although Ag/AgCl electrodes used in the experiment are performing well, it is not perfect as we still encountered problems such as i) the silver chloride

coating can worn out over time ii) the silver mesh can be corroded if left in the water without in use. Besides, no characterization was carried out to study the electrodes over-potential and polarization issues. Hence, it is necessary to look into all these aspects to enhance the electrode performance and maintain consistency in power generation.

8.2.1.4 Identify Better Material for The FO membrane and The EK Porous Medium

Continue to search for more suitable material for both the FO membrane as well as the EK porous media. Taking the cue from new avant-garde material with the aid of advance nano-technology could be leveraged to meet this objective. In conjunction, more new methods shall be developed to modify the performance of existing membrane and EK porous media. One possible way is to identify a more effective surfactant or protocol for achieving this purpose.

8.2.2 Development of New Applications

8.2.2.1 Continuous Operation Mode of FO-EK Power Generation Technique

The prototype system in the context of this study was performed in a batch mode. Hence, it is paramount to extend it into a continuous mode as part of the future work for more realistic application. Figure 8.2 is a schematic of a FO-EK power generating system in continuous mode operation. Unlike the batch configuration, this system comprises a spiral wound membrane instead of a flat sheet membrane in order to enhance the surface to volume ratio and generate higher volumetric flow rate.

However, to achieve the continuous operation condition, additional pumps are needed to circulate the feed and draw solutions as depicted by the figure. One key feature in this system is that the water flow driven by FO process (Q_{FO}) will be contributed to the total volumetric flow rate Q_{Total} at the feed side. The ratio between the permeation rate to the pump flow rate Q_{pump} need to be carefully adjusted so that net power is derived from the FO-EK process instead of the pumping work. Part of the flow will be channeled back to the reservoir after the FO process and for the power generation continuously. By doing so, a constant osmotic pressure gradient can be maintained across the FO membrane.

Figure 8.2 Schematic diagram of a FO-EK power generation system in continuous mode operation

8.2.2.2 FO-EK Powered CDI Desalination System

Other than abundant natural sources, anthropogenic saline water can also be readily obtained from industrial processes, such as brackish water and concentrated brine discharged from desalination plants. Therefore, FO-EK power generation can be integrated into existing RO

desalination plants where the discharged saline water can be recycled as the draw solution. Doing this would produce both economic and environmental benefits. Firstly, the extra power generated from the EK-FO technique can supplement the energy intensive RO processes. Secondly, environmental issues associated with RO plants for the disposal of concentrated brines would be mitigated.

Figure 8.3 Schematic diagram of a standalone FO-EK powered CDI desalination system.

Furthermore, a self-sustainable standalone water desalination system is conceptualized based on the capacitive deionization (CDI) principle. Besides, this system would be able to demonstrate the versatile functionalities of the FO-EK technology. The benefit is that the generated electrical field by the EK and FO technique can complement the CDI based desalination process. A

schematic diagram is presented in Figure 8.3 to illustrate such FO-EK powered CDI desalination system. CDI process works when ions in the salt solution driven by FO are adsorbed onto the charged electrodes surface. The electrodes are charged due to the applied potential. The relatively low potential (e.g. 1-2V) generated via EK method in the form of streaming potential or open circuit voltage is adequate for the CDI process to prevent electrolysis and to achieve desalination objective.

8.2.2.3 Energy Recovery from RO Pre-treatment Process

Figure 8.4 Concept of energy recovery from RO pre-treatment process derived from FO-EK energy harvesting technique.

The same FO-EK concept can be utilized for energy recovery during the water pretreatment processes such as in RO operation. Generally, RO membranes would have a thick support layer which acts like a porous medium. When salt water is pushed through (by external pressure input) the membrane as illustrated above, clean permeate which works like a feed solution will need to

flow through the porous substrate. This is analogous to the FO-EK power generation concept, based on which certain amount of power can be recovered during this process. Eventually, such recovered energy can partially offset the energy consumption in the energy intensive RO process.

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Appendix A

A1 Typical Results of Streaming Potential/Streaming Current by Polyethylene Porous Disc

Figure A1 Time evolution of flow induced streaming potential (OCV) curve driven by various concentrations of NaCl draw solutions ranging from 0.5M to 4M through polyethylene porous disc.

Figure A2 I-V curve at various concentrations of NaCl draw solutions (The figure shows the streaming current when potential=0 and the streaming potential when streaming current =0). Power curve is also illustrated on the same graph where the maximum power occurs at half of streaming potential (OCV) or when the external load resistance is equal to the EK power generator resistance. (Polyethylene porous disc)

A2 Determination of FO baseline (open) fluxes

FO baseline or open fluxes (i.e. without any applied pressure or resistance) were first characterized using a crossflow (counter current flow) setup as shown in Figure A3. A customized crossflow module (see Appendix B3) comprises a pair of symmetric rectangular channels with dimension of 3mm in height, 20mm in width and 250mm in length. FO membrane is sandwiched in between the two rectangular channels. Draw and feed solutions flow tangentially along the channel but in opposite direction at a flow rate of 400ml/min regulated by a peristaltic pump (Masterflex *L/S* model, Cole-parmer, IL). In this study, draw and feed solutions are continually fed through the channels in a closed loop configuration, which is termed as a continuous mode. Gravimetric method is used to measure the water flux performance by measuring the weight change of draw or feed solution reservoir on a balance. Since no constant concentration of draw solution is maintained, it will be diluted as time elapses and the net osmotic pressure gradient will be reduced with the water flux rate. In view of this, the average water flux of the initial 30 minutes of the operation is calculated and employed for comparison. The weight change is logged by a personal computer and fluxes are computed using Equation 5.1 in the main text.

Based on thin film model developed by the concept of concentration boundary layer, the mass transfer coefficient, h_m and the dimensionless number, Sherwood number Sh are linearly related by

where $d_h = \frac{4A_c}{P}$, A_c is the cross-sectional area of the channel and P is the wetted perimeter of

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and in turbulent region where $Re > 2100$

$$Sh = 0.04 Re^{0.75} Sc^{0.33}$$

A3

Here Re is the Reynolds number ($Re = \frac{U d_h}{\nu}$), Sc is the Schmidt number ($Sc = \frac{\nu}{D}$) and L is the length of the channel. It is noted that the above Sherwood relations are adapted from the model used commonly to describe the (external concentration polarization) ECP effects for RO and ultra-filtration processes ^[43, 75, 191]. However, in this study, mass transfer coefficient is determined by iteration method based on Equation 2.3 in the main text by using experimental open fluxes determined earlier. The equations shown above provide a direct method to estimate the mass transfer coefficient. It is found that the values obtained by iteration are within the order of magnitude as determined by other researchers.

A4 Determination of Pressure against Flow Rate Relationship and Permeability Constant

Figure A4 Schematic illustration of a method to characterize pressure as a function of applied flow rate across different types of porous media.

The pressure versus flow rate relationship across each types of porous media can be characterized using the setup depicted in Figure A4. A differential pressure transducer is connected along the pressure driven flow line. On the other hand, the true flow rate across the porous medium is measured using the gravimetric method. Results of the calibration curve of pressure vs flow rate is shown in Figure A5. Here the permeability constants, defined as the ratio of flow rate over pressure difference, are approximated as $2.82 \times 10^{-11} \text{ m}^3 \text{Pa}^{-1} \text{s}^{-1}$ and $1.54 \times 10^{-11} \text{ m}^3 \text{Pa}^{-1} \text{s}^{-1}$ for glass and PE porous media, respectively.

Figure A5 Calibrated relationship between the pressure difference developed across the porous medium and the FO-induced flow rate.

A5 Determination Structural Parameters of Porosity and Tortuosity

Porosity can be measured using dry and weight measurements of the porous structure as follows:

$$\varphi = \frac{(w_{wet} - w_{dry}) / \rho_w}{(AL)_p} \quad A4$$

where ρ_w is the water density, A and L are is the cross-sectional area and thickness of the porous medium respectively. Once the porosity is determined, tortuosity can then be computed by utilizing a permeability constant K relationship defined as following,

$$K = \frac{Q}{\Delta P} = \frac{Aa^2}{8\mu L} \frac{\varphi_p}{\tau_p} \quad A5$$

With known porosity and tortuosity, effective area of the porous media^[192] can then be determined by Eq. 4.48 in the main text or as follows

$$A_e = \frac{\varphi A}{\sqrt{\tau}} \quad A6$$

Meanwhile, total number of channels in a porous medium is calculated as

$$N = \frac{A_e}{\pi a^2} \quad A7$$

Figure A6 SEM images of a) Glass porous medium and b) Polyethylene porous medium c) FO pouch membrane d) FO cartridge membrane

Figure A7 Measured conductivity of feed solution after experiment. The conductivity increases with the applied concentration differences across the semipermeable membrane, indicating the salt leakage is more significant at high water fluxes.

A6 Power Density Calculation

Maximum power generated can be calculated as Equation 5.5 as

$$P_{\max} = \frac{V_{\max}^2}{R_{\text{Total}}} = \frac{(V_s / 2)^2}{R_{\text{Total}}} \quad \text{A8}$$

where the corresponding maximum output voltage $V_{\max}$ is half of the streaming potential voltage V_s . R_{total} is the total electrical resistance of the porous media column. Since porous medium is considered as an array of microchannels connected in parallel, the total resistance is equivalent to

$$\frac{1}{R_{Total}} = \frac{1}{R_{channel1}} + \frac{1}{R_{channel2}} + \dots + \frac{1}{R_{channelN}} \quad A9$$

and assume that all channels are identical, thus

$$R_{channel1} = R_{channel2} = \dots = R_{channelN} = R \quad A10$$

Substitute Eq.A10 into equation A9 and rearrange we get

$$R_{Total} = \frac{R}{N} \quad A11$$

where N is the number of channels in the porous medium which can be calculated by Equation A7. Hence based on the method described above, the total resistance per unit area of the porous medium can be reduced to a value of merely few tens of Ohms as the total current generated is the accumulation of individual channel. Therefore, power density is only dependent on the magnitude of flux generated across the porous medium by FO alone.

A7 Contact Angle Measurements by Captive Bubble Method

After membrane surface treatment with the additive solution, portion of the membrane is cut and then pasted on a transparent container and immersed in the solution of DI water. A 10 ml syringe is used to produce the bubble formed on the membrane. The volume of bubble formed is controlled via a program. Afterwards, images of the bubbles formed on the membrane are captured by a camera. The measurements are conducted by using a FTA 200 instrument as shown in Figure A8.

Figure A8 FTA 200 instrument used for measuring the contact angle of air bubble on a membrane surface submerged in water.

After the image has been captured, it is then displayed on the monitor. Contact angle is measured based on the contour of the bubble image. For each surface treatment condition under different additive concentrations, a minimum of 4 bubbles are measured. Furthermore, at least 3 sets of data are obtained for each bubble.

Figure A9 On screen measurement showing the bubble contact angle with a membrane surface

Figure A10 Actual experiment setup for characterization of membrane flux performance with DMAPS surfactant treatment and subject to a pressure difference regulated by a needle valve

Figure A11 Actual experiment setup for surface pre-treatment of porous media with SDS surfactant

Figure A12 Actual experiment set up for characterization of the stacking effect of multi units of EK power generator.

Appendix B

B1 FO-EK Experiment Actual Setup

Figure B1 Actual setup of a FO-EK power generation system including i) EK power generator ii) FO flow generator iii) feed solution reservoir iv) draw solution reservoir. The electrodes pair (acts as current collector) is connected to a source meter for measuring flow induced streaming potential and streaming current.

B2 Cross-Flow Module

Figure B2 Cross flow module showing top and bottom module with rectangular flow channels of dimensions 18mm x 3mm x 200mm. Membrane is sandwiched in between with O-ring to prevent from leakage.

B2.1 Cross-Flow Module Assembly Drawings

Cross flow channel Assembly
Louishon

Acrylic
16/6/09

B2.2 Cross-Flow Module - Single Side Drawings

B3 Customized Batch Module for PZT Experiment

Figure B3 Customized batch module (with side A and B) for testing the PZT induced surface vibration on a FO membrane

B3.1 Batch Module – Single Side Drawings

PZT DEVICE A

B4 FO Flow Generator – Single Side Module Drawings

Compartment x 5 pcs.
M6 Threaded x 2
M6 Clearance Hole x 3

B5 EK Power Generator Assembly

Figure B4 EK power generator assembly comprises i) acrylic holder side A and side B, ii) porous media holder, iii) porous media, iv) pair of Ag/AgCl mesh electrode, V) inlet and outlet fittings.

B5.1 Acrylic Holder – Single Side Drawings

B5.2 Glass Type Porous Media Holder Drawing

B5.3 Polyethylene Type Porous Media Holder Drawing

Appendix C Mathematical Derivation

A: Derivation of Equations 4.4 and 4.6

Here is the no derivation of Equation 4.4. The energy conversion efficiency η is by definition only as the electrical output power $W = I\Delta\phi$ (equation 4.3) over fluid power $W_F = Q(-\Delta P)$ in generation mode. It is noted that in the generation mode, the pressure decreases in the direction of fluid flow to provide mechanical power, and the voltage increases in the direction of current acting as a battery. Thus the sign for the voltage or streaming potential is positive while pressure difference is negative. So by definition, Equation 4.4 is expressed as:

$$\eta = \frac{I\Delta\phi}{Q(-\Delta P)} \quad 4.4$$

Substituting the Onsager relationship Equations 4.1 and 4.2 into equation 4.3 and 4.4, respectively. One can obtain the following as a function of phenomenological coefficients as,

$$W = M(-\Delta p)\Delta\phi - S(\Delta\phi)^2 \quad A1$$

$$\eta = \frac{-M(\Delta p)\Delta\phi - S(\Delta\phi)^2}{G(\Delta p)^2 + M(\Delta\phi)(\Delta p)} \quad A2$$

And to derive the maximum theoretical power output in generation mode, the following condition $\frac{dW}{d\Delta\phi} = 0$ is applied and to obtain the maximum streaming potential as Equation 4.7.

$$\Delta\phi_{\max W} = \frac{M}{2S}(-\Delta p) \quad 4.7$$

And substitute the above into Equation A2, and Equation A3 is obtained as following:

$$\eta = \frac{-M(\Delta p)\frac{M}{2S}(-\Delta p) - S\left(\frac{M}{2S}(-\Delta p)\right)^2}{G(\Delta p)^2 + M\left(\frac{M}{2S}(-\Delta p)\right)(\Delta p)} = \frac{\frac{M^2}{2S}\Delta p^2 - \frac{M^2}{4S}\Delta p^2}{G(\Delta p)^2 - \frac{M^2}{2S}\Delta p^2} = \frac{\frac{M^2}{4S}}{G - \frac{M^2}{2S}} = \frac{\frac{M^2}{4GS}}{1 - \frac{M^2}{2GS}} \quad A3$$

and with figure of merit defined as $Z = \frac{M^2}{GS}$, Equation A3 then becomes equation 4.6 as such,

$$\eta = \frac{\frac{1}{4}Z}{1 - \frac{1}{2}Z} = \frac{Z}{4 - 2Z} = \frac{Z}{2(2 - Z)} \quad 4.6$$

B: Derivation of Equations 4.9-4.19

Equation 4.9 is the generalized form of Poisson-Boltzmann equation which is also the governing equation for solving the potential distribution in the microchannel. Derivation of which is beyond the scope of this works. However, the entire derivation to reach the final analytical potential distribution is reproduced here.

$$\nabla^2\psi = -\frac{\rho_e}{\varepsilon} \quad 4.9$$

ρ_e is the net charge density which is defined as follows

$$\rho_e = \sum z_i e n_i = ze(n_+ - n_-) \quad 4.10$$

The ionic concentration can be determined using Boltzmann distribution as

$$n_{\pm} = n_b \exp(\mp \frac{ze\psi}{k_b T}) \quad 4.11$$

Thus for monovalent symmetric electrolyte solution, the net charge density becomes

$$\rho_e = ze(n_+ - n_-) = zen_b \left[\exp(-\frac{ze\psi}{k_b T}) - \exp(\frac{ze\psi}{k_b T}) \right] = -2zen_b \sinh \frac{ze\psi}{k_b T} \quad 4.12$$

Equation 4.9 would then become

$$\nabla^2 \psi = \frac{2Zen_b \sinh \frac{ze\psi}{k_b T}}{\epsilon_0 \epsilon_r} \quad 4.13$$

with an assumption of low surface potential $\frac{ze\psi}{k_b T} \ll 1$, the PB equation can be linearized

according to the Debye-Huckel Approximation^[118] with $\sinh \frac{ze\psi}{k_b T} \approx \frac{ze\psi}{k_b T}$, such that

Equation 4.13 becomes

$$\nabla^2 \psi = \frac{2Z^2 e^2 n_b \psi}{\epsilon k_b T} = \kappa^2 \psi \quad 4.14$$

In cylindrical coordinates, the linearized PB equation can be expanded as

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right) = \kappa^2 \psi \quad 4.15$$

Or can be written as

$$\frac{d^2\psi}{dr^2} + \frac{1}{r} \frac{d\psi}{dr} = \kappa^2\psi \quad \text{B1}$$

Solving the above by Bessel's modified equation as follow,

$$\psi(r) = C_1 I_0(\kappa r) + C_2 K_0(\kappa r) \quad \text{B2}$$

with appropriate boundary conditions,

$$\psi = \psi_s \quad \text{at} \quad r = a \quad \text{4. 16}$$

$$\frac{d\psi}{dr} = 0 \quad \text{at} \quad r = 0 \quad \text{4.17}$$

Applying boundary condition 4.17, Equation B2 becomes

$$\frac{d\psi}{dr} = \kappa C_1 I_1(\kappa r) + \kappa C_2 K_1(\kappa r) \quad \text{B3}$$

$$0 = \kappa C_1 I_1(0) + \kappa C_2 K_1(0) \quad \text{B4}$$

First term of right hand side is zero and therefore the constant C_2 must be zero to fulfill the condition. Hence Equation B2 is simplified and becomes

$$\psi(r) = C_1 I_0(\kappa r) \quad \text{B5}$$

Applying boundary condition 4.16 into Equation 4.15.5, becomes

$$\psi_s = C_1 I_0(\kappa a) \quad \text{B6}$$

And thus C1 is

$$C_1 = \frac{\psi_s}{I_0(\kappa a)} \quad \text{B7}$$

Therefore, the analytical solution for potential distribution in the channel becomes

$$\psi = \psi_s \frac{I_0(\kappa r)}{I_0(\kappa a)} \quad 4.18$$

where I_0 is the modified Bessel function of the first kind of zeroth order. Hence, with Equations 4.9 and 4.18, the net charge density would then be described as

$$\rho_e = -\varepsilon \nabla^2 \psi = -\varepsilon \kappa^2 \psi_s \frac{I_0(\kappa r)}{I_0(\kappa a)} \quad 4.19$$

C3. Derivations of Equation 4.33

From the main text, streaming current I_s is expressed as

$$I_s = 2\pi \int_0^a \rho_e(r) v_z(r) r dr \quad 4.32$$

Substituting Equations 4.19 and 4.27 into Equation 4.32, it can be found that

$$I_s = 2\pi \int_0^a \left[-\varepsilon \kappa^2 \zeta \frac{I_0(\kappa r)}{I_0(\kappa a)} \right] \left[\frac{a^2 - r^2}{4\mu} \left(\frac{\Delta P}{L} \right) - \frac{\varepsilon \zeta}{\mu} \left[1 - \frac{I_0(\kappa r)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{L} \right) \right] r dr \quad \text{C1}$$

Rearrange the above, Equation C1 becomes

$$I_s = \frac{-\pi\epsilon\kappa^2\zeta}{2\mu} \left(\frac{\Delta P}{L} \right) \int_0^a (a^2 - r^2) \frac{I_0(\kappa r)}{I_0(\kappa a)} r dr + \frac{2\pi\epsilon^2\kappa^2\zeta^2}{\mu} \left(\frac{\Delta\phi}{L} \right) \int_0^a \frac{I_0(\kappa r)}{I_0(\kappa a)} \left[1 - \frac{I_0(\kappa r)}{I_0(\kappa a)} \right] r dr \quad C2$$

And separate Equation C2 into two separate terms as follow

$$\begin{aligned} I_{s,1} &= \frac{-\pi\epsilon\kappa^2\zeta}{2\mu} \left(\frac{\Delta P}{L} \right) \int_0^a (a^2 - r^2) \frac{I_0(\kappa r)}{I_0(\kappa a)} r dr \\ &= \frac{-\pi\epsilon\kappa^2\zeta}{2\mu I_0(\kappa a)} \left(\frac{\Delta P}{L} \right) \left[a^2 \int_0^a r I_0(\kappa r) dr - \int_0^a r^3 I_0(\kappa r) dr \right] \end{aligned} \quad C3$$

And

$$\begin{aligned} I_{s,2} &= \frac{2\pi\epsilon^2\kappa^2\zeta^2}{\mu} \left(\frac{\Delta\phi}{L} \right) \int_0^a \frac{I_0(\kappa r)}{I_0(\kappa a)} \left[1 - \frac{I_0(\kappa r)}{I_0(\kappa a)} \right] r dr \\ &= \frac{2\pi\epsilon^2\kappa^2\zeta^2}{\mu I_0(\kappa a)} \left(\frac{\Delta\phi}{L} \right) \left[\int_0^a r I_0(\kappa r) dr - \frac{1}{I_0(\kappa a)} \int_0^a r I_0^2(\kappa r) dr \right] \end{aligned} \quad C4$$

Using integration by parts, the integration terms in C3 and C4 become

$$\int_0^a r I_0(\kappa r) dr = \frac{a}{\kappa} I_1(\kappa a) \quad C5$$

$$\int_0^a r^3 I_0(\kappa r) dr = \frac{a^3}{\kappa} I_1(\kappa a) - \frac{2a^2}{\kappa^2} I_0(\kappa a) + \frac{4a}{\kappa^3} I_1(\kappa a) \quad C6$$

$$\int_0^a r I_0^2(\kappa r) dr = \frac{a^2}{2} \left[I_0^2(\kappa a) - I_1^2(\kappa a) \right] \quad C7$$

Substituting Equations C5 to C7 back into Equations C3 and C4 gives

$$I_{s,1} = \frac{-\pi a^2 \varepsilon \zeta}{\mu} \left(\frac{\Delta P}{L} \right) \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \quad \text{C8}$$

$$I_{s,2} = \frac{-\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \quad \text{C9}$$

Hence, we obtain the streaming current as

$$I_s = -\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{L} \right) - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta \phi}{L} \right) \quad 4.33$$

D: Derivation of Equations 4.39 and 4.42

Streaming potential or open circuit potential with zero current can be found by invoking the condition of $I_s + I_c = 0$, where the conduction current I_c is written as

$$I_c = \frac{\Delta \phi}{R_T} \quad 4.34$$

Substitute Equations 4.33 and 4.34 to the zero current condition, yield

$$-\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{L} \right) - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta \phi}{L} \right) + \frac{\Delta \phi}{R_T} = 0$$

And rearrange the above; the streaming potential per unit pressure difference can be obtained

$$\frac{\Delta\phi}{\Delta p} = \frac{\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right]}{\frac{L}{R_T} - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right]} \quad 4.39$$

Total current is the summation of streaming current and conduction current $I_T = I_s + I_c$,

whereby the conduction current can be written in terms of Dukhin number $Du = \frac{\lambda_s}{a\lambda_f}$ and by

replacing the total resistance as $R_T = \frac{L}{2\pi a\lambda_s + \pi a^2\lambda_f}$, conduction current can be expressed as

$$I_c = 2\pi a\lambda_s + \pi a^2\lambda_f \left(\frac{\Delta\phi}{L} \right) = \pi a^2\lambda_f \left(\frac{2\lambda_s}{a\lambda_f} + 1 \right) \left(\frac{\Delta\phi}{L} \right) = \pi a^2\lambda_f (2Du + 1) \left(\frac{\Delta\phi}{L} \right) \quad C10$$

Hence the total current becomes,

$$I_T = -\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{L} \right) - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta\phi}{L} \right) + \pi a^2\lambda_f (1 + 2Du) \left(\frac{\Delta\phi}{L} \right) \quad 4.42$$

E: Derivation of Equations 4.47 and 4.51

Total volumetric flow rate Q across the entire porous medium can be described as

$$Q = N \cdot q \quad 4.47$$

where N is the total number of channel and q is the flow rate across each microchannel, and

they are given by

$$q = 2\pi \int_0^a v_z(r) r dr = \frac{\pi a^4}{8\mu} \left(\frac{\Delta P}{L_e} \right) - \frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{L_e} \right) \quad 4.28$$

$$N = \frac{A_e}{\pi a^2} = \frac{\varphi A}{\sqrt{\tau}} \cdot \frac{1}{\pi a^2} \quad 4.48$$

and the tortuosity is defined as

$$\tau = \left(\frac{L_e}{L} \right)^2 \quad 4.49$$

where A_e is the effective surface area of the porous medium. The total volumetric flow rate Q then becomes

$$Q = \frac{\varphi A}{\sqrt{\tau}} \cdot \frac{1}{\pi a^2} \left\{ \frac{\pi a^4}{8\mu} \left(\frac{\Delta P}{L_e} \right) - \frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{L_e} \right) \right\} \quad 4.47$$

$$Q = \frac{\varphi A}{\sqrt{\tau}} \cdot \frac{1}{L} \left\{ \frac{a^2}{8\mu} \left(\frac{\Delta P}{L_e/L} \right) - \frac{\varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{L_e/L} \right) \right\} \quad E1$$

$$Q = \frac{\varphi A}{\sqrt{\tau}} \cdot \frac{1}{L} \left\{ \frac{a^2}{8\mu} \left(\frac{\Delta P}{\sqrt{\tau}} \right) - \frac{\varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta \phi}{\sqrt{\tau}} \right) \right\} \quad E2$$

$$Q = \frac{\varphi}{\tau} \left\{ \frac{A a^2}{8\mu L} \Delta P - \frac{A \varepsilon \zeta}{\mu L} \Delta \phi \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \right\} \quad 4.50$$

And for total streaming current $I_{s,Total} = N I_s$ for the entire porous medium with account of geometric properties will be

$$I_{s,Total} = \frac{\varphi A}{\sqrt{\tau}} \cdot \frac{1}{\pi a^2} \left\{ -\frac{\pi a^2 \varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{L_e} \right) - \frac{\pi a^2 \varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta \phi}{L_e} \right) \right\} \quad \text{E3}$$

$$I_{s,Total} = \frac{\varphi A}{\sqrt{\tau}} \cdot \frac{1}{L} \left\{ -\frac{\varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{L_e/L} \right) - \frac{\varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta \phi}{L_e/L} \right) \right\} \quad \text{E4}$$

$$I_{s,Total} = \frac{\varphi A}{\sqrt{\tau}} \cdot \frac{1}{L} \left\{ -\frac{\varepsilon \zeta}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \left(\frac{\Delta P}{\sqrt{\tau}} \right) - \frac{\varepsilon^2 \kappa^2 \zeta^2}{\mu} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \left(\frac{\Delta \phi}{\sqrt{\tau}} \right) \right\} \quad \text{E5}$$

$$I_{s,Total} = -\frac{\varphi}{\tau} \cdot \left\{ \frac{A \varepsilon \zeta}{\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} \right] \Delta P + \frac{A \varepsilon^2 \kappa^2 \zeta^2}{\mu L} \left[1 - \frac{2}{\kappa a} \frac{I_1(\kappa a)}{I_0(\kappa a)} - \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \Delta \phi \right\} \quad 4.51$$