

EFFECT OF IONIC MOBILITY OF WORKING ELECTROLYTE ON EFFICIENCY OF ELECTROKINETIC ENERGY CONVERSION IN SUB-MICRON CHANNELS

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Abstract: In this study, the effect of the ionic mobility of a working electrolyte on the efficiency of electrokinetic energy conversion was experimentally investigated for various channel sizes. It is shown that the efficiency of electrokinetic energy conversion behaves differently with the ionic mobility depending on the channel size. Experimental results show that the electrolyte with lower ionic mobility performs better only when the channel size is larger than the Debye length (Channel height $\geq O(10 \lambda_D)$). Otherwise, the energy conversion efficiency was found to be independent of the ionic mobility of the working electrolyte.

Keywords: Electrokinetics; Energy conversion; Ionic mobility; Efficiency; Nanochannel

INTRODUCTION

In the present work, experimental investigations were systematically conducted to determine how the ionic mobility of the working electrolyte affects the efficiency of electrokinetic energy conversion in sub-micron channels. So far investigators have concentrated on reducing the channel size in improving the energy conversion efficiency [1, 2]. However, since electrokinetic energy conversion occurs in the working electrolyte, the properties of the working electrolyte also plays an important role in energy conversion efficiency. Therefore, an obvious question is what kind of working electrolyte should be used in achieving higher efficiency of electrokinetic energy conversion. To date, several researchers have been interested and seeking a proper answer to this question [3-5]. However, the selection of the best working electrolyte remains unclear. Furthermore, to the best of the authors' knowledge, there has been no experimental study comparing the efficiencies systematically with various electrolytes and channel sizes. The objective of this paper is to help eliminate ambiguity associated with the selection of the working electrolyte for electrokinetic energy conversion.

MATERIALS AND METHODS

According to a thermodynamic analysis [5], the Onsager reciprocal theorem relates the liquid flow rate Q and the electrical current I to the pressure difference Δp and the electrical potential difference $\Delta\phi$ across flow channels:

$$Q = G(-\Delta p) + M(-\Delta\phi) \quad (1)$$

$$I = M(-\Delta p) + S(-\Delta\phi) \quad (2)$$

Here, G represents the hydrodynamic conductance, M characterizes the electro-osmotic flow in Eq. (1) and the streaming current in Eq. (2), and S indicates the electrical conductance. G , M , and S are defined as

$$G \equiv -\left[\frac{Q}{\Delta p}\right]_{\Delta\phi=0}, \quad M \equiv -\left[\frac{Q}{\Delta\phi}\right]_{\Delta p=0}, \quad S \equiv -\left[\frac{I}{\Delta\phi}\right]_{\Delta p=0} \quad (3)$$

Generally, the maximum energy conversion efficiency is given as

$$\eta_{\max,\eta} = \frac{(1 - \sqrt{1 - Z})^2}{Z} \quad (4)$$

where $Z (=M^2G^{-1}S^{-1})$ is the figure of merit. The maximum conversion efficiency is reached when the following equations hold:

$$\Delta p_{\max,\eta} = \frac{G}{M}(1 - \sqrt{1 - Z})(-\Delta\phi) \quad \text{for power generation} \quad (5)$$

$$\Delta\phi_{\max,\eta} = \frac{S}{M}(1 - \sqrt{1 - Z})(-\Delta p) \quad \text{for pumping} \quad (6)$$

A direct measurement of the maximum efficiency ($\eta_{\max,\eta}$) may require a great deal of effort, because the pressure or the voltage should be precisely controlled to satisfy Eq. (5) or (6), respectively. In this study, instead of a direct measurement, the values of G , M , and S are experimentally obtained and the maximum efficiency is simply calculated with Eq. (4).

The microfluidic chip having sixteen 50 μm wide nanochannels, and two electrodes for the experimental investigation is shown in Fig. 1. The channel height was controlled at 200nm, 500nm, and 800nm in three cases. The fabrication process is shown in Fig. 2. The fabricated nanochannels were used in conjunction

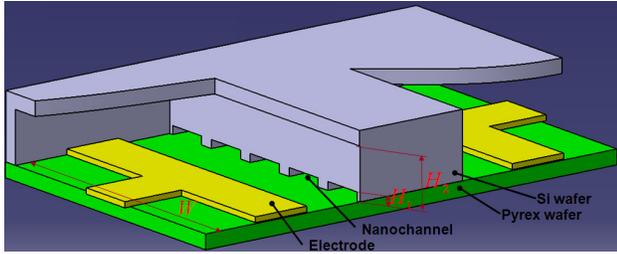


Fig. 1: Schematic diagram of the fabricated chip (not to scale).

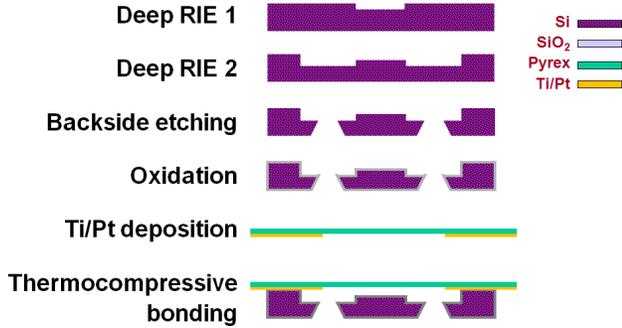
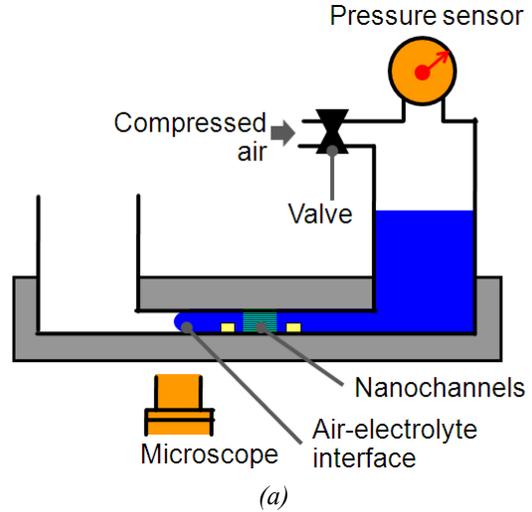


Fig. 2: Fabrication process.

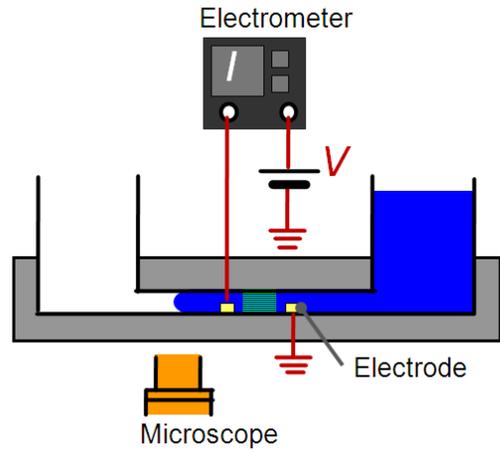
with the experimental apparatus shown in Fig. 3. First, in order to obtain the hydrodynamic conductance, the flow rate of a pressure-driven flow was measured at various pressure differences (Fig 3(a)). Secondly, in order to obtain the electrical conductance and the phenomenological coefficient, the current and the flow rate for the electro-osmotic flow were measured, respectively (Fig 3(b)). Potassium chloride, trimethylammonium formate, and tetrabutylammonium dihydrogen phosphate solutions with concentration of 10^{-5} M and pH values of 5.65 ± 0.55 were selected as the working electrolyte. As shown in Table 1, these electrolytes show very different ionic mobilities. The mobility of trimethylammonium ion is nearly the arithmetic mean of the mobilities of potassium and tetrabutylammonium ions. The mobility of formate ion is nearly the arithmetic mean of the mobilities of chloride and dihydrogen phosphate ions.

RESULTS AND DISCUSSION

Typical experimental results are presented in Fig. 4. Fig. 4(a) shows the electro-osmotic flow of the electrolyte. The flow rate was calculated by measuring the amount of the movement of the air-electrolyte interface at a given time interval. In order to eliminate the effect of the capillary-driven flow, the electro-osmotic flow rate was obtained by excluding the flow rate for pure capillary-driven flow. The



(a)



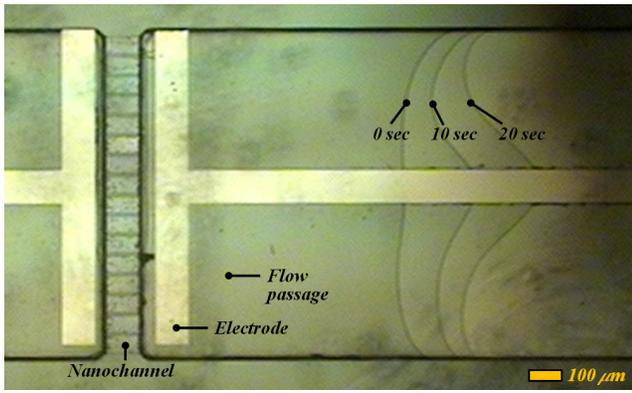
(b)

Fig. 3: Schematic diagram of the experimental apparatus for (a) the pressure-driven flow and (b) the electro-osmotic flow.

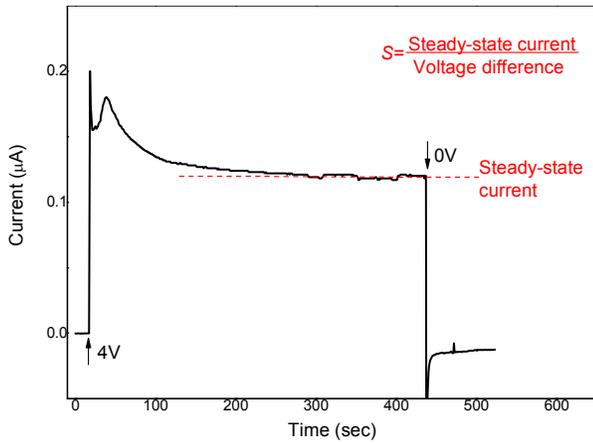
Table 1: Ionic mobilities (relative to K^+) [6, 7].

Cation	Mobility	Anion	Mobility
Potassium	1.00	Chloride	1.04
Trimethylammonium	0.642	Formate	0.743
Tetrabutylammonium	0.265	Dihydrogen phosphate	0.450

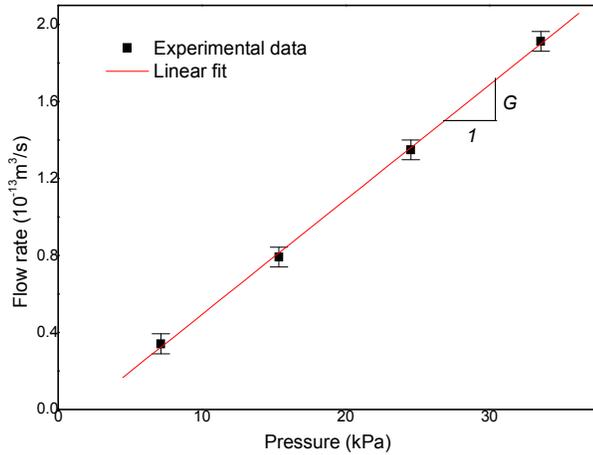
phenomenological coefficient M was then obtained by using Eq. (3). Fig. 4(b) shows the typical dynamic response of the current measurement for the electro-osmotic flow. Since pumping performance for steady operation is practically important, the current was measured after the signal reached a steady state. The electrical conductance S was then calculated with the



(a)



(b)



(c)

Fig. 4: Experimental results. (a) Electro-osmotic flow of electrolyte. (b) Current response for electro-osmotic flow. (c) Flow rates for pressure-driven flow.

measured current. Fig 4(c) is an example of the results for the pressure measurement of the pressure-driven flow. As expected, the flow rate was a linear function of the pressure drop and the slope of the linear curve is the hydrodynamic conductance G .

The hydrodynamic conductance G , the phenomenological coefficient M , and the electrical

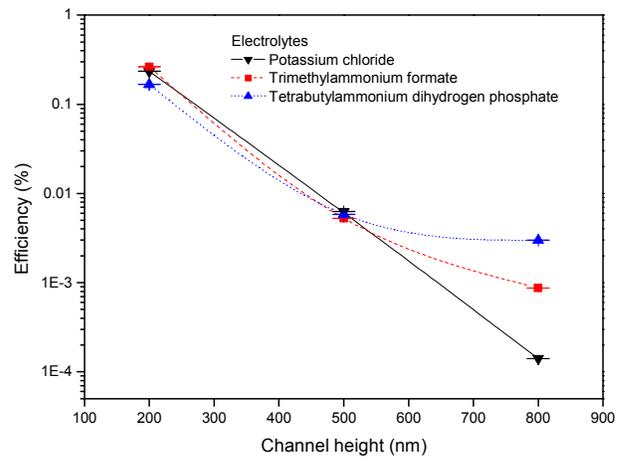


Fig. 5: Efficiency of electrokinetic energy conversion.

conductance S were experimentally obtained for the three electrolytes and three channel heights listed in Table 2. Finally, from the experimental data, the maximum efficiencies of electrokinetic energy conversion for various electrolytes and channel heights are presented in Fig. 5. The maximum efficiency shown in this study is much lower than that reported by van der Heyden et al. [4]. This can be ascribed to overpotentials of Pt electrodes are much higher than those of Ag/AgCl electrodes. Two very different efficiency trends are shown in Fig. 5. For the

Table 2: Summary of experimental results.

Electrolyte	H	$\eta_{max\eta}$	G	M	S
	nm	%	$10^{10} \text{ m}^3/\text{s Pa}$	$10^{10} \text{ m}^3/\text{s V}$	$10^9 \Omega$
Potassium chloride	200	0.23	33.6 ± 1.0	474 ± 11	71 ± 11
	500	0.0062	151 ± 9.0	126 ± 3.1	42 ± 1
	800	0.00014	290 ± 16	20.8 ± 0.5	26 ± 1
Trimethylammonium formate	200	0.26	33.3 ± 0.8	455 ± 11	59 ± 6
	500	0.0052	204 ± 9.7	185 ± 4.6	79 ± 5
	800	0.00087	141 ± 21	42.2 ± 1.0	36 ± 2
Tetrabutylammonium dihydrogen phosphate	200	0.16	14.4 ± 0.3	175 ± 4.3	32 ± 3
	500	0.0058	55.6 ± 1.6	62.4 ± 1.5	30 ± 2
	800	0.0029	348 ± 20	171 ± 4.2	70 ± 4

case of nanochannels with a height of 800 nm ($8.3\lambda_D$), the efficiency increases as the ionic mobility decreases. In contrast, for nanochannels with heights of 200 nm ($2.1\lambda_D$) and 500 nm ($5.2\lambda_D$), the experimental data show that the efficiency is mostly independent of the ionic mobility. Therefore, an electrolyte with low ionic mobility performs better only when the channel size is sufficiently larger than the Debye length (Channel height $\geq 10\lambda_D$ in this case).

As mentioned earlier, theoretical works [3, 5] concluded that the ionic mobility is the determining factor in electrokinetic conversion efficiency and that an electrolyte with lower ionic mobility provides higher efficiency. On the other hand, van der Heyden et al. [4] found that the efficiency is nearly independent of the ionic mobility of working electrolytes. The results in Fig. 5 indicate that the theoretical prediction is valid for flow channels sufficiently larger than the Debye length and that the conclusion presented by van der Heyden et al. is valid for smaller flow channels. Therefore, the results from the two groups are not contradictory but mutually complementary. In the theoretical analysis, the surface conductance was not considered to simplify the problem. In contrast, van der Heyden stated that their experimental data could be well explained only when the surface conductance was considered. As the channel size decreases, the surface area to volume ratio increases and the influence of the surface conductance increases [8]. For nanochannels, the electrostatic effects of the channel surface charge on the fluid dominates the transport phenomena [9]. When the surface conductance dominates the electrical current, the efficiency of electrokinetic energy conversion is most likely independent of the ion-mobility of the working electrolyte, and vice versa. This study presents the first experimental data showing that two different efficiency trends coexist. This may be shown by adequate mathematical modeling, but experimental confirmation is always worthwhile.

Another interesting fact shown in Fig. 5 is that the efficiency increases as the channel height decreases. This indicates that the efficiency of electrokinetic energy conversion would be maximized when the channel size is minimized if other practical aspects are disregarded. In addition, it can be inferred that the efficiency can be maximized when the electrical current is dominated by the surface conductance. Therefore, it could be concluded that how small the flow channel can be would be much more important than what kind of working electrolyte is used to

maximize the efficiency of electrokinetic energy conversion.

CONCLUSION

In the present work, experimental investigations were systematically conducted to determine how the ionic mobility of the working electrolyte affects the efficiency of electrokinetic energy conversion. It was shown that the efficiency of electrokinetic energy conversion behaves differently with the ionic mobility depending on the channel size. When the channel size is larger than the Debye length (Channel height $\geq 10\lambda_D$), an electrolyte with low ionic mobility shows superior performance. On the other hand, for nanochannels whose size is comparable to the Debye length, the surface conductance dominates the electrical current, and the energy conversion efficiency is mostly independent of the ionic mobility of the working electrolyte. In this case, the size of the flow channel is much more important than the selection of working electrolyte in maximizing the efficiency. This study provides insight into the selection of the working electrolyte for various microfluidic devices based on electrokinetic energy conversion.

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