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Effect of ionic mobility of working electrolyte on electrokinetic energy conversion in sub-micron channels

Dong-Kwon Kim [a], Duckjong Kim [b],*, Sung Jin Kim [c], Sang-Jin Park [b]

[a] School of Mechanical Engineering, Ajou University, Suwon 443-749, South Korea
[b] Korea Institute of Machinery and Materials, Daejeon 305-343, South Korea
[c] Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, South Korea

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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. Potassium chloride, trimethylammonium formate, and tetrabutylammonium dihydrogen phosphate solutions with very different ionic mobilities at a concentration of 10^{-5} M were used as the working electrolytes. The efficiencies of electrokinetic energy conversion for 50 μm-wide nanochannels with heights of 200 nm, 500 nm, and 800 nm were obtained. We show that the efficiency of electrokinetic energy conversion behaves differently with respect to the ionic mobility depending on channel size. Experimental results showed that the electrolyte with lower ionic mobility performed better only when the channel size was larger than the Debye length (Channel height $\geq 0\ (10\lambda_D)$). Otherwise, the energy conversion efficiency was found to be independent of the ionic mobility of the working electrolyte.

1. Introduction

In the last decade, various microfluidic devices based on electrokinetics have been proposed and demonstrated. Among them, electrical power generation using electrokinetics has attracted attention due to its great potential for a breakthrough in the field of mobile power sources. Yang et al. [1] first reported a microfluidic battery using electrokinetic phenomena. A porous glass filter 20 mm in diameter with pore sizes from 10 to 16 μm was used to obtain a current of 1–2 μA from a 30 cm hydrostatic pressure drop. The maximum efficiency was estimated to be on the order of 0.01%. Since then, many studies have focused on improvement of electrokinetic energy conversion. Lu et al. [2] obtained an efficiency of 0.77% by having KCl electrolyte flow through a nano-porous membrane with a pore size of 200 nm. Recently, Xie et al. [3] achieved an efficiency of 5% by using KCl solution and nanopores with a small radius of 31 nm. Thus far, investigators have concentrated on reducing channel size in improving energy conversion efficiency. However, since electrokinetic energy conversion occurs in the working electrolyte, the properties of the electrolyte play an important role in energy conversion efficiency. Therefore, we wish to know what kind of working electrolyte should be used in achieving a higher efficiency of electrokinetic energy conversion.

Min et al. [4] and Xuan and Li [5] carried out theoretical analyses of electrokinetic energy conversion in micro- or nanometer-sized channels. They concluded that ionic mobility is one of the most important parameters in electrokinetic energy conversion and that an electrolyte with lower ionic mobility provides higher efficiency. More recently, van der Heyden et al. [6] experimentally investigated the effect of ionic mobility on electrokinetic conversion efficiency in a nanochannel. They compared the efficiencies for potassium chloride and lithium chloride solutions with very different mobilities, and found that efficiency is nearly independent of the ionic mobility of the working electrolyte. As indicated by these contradictory results, selection of the best working electrolyte remains unclear. Furthermore, to the best of the authors' knowledge, there has been no experimental study systematically comparing efficiencies using various electrolytes and channel heights.

The objective of this study is to help eliminate the ambiguity associated with the selection of a working electrolyte for electrokinetic energy conversion. To this end, experimental investigations were systematically conducted to examine the effect of ionic mobility of the working electrolyte on the efficiency of electrokinetic energy conversion for various electrolytes and channel sizes. Potassium chloride, trimethylammonium formate,

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* Corresponding author. Tel.: +82 42 868 7121; fax: +82 42 868 7335.
E-mail address: dkim@kimm.re.kr (D. Kim).

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Nomenclature

H_1	Height of nanochannels
G	Hydrodynamic conductance
I	Electrical current
M	Phenomenological coefficient
Δp	Pressure difference
Q	Flow rate
S	Electrical conductance
Z	Figure of merit ($= M^2 G^{-1} S^{-1}$)
$\Delta\phi$	Electrical potential difference
$\eta_{max\eta}$	Maximum energy conversion efficiency
λ_D	Debye length

and tetrabutylammonium dihydrogen phosphate solutions with very different ionic mobilities at a concentration of 10^{-5} M were chosen as the working electrolytes. The efficiencies of electrokinetic energy conversion for nanochannels with heights of 200 nm, 500 nm, and 800 nm were experimentally determined.

2. Materials and methods

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

$$Q = G(-\Delta p) + M(-\Delta\phi) \tag{1}$$

$$I = M(-\Delta p) + S(-\Delta\phi) \tag{2}$$

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

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

Generally, the maximum energy conversion efficiency is given as

$$\eta_{\max\eta} = \frac{\left(1-\sqrt{1-Z}\right)^2}{Z} \tag{4}$$

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

$$\Delta p_{\max\eta} = \frac{G}{M}\left(1-\sqrt{1-Z}\right)(-\Delta\phi) \quad \text{for electrokinetic power generators} \tag{5}$$

$$\Delta\phi_{\max\eta} = \frac{S}{M}\left(1-\sqrt{1-Z}\right)(-\Delta p) \quad \text{for electrokinetic pumps} \tag{6}$$

For electrokinetic power generators, the maximum efficiency is given by the ratio of the maximum electrical energy that can be harvested by an external device to the mechanical energy input from the working fluid. For eletrokinetic pumps, the maximum efficiency is the ratio of the maximum mechanical energy generated in the nanochannels to the electrical energy input from an external device. A direct measurement of maximum efficiency $\eta_{max\eta}$ may require considerable effort because the pressure or the voltage should be precisely controlled to satisfy Eqs. (5) or (6), respectively. In this study, instead of a direct measurement, the values of G, M, and S were experimentally obtained and the maximum efficiency was simply calculated using Eq. (4).

We developed a microfluidic chip having nanochannels, a flow passage, and electrodes, as shown in Fig. 1. The chip was fabricated on a silicon wafer. The fabrication process is shown in Fig. 2. Initially, sixteen 50 μm-wide channels were etched by the first deep reactive ion etching. The channel height H_1 was controlled at 200 nm, 500 nm, and 800 nm in three cases. The flow passage ($W = 1$ mm, $H_2 = 20$ μm) connecting the nanochannels with the inlet and outlet ports was etched by the second deep reactive ion etching. The inlet and outlet ports were then etched from the backside of the wafer. After the etching processes, a silicon dioxide layer was formed on the channel surface by thermal oxidation. Titanium and platinum layers functioning as electrodes were deposited on a Pyrex 7740 glass cover. The Pyrex cover was then thermocompressively bonded to the silicon wafer to seal the flow channels.

The fabricated nanochannels were used in conjunction with the experimental apparatus shown in Fig. 3. To obtain the hydrodynamic conductance G, the flow rate of a pressure-driven flow was measured at various pressure differences (Fig. 3(a)). Compressed air was used to drive an electrolyte through the nanochannels. While the pressure difference was measured with a differential pressure transducer (Validyne DP15), the flow rate through the nanochannels was measured from the captured images of the movement of the air–electrolyte interface. A similar flow measurement method was employed in a test of a magnetohydrodynamic micropump as described in [7]. Experiments were conducted for four pressure differences in the range of 0–40 kPa. The electrical conductance S and the phenomenological coefficient M were obtained from the measured current and flow rate (Fig. 3(b)). The electrokinetic behavior is expected to be linear if the electrostatic double layers are not significantly distorted by the fluid flow or by the applied electrical potential difference [8], and the flow rate and the current are zero when the electrical potential difference is zero. Therefore, using Eq. (3), we calculated M and S from the experimental data on the flow rate and the electrical current for the applied electrical potential difference. While the flow rate was obtained from the captured images of the movement of the air–electrolyte interface, the current across the nanochannels was measured using an electrometer (Keithley 6514 programmable electrometer). The voltage difference across the nanochannels was fixed at 4 V.

Potassium chloride (KCl), trimethylammonium formate ($(CH_3)_3N\cdot HCOOH$), and tetrabutylammonium dihydrogen phosphate ($(CH_3CH_2CH_2CH_2)_4N\cdot[OP(OH)_2O]$) solutions with concentration of 10^{-5} M and pH values of 5.65 ± 0.55 were selected as the working electrolytes. As shown in Table 1, these electrolytes show very different ionic mobilities [9,10]. The mobility of a trimethylammonium ion is nearly the arithmetic mean of the mobilities of potassium and tetrabutylammonium ions. The mobility of the formate ion is nearly the arithmetic mean of the mobilities of chloride and dihydrogen phosphate ions.

3. 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 over a given time interval. To eliminate the effect of capillary-driven flow, the electro-osmotic flow rate was obtained by excluding the flow rate for pure capillary-driven flow.