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Full paper

High-voltage nanofluidic energy generator based on ion-concentration-gradients mimicking electric eels☆

Cong Wang[a], Eunpyo Choi[b], Jungyul Park[a,c,*]

[a] Department of Mechanical Engineering, Sogang University, 35 Baekbeom-ro (Sinsu-dong), Mapo-gu, Seoul 04107, Korea
[b] School of Mechanical Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, Korea
[c] Interdisciplinary Program of Integrated Biotechnology, Sogang University, 35 Baekbeom-ro (Sinsu-dong), Mapo-gu, Seoul 04107, Korea

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ABSTRACT

Although rapid advances have been made in micro/nano-scale devices, there is still a lack of clean and sustainable power source for them. Here we propose a high voltage nanofluidic energy generator inspired by electrical eel using ion-concentration gradients, which converts Gibbs free energy into electricity without any pollutants. The high voltage can be induced by alternatively multi-stacking cation and anion-exchange nanochannel network membranes (CE-NCNMs and AE-NCNMs) in a confined microscale space. These membranes were constructed by in situ self-assembled nanoparticles with hydroxyl and amine groups, respectively. The multiple stacks of CE-NCNMs & AE-NCNMs were successfully realized by precisely guiding the nanodrops with the suspended positively or negatively charged nanoparticles into the desired positions in the multilayered microchannel platform. The performance of the proposed nanofluidic energy generator was quantitatively investigated by changing nanoparticle species, intermembrane distance (IMD), and environmental temperature. Interestingly, we found that our optimized IMD (~80 μm) is very similar to the inter-cell membrane distance of electrocytes in natural electric eels and the diffusion potential of a single full cell at this IMD (~138 mV) is also similar to the net potential across a single electrocyte (~150 mV). This optimized IMD is verified through not only electrical measurement but also by fluorescent tracing and numerical analysis using multiphysics simulation. The high voltage of up to 1 V achieved by stacking 20 full cells is, to the authors' knowledge, the highest value yet obtained by microfluidic systems harnessing ion-concentration gradients.

1. Introduction

Clean and sustainable renewable energy sources, such as solar [1,2], wind [3,4], biomass [5,6], or geothermal energy [7,8], have received significant attentions as they supply electricity with zero or almost zero emission of both air pollutants and greenhouse gas. One promising renewable-energy-generation technology is ion-concentration-gradient-based reverse electrodialysis (RED) [9,10]. By establishing an ionic-concentration gradient, which widely exists in nature or in human bodies, across ion-exchange membranes, the Gibbs free energy can be converted into electricity. The potential capacity of energy generation from salinity gradients by mixing fresh and sea water is vast. Each cubic meter of fresh water can generate 1.4 MJ of energy when mixed with the same amount of seawater, and 2.25 MJ when mixed with an excess of seawater [11]. Since this system does not rely on any mechanical moving parts such as turbines or motors, the damage from wear and replacement for these parts can be avoided. Electric eels already adopt this novel power-generation mechanism for high voltages up to 600 V using thousands of specialized cells called electrocytes (Fig. 1(a, b)) [12,13]. In their inactive state, these cells contain relatively high concentrations of potassium ions (K^+) and low concentrations of sodium ions (Na^+) compared to the external cell membrane. In the active state, the innervated membrane is triggered by a neurotransmitter called acetylcholine, allowing ion flux through the membranes on both sides under polarized concentration gradients of Na^+ and K^+. The net potential across single electrocyte can be raised to be ~150 mV, which is the sum of all transmembrane potentials (Fig. 1(c)) [13,14].

By mimicking electric eels, we present a high-voltage nanofluidic energy generator harnessing ion-concentration gradients using a stack of reverse electrodialysis (RED) cells (Fig. 1(d)). Although several nanogenerators with stacking structures have been previously reported for the generation of high voltage or current based on the triboelectric effect [15–18], a nanofluidic energy generator based on RED has not yet been reported. This is due to the limitations of the intrinsic fabrication

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* Corresponding author at: Department of Mechanical Engineering, Sogang University, 35 Baekbeom-ro (Sinsu-dong), Mapo-gu, Seoul 04107, Korea.
E-mail addresses: eunpyochoi@chonnam.ac.kr (E. Choi), sortpark@sogang.ac.kr (J. Park).

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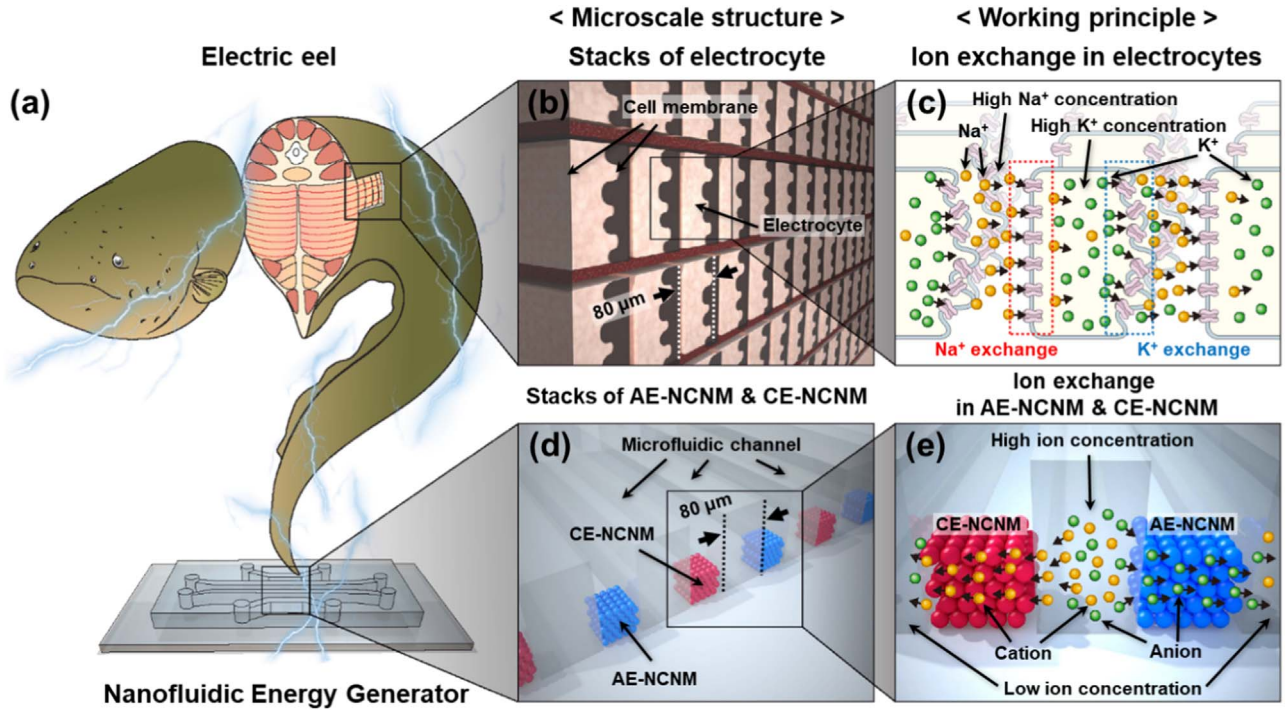

Fig. 1. (a) Schematic of the electric-eel-inspired nanofluidic-energy generator: Microscale structure with multiple stacks of (b) electrocytes in electric eels and (d) CE-NCNMs & AE-NCNMs in a microfluidic channel, and the working principle of high-voltage generation based on the ion-concentration gradient across the ion-exchange membrane. (c) Innervate cell membranes of electrocytes and (e) a single full cell of artificial CE-NCNM & AE-NCNM repeated in a nanofluidic energy generator.

method (a complicated process), and also due to the high cost, low pore density, and the difficulties in minimization and integration into a microsystem. Hence, they only have a half-cell structure, indicating that only the cation- or anion-exchange membrane was realized in the micro-scale device [19,20]. The generated electrical potential across the entire nanofluidic energy generator was very limited (~60 mV (Max.) from Choi et al., [21] ~100 mV (Max.) from Kim et al. [19] and ~70 mV (Max.) from Kwon et al., [22] and ~120 mV (Max.) from Gao et al. [23] obtained with a bipolar ion diode membrane composed of mesoporous carbon and macroporous alumina). In this study, this critical limitation is overcome by controlling nanoparticle self-assembly at desired positions using simple microfluidic principles: capillary force and pressure drop. In our previous studies, we have experimentally and theoretically demonstrated the electrokinetics properties of the ion-exchange membrane based on self-assembled nanoparticles. The interstices between self-assembled nanoparticles serve as 3-dimensional nanochannel networks that induce selective ion transport and enable high ionic current for efficient power generation [21,24]. Herein, we refer to this formed ion-exchange membrane as the nanochannel networks membrane (NCNM). NCNMs constructed by nanoparticles with hydroxyl and amine groups act as cation- and anion-exchange NCNMs (CE-NCNMs and AE-NCNMs), respectively. As shown in Fig. 1(e), the ion concentration gradient across the CE-NCNMs or AE-NCNMs causes selective ion diffusion and ionic current. The opposite ion selectivity of the CE-NCNMs and AE-NCNMs induces cation and anion transport in an opposite direction across the CE-NCNM and AE-NCNM, respectively, so that it results in an equivalent directional ionic current. The potential in a single full cell is the sum of all the diffusion potentials through the CE-NCNMs and AE-NCNMs. If a single full cell with CE-NCNM and AE-NCNM pair connects to another in series, the potential of each single cell can be added to reach a high electric potential in multiple cells. A detailed explanation of the configuration and the equivalent electric circuit of the multi-stack nanofluidic energy generator are shown in Fig. S1. In addition to the CE-NCNM and AE-NCNM, the single full cell of the nanofluidic energy generator is composed of two compartments filled with the diluent (i.e., low-ion-concentration solution) and concentrate (i.e., high-ion-concentration solution). To improve power-generation performance, the effects of nanoparticle material, intermembrane distance (IMD), and environmental temperature were explored quantitatively.

2. Materials and Methods

2.1. Fabrication process of nanofluidic energy generator

The proposed nanofluidic energy generator was fabricated by hybridization of the conventional photolithography and microfluidics-based control mechanisms of nanoparticle self-assembly, as reported previously [21,24–26]. The microchannel system of the nanofluidic energy generator was fabricated by standard photolithography, as shown in Fig. 2(a): (a-1) the SU-8 master mold on the silicon substrate is composed of deep and shallow layers; after (a-2) PDMS demolding and (a-3) bonding with glass substrate, the multilayered microchannel system is constructed, and the deep and shallow channels are used as main and filling channels, respectively. For the in situ formations of CE-NCNM and AE-NCNM with the designed shape in the desired positions, the filling channels were designed to guide the nanodrops containing positively or negatively charged nanoparticles into the desired regions as shown in Fig. 2(b) [21,27,28]. Additionally, the size of the designed regions could be modified as needed. First, a 2 μl drop of the nanoparticle suspension was introduced into the filling channel (Fig. 2(c)) and was allowed to flow into the desired position by capillary force and pressure drop. The solution in the filling channel was stopped at the interface between the main and filling channels due to negative neck pressure induced by the height difference and a large expansion angle (Fig. 2(d)). Subsequently, the nanoparticle suspension was dried using an air-flow through the contiguous main channels (Fig. 2(e)). After complete evaporation of the solution in the filling channel, the CE-NCNM connecting the two contiguous main channels was realized (Fig. 2(f)). Finally, all the CE-NCNMs were sequentially obtained; then, the AE-NCNMs were constructed in the same manner (Fig. 2(g)). The real-time in situ formation of NCNM in the filling channels is shown by