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Self-beating gel pump powered by chemical energy

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Abstract—**Many examples of microfluidic systems have been studied in various fields. Normally, micropumps in microfluidic systems are powered by electricity or heat generated from electric energy and the actuation is controlled by on–off switching of external inputs. Herein we report a novel autonomous flow control inside microfluidic channels powered by self-oscillating gels without external control devices. Self-oscillating gels exhibit a volume oscillation driven by the oscillatory Belousov–Zhabotinsky (BZ) reaction. Our approach greatly simplifies the microfluidic system construction because there is no need for the electric wiring and source. In this paper, we first demonstrate a directional fluid pumping within microfluidic channels and a directional flow rate was 0.02 µL/min utilizing self-oscillating gels. This self-actuated pump could serve as a new framework for microfluidic devices.**

I. INTRODUCTION

Many kinds of stimuli-responsive polymer gels have been widely studied and attempted to create soft actuators or micro pumps [1-10]. These materials that swell or shrink in response to external changes such as temperature, pH, electric field, and light are promising in various fields. Recently, many research groups have attempted to incorporate these intelligent materials into micro devices or soft actuators [1-3]. For example, the flow control in microchannels by using the microelectromechanical systems (MEMS) technology and poly(N-isopropylacrylamide) (PNIPAAm), a thermosensitive polymer, has been demonstrated [1]. In general, micropumps in microfluidic devices are made of piezoelectric elements [11], shape-memory alloys [12], etc. In most cases, these systems require complex fabricated circuits or external control devices. If gel actuators were to display independent motions such as self-oscillation, novel self-beating micro pumps could operate without external control devices. Recently, several groups have created autonomous actuators by using cells, biopolymers and cultured cardiomyocytes [13-16]. But the problem is that these materials based on the bio system work for only few days in such devices. On the other hands, our approach is to create a completely artificial devices and overcome these problems using autonomous gel actuator without relying on cells, biopolymers and so on.

Until now, we have studied the self-oscillating polymer gels driven by chemical energy of the oscillatory Belousov-Zhabotinsky (BZ) reaction [17, 18]. In an unstirred condition, chemical waves and pattern formations as the reaction-diffusion system are generated. The overall process of this reaction is the oxidation of an organic substrate by an oxidizing agent in the presence of the catalyst under acidic conditions. In the reaction process, there are periodic concentration oscillations of some reactants such as the metal catalyst moiety: $\mathrm{Ru(bpy)_3}^{2+} \leftrightarrow \mathrm{Ru(bpy)_3}^{3+}$. The Field-Koros-Noyes (FKN) mechanism explains the overall process of the BZ reaction [20]. According to the FKN mechanism, the overall reaction is divided into the following three main processes: consumption of Br^- ions (process A), autocatalytic formation of $\mathrm{HBrO_2}$ (process B), and formation of Br^- ions (process C).

$$\mathrm{Br}O_3^- + 2Br^- + 3H^+ \rightarrow 3HOBr \qquad \text{(A)}$$

$$\mathrm{Br}O_3^- + HBrO_2 + 2M_{red} + 3H^+ \rightarrow 2HBrO_2 + 2M_{red} + H_2O \qquad \text{(B)}$$

$$2M_{ox} + MA + BrMA \rightarrow fBr^- + 2M_{red} + \ other\ products \qquad \text{(C)}$$

The factor *f* denotes the number of bromide ions produced as two oxidized metal ions ($\mathrm{M_{ox}}$) are reduced ($\mathrm{M_{red}}$). In our gel system, $\mathrm{M_{ox}}$ and $\mathrm{M_{red}}$ represents $\mathrm{Ru(bpy)_3}^{3+}$ and $\mathrm{Ru(bpy)_3}^{2+}$, respectively. In processes B and C, the $\mathrm{Ru(bpy)_3}$ moiety in the gel works as the catalyst: the reduced $\mathrm{Ru(bpy)_3}$ moiety is oxidized (process B), and the oxidized one is reduced (process C). Therefore, as the initial concentration of the MA increased, the mole fraction of the reduced $\mathrm{Ru(bpy)_3}$ moiety in the gel increased in accordance with the FKN mechanism. The Oregonator model is used to describe the FKN mechanism. Here, we explain the Tyson and Fife version of the Oregonator that approximates the FKN mechanism by the following sequence of reactions:

$$\mathrm{A} + \mathrm{Y} \xrightarrow{k_1 H^2} X + P,$$
$$\mathrm{X} + \mathrm{Y} \xrightarrow{k_2 H} 2P,$$
$$\mathrm{A} + \mathrm{X} \xrightarrow{k_3 H} 2X + 2Z,$$
$$\mathrm{X} + \mathrm{X} \overset{k_4}{\rightarrow} A + P,$$
$$\mathrm{B} + \mathrm{Z} \overset{k_5}{\rightarrow} \frac{1}{2} fY,$$

where A=[$\mathrm{BrO_3}^-$], B=[all oxidizable organic species], H=[H^+], P=[HOBr], X=[$\mathrm{HBrO_2}$], Y=[Br^-], and Z=[$\mathrm{M_{ox}}$]. The Oregonator model treats the concentrations of A, B, and P, as well as the concentration of the hydrogen ion H, as constants. The reaction rate equations for the species X, Y, and Z are as follows:

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$$\frac{dX}{dt} = k_1H^2AY - k_2HXY + k_3HAX - 2k_4X^2,$$
$$\frac{dY}{dt} = -k_1H^2AY - k_2HXY + \frac{1}{2}fk_5BZ,$$
$$\frac{dZ}{dt} = 2k_3HAX - k_5BZ.$$

According to the ref. [19], the concentration Y is known to change in time much faster than X and Z. So Y can be excluded from the reaction rate equations by employing the steady-state approximation $dY/dt = 0$. Thus, the reaction rate equations are scaled as follows:

$$\frac{du}{dt} = u - u^2 - fv\frac{u-q}{u+q},$$
$$\frac{dv}{dt} = \varepsilon(u - v).$$

The scaling parameters are $u = X/X_0$, $X_0 = k_3HA/2k_4$, $v = Z/Z_0$, $Z_0 = (k_3HA)^2/k_4k_5B$, $\varepsilon = k_5B/k_3HA$ and $q = 2k_1k_4/k_2k_3$, respectively. Fig.1 shows the simulation result of the above equations. From this simulation, the concentration v oscillates under specific conditions. In our oscillating gel system, the volume change of the gel is explained by a change of the Flory Huggins interaction parameter [20], χ, which is induced by the hydration and dehydration of the polymer chain due to the valance change of the metal catalyst ($Ru(bpy)_3^{2+} \leftrightarrow Ru(bpy)_3^{3+}$; v) [21, 22]. In statistical thermal mechanics, χ is defined as the $\Delta G/k_BT$, where ΔG, k_B and T represents the difference in free energy of a solvent molecule that is surrounded entirely by polymer molecules compared with the one that is surrounded by solvent molecules of the same kind, Boltzmann constant and absolute temperature.

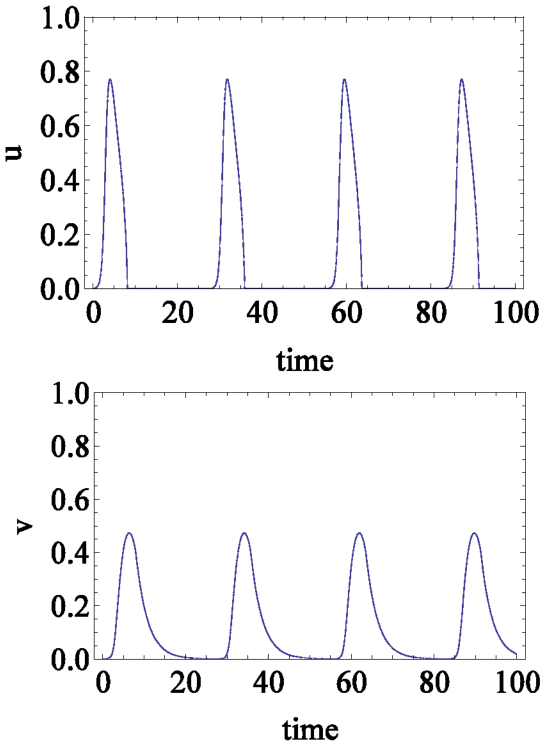

Figure 1. Simulation result. $\varepsilon = 0.354$, $q = 9.52\times10\text{-}5$, $f = 0.648$, $u(0) = 10^{-3}$, $v(0) = 10^{-3}$.

Thus with increasing in the mole fraction of the reduced $Ru(bpy)_3$ in the gel, the shrinking force originating in the hydrophobic reduced $Ru(bpy)_3$ greatly increased as well. So, gel swells at the oxidation state of the metal ion as shown in Fig. 2. Previously, the conventional self-oscillating gel generated the small mechanical oscillation because the response of the gel was very slow. To produce the large mechanical oscillation, the self-oscillating gel has to response firstly to the change in the charge density of $Ru(bpy)_3$. For realizing this purpose, we prepared the microphase-separated self-oscillating gel. And we succeeded in the realization of a large mechanical oscillation of a polymer gel at the macroscopic scale [9]. Thus, by building the self-oscillating gel into the microfluidic chip, a novel chemical micropumps could be expected without relying on external devices.

In this study, we demonstrate the self-beating gel pump powered by the self-oscillating gel.

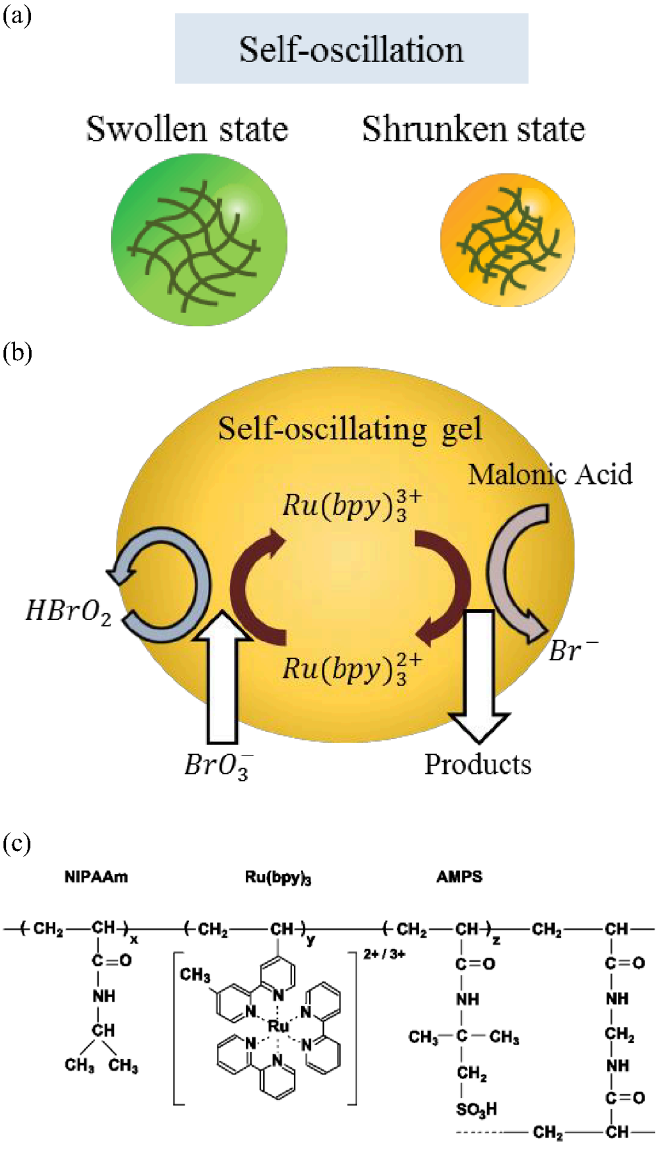

Figure 2. The self-oscillating gel. (a) Swelling-shrinking image of self-oscillating gel. (b) Working principle of self-oscillating gel. (c) Chemical structure of self-oscillating gel.

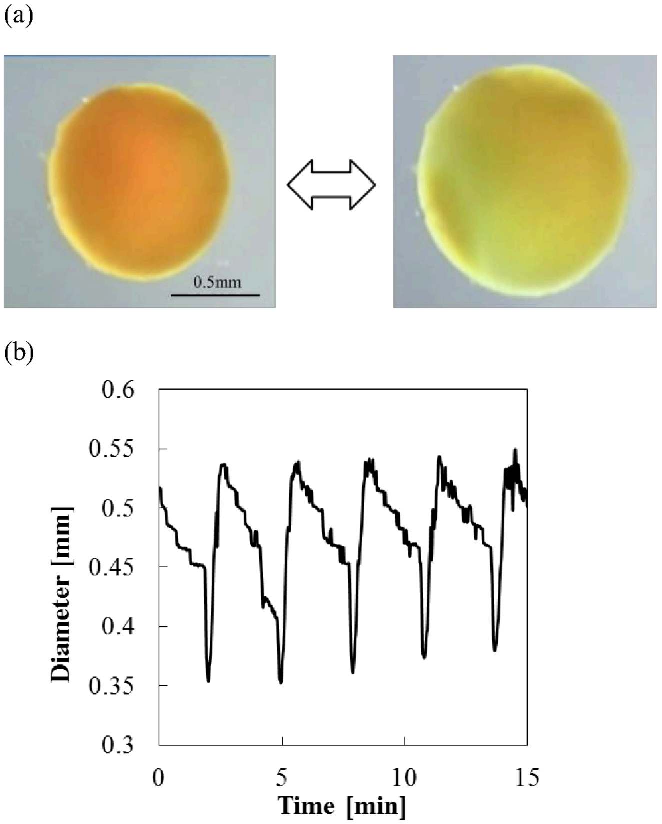

Figure 3. (a) Swelling-shrinking image of self-oscillating gel. (b) Working principle of self-oscillating gel.

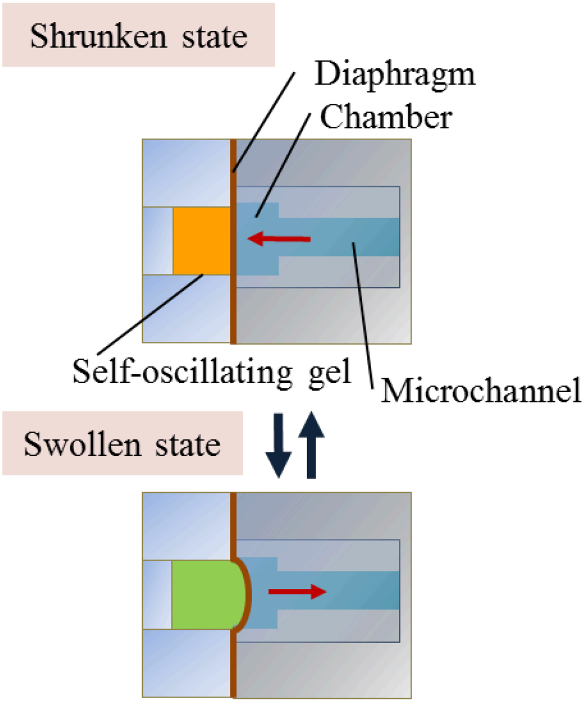

Figure 4. Design of micro gel pump powered by self-oscillating polymer gel. The microchip comprises four components i.e., Self-oscillating gel, diaphragm, chamber layer, and microchannel layer.

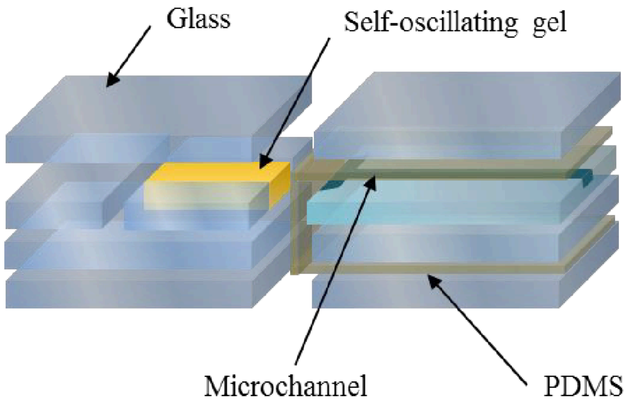

Figure 5. Schematic diagram of the 3D-micropump.

Fig. 4 shows the design and working principle of an actuated pump on chip using a self-oscillating polymer gel as the fluid pumping system. The flow in the microchannel is driven by swelling-shrinking behavior of the polymer gels. The proposed gel pump is shown in Fig. 5.

II. MATERIALS AND METHODS

A. *Fabrication of a microchip*

The microchip consists of four components: Self-oscillating gel, chamber layer, diaphragm membrane, and microchannel layer.

The master templates were fabricated by glasses. A microchip was assembled from the PDMS components. A diaphragm membrane was first attached to the chamber layer. The PDMS was (1) prepared by mixing prepolymer base with a curing agent in a 10 : 1 ratio by weight; (2) degassed under mild vacuum until the bubbles generated during stirring disappeared for the complete curing of PDMS; (3) spincoated with a 10 mm layer of prepared PDMS prepolymer; (4) attached to the fabricated chamber layer; (5) heated in an oven at 120 °C for 1 hour to harden the spin-coated PDMS membrane; and (6) peeled off with the chamber layer.

B. *Preparation of self-oscillating gel*

The poly(NIPAAm-*co*- Ru(bpy)$_3$-*co*-AMPS) gels were prepared as follows: 0.156 g of N-isopropylacrylamide (NIPAAm), 16.2mg of ruthenium (4-vinyl-4'-methyl-2,2'-bipylridine) bis (2,2'-bipyridine) bis (hexafluorophosphate) (Ru(bpy)$_3$) as a metal catalyst for the BZ reaction, 2.8mg of N,N'-methylenebisacrylamide (MBAA) as a cross-linker, and 6.6mg of 2,2'-azobis (isobutyronitrile) (AIBN) as an initiator were dissolved in O$_2$-free methanol (0.5ml). 5.5mg of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was dissolved in O$_2$-free pure water (0.5ml). Then the two solutions were mixed together. The monomer solution was injected into a casting mold. And then the monomer solution was polymerized at 60°C for 18 hours. After polymerization, the gels were soaked in pure methanol for a week to remove unreacted monomers. The gels were carefully hydrated through dipping it in a graded series of methanol-water mixtures, for 1 day each in 75, 50, 25 and 0%.

C. Preparation of BZ solution

The BZ solution were prepared as follow: malonic acid (62.5mM), sodium bromate (84mM), and nitric acid (0.894M). Then the three solutions were mixed together. The prepared gel was immersed in the solution at 17°C.

III. EXPERIMENT

We investigated the relation between the swelling pressure of the self-oscillating gel and the displacement of the PDMS membrane (a diaphragm). Firstly, we calculated the theoretical value of the displacement of the PDMS membrane. We constructed a simple model to optimize the design of the pump. The objective is to determine the relationship between the membrane deflection (*y*), the membrane thickness (*t*), and the length of the PDMS membrane (*l*), from a swelling pressure driven by a self-oscillating gel as shown in Fig. 6. Here we consider a thin square membrane that is clamped along the perimeter and subjected to a uniform swelling pressure driven by the self-oscillating gel. We employed the membrane theory [23, 24].

Let us T and p define as the tension per unit length of the PDMS membrane and swelling pressure of the self-oscillating gel, respectively. The restoring force due to tension in the membrane is $2l^2 T sin\theta$. Force equilibrium requires: $2l^2 T sin\theta - l^2 p = 0$, where $sin\theta \approx dy/dl$. The solution is given by

$$y = \frac{pl^2}{4T}, \qquad (1)$$

The strain along the *x* axis direction *l* is

$$\varepsilon_r = \frac{1}{l}\int_0^l \sqrt{1 + y'^2}dl - 1 \approx \frac{p^2 l^2}{24T^2}, \qquad (2)$$

since the bending moments are negligible, $\varepsilon_\theta = 0$, implying that the tangential and radial stresses are related by $\sigma_\theta = \nu\sigma_r$, where ν is the Poisson's ratio of the PDMS membrane. Together with Hooke's law $\varepsilon_r = \sigma_r / E'$, where $E' = E/(1 - \nu^2)$ and E is the Young's modulus of the membrane material, we have

$$T = \sigma_r t = \frac{\varepsilon_r E}{1 - \nu^2} \mathrm{t} = \left\{\frac{Etp^2 l^2}{24(1 - \nu^2)}\right\}^{\frac{1}{3}}, \qquad (3)$$

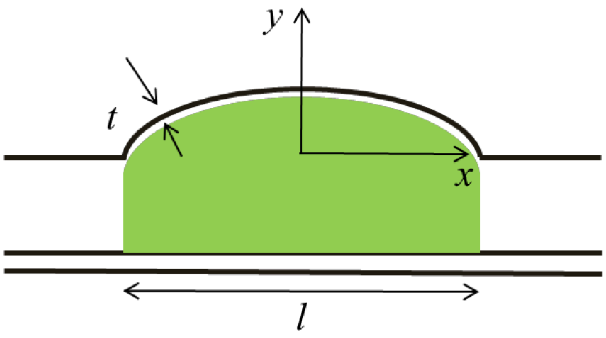

Figure 6. Schematic illustration of the diaphram

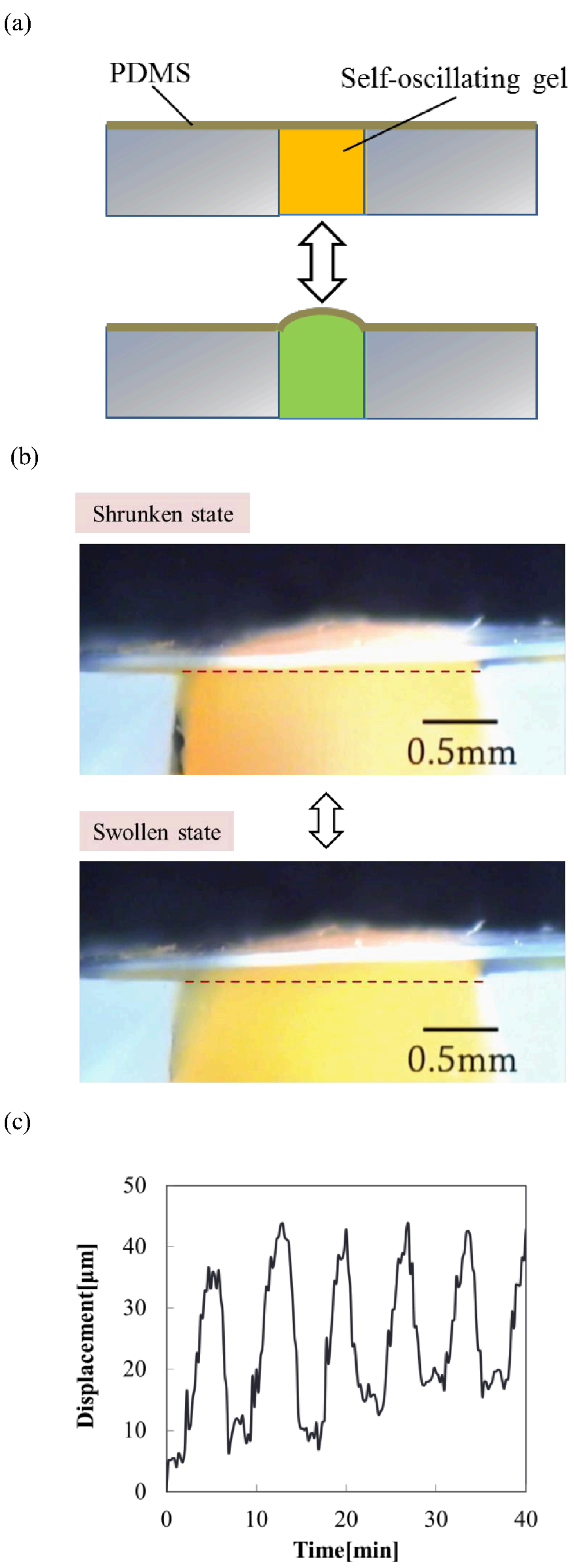

Figure 7. (a)Image of displacement of PDMS membrane by self-oscillating gel. (b) Image of displacement of PDMS membrane by self-oscillating gel. (c) The microscope was focused on the center of the PDMS membrane and the images were recorded.

which together with (1) gives

$$y_{max} = \frac{l^{\frac{4}{3}}}{4}\left[\frac{24(1-\nu^2)p}{tE}\right]^{\frac{1}{3}}. \tag{4}$$

Poisson's ratio of the PDMS membrane ν is 0.2. The swelling pressure of the gel p is 1.0 kPa. Young's modulus of the membrane material E is 750 kPa. The length of gel l is 0.5 mm. The membrane thickness t is 0.02 mm. The calculation result shows $y_{max} = 0.11$ mm.

Fig. 7(a) shows the part of displacement of a PDMS membrane by the self-oscillating gel. And Fig. 7(b) shows the image of a PDMS membrane by the self-oscillating gel. Fig. 7(c) shows the displacement time-course trajectory for a PDMS membrane as directly observed by the video. As a result, the maximum displacement was about 40 μm.

IV. RESULT AND DISCUSSION

A. *Fluid actuation on microchips.*

The spherical polystyrene tracking particles (Polybead, 1 μm diameter, Polysciences) were dispersed in solution, and microchannel fluid movement were observed directly by using a stereoscopic microscope (SZX16, Olympus) with an objective lens. The microscope was focused on the center of the microchannel and the images were recorded by personal computer through a CCD camera. Temperature was maintained at 17 °C during the observation using a constant temperature water tank (NCB-1200, EYELA). Fig. 7 shows the motion of polystyrene micro particles in the microchannel. The displacement time-course trajectory for a select particle near the center of the channel as directly observed by a CCD is plotted in Fig. 7(b). Particle displacement to the right (x) was measured directly from sequential video frames. Displacement at $t = 0$ min was defined as $x = 0$ μm. The fluid oscillating frequency was 0.002 Hz and the maximum linear displacement was 359.3μm.

B. *Estimation of potential performance of self-oscillating gel pump.*

From the position of the select particle near the center of the channel and microchip dimensions, we estimated the following parameters regarding the performance of the fluid movement: the volume change in the chamber per displacement (ΔV), position of the center of the diaphragm (y_0) and the expected flow rate to regulate the flow direction of the actuator without the loss (FW). In our rough estimation, it is assumed that the stress on the membrane was uniform. For small positions, y (the vertical position of a square diaphragm where the distance from the diaphragm is l) is approximated to the following equation:

$$y = y_0\left(1 - \frac{l^2}{{l_0}^2}\right)^2, \tag{5}$$

where l_0 is the length of the diaphragm (Fig. 7(a)). Therefore, ΔV is calculated as the following:

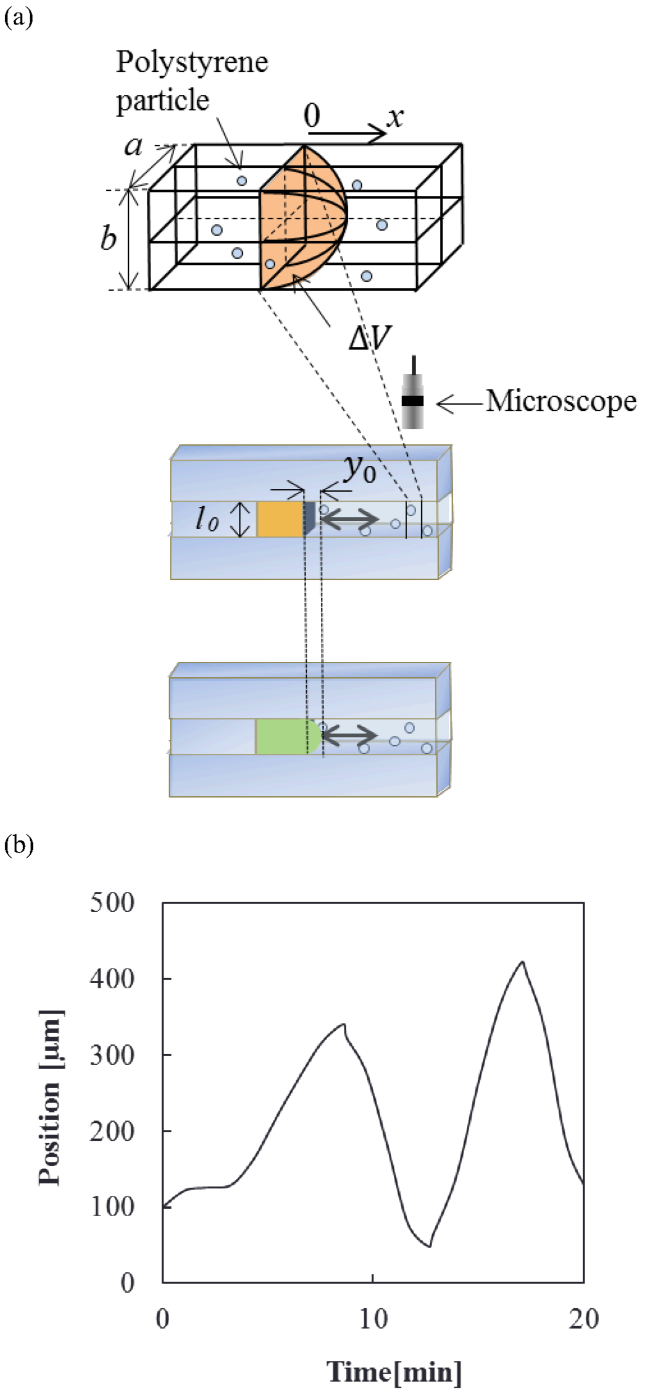

Figure 8. (a) Schematic view describing the observation method and parameters to calculate the performance of the fluid actuation on-chip. (b) Position time-course of one particle near the center of the channel for 20min at 17 °C.

$$\Delta V = \int_0^{y_0} l^2 dy. \tag{6}$$

From the position of one particle near the center of the channel (x), ΔV is estimated using the following approximation for volume change in a square geometry [15].

$$\Delta V = 0.47xab, \tag{7}$$

where a and b are the width and the depth of the microchannel, respectively as shown in Fig.7(a). Here we used the following values: l_0 = 100 μm, a = b = 100 μm and x = 359.3 μm. From eqn. (6, 7), ΔV was estimated as 0.169 nm^3. The flow rate was calculated from the following equation on the assumption that the resistance of the reflux was negligible:

$$FW = f\Delta V. \tag{8}$$

where f is the oscillation frequency. And frequency f was measured as 0.7 Hz at 17 °C and ΔV = 0.169 nm^3, respectively. Therefore, FW = 0.02 μL/min. Here, the estimated parameters are summarized for the device driven by the self-oscillating gel: ΔV = 0.169 nm^3; FW= 0.02 μL/min. It is assumed that the flow rate can be controlled by changing the concentration of the BZ solution and temperature [8, 19].

V. CONCLUSION

In this paper, we demonstrated a novel self-beating gel pump prototype. The pumping action is powered by only chemical energy of the BZ reaction without any external inputs, unlike conventional actuators. From the point of view of the practical use, the check valve is considered essential to control the flow direction in the microchannel. In the future, the self-beating gel pumps demonstrated here would be expected to the various fields, as novel biomimetic devices that exhibits autonomous motion as if it is alive.

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