DEVELOPMENT OF A HIGH EFFICIENT PROTON CONDUCTOR MEDIA USING EXTENDED-NANO SPACE UNDER THE OUTER ELECTRIC FIELD

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ABSTRACT

We report on realization of enhanced proton (H^+) conductivity in extended-nanochannels (ENCs) with the diameter of 250 nm in a micro-fluidic device, which was fabricated in combination with fused silica and $LiNbO_3$ (LN) ferroelectric materials with a thin SiO_2 film sputtered on them in advance. We detected the optimal thickness of a SiO_2 film where the deposited material would not affect spontaneous polarization in a $LiNbO_3$ material, which enables us to control the surface potential for efficient H^+ transport in ENCs. Here we describe the device concept, the outer electric field effect on ENCs and demonstrate the device working principle.

KEYWORDS: Extended-nanochannels on fused silica, $LiNbO_3$, Spontaneous polarization, Proton mobility

INTRODUCTION

Recently micro fuel cells (MFCs) have been considered as micro power sources analogous to existing batteries. However, the MFC technology requires stable and high H^+ conducting materials, operating at ambient conditions, and the external fuel supply system. In response to this issue, we designed the device that combines MFC with the on-chip micro-fluidic system for hydrogen generation via photoelectrochemical water splitting [1]. Then we fabricated two independent micro-fuel generation and micro-fuel cell devices, built on separate microfluidic chip platforms [2, 3]. In the both devices, the ENCs were used as the H^+conductor and separator, with consideration of our previous report [4] on unique water properties in ENCs, especially at high H^+ diffusion rate. Nevertheless, the fabricated devices showed quite low efficiency due to limited H^+ transport in the ENCs. From our previous experimental results [2, 3], we estimated that one nanochannel can transfer ~ 0.07 nA of energy. One approach to increase the H^+ conductivity is based on controlling the surface potential in the ENC, which will result in H^+ distribution changes near the nanochannel wall (within 50 nm) where the H^+ transfer phase is located, as we reported [4]. For this reason, we proposed to fabricate extended-nano space in combination with a LN single crystal material, where the surface crystal spontaneous polarization was detected [5], and thus we expect that we can increase the surface potential in ENCs due to the outer electric field phenomenon. Figure 1 shows the design of an extended-nanochannel which is based on the LN material. The bottom part of the extended-nano space consists of the LN material, which is covered by a thin SiO_2 film. In the present design we show the main functionality of an ENC, where the H^+ distribution is mainly localized in the proton transfer phase within 50 nm near the nanochannel wall due to the changes in surface potential by the outer electric field.

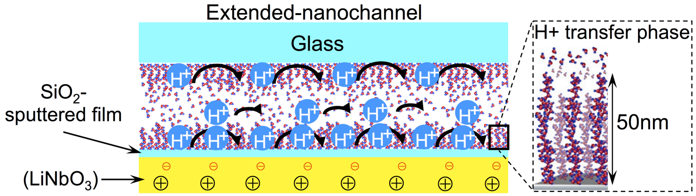

Figure 1. Design of an extended-nanochannel based on the LN material.

EXPERIMENTAL

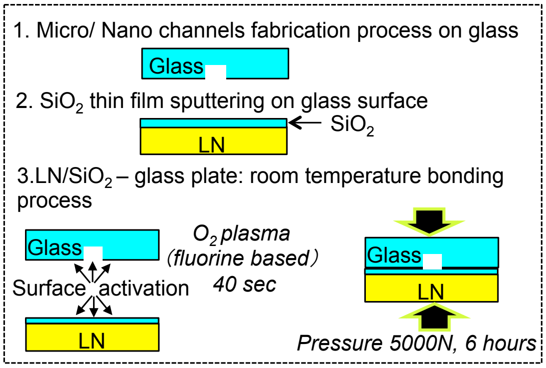

Figure 2. Schematic illustration of the fabrication process of the proposed LN-based extended-nanochannels microfluidic chip.

We designed and fabricated extended-nano space in combination with an LN single crystal material on one fused silica microfluidic chip platform. This device consists of two U-shaped microchannels (600µm wide and 6 µm deep) bridged by extended-nanochannels with the diameter of 250 nm and length of 400 µm (Fig. 3a). The chip fabrication protocol is schematically shown in Figure 2. All micro/nano channels were prepared on fused silica plates by standard electron beam lithography and lift-off processes on which we reported in our recent works [2-4]. In the next step, we covered the LN materials with thin SiO_2 films (LN/SiO_2) with the help of a r.f magnetron sputtering technique. After all necessary fabrication processes, a glass plate, with extended-nano channels and micro-channels fabricated on it, was bonded with the LN/SiO_2 substrate. Due to the differences in thermal expansion coefficient of fused silica and LN materials, we developed new parameters for the room temperature bonding process. At first, the both substrates were exposed by O_2 (fluorine based) plasma process for 30 seconds. After that, the substrates were aligned and pressed together, at the pressure of 5000 N for 6 hours. Using such parameters, we reached the bonding strength of ~ 0.6 J/m^2 and this value corresponds to ~ 500 kPa of the leakage test.

RESULTS AND DISCUSSION

To verify H^+ conductivity in ENCs, a pH fluorescence probe microscopy technique was used [4] (Fig. 3a). However, such a technique is more applicable for the fused silica based microfluidic chip, due to high transparency of the fabricated device. At present work, we fabricated a microfluidic-chip, with LN/SiO_2 on its one side, and found that the transparency of such a device is lower in comparison with fused silica based devices. For that reason, we decided to use the laser assisted fluorescence probe microscopy to detect the protons diffusion on extended-nanochannels. The basic operation procedure is shown in Figure 3a, where solutions 1 and 2 were applied to the left and right microchannels at different pressure of 10 kPa and 300 kPa, respectively. At the present pressure conditions the extended-nanochannels were filled with solution 2, and then the pressure was reduced to 0 Pa to stop the flow in the both microchannels. In the next step, the laser light was applied to the nanochannels area, and under such conditions, H^+ started to diffuse from the left to the right side of the nanochannels where fluorescence intensity decreased due to the decrease in pH, as shown in Figure 3b. The moving front of H^+ was recorded by a speed camera, and then the proton diffusion rate was calculated following our reported recipe [4].

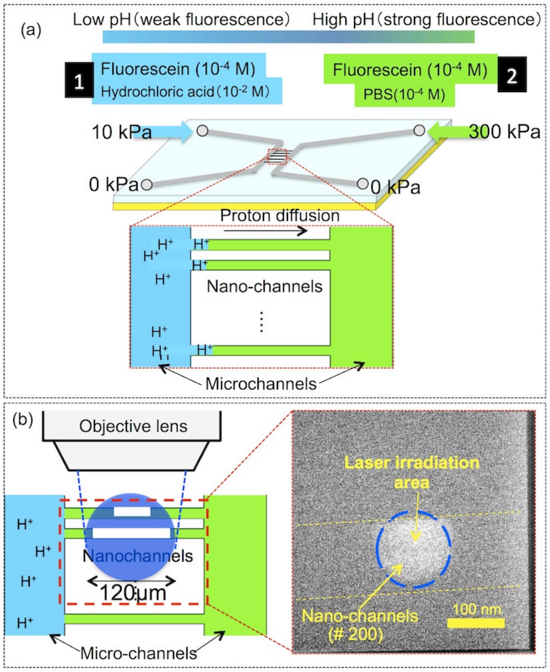

Figure 3. (a) Schematic illustration for H^+ diffusion measurements in extended- nanochannels. (b) Results of the observation of laser based induced fluorescence on the fabricated device.

We fabricated a few micro/nano fluidic devices with constant nanochannels sizes of 250 nm (Fig. 4a-b), but with SiO_2 films of different thicknesses on the LN material, in order to detect the optimal thickness where the electric outer field effect will enhance the H^+ conductivity. As we expected, the highest conductivity was realized in the device where the SiO_2 thickness was 5 nm, and the result on H^+ diffusion coefficient was 1.4x higher in comparison with the bulk value (Fig. 4a). These phenomena can be explained with consideration of the surface potential which is much higher at a thin sputtered SiO_2 film (Fig.4b). Also, these results clearly demonstrate the verification of the proposed outer electric field phenomenon (due to spontaneous polarization of the LN material) that changed H^+distribution in the proton transfer phase of the extended nanochannel.

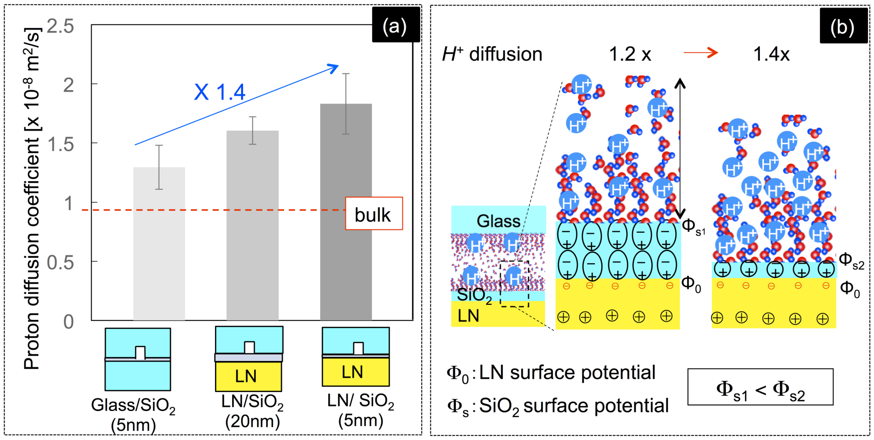

Figure 4. (a) Proton diffusion coefficient for LN based micro/nano fluidic devices- thickness effect of the SiO_2 *sputtered film. A glass/*SiO_2*-based device is shown for comparison. (b) Expected mechanism for* H^+ *transport in the ENC, which depends on the surface potential of the sputtered* SiO_2 *thin film due to the electrical outer field effect.*

CONCLUSION

In conclusion, we have successfully designed and fabricated a microfluidic chip based on the LN material, where a new idea of utilizing spontaneous polarization to the nanochannels surface potential control for efficient H^+ transport in ENCs has been realized. Presently, our efforts focus on the MFC device fabrication using the LN ferroelectric material where nanochannels will be fabricated, and a double enhancement in the H^+ conductivity is expected.

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