DEVELOPMENT OF HIGH-EFFICIENT PROTON CONDUCTOR NANOCHANNELS ARRAY BASED ON FERROELECTRIC MATERIAL

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ABSTRACT

In this work, we report on the possibility of controlling the surface potential of extended-nano channels (ENCs) made in a system of SiO_2/$LiNbO_3$ (LN), which can promote improvement of the proton diffusion rate. We detected the optimal thickness of a SiO_2 film which is ~ 5 nm, where the deposited material would not affect spontaneous polarization of the LN material, which results in enhanced proton transport in ENCs. Here, we describe the device concept, the effect of SiO_2 thickness on the LN surface potential, demonstrate the device working principle and show its enhancement of 2.5 times in proton diffusion in comparison to the balk value.

KEYWORDS: Extended nano channel, Proton conducting media, Ferro-electric material

INTRODUCTION

Micro fuel cells (MFCs) are gathering attention as the next generation of micro power sources. However, conventional MFCs' performance gets worse during operation due to proton conducting media degradation. The conventional proton exchange membranes (PEMs), such as Nafion based membranes, can easily degrade during operation, because high temperature and humidity are necessary to reach the appropriate proton (H^+) diffusion rate. On the other hand, our laboratory has discovered unique water properties in ENCs, such as high viscosity, low dialectical [1] constant and enhanced proton mobility [1]. In our previous research [2], we designed and fabricated a MFC device where we proposed to utilize an ENC made in fused silica as a new class of H^+ conducting media. Our approach to use ENCs for H^+ transport has a few advantages over conventional PEMs: 1) made on a fused silica plate, which means that it will not degrade during its operation; 2) H^+ mobility in glass-made ENCs does not require high temperature to reach the enhanced H^+ mobility [1]. However, the fabricated MFC device showed a quite low efficiency due to limited proton transport in ENCs in comparison with conventional MFC based on the PEM membrane. With response to this issue, one approach to increase H^+ diffusion 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, and thus we expect that we can increase the surface potential in ENCs due to the outer electric field phenomenon. As a result, introducing a LN material improved proton conductivity up to 1.4 times compared to the glass-based ENCs [3].

In this work, we detected the optimal thickness of a SiO_2 film where the deposited material did not affect spontaneous polarization in the LN material by measuring its surface potential. Also, we describe the device concept, the effect of SiO_2 thickness on the LN surface potential and demonstrate the device working principle.

THEORY

According to the proton transfer phase theory for extended nanochannels [4], the effect of the H^+ transfer phase is dominant in the range of 50 nm near the nanochannels walls. In this phase, the water molecules are loosely structured and through this structure, proton hopping occurs. Consequently, the proton diffusion in the channel accelerates.

In order to enhance the proton mobility in ENCs, we attempted to increase H^+ concentration in the nanochannels H^+ transfer phase, which resulted in a higher proton mobility, as shown in Figure 1.

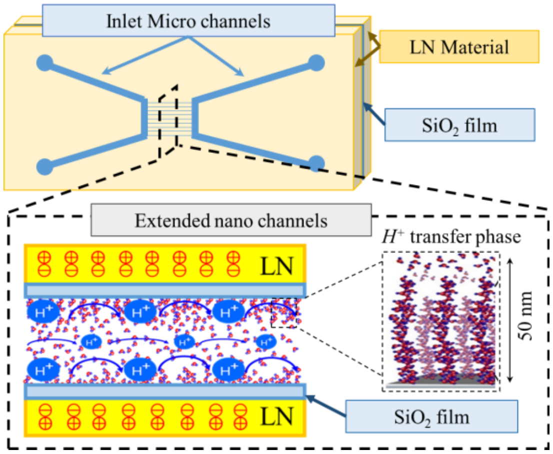

Figure 1: Conceptual design of a LN material-based proton conductor device. (The inset figure corresponds to the main functionality of ENC, where the distribution H^+ is mainly localized in the proton transfer phase within 50 nm near the nanochannels wall due to the changes in the surface potential in the system SiO_2/LN-SiO_2/LN due to outer electric field.)

EXPERIMENTAL

In order to detect the optimum thickness of a SiO_2 film which will not affect spontaneous polarization in the LN material, we performed a series of experiments. At first, the LN material was cut in small samples with the size of 1x1 cm. Then the LN samples were covered by SiO_2 with the help of a r.f. magnetron sputtering technique with various thickness from 3 nm to 20 nm. In the next step we measured the surface potential on the system of SiO_2/LN fabricated samples. The schematic diagram of the experimental arrangement is shown in Figure 2, and more details can be found elsewhere [6].

To confirm the SiO_2 film thickness dependency on proton mobility in the system of SiO_2/LN-Glass, we designed and fabricated extended-nano space in combination of a LN single crystal material on a fused silica microfluidic chip platform in the analogy with our previous work [3]. We fabricated devices with various SiO_2 film thickness starting from 5 nm to 20 nm. All the micro/nano channels were fabricated on a fused silica glass plate, and bonded with a sputtered SiO_2/LN material with the help of a low temperature technique [4], due to the differences in thermal expansion coefficient of fused silica and LN materials.

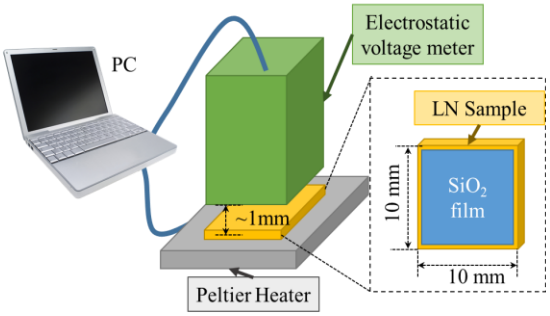

Figure 2: A schematic diagram of the experimental arrangement for recording and reading surface potential.

RESULTS AND DISCUSSION

Figure 3 shows the result of the surface potential measurement. These results clearly demonstrated that the thickness of a SiO_2 deposited film affected the surface potential in the LN material. It was detected that 5 nm of the SiO_2 film is the optimum thickness which can be used for the proposed device.

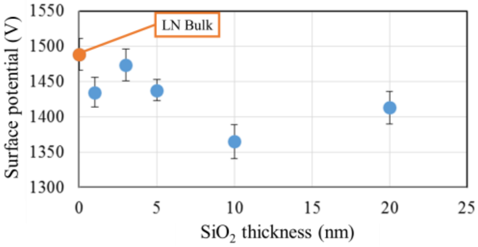

Figure 3: The surface potential dependency on the thickness of sputtered SiO_2 /LN fabricated samples.

In the next step we fabricated extended-nano space in combination with a LN single crystal material with various thickness of a sputtered SiO_2 film as we mentioned above. To verify H^+ conductivity in ENCs, a pH fluorescence probe microscopy technique was used [1, 3] (Figure 4). The basic operation of laser induced fluorescence spectroscopy was based on the following. At first, the microchannels were filled with low and high pH solutions with different pressure, as shown in Figure 4. At such pressure conditions extended-nano channels were filled with solution with high pH, and then the pressure was reduced to 0 Pa to stop the flow in the both microchannels. Under such conditions, H^+ diffused from the left to the right side of the nanochannels where fluorescence intensity decreased due to the pH decrease. Through the microscope lens in its combination with the speed camera the moving front of H^+ was recorded. The proton diffusion rate afterwards could be calculated according to the reported recipe [1].

Figure 5 shows the results in the proton diffusion experiments. The results showed that the proton diffusion was dependent on SiO_2 sputtering thickness. The relation behavior between proton diffusion and SiO_2 thickness showed to be quite similar as in the case of a surface potential dependency. The proton diffusion was enhanced up to 1.5 times of the diffusion inside glass-based ENCs. These results clearly confirmed that the optimum SiO_2 sputtering thickness of the LN material is 5nm.

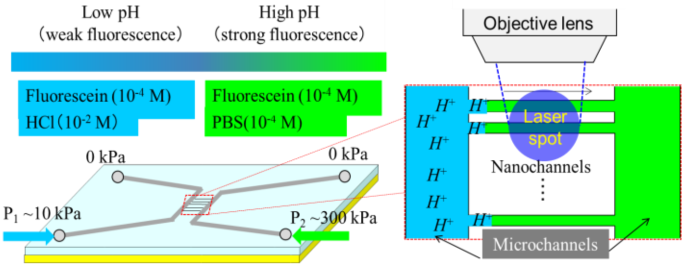

Figure 4: Schematic illustration of a laser induced fluorescence spectroscopy.

Finally, we fabricated ENCs on LN materials and covered them with the SiO_2 film 5 nm thick and evaluated the proton diffusion coefficient. It became clear that the proton diffusion rate was enhanced up to 2.5 times compared to the bulk constant and 1.8 times of glass-based ENCs. The result showed the both side effect of LN could enhance the proton mobility (Figure 5).

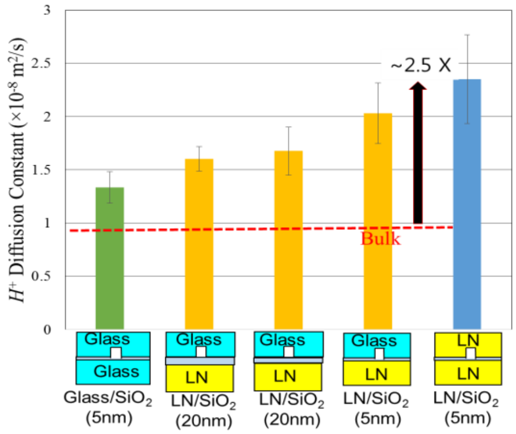

Figure 5: Proton diffusion coefficient for LN based micro/nano fluidic devices-thickness effect of the SiO_2 sputtered film. For comparison, glass-glass and SiO_2/LN-SiO_2/LN devices are presented in the left and right side of the graph, respectively.

CONCLUSION

In conclusion, we detected the optimal thickness of a SiO_2 film where the deposited material would not affect the spontaneous polarization of the LN material. Also, we successfully designed and fabricated a microfluidic chip based on the combination of LN and glass materials, as well as solely on LN materials. Here we demonstrated our idea of utilizing spontaneous polarization to the nanochannels surface potential control for efficient H^+ transport in ENCs and showed results in proton diffusion enhancement of 2.5 times in comparison to the bulk value.

ACKNOWLEDGEMENTS

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