

Report on Visit to MESA+ Institute for Nanotechnology of University of Twente by International Training Program

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This report describes the research activity during long-term research program in the International Training Program of young researchers sponsored by Japan Society for the Promotion of Science.

I visited to Twente University of Twente MESA+ Institute for Nanotechnology in the Netherlands from October 22 to December 22, 2012 by the program for incubating young researchers on plasma nanotechnology materials and device processing conducted by Plasma Nanotechnology Research Center in Nagoya University. Here, I report on the research environment and my research progress.

1. The research environment

MESA+ Institute for Nanotechnology, which is located in University of Twente, the Netherlands, is one of the most important institutes for nanotechnology all over the world. This institute is one of central institutes which leads NanoNed, the national project for nanotechnology in the Netherlands, and has the huge infrastructure for research of material and fabrication technology. This institute consists of 19 groups of various fields, such as physics, electrical engineering, chemistry and mathematics. Activating the collaborative research between each group, this institute aspires to achievement of breakthrough in the nanotechnology.

I engaged in the research activity in BIOS group directed by Prof. van den Berg. This group research mainly aims to contribute to the improvement of the quality of life by combining the micro- and nanotechnology with chemistry, physics and life science, using the microfluidic device called Lab-on-a-Chip.

BIOS group has around 50 members, 6 scientific staffs, 4 technical staffs, 10 postdoctoral fellows (Postdocs), 22 Ph.D. students, 3 master students and so on. Each scientific staff directs his/her own research projects with several Postdocs and Ph. D. students.

Ph. D. students usually begin their research at 9 a.m. and finish it at 6 p.m. and leave the institute immediately. This style is far different from that in Japanese laboratories. They seemed to be very good at switching on and off. In addition, scientific staffs expect a lot from Ph.D. students and discussed with them very frankly. I also discussed with my supervisor once a week and it helped me to understand my research.

2. Research progress

In this program, I conducted experiment to measure the chloride ion (Cl⁻) behavior in nano scale space with supervision of Prof. Eijkel in BIOS group. In the following part, details of this research are described.

2.1. Introduction

Since Cl⁻ ingress into concrete structures cause the deterioration of steel bar inside, it is required to predict precisely Cl⁻ ingress behavior for durability design. In standard specification for concrete structure, prediction for Cl⁻ ingress is based on Fick's diffusion law. But it has been reported by recent analysis of real structures that there is possibility of stagnation of Cl⁻ ingress into the high quality concrete structures at a certain point. This shows that current method to predict Cl⁻ ingress might overestimate and the design might become uneconomical in case of the high quality concrete. If stagnation of Cl⁻ ingress is taken into account in durability design, rationalization of design can be expected. But its mechanism has a lot of unknown factors.

Some researchers have reported that its mechanism might be as followings; Cl⁻ cannot enter into pores, which sizes are under a certain threshold value, by the electrical interaction between pore wall and ion even if the pores are filled by water. Though a numerical analysis shows that the threshold size of that pores is considered to be around 10nm, no experimental validation is conducted so far due to the difficulty of direct observation of Cl⁻ behavior in concrete.

So in this research we conduct the optical experiment by using glass micro/nano chip and MQAE, a fluorophore which fluorescence intensity decreases by reacted with Cl^- , in order to understand the relationship between pore size and Cl^- behavior.

2.2. Experiment

The micro/nano chip is consisted of 2 U-shaped micro channels (Depth: $30\mu\text{m}$, Width: $500\mu\text{m}$) and 32 nano channels (Depth: 95, 28, 16nm, Width: $5\mu\text{m}$, Length: $500\mu\text{m}$) which are bridged between micro channels. (Photo1 and Fig.1) The chip is fabricated by photo lithography and wet etching. After etching micro channels on upper substrate and nano channels on bottom substrate, they are bonded by thermal bonding.

MQAE, a fluorophore which fluorescence intensity decreases by reacted with Cl^- , is used to detect Cl^- in nano channels. MQAE is a monovalent cation and its fluorescence intensity decreases as concentration of Cl^- increases. Also its fluorescence intensity decreases by Br^- , I^- and SCN^- , but not affected by NO_3^- , SO_4^{2-} and HCO_3^- .

Two properties of MQAE should be understood quantitatively before this experiment. First one is photo bleaching, that is fluorescence intensity of MQAE decreases as it is excited by a mercury lamp. In order to understand this, we keep exposing 0.25mM MQAE solution in $500\mu\text{m}$ gap

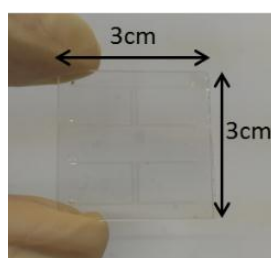


Photo1. Micro/nano chip

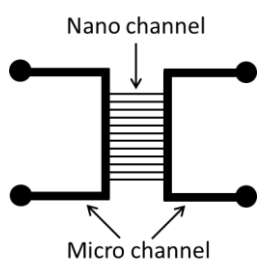


Figure1. Chip design

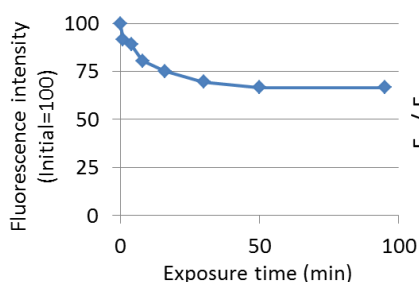


Figure2. Photo Bleaching

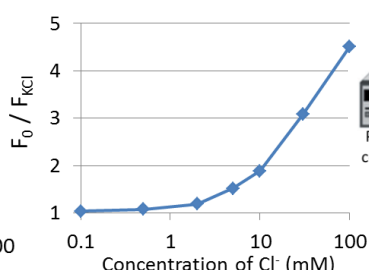


Figure3. Quenching Plot

between two glasses and measure the exposure time and its fluorescence intensity. Fluorescence intensity of MQAE is obtained by imaging analysis. The result is shown in Fig.2. It is confirmed that the intensity decreases drastically in first 10 minutes and reaches the steady state with 70% intensity compared with the initial intensity. Not like other fluorophores, the intensity doesn't become zero. It might be because of the back ground effect. But at least we can confirm that the drastic decrease of fluorescence intensity should be taken into account for the experiment.

Second property of MQAE is quenching, that is fluorescence intensity of MQAE decreases by reacted with Cl^- . In order to understand this quantitatively, we measure the change of fluorescence intensity of 0.25mM MQAE with KCl solution with various concentrations by the same method as the photo bleaching measurement. The measurement is conducted 3 times and the averaged result is showed in Fig.3. The vertical axis in Fig.3 shows the ratio of fluorescence intensity of only MQAE solution (F_0) to fluorescence intensity of MQAE with KCl solution (F_{KCl}). As shown in Fig.3, it is confirmed quantitatively that the intensity decreases as concentration of KCl solution increases.

The experimental set-up is shown in Fig.4. The inlets of micro channels are connected with the pressure controller by glass capillary tubes and connectors and solution flow is controlled by pressure. Fluorescence microscope is used for observation. In addition, it is reported that decrease of pH in nano channels might cause decrease of fluorescence intensity of MQAE. In order to avoid this, phosphate buffer solution (PB) is used in this experiment.

The experimental procedure is as followings. First, right micro channel is filled with 1mM PB by pressure $P_R=200\text{mBar}$ for 30 minutes. Then, left micro channel is

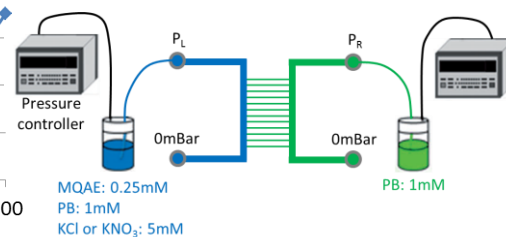


Figure4. Experimental set-up

filled with 0.25mM MQAE solution, 1mM PB and 5mM KCl solution (they are mixed with 1:1:1 volume ratio) by pressure $P_L=100\text{mBar}$. After fluorescence from left micro channel is seen, we stop the flow by $P_R=P_L=0$ and take the microscope photos for each time. Fluorescence intensity from nano channels is measured by imaging analysis of these photos. In order to avoid photo bleaching, MQAE is exposed by mercury lamp only when microscope photos are taken. Also we replace KCl solution to KNO_3 solution and conduct the same measurement to compare their fluorescence intensity. If the thickness of electrical double layer overlaps the depth of nano channel, MQAE (a monovalent cation) can easily enter into nano channel, while Cl^- cannot enter into due to the electrical interaction. In the result, it is expected that the difference between fluorescence intensity of case KCl and case KNO_3 becomes minor.

2.3. Result

Photo2 shows the microscope photos for each time in case of KNO_3 and nano channel depth 95nm. From these photos, it is confirmed that MQAE diffuses one-dimensionally in nano channel from left to right.

Fig.5 shows the comparison between fluorescence intensity of case KCl (F_{KCl}) and case KNO_3 (F_{KNO_3}) at 45

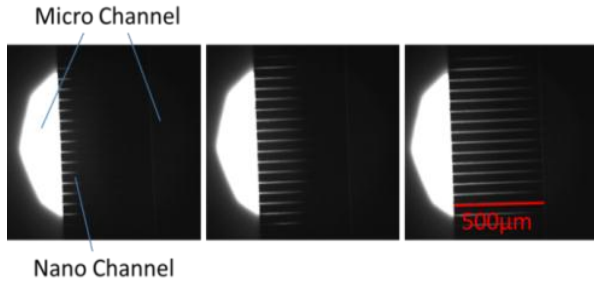


Photo2. Fluorescence microscope photos (2min, 10min and 30min from left)

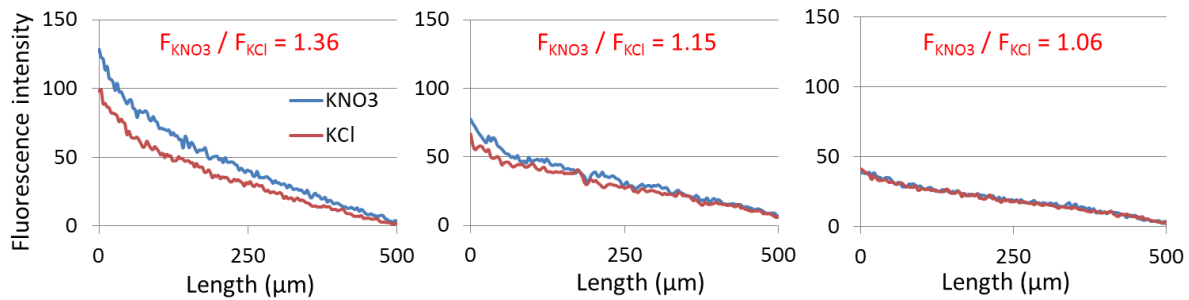


Figure5. Comparison between F_{KCl} and F_{KNO_3} at 45 min (channel depth 95, 28 and 16nm from left)

minutes. By this point MQAE diffusion has reached the steady state in any cases of channel depth 95, 28 and 16nm. Since F_{KCl} is less than F_{KNO_3} in case of 95nm, it is confirmed that Cl^- enters into nano channel. Ratio of fluorescence intensity is $F_{\text{KNO}_3}/F_{\text{KCl}}=1.36$. In case of 28nm, that ratio becomes $F_{\text{KNO}_3}/F_{\text{KCl}}=1.15$ and it means less Cl^- could enter into nano channel than case 95nm. Especially in case of 16nm, that ratio becomes $F_{\text{KNO}_3}/F_{\text{KCl}}=1.06$ and it means almost no Cl^- could enter into nano channel. Debye length, which is considered to be thickness of the electrical double layer, becomes 6.7nm calculated by concentrations of solution which are used in this experiment. Therefore, since 13.4nm is inside of the electrical double layer in 16nm depth nano channel, only 2.6nm remains practical diffusion area for Cl^- and it suppresses Cl^- diffusion drastically.

2.4. Comparison between experiment and theory

Plečis et al. defines the Exclusion-Enrichment coefficient β in order to quantify the effect of the electrical interaction on Cl^- behavior in nano scale space as followings.

$$\beta = \frac{C_{\text{eff}}(x)}{C^*(x)} = \frac{\langle C(x, z) \rangle_z}{C^*(x)}$$

Where $C_{\text{eff}}(x)$ is concentration of ion with the electrical interaction and $C^*(x)$ is concentration of ion without the electrical interaction. First, the experimental value of β (β_{exp}) should be obtained by our results. Concentration of Cl^- in nano channel can be obtained by quenching plot and fluorescence intensity ratio $F_{\text{KNO}_3}/F_{\text{KCl}}$. Then, β_{exp} can be obtained by dividing them by bulk concentration of Cl^- 5mM.

Then, the theoretical value of β (β_{pre}) can be expressed as following equation by using Plečis's paper as a reference.

$$\beta_{pre} = \frac{1}{h} \int_0^h \exp\left(-q \frac{\zeta \cosh((h/2-z)/\lambda_D)}{\cosh(h/2\lambda_D)} / k_B T\right) dz$$

From this equation, not only Debye length λ_D , but also the net charge q of the diffusing species and the zeta potential ζ of the glass surface are important parameters in the quantification of ion behavior with the electrical interaction. Therefore, the zeta potential of the glass surface which is used in this experiment should be determined in order to compare the experimental value with the theoretical value. Kirby et al. have reported that for a 1:1 inorganic electrolyte, the zeta potential of glass varies linearly with the logarithm of the bulk concentration, leading to the following expression of ζ ,

$$\zeta = a_0 + a_1 \log(c)$$

Where a_0 and a_1 are two constants depending on surface properties and the solution composition. Experimental studies by Kirby et al. have shown that for Pyrex and KCl solutions, a_0 can be taken as 0 mV and a_1 depends on bulk pH, temperature and so on. In this experiment, pH of solution is 7.4 and temperature is 25 degrees Celsius. In this condition, a_1 could be taken 30mV by using past experimental studies as references. Therefore, we have obtained all parameters required to calculate β_{pre} value by the numerical analysis.

Fig.6 shows the comparison between β_{exp} and β_{pre} . Though we have only three experimental values, it is confirmed that at least these experimental values agree well with the theoretical curve. Therefore, it is considered that it shows the reliability of this experimental results and the possibility of quantification of ion behavior with the electrical interaction in nano scale space.

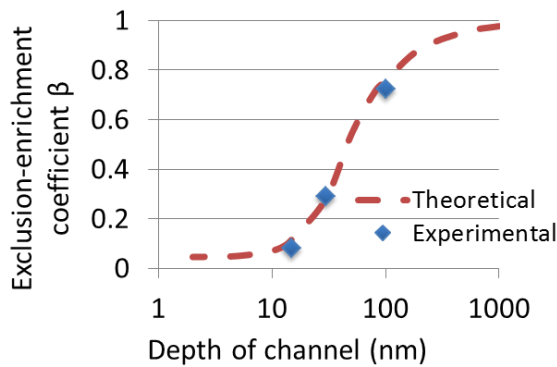


Figure6. Comparison between β_{exp} and β_{pre}

2.5. Conclusion

In this study, it is confirmed that Cl⁻ ingress into the space which size is almost same as Debye length is suppressed drastically. Since the main pore size in concrete is considered to be from μm to nm scale, it is considered that the phenomenon seen in this study might cause the stagnation of Cl⁻ ingress into concrete. But in order to suppress Cl⁻ ingress into concrete, the zeta potential of pore wall surface in concrete should be negative. Therefore, it is required to measure the zeta potential of pore wall surface in concrete in order to verify the possibility shown in this study.

3. What I got from this program

In this program, I have learnt not only knowledge on my study, but also communication skill in English. In addition, I feel my view has been broadened through touching cultures and arts which are different from Japanese ones and having communication with a lot of people with various backgrounds. I think that this program gave me a very good opportunity to think about my research itself and research carrier.

Finally, I deeply acknowledge Prof. Toyoda, Associate Prof. Kaji and Ms. Era in Nagoya University, Associate Prof. Hibara in Tokyo University IIS and those who gave me this precious opportunity. Also I really appreciate Prof. Eijkel, Dr. Le Gac and those who support my research activity in University of Twente and Ms. Fukuyama in Tokyo University for her great support in the process of fabrication.