Report for Long-Term Overseas Dispatch Program in MERIT

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1. Outline

This is the report for the visit to Truls Norby's lab at Department of Chemistry in University of Oslo, Norway from 9/4 to 11/17.

2. Backgrounds

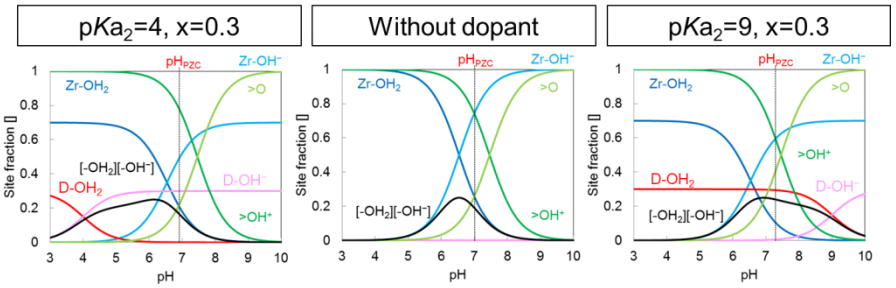
Prof. Norby is, needless to say, a famous professor about bulk ion conductors and authority of Solid State Ionics. He is a Japanophile and has been my supervisor's friend for about 30 years. Actually, there was a Japanese guest from Waseda University and one of the members decided to go to Japan for collaborative research during my short visit. Actually I have also seen him in international conference several times and I had a chance to see Ph. D defense of a student who studied proton conduction on oxide surface. Here, I was really impressed with his research and would like to touch the essence of their research. Therefore, I have asked Prof. Norby for this short visit via my supervisor. Here, I would like to mention the research done by the Ph. D student briefly. Proton conduction on the oxide surface is inversely proportional to the temperature under fixed partial pressure of water, since it is proportional to thickness of hydrated multilayer accumulated on the surface. In their research, by fixing the relative humidity and thickness of hydrated multilayer, they could successfully reveal the reason why proton conduction on the surface shows negative apparent activation energy and apply the equation of bulk ionic conductor to these surface migration phenomena.

In this overseas dispatch program, we conduct the research to improve the understanding about the effect of surface acidity and basicity on the proton conduction, by combining my knowledge about acid base chemistry on oxide surface obtained from *ab initio* molecular dynamic simulations with the sophisticated skill for conductivity measurement in Prof. Norby's group, which even could analyze proton conductivity as a function of thickness of water layer.

3. Research Contents

Proton migration property on single oxide surface is determined by the equilibrium of deprotonation reactions of hydroxyl groups on metal and oxide ions, $M\text{-}OH_2 \leftrightarrow M\text{-}OH^- + H^+$ pKa$_1$, and $>OH^+ \leftrightarrow >O + H^+$ pKa$_0$. Note that pKas are the acid dissociation constant for them. On the other hand, in case of binary oxide, it is considered that the proton migration property could be determined from the equilibrium of deprotonation reactions of hydroxyl group on the matrix and dopant site according to Tanabe's theory. Thus, it

can be discussed by adding the following equilibrium, D-OH_2 ↔ D-OH^- + H^+ pKa_2. (Here, D represents dopant metal ions on surface.) According to our previous research, proton conductivity is proportional to the products of site fraction of H_2O adsorbates on metal ion sites, [-OH_2][-OH^-]. The figure shows the schematic image of predicted equilibrium of site fraction of hydroxyl groups on doped ZrO_2 as a function of pH in hydrated multilayer on the surface. Based on this figure, it is predicted that acid dopant increase proton conductivity in lower pH compared to pH_{PZC}. On the other hand, by introducing the basic dopant, it seems that proton conductivity is maintained in higher pH.



Schematic image of site fraction of each adsorbate on ZrO_2 as a function of pH

Here, proton conductivity of doped ZrO_2 under wet-N_2 and wet-NH_3 to analyze the effect of dopant and their response against pH-modified condition. Under wet NH_3 atmosphere, proton conductivity decreases on pure ZrO_2, because of the neutralization of protonic carriers on the surface by basic NH_3. Since, at around room temperature, concentration of basic hydroxide ions in NH_3-saturated water is to the degree of 0.01(mol/L), which corresponds to pH≈12, it is considered that concentration of protonic carriers on ZrO_2 surface is larger than 0.01(mol/L), quite high concentration if we could consider [H^+] in the same manner as liquid. Also, contrary to my prediction, proton conductivity of ZrO_2 with acidic dopant was maintained under NH_3, but that with basic dopant decreased under NH_3. Therefore, we are now examining the mechanism of it.

4. Life in Oslo

Norway is a one of the wealthiest country and famous for oils and natural gas. Also, it is well known as a welfare state. However tax and living cost are too expensive because of it. If we consider foreign exchange ratio, living cost is almost doubled compared with that of Japan. For example, 500ml bottle of Coca Cola costs 250 yen in super market and Mc' Donald's meal costs more than 1000 yen. Therefore, except for lunch, which I utilized cafeteria in university, I have hardly eaten out but cooked meals by myself. (Note that even for students and staffs in Oslo it seems that living costs are quite high and comparable number of the members made their lunch by themselves.) Otherwise, food and commodity expenses exceed far from 50,000 yen although I have stayed in Oslo alone. However, Oslo city is quite safe and all the citizens are kind inversely

proportional to the living costs. Therefore, I have never felt any anxiety, even if I returned home in late at night at around 12. In Oslo, they tend to spend their time with their family, work from 9 to 17 o'clock and hardly do overtime work and, unfortunately almost all the shops are closed on Sunday, although I have lived in the city center. (Unfortunately, I need to go to the university for the experiment on the weekend to summarize it during this short visit.) It is a big advantage that there is no seniority system. In Oslo, all the member call Prof. Norby as "Truls" (his given name), and even say some joke and even make fun of him. I think this really frank relationship between members and working environment drastically increase the efficiency of the work and feel that we should change working environment in Japan including cultural and conscience part of managers.

About master students in this group, half of them go to companies after completion of the master course and the rest of them go to the doctor course after graduation. The biggest difference between Japan and his group is that all of the doctor course students apply to collaborative research projects with companies, receive salary from them, and study freely within the range of the project. (It is considered that this is because Prof. Norby is really good at drawing money and project from companies.) It seems that doctor course students are easy to do their research and what they want to do in the range of their project, although they must be responsible for all their work. The defense to win the doctor title is a bit different in Oslo, which is consisted of "Trial Lecture" and usual presentation in front of the referees (although presentation is a kind of theater-type one, opened for everyone.) In the trial lecture, the candidate is given a theme, looks up the theme for 2 weeks and presents it in front of the audience to test whether the candidate could explain scientific topic for the beginners. Therefore, it seems that not only the professional knowledge in particular field of science but also broad knowledge and skill for presentation to explain it are demanded for scientists in this country and they try to educate such kind of doctors by their program.

Acknowledgement

I really would like to appreciate Prof. Norby and all the members in his group, especially Dr. Vøllestad for giving me a really good opportunity to study in Oslo, fruitful discussion about the proton migration on the surface and helping for the preparation of these experiments. Also, I would like to thank all the professors and staffs in MERIT and my supervisor, Prof. Yamaguchi who sincerely arranged this visit to Oslo.