別紙様式３

学業及び研究等の進捗状況等報告書
Report of Research Progress and Future Research Plan

※ 本報告書は「4.指導教員からのコメント」を除き、北海道大学私費留学生特待プログラム」のHPに掲載します。(https://www.oia.hokudai.ac.jp/cier/own-scholarship/)
*This report other than "4. Comments from your supervisor" will be published on the website of "Hokkaido University Special Grant Program for Self-Supported International Students".
(https://www.global.hokudai.ac.jp/admissions/scholarships/scholarships-for-prospective-students/)

氏名 Name	ZHU RUIJIE	学　年 Year	D3
所属学院等名 Graduate School	総合化学院		
所 属 専 攻 名 Major	総合化学専攻		
所属研究室等名 Laboratory	界面電子化学研究室		
指導教員職・氏名 Supervisor	幅崎　浩樹		

１．研究テーマ名 Research theme

Suppressing dendrites growth of metal anodes from adjusting electrode-electrolyte interface for the development of next-generation high-energy-density batteries

2．研究等の進捗状況等 Research progress, etc.

研究の概要、独創性、状況等を含めて具体的に記入のこと。
※研究成果の発表・公表実績がある場合については学会名、掲載紙等の情報を含め詳細を記載すること
In detail, including the outline, originality and so on.
*Please state the name of academic conferences, journals or transactions if you have presented your research or your research was published.

In this semester I completed my doctoral thesis for my degree. During the years of my PhD program, I advanced my research on the growth and limitation of zinc dendrites in aqueous zinc ion batteries and obtained some important conclusions.

Rechargeable aqueous zinc-ion batteries (RAZIBs) are a class of safe, efficient, low-cost batteries with promising applications. The aim of my research is to improve the cycle life of the zinc anodes in RAZIBs and thus improving the performance of RAZIBs. The use of zinc metal anodes in RAZIBs is hindered by the growth of Zn dendrites. In my study, I investigated the origin of Zn dendrites and found that the zinc hydroxy sulfate (ZHS) brought about by the parasitic hydrogen evolution reaction (HER) plays a key role. The uniformity of Zn deposition can be improved by applying external stress to the Zn anode surface or by polishing the Zn metal surface. Based on the discovering, the use of niobium (Nb) metal as a coating for the anode current collector can also optimize the Zn deposition behavior. The combination of different research fields will help to develop high-energy-density batteries for sustainable energy storage. And I believe that this research sheds light on dendrite growth mechanisms in RAZIBs and proposes effective strategies to improve cycling performance of zinc metal anodes and develop high-energy-density batteries for sustainable energy storage.

The achievements published during my doctoral course are shown here:

1. Ruijie Zhu, Huijun Yang, Laras Fadillah, Zetao Xiong, Damian Kowalski, Chunyu Zhu, Sho Kitano, Yoshitaka Aoki, Hiroki Habazaki, "A lithiophilic carbon scroll as a Li metal host with low tortuosity design and "Dead Li" self-cleaning capability", *Journal of Materials Chemistry A*, 2021, 9, 13332-13343.

2. Ruijie Zhu, Huijun Yang, Wei Cui, Laras Fadillah, Tianhong Huang, Zetao Xiong, Chunmei Tang, Damian Kowalski, Sho Kitano, Chunyu Zhu, Daniel R. King, Takayuki Kurokawa, Yoshitaka Aoki, Hiroki Habazaki, "High strength hydrogels enable dendrite-free Zn metal anodes and high-capacity Zn–MnO_2 batteries via a modified mechanical suppression effect", *Journal of Materials Chemistry A*, 2022, 10, 3122-3133.

3. Ruijie Zhu, Zetao Xiong, Huijun Yang, Tianhong Huang, Seongwoo Jeong, Damian Kowalski, Sho Kitano, Yoshitaka Aoki, Hiroki Habazaki, Chunyu Zhu, "A low-cost and non-corrosive electropolishing strategy for long-life zinc metal anode in rechargeable aqueous battery", *Energy Storage Materials*, 2022, 46, 223-232.

4. Ruijie Zhu, Zetao Xiong, Huijun Yang, Ning Wang, Sho Kitano, Chunyu Zhu, Yoshitaka Aoki, Hiroki Habazaki, "Anode/Cathode Dual-Purpose Aluminum Current Collectors for Aqueous Zinc-Ion Batteries", *Advanced Functional Materials*, 2022, 2211274.

3．今後の研究計画等 Future research plan

現在までの進捗状況等を踏まえ、今後の研究発表等を含めて具体的に記入のこと。
In detail, based on current progress, including a future research presentation plan.

My dissertation reveals a strong relation between Zn dendrites growth and ZHS formation in mildly acidic electrolytes. The three conditions of HER ratio, current densities, and Zn deposition substrates are shown to greatly affect Zn deposition morphology and deposition reversibility. Also, optimization at the anode-electrolyte interface has been shown to be effective in improving the electrochemical performance of Zn anode. Among them, the use of polymer separators (or semi-solid electrolytes) with high mechanical-strength can limit the generation of Zn dendrites during long-term plating/stripping cycles; reducing the current proportion of HER in the total current, i.e., increasing the Faraday efficiency of Zn plating, will effectively limit the generation of ZHS and improve the Coulombic efficiency of the Zn plating/stripping. Considering that charging/ discharging batteries at very high current densities is not achievable in practice, most batteries will be used in the rate range of 0.3 C - 2 C (corresponding to charging current-densities of about 1 - 8 mA cm^{-2} for 4 mAh cm^{-2} capacity), it is also important to ensure the cycling performance of the Zn anode when charging and discharging at low current densities. Hence, the development of polymeric separators/electrolytes that can simultaneously inhibit HER and have high mechanical-strength would be a highly likely way to help achieve a high-performance Zn anode.

In the subsequent studies, hydrogel electrolytes that can simultaneously reduce the activity of water molecules at the electrode-electrolyte interface without affecting zinc-ion transfer will be prepared by compounding hydrophilic hydrogel networks and hydrogel networks with hydrophobic properties. The hydrogel with double networks can be mechanically strong, while the hydrophobic network will reduce the proportion of water molecules at the interface. Furthermore, nanoparticles that can be used as anti-corrosion coatings (e. g. zeolite imidazolate framework, ZIF) will be added to the hydrogels to enhance the mechanical strength of the hydrogel while further reducing the possibility of HER occurrence at the interface. The development of the functionalized hydrogel electrolytes will provide a more comprehensive understanding of the study of Zn metal anodes and RAZIBs.

A part of the subsequent research publications is planned as follows (includes papers as first or corresponding author):

1.Understanding the electrochemical behavior of Zn anodes in aqueous electrolytes by 3-electrode AC-impedance testing, **in preparation.**

2. Ice crystal sublimation for easily producing MnO_2 cathode with hierarchically porous structure and high cyclic reversibility, *Nanoscale*, **under peer review.**

3. Enabling hydrophilic binders bonded MnO_2 cathodes via hydrogels based quasi-solid-state interface, **in preparation.**

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氏名 Name	Onuh Amarachukwu Faith	学　年 Year	D3
所属学院等名 Graduate School	Environmental Science		
所 属 専 攻 名 Major	Division of Biosphere Science Molecular Biology Course		
所属研究室等名 Laboratory	Miwa laboratory		
指導教員職・氏名 Supervisor	Miwa, Kyoko		

１．研究テーマ名 Research theme

The involvement of Golgi localized proton pyrophosphatase (AVP2;1) in amelioration of low boron stress in plants

２．研究等の進捗状況等 Research progress, etc.

研究の概要、独創性、状況等を含めて具体的に記入のこと。
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Boron (B) is a trace mineral nutrient required by plants and its deficiency affects crop yield (Yan et al., 2006). The major role of B identified thus far in plants is the crosslinking of rhamnogalacturonan II (RG-II), a pectin polysaccharide in cell wall. RG-II is synthesized in the Golgi in an acidified state. In the Golgi compartment, the type II proton pyrophosphatase (AVP2;1) plays a role of proton pumping coupled with pyrophosphate hydrolysis possibly for maintenance of Golgi acidification. While the enzymatic activity and expression patterns of AVP2;1 have been previously revealed, its mutant phenotype and role in plants remains unknown. The aim of this study therefore was to explore the physiological role of AVP2;1 in *Arabidopsis thaliana*. In the screening of mutants under low boron, a mutant carrying a missense mutation in *AVP2;1* was isolated. This mutant showed increased primary root growth under low B conditions but no significant difference under normal B conditions compared to wildtype plants. T-DNA insertion mutants showed a similar phenotype of enhanced root growth under low B suggesting that reduced function of AVP2;1 was responsible for the improved root growth. The root cell observation of plant lines revealed an increase in meristematic zone length, cell number in meristem and length of matured cell in *avp2;1* mutants compared to wildtype under low B. To explore the possible mechanism behind the increased root growth and root cell under low B in *avp2;1* mutants compared to wildtype Col-0, changes in cell wall components were considered as B function in cell wall stability. Analysis of the root cell wall revealed that calcium concentration was reduced in mutant root cell wall under low B condition and RG-II specific sugars also tended to be decreased in mutant root cell wall under low and normal B conditions, showing changes in *avp2;1* mutants cell wall. Together with the previous study and my analysis of mutant of tonoplast localized proton pyrophosphatase *AVP1*, a homolog of *AVP2;1*, it is suggested that the proton pumping component of AVP2;1 may possibly be the key component for plant growth. With the assumption of the proton pumping activity as the key for improved root growth, reduced proton pumping due to the reduced function of AVP2;1 in *avp2;1* mutants were considered to affect the activity of pectin (RG-II) synthesis enzymes such as glycosyltransferase in the Golgi apparatus. This effect of *AVP2;1* mutation on glycosyltransferase could lead to reduced amount of pectin (RG-II) been synthesized. The implication of the reduction of RG-II in mutants is that the amount of boron required for crosslinking of RG-II would be reduced and hence the improved root growth of mutants under low boron supply. To support this, previous studies have implied that pectin amount or RG-II amount determines sensitivity to B deficiency hence the reduced sensitivity to low B in *avp2;1* mutants. Taken together, this study proposes that reduced B requirement by changes in cell wall component may be the probable mechanism behind *avp2;1* mutant phenotypes. This supports the idea that AVP2;1 plays a role in proton pumping and acidification of Golgi apparatus for maintenance of pectin synthesis.

Published works:

- Onuh AF, Miwa K. Mutations in type II Golgi-localized proton pyrophosphatase *AVP2;1*/*VHP2;1* affect pectic polysaccharide rhamnogalacturonan-II and alter root growth under low boron condition in *Arabidopsis thaliana*. Frontiers in Plant Science 14:1255486 (2023)
- Onuh AF, Miwa K. Regulation, diversity and evolution of boron transporters in plants. Plant and Cell Physiology, Vol.62, No. 4, pp590-599 (2021)

Academic conferences:

- Onuh AF, Miwa K. Functional characterization of *AVP2;1* under low boron condition. Annual boron meeting, Wakayama, Japan. (2019/11). (Oral presentation)
- Onuh AF, Miwa K. Reduced function of *AVP2;1* confers low-boron tolerance in *Arabidopsis thaliana*.61st Japanese Society of Plant Physiologists, Osaka, Japan. (2020/03). (Poster presentation)
- Onuh AF, Miwa K. Mutations in a Golgi localized proton pyrophosphatase *AVP2;1* alleviates low-boron stress in *Arabidopsis thaliana*. 62nd Japanese Society of Plant Physiologists, Shimae, Japan. web meeting. (2021/03). (Poster presentation)
- Onuh AF, Miwa K. The effect of Golgi localized proton pyrophosphatase, *AVP2;1*, mutation on boron stress. Annual boron meeting, Tokyo, Japan. (2022/09). (Oral presentation)
- Onuh AF, Miwa K. Mutations in Golgi-localised proton pyrophosphatase, *AVP2;1* enhances root growth under limited boron supply by changes in cell wall stability. 33rd International Conference on Arabidopsis Research, Makuhari Messe, Chiba, Japan. (2023/06). (Poster presentation)

３．今後の研究計画等 Future research plan

現在までの進捗状況等を踏まえ、今後の研究発表等を含めて具体的に記入のこと。
In detail, based on current progress, including a future research presentation plan.

Preparations are currently ongoing for the presentation of this work during my PhD defense as a requirement for the completion of my doctoral study.

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氏名 Name	Md Menhazul Abedin	学　年 Year	D3
所属学院等名 Graduate School	Graduate School of Chemical Sciences and Engineering		
所 属 専 攻 名 Major	Chemical Sciences and Engineering		
所属研究室等名 Laboratory	Laboratory of Molecule and Life Nonlinear Science		
指導教員職・氏名 Supervisor	Prof. Tamiki Komatsuzaki		

１．研究テーマ名 Research theme

Multi-armed Bandit Algorithm for Sequential Experiments of Molecular Properties with Dynamic Feature Selection

２．研究等の進捗状況等 Research progress, etc.

My research topic is the acceleration of designing chemical reactions and finding the target molecule whose property (such as drug efficacy and solvation affinity) is the highest using a reinforcement learning, linear bandit (Optimistic in the face of uncertainty linear bandit-OFUL) framework. Precisely, the objective of the research is to find the molecule including catalyst to own the highest/lowest quantity desired by chemists such as hydration free energy, and reaction enantioselectivity, solvation affinity etc., by fewer experiments as possible via bridging chemistry and information science.

For instance, to find molecules having lower hydration free energies is important because it implies the larger solubility of the molecules. My problem setting in this research is to find the lowest hydration free energy molecule by fewer experiments as much as possible using linear bandit algorithm. Linear bandit is an algorithm which assumes the feature variables to characterize each molecule or their power series are linearly related to a target quantity. Currently, I have developed a method based on the algorithm and evaluating the performance by using FreeSolv benchmark data, which contains experimental and calculated hydration free energies of 642 molecules. Well-known topological fragment's features are used in the current analysis. However, having the cleaning steps, the total number of features are more?? than the sample size. Therefore, LASSO (least absolute shrinkage and selection operator) regression analysis is used for feature selection to cut away the irrelevant features. Before applying our algorithm on the real data, I investigated two synthetic datasets. Four analyzing protocols has been applied on the data such as i) OFUL with all features (OFUL-AF), ii) OFUL with selected features (OFUL-SF), iii) Bayesian Optimization (BO) and iv) Random search (RS).

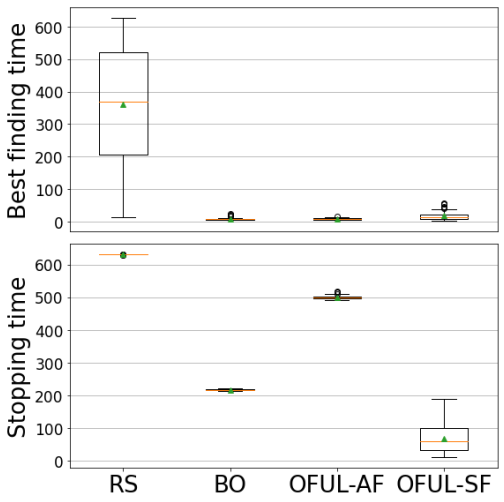

Figure 1. Boxplots for the time of finding the molecule of ground truth (upper) and stopping time (lower) in case of Hydration free energy

Findings of my research is briefly explained bellow: Figure 1 illustrates the boxplots for the time required to find the molecule of ground truth and the stopping time to confirm the found molecule is the best within some error bound for hydration free energy of molecule. The statistics are based on 50 runs. The median values for the best molecule finding time are approximately 370.0, 7.0, 7.0 and 13.0 iteration steps for RS, BO, OFUL-AF, and OFUL-SF, respectively. I observed that BO and OFUL-AF gets the same score, and OFUL-SF takes more 6 iterations to finds the best molecule, but RS takes huge iteration. So, the performance of BO, OFUL-AF and OFUL-SF are almost nearby.

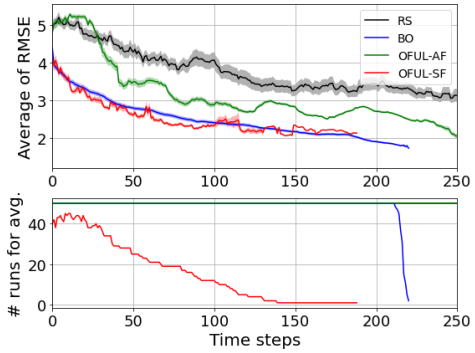

Figure 2. Average of RMSE for FreeSolv

To confirm the performance of the methods, I focus on the stopping time. Median stopping time for RS, BO, OFUL-AF, and OFUL-SF are around 632.0, 217.0, 499.0 and 59.0 iteration steps, respectively. It is observed that OFUL-SF can stop experiments within one ninth of the total number of candidate molecules whereas the nearest competitor is BO, but RS and OFUL-AF shows far distant from OFUL-SF. I also confirmed methods apart from OFUL-SF attain a success rate of 100 percent, whereas OFUL-SF achieves a success rate of 90

percent. This success rate can be increased using smaller error rate (δ).

To check the fitness of the models, I looked at the RMSE of each of the models. Figure 2 (upper) illustrates the average root mean square error (RMSE) across the different methods over the 50 runs along with standard error. It shows average RMSE of OFUL-SF and BO close to each other i.e., comparable but RS and OFUL-AF are much larger. This is an indication that OFUL-SF and BO give a better model than RS and OFUL-AF. Figure 2 (lower) shows that some of runs of OFUL-SF stops at the very beginning and all the runs stopped before 200 iteration steps, but any runs of BO never stops before 200. Again, since OFUL-SF does not find features for some of the runs, the average RMSE is calculated from less than 50 runs at the beginning of the experiment.

Conference and poster presentation:

- "Desired property screening of molecules utilizing Linear Bandit Algorithm", 14th CSE International Summer School and the 11th ALP International Symposium; 31 August- 1 September 2023, Chippubetsu, Japan.
- "Linear Bandit Algorithm for the Sequential Experiments of Molecular Properties", Hokkaido university theoretical chemistry workshop; 17 August 2023, Japan.
- "Sequential Experiments of Molecular Properties Under Linear Bandit Framework", ICAT International Symposium on Catalysis 2023; July 18-19, 2023; Hokkaido University, Japan.

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In detail, based on current progress, including a future research presentation plan.

In this year I would like to publish my research in a scientific journal. Currently my manuscript is under evaluation within my research team and collaborators. I am optimistic that I will be able to publish my research in the near future. I also interested in expanding this research to include some other chemistry data as well. Ultimately, this study will contribute significantly to the existing body of knowledge and pave the way for further advancements in the field.