

Report on MERIT Long-term Overseas Dispatch

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My long-term overseas dispatch was conducted under the supervision of Professor Clare Grey at Department of Chemistry in University of Cambridge from 9th July to 22th September. During the stay, my was registering local structure analysis using solid state Nuclear Magnetic Resonance (ss-NMR) spectroscopy for a new Na-ion battery electrode.

The city of Cambridge is a university-city and county town of Cambridgeshire in United Kingdom. It lies on about 80 km north of London and the trip takes about an hour by train. The University of Cambridge is regularly nominated among the world's best universities, and has produced many of famous scientists and natural philosophers (eg. Sir Isaac Newton, Charles Darwin, Stephen Hawking, John Maynard Keynes, and etc.). I noticed that the educational system in UK is totally different from that in Japan in terms of required years for graduation, the college system (Fig.1), the university-going rate, the entrance examination system, the laboratory system, and others. Discussion about these topics among laboratory members are exciting, providing me a good opportunity to understand both pros and cons sides of the Japanese educational system.

The Grey group is a world-leading laboratory with outstanding results for secondary batteries, electrochemical capacitances, and fuel cells. Especially, the group is an authority of solid-state chemistry with analytical techniques, such as ss-NMR, and X-ray total scattering. I was impressed with the fact that all the members in the group are truly self-motivated, and international. They are holding/attending workshops constantly and eager for every discussions. Discussions with contemporary scientists from various backgrounds were really informative and stimulating for me.

Research subject: Reaction mechanism analysis for a new Na-ion battery cathode material with solid-state Nuclear Magnetic Resonance (ss-NMR) spectroscopy



Fig. 1 King's college: One of the 31 colleges under the University of Cambridge.

The current Li-ion batteries have dominated global markets of secondary batteries. However, rapid expansion of their application has triggered the growing concerns on scarcity and rising costs of Li resources. As one of the most realistic alternatives, Na-ion batteries re-attract massive attention owing to the abundance of sodium, lower cost, and sustainable production, though their energy densities and voltages are not competitive with those of Li-ion batteries. In this pursuit, we have explored Na-Fe-S-O phase diagram and discovered *alluaudite*-type sodium iron sulfate, registering higher voltage than a commercial cathode material, olivine-type LiFePO_4 .¹

Here, I aimed to reveal local structure changes of sodium iron sulfate during electrochemical charging/discharging processes with ss-NMR spectroscopy (Fig. 2). I got a chance to discuss with a postdoc and a graduate student in the group soon after the arrival and thus started my research very smoothly. All the experimental work has been done with Dr. Oliver Pecher, and Kent Griffith. They carefully guided me how to deal with NMR machines and analyze the data step-by-step even though they were really busy with their own researches. Owing to their help, we successfully finished all of the scheduled experiments during the stay.

NMR spectroscopy is one of the most straightforward techniques for revealing local structures of crystal, semi-crystal and amorphous phases. NMR techniques were used to be applied for structure analysis of liquid organic materials because chemical bonding states are easily identified by slightly different resonance frequencies. But for solid materials, very slow movements of molecules/atoms emphasis interactions (dipolar-dipolar interaction, chemical shift anisotropy, and quadruple interaction) results in an extremely broad peak in NMR spectrum. In fact, we performed ss-NMR for ^{23}Na nucleus (spin: $I = 3/2$), where charge density is not spherically symmetric. This anisotropic nuclei

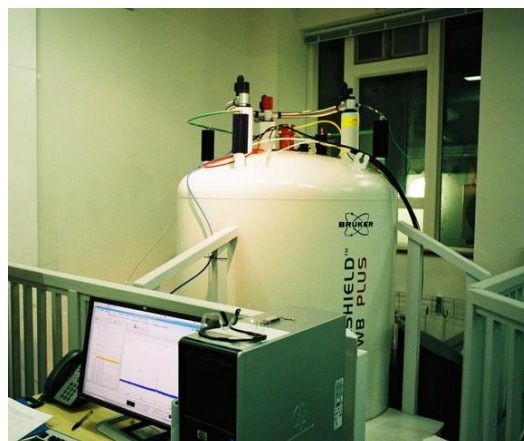


Fig. 2 Bruker AvanceIII: One of ss-NMR magnets in Grey group.*

*<http://www.ch.cam.ac.uk/group/grey/lab-facilities>

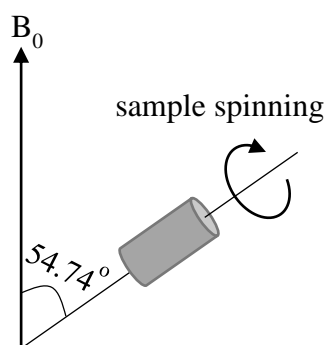


Fig. 3 Image of magic angle spinning (MAS) in ss-NMR. The sample (shown in gray color) is spinning with high frequency at the magic angle $\theta_m (=54.74^\circ)$ with respect to the direction of magnetic field B_0 .

environment produce quadruple interaction and its first-order is proportional to $3\cos^2\theta-1$. Thus, quadruple interaction can be partially averaged by spinning the sample with high frequency at the magic angle $\theta_m = 54.74^\circ$, where $3\cos^2\theta_m - 1 = 0$ (Fig. 3). By adopting this magic angle spinning (MAS) technique, the spectrum became much narrower for better identification of the spectrum, and site selective reaction during charging/discharging processes was suggested. In future, I am planning to pursue the joint-research for reporting on a journal based on these results.

Moreover, I re-realized the importance of discussion with researchers from different fields. During the stay, discussion with the collaborators, Kent and Olli was sometimes not easy especially in the initial stage, because their points of view were different based on their own backgrounds. However, we respected differences in opinions, listened carefully, and studied basic theories if necessary. In fact, many of our idea were useful in subsequent experiments. At present, this is one of the most precious lessons I learnt during the stay, contributing to a better understanding of solid chemistry also. These experiences will be indispensable for my future researches.

Acknowledgements

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References

1. P. Barpanda*, G. Oyama*, S. Nishimura, S. C. Chung, A. Yamada, *Nat. Commun.* 2014, 5, 4358. (* authors with equal contribution)