

MERIT overseas study report

Department of Applied Chemistry, Miyayama lab.

D2 Hiroyuki Koshikawa

1. Overview

I visited a laboratory of Professor Timo Jacob at Ulm University in Germany from June 2nd to July 16th in 2016. I studied lithium ion concentration profile in a nonaqueous electrolyte under current flow condition using confocal Raman microspectroscopy.

2. Background

A lithium (Li) metal electrode is one of the promising materials for solving energy problems owing to its high theoretical specific capacity (about 10 times higher than that of carbon materials employed in conventional Li-ion batteries). The performance of Li metal-based batteries has been often discussed in view of the properties of bulk electrolytes such as ionic conductivity and those of surface layers formed at a Li deposits-electrolyte interface. Then, various kinds of electrolytes and additives have been investigated using that knowledge, but a battery system exhibiting sufficient activity for the application as next-generation batteries has not been realized yet. Although electrodeposition processes are significantly influenced also by ion flux in the vicinity of an electrode, it has not been thoroughly investigated yet. Therefore, I try (1) to examine the coordination structures around Li ions and the ion concentration profile near an electrode, and then (2) to develop novel battery materials based on that knowledge.

I got interested in a laboratory of Professor Timo Jacob doing basic research of metal deposition when thinking about overseas study. In addition, Professor Kohei Uosaki, the fellow of National Institute for Materials Science and one of my supervisors, is fortunately his friend. This overseas study has been realized by his kind introduction of me to Professor Jacob.

3. Research activity in Germany

I set the purpose of this stay as establishing an evaluation system of Li ion distribution to achieve the purpose (1) written above. Confocal Raman microspectroscopy was employed owing to its high spatial resolution and its sensitivity to Li coordination environments. For most of the time, Dr. Attila Farkas, a scientific staff, kindly took care of me.

As mentioned above, there is a research group studying metal deposition, and they are especially good at in situ analysis of metal deposition reactions using a scanning tunneling microscope. They also possess a homemade electrochemical cell for Raman measurements. However, when I communicated with them beforehand, they told me that they had had no experience of conducting Raman analyses in an experimental system I proposed. We shared the experimental plans and got

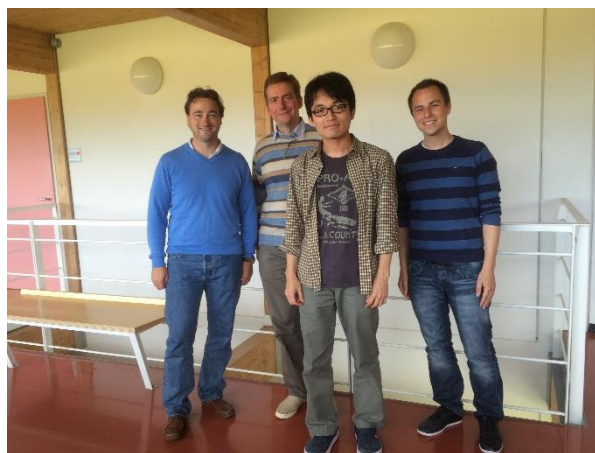
sure that we could advance the research, but encountered some problems when starting experiments. An existing homemade electrochemical cell had to be improved. We asked a factory in the university, and also made modifications by ourselves at the laboratory.

After the cell modification, we moved to main experiments using a confocal Raman microscope. Measurements were conducted with the help of Sebastian Horvat, a Ph. D candidate. In order to examine Li ion distribution in the vicinity of an electrode, the position of an electrode surface has to be firstly determined as a reference point. Since we were not sure that the previous knowledge reported in different experimental systems could be also applicable to mine, a simple setup constructed through the discussion with Attila was utilized. Besides, Attila and Sebastian gave me a plenty of advice about the accuracy of Raman spectra and how to interpret them. Thanks to their much help, observed Li ion concentration change was qualitatively reasonable, indicating that the experimental setup worked well. However, measurement conditions such as recording time and current density should be compared and further optimized to obtain quantitatively reliable data. I am continuing this work based on the knowledge gained thorough this stay, keeping contact with them.

Through this stay, I could especially enhance the ability to immediately construct a simple but reliable experimental setup and that to imagine the occurring phenomena from electrochemical data, and could acquire the knowledge of Raman and related microspectroscopies. As I tend to use electrochemical and other analytical methods just as tools for developing good materials in my research life, I strongly feel that a sense of fundamental science should be cultivated further during my Ph. D course. This was also the reason why I have chosen this laboratory. The stay was so meaningful for me.

4. Life in Germany

The city Ulm, lying in the south part of Germany, is a very beautiful place where the Danube flows through. Ulm is also the birthplace of Einstein and the north part of the city where Ulm university stands is called “Wissenschaftsstadt”, meaning a science “city in English. There are about 50 members in the laboratory I stayed, and many members gather in a party room with some cake, celebrating his or her birthday or completion of the thesis. In addition, time spent alone or with family are respected in Germany. To say nothing of working hours, we could not have supper at a university’s cafeteria,



With kind laboratory members
From the left: Professor Timo Jacob, Dr. Attila Farkas, I and Sebastian Horvat

and many shops in the city are closed on Sunday.

Let me explain about the carrier in the school which the laboratory belongs to. As in the case of Japan, a master's course and a doctoral course are separated, but more than half proceed to a doctoral course. There exists laboratories of companies such as Daimler and Siemens in the campus of Ulm university, and graduate students can work as interns or conduct collaborative researches. In some cases, they can work as permanent employees at those companies after finishing their Ph. D courses, being a typical example of academic-industrial collaboration. Besides, doctoral students have to spend about one day per week teaching bachelor students. More tough doctors can be produced through these various tasks inside and outside laboratories.



The view of Ulm city from the top of Ulm Minster, the tallest (162 m) church in the world

Acknowledgement

I really thank Professor Timo Jacob, Dr. Attila Farkas, Sebastian Horvat and other laboratory members for accepting and supporting me both for research and daily life, thank Professor Kohei Uosaki for kindly introducing me to Professor Jacob, thank Professor Kazuhito Hashimoto, Professor Masaru Miyayama, Professor Masaaki Tanaka and other related staff at the University of Tokyo for allowing my overseas study and for giving me helpful advice and thank a MERIT program for giving me such a valuable opportunity.