SCIENTIFIC INSTRUMENT NEWS

INTERVIEW

14

In October 2019, Asahi Kasei Corporation Honorary Fellow Dr. Akira Yoshino won the Nobel Prize in Chemistry. Dr. Yoshino was awarded for his achievements in perfecting the basic principles of lithium-ion batteries (LIBs), which are now so indispensable to our everyday life. Hirohide Otobe, Expert at Asahi Kasei's Platform Laboratory for Science & Technology, was one of those who supported the Yoshino team in advancing the practicality of LIBs. This time, I visited Otobe to talk to him about the role of electron microscopes in Asahi Kasei product development over his nearly 30 years supporting company research and development.

Developing Various Observation Methods to Solve In-House Developer Challenges

Supporting Development by Making the Unseen Visible

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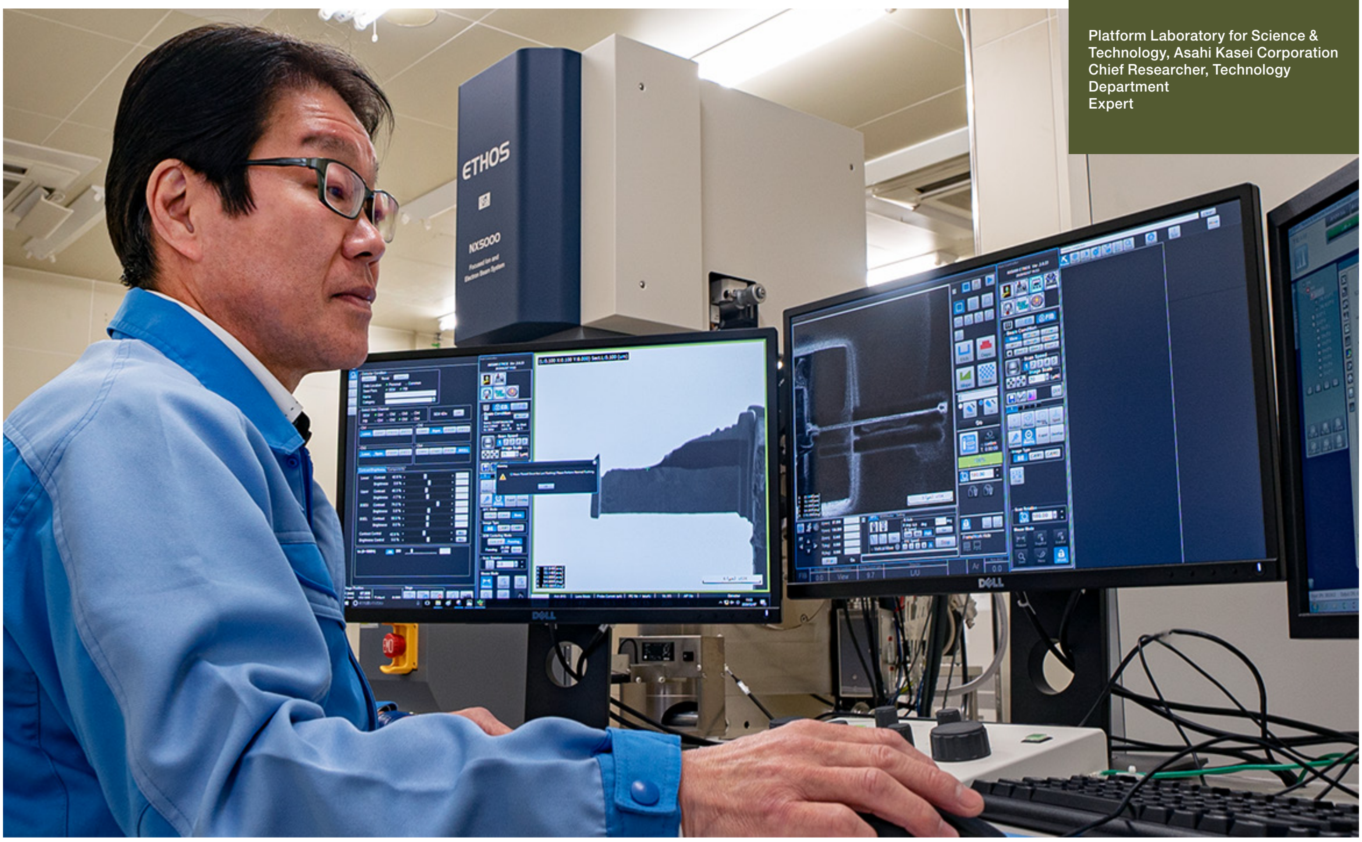

1. In Pursuit of a Practical Lithium-Ion Battery

LIB research began in 1981 when Dr. Yoshino started researching polyacetylene, a conductive polymer. Yoshino found that polyacetylene could be used as an electrode for rechargeable batteries and moved forward with research on negative electrodes in particular. Then, in 1985, Yoshino's team switched to lithium cobaltate (a metal oxide with lithium ions) for the positive electrode and from polyacetylene to carbon-based material for the negative electrode, completing the basic structure of the world's first lithium-ion battery (LIB).

There were still many challenges left before LIBs would reach the market, however. One that was considered the most important was safety measures to prevent issues such as ignition. For LIBs to be mounted in green vehicles and other mobility applications in addition to mobile IT devices, they would have to be kept from igniting or exploding in the event of an impact.

Positioned between the LIB positive and negative electrodes, a separator serves both to allow lithium ions to flow between the two electrodes and to prevent short circuits. For the separator, Asahi Kasei used a polyolefin microporous membrane with a thickness of 20 μm or less. In the case of a thermal runaway in the LIB, the separator melts to fill the micropores and works as a fuse to stop battery function. Asahi Kasei was the first company in the world to mass-produce the separator, establishing it as the de-facto standard. This technology was important in ensuring the safety of LIBs and gaining social acceptance. Demonstrating his skills in structural analysis and evaluation of these separators was none other than Otobe.

Otobe reflects on his experiences at the time. "We analyzed the 3D structure of the separator using a FIB-SEM (focused ion beam (FIB) scanning electron microscope (SEM)), and measured the diffusion of lithium ions using nuclear magnetic resonance (NMR) spectroscopy. We ran simulations based on the results. What was particularly memorable for me in separator development was examining what structures led to the best battery properties."

2. Technology Built on the Achievements of Their Predecessors

While ion beams are capable of performing multi-slicing of porous material, cross-sectional 2D images are not possible as depth is visible with SEM. Without a 2D binary image, the 3D structure cannot be reconstructed. Therefore, Otobe's team pre-filled the porous holes with resin. However, just filling the holes was not enough to achieve sufficient contrast. "I kept wondering what I could do to get a complete 2D binary image, and what I came up with was electronic staining. I think the point of that work was to apply the company's know-how regarding electronic staining."

Thus, using FIB-SEM, Otobe's team performed repeated slicing and observation to reconstruct the structure from the large number of SEM images produced. By doing so, they were the first in Japan to successfully visualize the 3D structure of a separator.

They presented the results at the Electrochemical Society of Japan's Battery Symposium in Nagoya. The scale of the impact was apparent when Otobe finished his lecture: attendees from companies in the analytical sector were lined up to trade business cards with him.

Otobe remains modest. "Again, it was all due to staining technology that our company has been working on for the last 30 to 40 years. We inherited generations of know-how built on the efforts of our pioneering predecessors working with microscopy and NMR. The way I see it, we achieved what we did by repeatedly taking on new challenges on the backs of their efforts."

Currently, the company manufactures Hipore as wet membrane separators and Celgard as dry membrane separators, both with greatly improved battery safety. Still, they make daily progress on their separators, making them stronger and thinner in pursuit of higher energy density.

3. Turning Point: The Electron Microscope

The year that Otobe joined Asahi Kasei, 1987, was also the year that Nippon Telegraph and Telephone Corporation (NTT) started its mobile phone services. It was the very beginning of the mobile era.

In addition to electronics, Otobe professes to originally being a physics guy. “As a student, my research thesis was on increasing the density of optical disks. We wielded lasers around the lab,” says Otobe.

“I aspired to study the sciences because I hated memorizing things. I joined Asahi Kasei with a desire to build systems. I knew absolutely nothing about chemistry when my boss told me ‘You just joined a chemical company, so you better study up on your structural formulas. No excuses.’”

It was his second year with the company, when Otobe was working on optical disc development, that he first encountered the Hitachi S-430 electron microscope as an evaluation tool. He saw the appeal of the images. After that, he moved to the Analysis Center, which was the predecessor to the Platform Laboratory for Science & Technology, where he specialized in SEM analysis.

“That’s where the fun started. Every day at the office felt like I was jumping into a microscopic world. Also, one corner-cutting in specimen preparation and you get false images; prepare well, and you get to see the true form of the specimen. We got to see this true form before even the developers. I got more and more immersed in the joy of my work.”

As Otobe tells it, he wouldn’t be who he is today if he hadn’t encountered the electron microscope when he did for analytical evaluation, going as far as to call it the turning point in his career. Subsequently, he supported in-house developers and devoted himself to developing new techniques for electron microscopy observation.

“When I was young, I developed a bunch of observation methods. One such method was non-dry SEM observations of wet specimens using an ionic liquid, as I co-presented at conferences with someone from Hitachi High-Tech.”

4. Making a Daily Practice of Observation

The specimen chambers of SEMs are under a high vacuum, and it is common to dry wet specimens when observing them. However, no matter what method was used, drying would inevitably result in structural changes, preventing observation of structures in their aqueous state.

Thus, Otobe’s team focused on ionic liquids, which Professor Kuwabata of Osaka University had started researching at the time. Otobe’s team developed a method for replacing the moisture in a wet specimen with an ionic liquid and observing it using high-vacuum SEM. This enabled SEM observations with the structure still in its swelled, wet state.

“There was a longstanding need to observe Bemberg® (material name: Cupro), the company’s material used in suit lining and such because of its excellent absorption and desorption properties, for structural changes during moisture absorption and desorption. Developing this method made it possible to observe the hygroscopic state using high-vacuum SEM.”

The results confirmed that the fiber diameter in Bemberg® was 12% larger during moisture absorption, says Otobe.

Also, some gears for copiers manufactured by the company are made of a highly self-lubricating resin called polyacetal. If these parts are charged with electricity during use, copier toner adheres to them. To combat this, a conductive additive called carbon black is added to prevent charging. Given the effect that the dispersion state of this carbon black has on the surface resistance, there was a need to observe it under an electron microscope for evaluation.

Conventionally, a transmission electron microscope (TEM) had been used to evaluate the distribution of carbon black. However, given the difficulty in evaluating the distribution of the outermost surface of the molded resin with TEM, no discussion of any direct relationships with surface resistance was possible. Thus, Otobe used SEM with a retarding mechanism set up to create a specimen so that the retarding voltage could be applied only to the surface of the molded resin piece, and optimized the observation conditions.

He succeeded in selectively visualizing only the carbon black, which decreases the surface resistance. This provided quantitative proof of the difference in surface resistance values.

“I still work with the younger staff everyday on making heretofore unseeable things visible,” says Otobe with regard to his efforts. “Together with the staff over at Hitachi High-Tech, we’ve been able to visualize many things. During high-resolution observation of wet specimens using ionic liquids, damage due to electron irradiation was causing issues with observations. The Hitachi High-Tech team proposed low-temperature observations to reduce the damage. With that, we were able to evaluate fine-grained structures to resolutions of about 10 nm. That wouldn’t have been possible without the help of Hitachi High-Tech. Thinking about it, I cannot find the words to express my gratitude to Hitachi High-Tech,” Otobe adds.

5. Providing Solutions, Not Data

Producing profit is how a company recognizes the worth of their engineers. This is what sets apart engineers from researchers in academia. “My job involves making the unseen visible, but the real objective is to tie that into product development,” says Otobe.

“Our observations to date and moving forward have a singular purpose: to answer developer questions. Devising a way to observe aqueous specimens, visualizing the resistance of resins, and all the rest—all were to resolve problems encountered by our developers.”

After 30-plus years devising new electron microscope observation techniques and his contributions to technological development, I asked Otobe what he sees as the role of his current workplace, the Platform Laboratory for Science & Technology (PLST).

“In the past, the PLST has primarily been engaged in providing material analysis and computer simulation results.

Now though, at every opportunity, I tell our staff that we offer solutions.” Yes, we do observe, measure, and respond to what the developers want to see. Beyond that, we also ask developers what the problem is and work up a solution together. We design analysis methods to solve the problem and compare results with the physical property data collected by the developers.”

They provide solutions, not data. Thus, the PLST has annual contracts with each development team. Their staff attends monthly review meetings to determine situations and provide advice.

“Working as part of a team is difficult, of course, but to get results, you have to feel the pain points along with the developer. Recently, we’ve gotten increasingly higher assessments for PLST joint projects and are receiving more orders.”

I also asked Otobe what the office reaction was when he first heard that Dr. Yoshino was going to win the Nobel Prize. “When I first heard the news, I had just finished a meeting and was out for drinks with some colleagues. A colleague got a message on his smartphone, and we all cheered. The waiters asked us what happened, and we told them that someone at our company had just won the Nobel Prize. They gave us a free bottle of saké to celebrate. I had one drink too many, all thanks to Yoshino and his Nobel Prize,” he jokes. Asking around at Asahi Kasei, the award announcement was a long time coming.

6. Using AI and MI in Pursuit of the Ideal Structure

For my closing question, I asked Otobe about the future of PLST. “Our goal is to propose an ideal structure to the developer. In pursuit of that goal, we look to leverage AI technology and MI (materials informatics) based on Big Data to calculate parameters that demonstrate a correlation between the 3D structure and features of the products. Developers are always chasing more functionality. From an analysis standpoint, we always wind up probing for what the developers want, asking with every proposal, ‘Is this it?’” I also think handing the developer models printed on a 3D printer would be an improvement.”

In efforts to accelerate and streamline technological development, things are expected to revolve more and more around data science. However, in Otobe’s opinion, data are just numerical values. “Computational chemistry certainly is a larger factor than before; this is true. However, proposals will only come to life when computational chemistry is tied into the actual product.” He closes emphatically: “There’s absolutely no way to get around detailed observations of fine-grained structure in real space.”

(Interview/article: Toshinari Yamaguchi)

Editor’s Notes

Throughout the interview, Otobe repeatedly described microscopy as “fun.” It’s easy to imagine the joys of that first time you think, test, and then get to actually observe something that no one else has ever seen. I asked Otobe about his current challenges. “Every day we’re expected to produce ever finer details. That’s the everyday struggle. I’d love to reconstruct 3D images of nanoscale polymer materials at resolutions smaller than 10 nm.” In terms of batteries, Otobe is also interested in operando measurements performed in the actual operating environment. “I wonder how we can observe a battery with the positive and negative electrodes, separator, and electrolytic solution all in place.” Apparently, his intellectual curiosity knows no bounds. Solutions obtained using electron microscopes will revolutionize our society. It is my sincere hope that the technological innovations of Otobe’s team will improve people’s lives someday.