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SCIENCE & METROLOGY SOLUTIONS

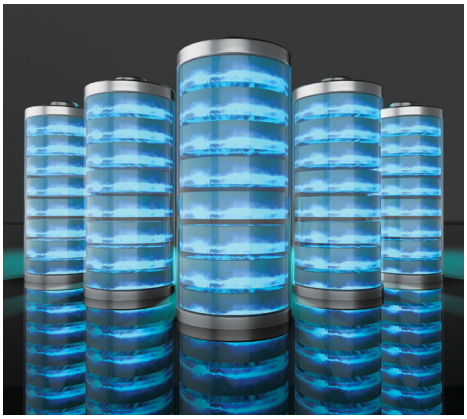
AMETEK
MATERIALS ANALYSIS DIVISION

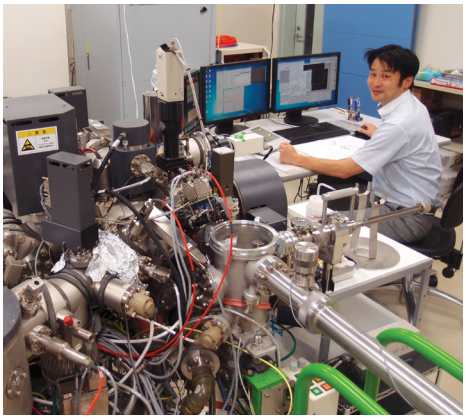
Revelatory results for lithium research with a CAMECA SIMS at Tohoku University

A SUCCESS STORY FROM CAMECA

CAMECA SIMS Advantages

- High-performance, universal magnetic sector secondary ion mass spectrometer
- Utmost-precision elemental & isotopic analysis
- Unshakable reliability
- Extreme sensitivity
- Best detection limits on light & trace elements
- Unparalleled depth/diffusion profiling
- Wide versatility
- Materials science
- Semiconductors
- Metallurgy
- Environment





The Challenge

More than a decade ago, researchers at Tohoku University in Sendai, Japan, launched several basic research efforts as part of a national green technology initiative. These included studies aimed at improving fuel cells and batteries.

Dr. Takamichi Miyazaki is head of operations and management for the university's Instrument Analysis Group, which supplies a range of analytical instruments used by researchers. As the green program has progressed, Dr. Miyazaki and his team have provided tools and insights to help answer key questions, including one in a recent study: during ion transport in a secondary lithium-ion battery, what is the lithium diffusion coefficient in the cathode material? The answer could have important implications for improving battery designs.

Previous researchers had tried to characterize lithium diffusion coefficients, but their methods (NMR, electrochemical, etc.) were indirect and lacked reliable results. The Tohoku researchers needed to establish those coefficients with precision.

The Instrument

They turned to their high-performance, universal magnetic sector secondary ion mass spectrometer (SIMS): the IMS 7f from CAMECA.

Dr. Miyazaki and his group had overseen installation of the instrument in March 2011. The IMS 7f met its first challenge, not even a week later — when the devastating Tohoku earthquake struck. Although the entire lab moved laterally 3 feet and the violent shaking broke several other analyzers, the CAMECA SIMS emerged unscathed.

In addition to rugged reliability, CAMECA designed the IMS 7f for precise measurement of challenging light elements such as lithium, with good sensitivity and low background. It features ultra-high vacuum in the analysis chamber, plus a high sputter rate to minimize residual gas contribution.

"That design means you can achieve much lower detection limits than a time-of-flight SIMS, where you couldn't get such optimized, stable vacuum levels," says Dr. Miyazaki. "Our university has a TOF SIMS. But when they heard these new detection limits, many researchers gave up using it and came over to the CAMECA SIMS."

Additionally, the IMS 7f provides a high-density primary ion beam with superior beam current stability, as well as sub-micron lateral resolution and nanometer depth resolution.

"That stability is comparable to our field emission electron beam analyzer," Dr. Miyazaki says. "And you get excellent performance with small beam diameters, enabling high spatial resolution."

The instrument's design is optimized for depth profiling and diffusion profiling. "In measuring the tracer diffusion coefficient, we adopted a combination of depth profiling and planar point analysis," Dr. Miyazaki says. "Again, this required long-term stability and optimized primary beam focusing. Whoever developed that design is great!"

The IMS 7f, forerunner to the current IMS 7f-Auto model, is designed for versatility in multiple applications. Tohoku researchers, as well as collaborators from south Asia and the rest of the globe, have relied on the university's CAMECA SIMS for everything from basic research in physics, chemistry, and geology to studies of hydrogen embrittlement in steels or radioactive materials in animal horns.

Finally, the Tohoku University group added a special accessory to their SIMS: a unique CAMECA transfer suitcase, which maintains an in-transit sample within an argon atmosphere, avoiding oxidation or other reactions with ambient air.

The Work

The study focused on the tracer diffusion coefficient of lithium manganese oxide ($LiMn_2O_4$) thin films. Other methods had shown discrepancies amounting to several orders of magnitude. So instead, the research group at Tohoku University undertook its critical measurements of the coefficient using isotope ion-exchange and SIMS line analysis.

An important enabler: since the ^6Li and ^7Li isotopes in the tracer exhibited the same chemical properties, their ionization and detection efficiencies remained almost constant — permitting quantitative isotope ratios to be determined from SIMS counting rates.

"With a time-of-flight SIMS, you couldn't measure these ratios," explains Dr. Miyazaki. "But with the magnetic detector IMS 7f SIMS, you can always get highly reproducible data. It was a very stable measurement: every day, every time."

The study also benefitted from using the CAMECA SIMS and the group's TEM/SEM in combination. "The work gave us a diversified perspective due to the very small quantities and extremely fine-scale information."

The Results

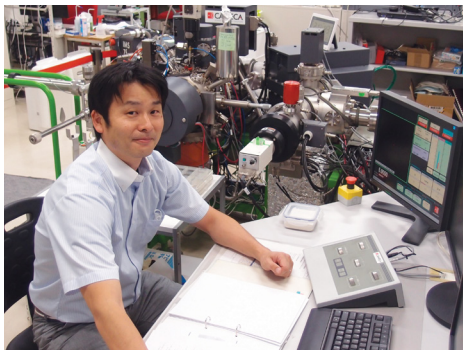
The value of the lithium tracer diffusion coefficient — directly observed, accurately measured, and extrapolated to room temperature — was considerably smaller than the chemical diffusion coefficient previously shown. The researchers believe this ion transport value exhibits some unique characteristics, and varies considerably depending on the precise composition of the lithium cathode material.

Further understanding may well help cell designers improve charge/discharge capabilities and lifespan.

The Future

"I'm glad to share our results on the CAMECA SIMS with my colleagues and other researchers," says Dr. Miyazaki. "I discuss the direct measurement of the lithium-ion movement, and this unique combination of SIMS and TEM/SEM."

"The results from these projects are starting to be recognized in the field, and by battery manufacturers," he reports. "We have high expectations for more valuable work in the future."



Dr Takamichi Miyazaki
Free man
Tohoku University Instrument Analysis Group

About the Group

Tohoku University in Sendai is one of Japan's three designated National Universities. At Tohoku, the 10-member Instrument Analysis Group provides systems and support for an array of analytical instruments used by university researchers, as well as by selected scientists and engineers from organizations worldwide. Equipment includes a dynamic secondary ion mass spectrometer (SIMS), a transmission electron microscope/scanning transmission electron microscope (TEM/STEM), a scanning electron microscope (SEM), and an atomic force microscope (AFM).

About CAMECA

CAMECA is a world-leading supplier of microanalytical and metrology instrumentation for research and process control. Our instruments measure elemental and isotopic composition in materials down to atomic resolution. Advanced CAMECA technologies include secondary ion mass spectrometry (SIMS), atom probe tomography (APT), electron probe microanalysis (EPMA), and low-energy electron-induced X-ray emission spectrometry (LEXES). We address challenging characterization needs in diverse markets, from materials sciences, cosmochemistry, geology, and life sciences to environmental, nuclear, and semiconductor research.

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