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A Chance Encounter with Ionic Liquids Yields a Strong Bond to the World of Electron Microscopy

The Development of Real-time Methods for Observing Chemical Reactions

Professor Susumu Kuwabata is Dean of the Osaka University Graduate School of Engineering and Director of Osaka University's Research Center for Ultra-High-Voltage Electron Microscopy; his specialty is electrochemistry, and he has professed a boundless love for electron microscopy. We asked Professor Kuwabata to discuss his research—and how he came to be involved with electron microscopy.

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Osaka University: A pioneering institution pulling Japan into the modern era of electron microscopy

The expansive grounds of Osaka University's Suita Campus are home to one particularly distinctive building exuding an unmistakable sense of history: the Research Center for Ultra-High-Voltage Electron Microscopy.

The long history of electron microscopy at Osaka University (OU) dates all the way back to the completion of Japan's first electron microscope in 1939. Later, OU also played a pioneering role in leading Japan into the era of ultra-high-voltage electron microscopy: in 1970, a joint team of researchers from OU and Hitachi Central Research Laboratory developed the world's first ultra-high-voltage electron microscope—with a standard operating voltage of 2 million volts—and installed it at the Suita Campus. This was the impetus for the founding, in 1974, of the Research Center for Ultra-High-Voltage Electron Microscopy as a campus-wide shared educational facility.

The Research Center for Ultra-High-Voltage Electron Microscopy at Osaka University's Suita Campus was founded in 1974. Today, the Center is a campus-wide shared educational facility used by researchers in a wide range of academic disciplines.

Today, the Center is home to some 20 electron microscopes, ranging in size from small to large and crowned above all by one prize possession: the H-3000, a 3-million-volt ultra-high-voltage system developed by Hitachi Central Research Laboratory. These instruments are used by OU researchers spanning a diverse spectrum of scientific and engineering fields to investigate specimens ranging from inorganic materials to biological samples. The Director of the Center is Professor Susumu Kuwabata, who also serves as the Dean of OU's Graduate School of Engineering.

Professor Kuwabata describes the H-3000 this way: "This microscope boasts the highest accelerating voltage of any ultra-high-voltage electron microscope in the world, and one of its key features is that its electron beam can pass through even the thickest specimens to yield high-resolution microscope images. More specifically, depending on the type of specimen, the beam can pass through biological samples with thicknesses on the order of 10 microns and through inorganic samples with thicknesses on the order of 3-5 microns. For example, blood vessels have circular cross sections, and conventional electron microscopes weren't able to see anything but just plain rings. But the realization that there was some thickness there finally allowed the first observation that in fact we were looking at tubes. And there are many other examples like this, where the ability to observe thick specimens allowed new things to be understood for the first time. The ability of the H-3000 to acquire 3-dimensional images by rotating specimens during observation is another major advantage."

Today, ultra-high-voltage electron microscopes like the H-3000 are installed not only at OU but at many other universities as well. This has spurred the creation of a nationwide network of universities possessing these instruments, who come together to share a broad diversity of microscopy images. Efforts are also in progress to develop remote-control protocols through which ultra-high-voltage electron microscopes can be used by researchers at universities and other institutions lacking systems of their own.

The H-3000 electron microscope at OU's Research Center for Ultra-High-Voltage Electron Microscopy is a 3-million-volt system developed by Hitachi Central Research Laboratory. Images acquired by this instrument may be shared not only among users of the Center, but more broadly through a nationwide consortium of universities equipped with ultra-high-voltage electron microscopes.

Focusing on the non-volatility of ionic liquids

Professor Kuwabata specializes in *electrochemistry*, a branch of chemistry that studies chemical reactions induced by electron-motion between substances and chemical species. Electrochemistry encompasses the study of common devices such batteries and of familiar phenomena such as electrolysis and artificial photosynthesis.

But how did electron microscopy become a tool so near and dear to Kuwabata's heart? Kuwabata credits a chance encounter with *ionic liquids*. Discovered in 1914 by the chemist Paul Walden (1863-1957), ionic liquids are varieties of salts that can stay as liquids even at room temperature; here the term "salts" refers to compounds consisting of positive ions electrostatically bound to negative ions. Most salts, including common table salt (sodium chloride, NaCl), are solids at room temperature, and for this reason it was long believed that *all* salts share this property; indeed, ionic liquids continued to attract minimal attention for many years following Walden's discovery, and it wasn't until the 1990s, with the development of ionic liquids that remain stable in air, that interest in ionic liquids began to explode. "It was around this time that I first learned of the existence of ionic liquids, and I found them incredibly fascinating," Kuwabata explains. "Of course, my fellow electrochemists were all thinking about applications to electrolytic solutions, whereas my ideas"—as he recounts with an impish glint in his eye—"went in a very different direction."

Kuwabata focused on what he saw as the single greatest advantage of ionic liquids: their *non-volatility*. "Ionic liquids are the only liquids that don't evaporate," he explains. "For example, the electrical neutrality of the water molecule, H_2O, has the consequence that water molecules are easily separated from each other via boiling or evaporation. But the atoms comprising ionic liquids, although not so tightly bound as in solid salts, are nonetheless held together by strong electrostatic attractions between positive and negative ions, making them particularly difficult to separate and send off in separate directions—even when subjected to heating or vibration. So one day it dawned on me"—and here the Professor's eyes are positively *shining*—"that this non-evaporating behavior could be exploited for electron-microscope observation of specimens *as they exist in their natural state*, with no need to dry specimens for observation."

Ionic liquids, which exist in liquid form at room temperature, are compounds consisting of positive ions bound to negative ions by attractive electrostatic forces. The strength of these forces ensures that ionic liquids, unlike water and most other liquids, staunchly resist evaporation—even when heated or placed in a vacuum.

The need to preserve the high-vacuum state within electron microscopes had conventionally required observation specimens to be completely dried before they could be observed. But the ability to observe specimens immersed in ionic liquids could allow direct investigation of living organisms in their natural state—and of the progress of chemical reactions in ionic liquids. Moreover, Kuwabata reasoned that the high ionic conductivity of ionic liquids should prevent the accumulation of static charge under electron-beam irradiation, avoiding a phenomenon that could otherwise prohibit image acquisition.

Doing his best to keep his excitement in check, Kuwabata immersed a biological sample in an ionic liquid, mounted the specimen in his laboratory's scanning electron microscope, and conducted an observation. The results confirmed his hypothesis: the electron beam passed through the ionic liquid without generating static-charge buildup, yielding clear microscope images. As expected, the ionic liquid did not evaporate inside the SEM. Kuwabata's next attempted the challenge of following the detailed evolution of battery charging/discharging processes and other electrochemical reactions through real-time SEM observation. This was followed by yet another breakthrough: in 2008, Kuwabata and a research group at Nagoya University dissolved silver ions in an ionic liquid, passed an electric current through the liquid, and carried out the world's first successful observation of the dendritic growth process of silver deposits on electrode surfaces—a result that was widely heralded in newspapers and other media outlets.

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Kuwabata's achievements noted in high-school chemistry textbooks

"As it turned out, placing ionic liquids in SEM specimen chambers required a little retuning of the basic SEM system," Kuwabata recalls. "So we asked the folks at Hitachi High-Tech if they could help us out, and they came up with some perfect solutions."

With a track record of successful SEM observations bolstering his confidence, Kuwabata next started thinking about using ionic liquids for transmission electron microscope (TEM) experiments. Compared to SEM, TEM offers higher resolution and higher performance—but at considerably higher cost. "So, anybody with a little common sense understood that, just because you could put one of these things in a SEM, it didn't necessarily follow that you could put one in a TEM!" Kuwabata laughs. "Back then, when I told the folks at Hitachi High-Tech that I wanted to put an ionic liquid in a TEM, they looked at me and said—'Stick an ionic liquid in a TEM? Absolutely no *way* we're doing that!' But eventually they were gracious enough to give it a try. And I still remember the moment we all saw the first TEM image of an ionic-liquid specimen—the Hitachi High-Tech guys all got really excited and kept saying 'Holy cow! This is incredible!' And ever since then," Kuwabata laughs, "I've had a very favorable relationship with the folks at Hitachi High-Tech."

"You know," he continues, "if it hadn't been for all the cooperation we got from the Hitachi High-Tech team back then, we may well have been scooped by some overseas researcher in attempting the world's first TEM observations in ionic liquids. This is another reason I've always been grateful to Hitachi High-Tech."

Kuwabata's accomplishments have even made their way into high-school chemistry textbooks. Previous-generation textbooks contained statements like "Ionic crystals, such as sodium chloride, typically have high melting points and are solids at ambient temperature and pressure." However, many newer textbooks follow the lead of Keirinkan's high-school chemistry text, which now includes a sidebar noting that "Salts existing as liquids at room temperature are known as *ionic liquids*"—and features an electron microscope image of scales on a butterfly wing captured by Professor Kuwabata.

"When that textbook arrived," Kuwabata recalls, "I immediately turned to the Acknowledgements section at the end, where they list credits for all materials supplied to the book, and, sure enough,

"My laboratory's achievements have even made it into high-school chemistry textbooks." Kuwabata says. Newer editions of the textbook in question include a sidebar discussion stating "Salts existing as liquids at room temperature are known as *ionic liquids*."

there it was, right there in print: *Kuwabata Laboratory, Osaka University Graduate School of Engineering*. I was so thrilled that I took the book into the lab and showed all my students, who were pretty excited as well—'That's so cool!' they all said. So then I asked them: 'By the way, when you guys were in high school, did you ever open your textbook to the Acknowledgements page and read all the names?' And of course they all said 'No, sir—we never even knew such pages existed!' And I said 'That's right—because the only reason these pages *do* exist is to flatter the people listed on them!' and we all laughed."

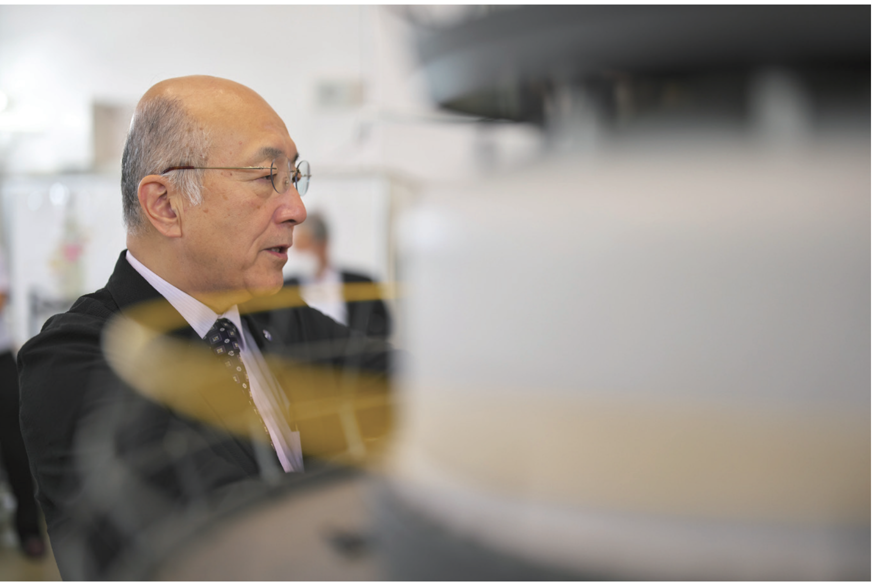
As awareness of ionic liquids continues to grow, Kuwabata says he dreams of that happy future day when their existence will merit not just sidebars—but *full sections* in chemistry textbooks.

Electron microscopes as extensions of film cameras

But how did Kuwabata first hit on the idea of putting ionic liquids in electron microscopes? "Actually," he explains, "I had been a total camera freak ever since elementary school." This was before the days of digital cameras, when photographers had to take film to photo studios to have pictures developed and printed. But young Kuwabata was developing and printing his *own* snapshots already by his first year of junior high school.

Of course, the digital cameras in modern smartphones are extremely high-performance instruments allowing anyone to take close-up shots with ease, but things weren't so easy with the film cameras of Kuwabata's youth. Capturing close-up images—of, say, a tiny insect—required specialized tools, such as close-up lenses, and the photographic skills to use them. "All through those years, from elementary school to high school," recalls Kuwabata, "my burning passion was to use film cameras to capture the microscopic world in the greatest possible detail."

But later, when Kuwabata became a student at Osaka University and belonged to a research laboratory one day, he got a big surprise—the lab was equipped with a Hitachi S450 SEM system. He asked a professor in the laboratory how to use the instrument, and was told "Just put the specimen in here and go like this to make an observation—and you can even push this button to capture an image." Kuwabata was astonished to see how easy it was



Kuwabata says he's been a total camera freak ever since elementary school—and that he sees electron microscopes as extensions of ordinary cameras.

to observe the microscopic world—and even to acquire high-resolution images with just the touch of a button.

"In our electrochemistry research, using electron microscopes wasn't something we needed to do every day, but in my heart I always held on to the hope that someday I'd use electron microscopes to capture images that would take people's breath away," Kuwabata recalls. "Because, to me, electron microscopes were just extended versions of ordinary cameras. I think that's how I wound up asking myself why I couldn't use ionic liquids for electron-microscope observations."

Choosing a life of electrochemistry research

How did Kuwabata wind up choosing electrochemistry as his field of specialty? "The experience that first got me interested in electrochemistry," he recalls, "was my discovery of batteries, probably around my 3rd year of junior high school."

At that time, most batteries were of the disposable dry-cell variety, but one day young Kuwabata came across a radio and cassette player in his house, and, reading through the user's manual, his eyes fell on the phrase *NiCad battery*—and specifically what came after: *Battery may be recharged and reused multiple times*. This was music to Kuwabata's ears: Having long been forced to save up his paltry allowance to purchase costly batteries, "now I could just charge up my batteries at home—and save my allowance!" he grinned. "Of course, at that time, NiCad batteries were pretty expensive—I remember it's around 6,000 yen. But, in the long run, it seemed obvious to me that they represented an enormous savings compared to disposables."

Kuwabata treasured his precious NiCad batteries so much he barely used them—and yet, after constant recharging, the devices stopped working after just a month or so. "It wasn't until after I became an electrochemistry researcher that I learned that NiCad batteries quickly stop working after repeated recharging," he recalls. "I hadn't understood this back in junior high school, and I found it so incredibly disheartening that I vowed, right then and there, to build a battery someday that could be recharged over and over again without ever breaking down."

Kuwabata's high-school years were rocked by another calamitous event: In 1973, the oil-producing nations of the Middle East raised crude-oil prices by 70%, plunging Japan into a full-blown oil shock. Amid the ensuing search for alternative energy sources, the discovery of the Honda-Fujishima effect cast a bright spotlight on research into photocatalysts as ideal sources of energy. This effect involves a titanium-dioxide electrode and a platinum electrode immersed in water; when light shines on the titanium-dioxide electrode, the water decomposes to yield oxygen and hydrogen, generating a flow of current between the electrodes. The possibility of a revolutionary new technology, capable of converting light energy simultaneously into electrical energy and chemical energy, became a focus of intense global interest—and, to this day, Kuwabata still has several carefully-preserved newspaper articles from that time. "That's what convinced me I wanted to major in something at college that would give me a chance to study batteries and photocatalysts," Kuwabata explains. "And it was right around then that my father gave me a pamphlet for Osaka University, and right there on the page for the Applied-Chemistry Major in the School of Engineering was the word *electrochemistry*! I said, yes! This is it! This is exactly what I want to study!"

Kuwabata eventually got his wish, entering the Osaka University School of Engineering and majoring in applied chemistry. What sort of research did he pursue? "In battery research, interfaces between solid electrodes and liquid electrolytes are extremely important," Kuwabata explains. "And yet, what's surprising is that, if you look at these interfaces under electron microscopes, you can't tell where the solid ends and where the liquid begins—the boundary is actually quite fuzzy. In fact, the boundary between liquid and gas isn't very clear either. The professor in the laboratory I joined used to say 'If you think of it like an ocean, then these interfaces are like the beach.' When waves come in, there's a moment when you can't tell where the ocean ends and where the sand begins—and interfaces in batteries are very similar. So that got me interested in studying interfaces in batteries and other systems."

Interfaces in batteries are crucial indeed—the scant few nanometers of interface between electrodes and electrolytic solutions are responsible for generating current flows, and thus, without the ability to observe interfacial phenomena, it is nearly impossible to understand the mechanisms governing power generation. This was the impetus that made Kuwabata so eager to observe solid/liquid interfaces with electron microscopes. Of course, at the time, the notion of inserting liquids into electron microscopes was totally unheard of, and it would be another ten-plus years before Kuwabata experienced his fateful encounter with the world of ionic liquids.

Continuing to solve energy problems —well beyond retirement

Professor Kuwabata retires in 2023 academic year, but says he plans to continue working on energy problems.

At present, Japan's Ministry of Education, Culture, Sports, Science and Technology, together with the Japan Science and Technology Agency (JST), are promoting a program known as Green Technologies of Excellence (GteX), to be implemented over a five-year interval beginning in October 2023. Amid efforts toward carbon neutrality from nations around the world and a rapid growth in investments targeting green transformation (GX), GteX represents a collaborative effort among Japanese government, academia, and industry players to create new technologies and train new leaders to promote GX innovations and achieve carbon neutrality by 2050. More specifically, GteX focuses on three specific sectors—*revolutionary batteries* (*energy-storage technology*), *hydrogen-conversion technology*, and *biomanufacturing technology*, and Professor Kuwabata serves as a Program Officer (PO) in the revolutionary-batteries sector.

"Going forward, I'm hoping to continue using electron microscopes for electrochemistry research, while helping to supervise researchers working today in R&D for revolutionary new types of batteries," Kuwabata explains with an air of fierce commitment. "I am not at all ready to just kick back and relax!"

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Professor Kuwabata poses in front of the H-3000 ultra-high-voltage electron microscope.

Reported and written by Kumi Yamada. Photographs by Yuki Akiyama.