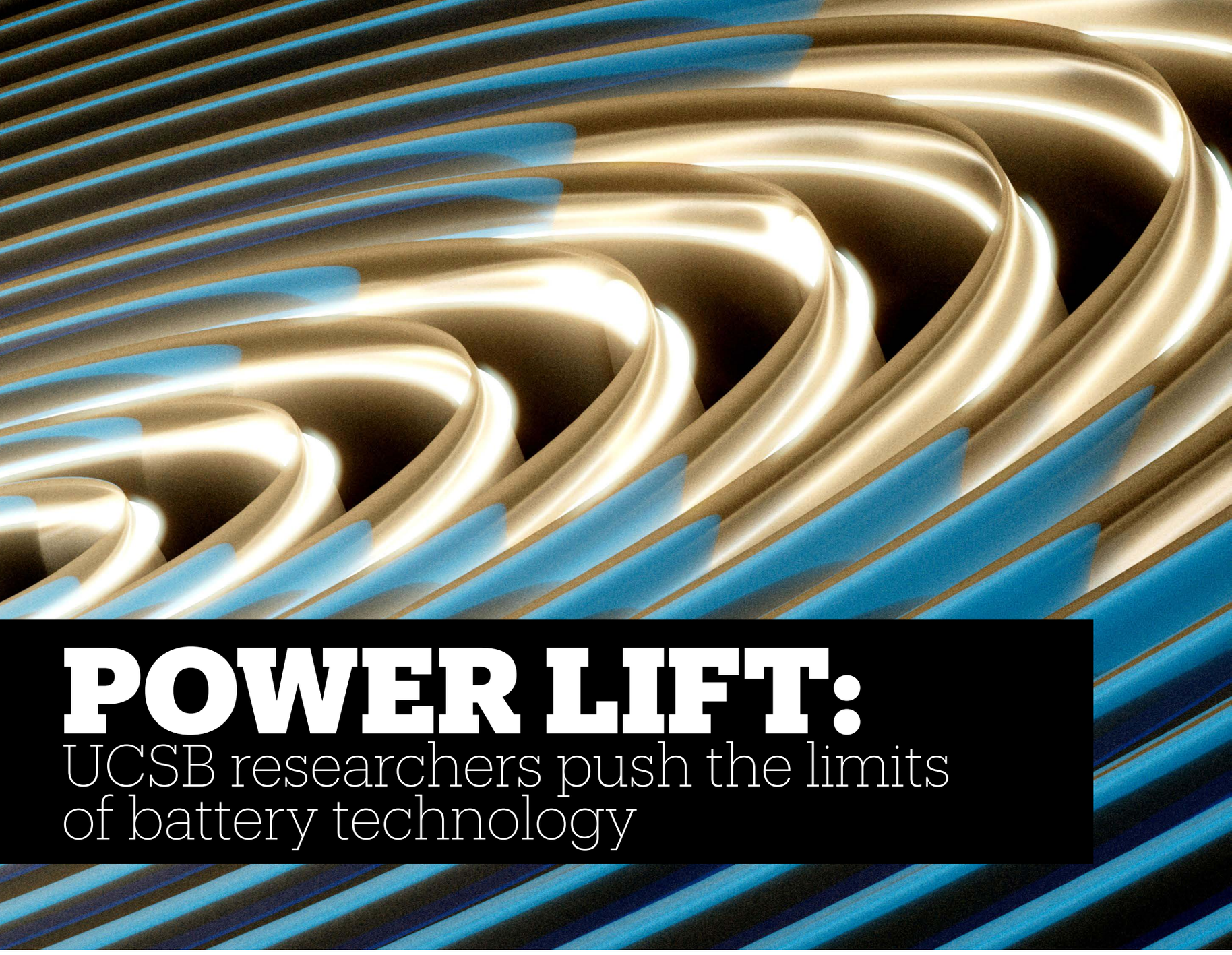


POWER LIFT:
UCSB researchers push the limits of battery technology

Now more than at any other time in human history, batteries are a big deal, and no wonder; we will need billions of new and better batteries to power our imagined carbon-neutral future, most notably for electric vehicles (EVs), handheld electronic devices, and battery "farms" for storing energy produced intermittently by renewable energy sources such as the sun and wind. Visions for — and prototypes of — electric big-rig trucks, airliners, and almost anything else that currently runs on fossil fuel are in the offing.

There is work ahead. "We're still very far from being a carbon-neutral society," says **Raphaële Clément,** an assistant professor in the Materials Department at UC Santa Barbara and an expert in using nuclear magnetic resonance (NMR) spectroscopy to characterize materials, including those being developed as battery materials. "Achieving a fifty-percent reduction in U.S. greenhouse gas pollution from 2005 levels by 2030, a goal that was announced by President Biden at the Leaders Summit on Climate in 2021, will require building enough storage facilities [farms], and diversifying the chemistry portfolio of batteries to make it possible to build such storage units at the necessary scale."

Additionally, she notes, at least some of those new technologies will need to be made from earth-abundant elements that are, perhaps, less energy dense but adequate for grid storage, where having a high energy-to-weight ratio is not as much of a concern as it is for, say, EVs, since the batteries are stored in one place. The important concerns are, rather, low cost, sustainability, and durability to keep maintenance costs down. On the EV front, better batteries are needed that will last longer, extend driving ranges, charge in a few minutes, and incorporate elements that are abundant, cheap, and mined in ethical and sustainable ways.

Clément is one of some twenty faculty members, most of them in the College of Engineering (COE), who conduct battery research at UCSB. Having

won a National Science Foundation Early CAREER Award in 2022, Clément is working on materials that could be used in a sodium-ion battery, an alternative to the lithium (Li)-ion battery. She works with numerous colleagues who are developing theoretical models, creating computer simulations to test theory, advancing new technologies, and planning pathways to large-scale production.

Among that group is one of the COE's newest faculty members, **Jeff Sakamoto,** a world-leading battery expert whose research is focused entirely on batteries and who helped to build a battery pilot and test plant during his ten years at the University of Michigan (UM). He came to UCSB last November with appointments in both the Materials and Mechanical Engineering Departments and is ideally positioned to anchor the university's strong team of battery researchers.

> **"The migrating electrons can do work. It's a genius invention from two hundred years ago."**

(Not) a Simple Thing

A battery may seem a relatively simple thing, consisting of an anode, a cathode, a liquid electrolyte, and current collectors made of aluminum on the cathode side and copper on the anode side (for a Li-ion cell). Enabling batteries that are energy-dense, powerful, safe, and environmentally sustainable, however, requires operating at the cusp of material stability and instability, and changing the materials chemistry of one battery component often requires changes to one or more — or even all — of the other components.

At a basic level, all batteries function in the same way, by separating electrons from atoms and shuttling the resulting ions inside a cell between the cathode and the anode — electrodes that store chemical energy — while the freed electrons flow through an external circuit to power a device or allow charging. The electrolyte, interposed between the electrodes, has the single function of transporting ions.

"The migrating electrons can do work," notes materials and chemistry professor **Ram Seshadri,** who is also the associate dean for research at the COE and the director of the UCSB Materials Research Laboratory. "It's a genius invention from two hundred years ago that allows chemistry to be separated by transporting the ion through one channel and the electron through another."

Lithium has only one electron and the highest *electrochemical oxidation* potential — the tendency to lose an electron — of any element on the periodic table. That is what makes it such a valuable battery element. When a Li-ion battery is charged, the cathode — the higher-voltage of the two electrodes —simultaneously releases a Li-ion and an electron. The Li-ions then flow through the liquid electrolyte and are inserted into the anode material, where they recombine with an electron released from the cathode. Essentially, the charging process involves changing the Li-ion concentration in the electrodes to increase the chemical energy stored in the battery.

In the discharged state, Li-ions prefer to be in the cathode material rather than in the anode. The charging process overrides that affinity, forcing Li-ions to flow in a direction opposite the natural flow, to the anode. The anode is typically made of graphite, which consists of layers of carbon atoms, the carbon layers being held together by weak bonds. That unique bonding in graphite makes it easy for Li to be inserted between and extracted from the rows of carbon atoms. Once the graphite is full and cannot intercalate (absorb) more Li, the battery is fully charged.

The chemical potential energy accumulated in the electrodes has now been maximized and can be converted to electrical energy during discharge, which repeats the process of transporting Li-ions and electrons, but in the opposite direction. As the electrons travel through the external circuit back to the cathode, they convert the chemical energy stored during charging into electrical energy to power an EV, a cell phone, or any other battery-enabled device.

Li-ion batteries, currently the world's leading battery technology, the power of which Tesla and other EV companies demonstrated by employing them in massive arrays of more than seven thousand cells to power each of their vehicles, are a well-developed technology, but they have limitations.

Some of the highly collaborative faculty researchers who are pursuing new battery technologies at UCSB (from left): Ananya Balakrishna, Yangying Zhu, Rachel Segalman, Glenn Fredrickson, Robert McMeeking, Ram Seshadri, Anton Van der Ven.

For instance, ideally, the anode could be made of pure metallic lithium, which would increase the energy density of the battery, defined as "energy per given unit of battery size. "But, practically speaking, you can't do that," says UCSB materials professor **Anton Van der Ven,** who is known for his work building computational models of materials at the atomic scale. "That's because lithium is highly reactive and deposits non-uniformly at the anode." Those deposits are highly problematic, sometimes growing as fingers — called *dendrites* — that penetrate back through the electrolyte, short-circuiting the battery when one of them makes contact with the cathode." The fires in EVs we hear about on the news are sometimes the result of such short-circuits.

The UCSB Research Mix

To address those and other issues, a group of COE faculty from the Materials, Chemical Engineering, and Mechanical Engineering Departments are working together on every aspect of batteries, including new chemistries and recycling.

Through various collaborations, Ram Seshadri has demonstrated that calcium can be employed effectively as an anode in primary cells (defined as able to be discharged only once), has contributed a better understanding of sulfur redox in lithium sulfur batteries, and has conducted research to develop new cathode materials. His group is known for its anomalous use of household microwave ovens to prepare battery materials in a rapid, efficient method that takes minutes rather than hours.

More recently, Seshadri has also focused on recycling, and specifically the structures and compositions of products that are obtained while reclaiming components from used and dismantled batteries. He is interested, for example, in recovering lithium, nickel, cobalt, and graphite from cathodes and anode mixtures. "Heat treatment [used to eliminate certain chemicals at end of life] results in all sorts of new chemistry," he says. "We are trying to decipher those chemical changes as a step to developing efficient recovery techniques."

Clément complements her investigations of new materials for a possible sodium-ion battery — sodium being much cheaper and more abundant than lithium — by contributing her expertise in NMR spectroscopy to study new materials for lithium-based batteries. This powerful technique, which requires expensive instrumentation and a high level of expertise, makes it possible to analyze the atomic structure of a material by tracking interactions between nuclear and electronic spins, allowing Clément to study the charge-discharge processes in battery materials at the most fundamental level.

Sakamoto, an expert in fabricating ceramics for energy technologies, is continuing work he began at UM to develop a solid-state Li-ion conducting ceramic electrolyte, which would replace the liquid electrolyte in current Li-ion batteries. That effort involves advancing not only fundamental materials

science, but also the understanding of processes — how chemistry and electrochemistry affect the actual mechanical properties of a battery — with further considerations regarding how to manufacture such a battery.

"Making solid electrolytes work is a huge challenge, primarily because there are so many complicated reactions at the anode and cathode side, as well as complex chemomechanical reactions that can cause [the above-mentioned] lithium dendrites to penetrate and cause a short-circuit," he says.

Because Li metal is significantly softer than a typical ceramic electrolyte, scientists initially thought that Li dendrites would not penetrate solid-state electrolytes, but it turns out that they can. There is still a healthy debate within the scientific community as to how that is physically possible, but the prevailing theory is related to the imperfections or defects in the ceramic electrolytes. According to that view, Li metal deposition causes localized build-up of pressure sufficient to cause the ceramic to crack. Once a crack forms, it is quickly filled by Li metal and the crack or Li metal dendrite grows toward the cathode, eventually contacting it and causing short-circuiting to occur.

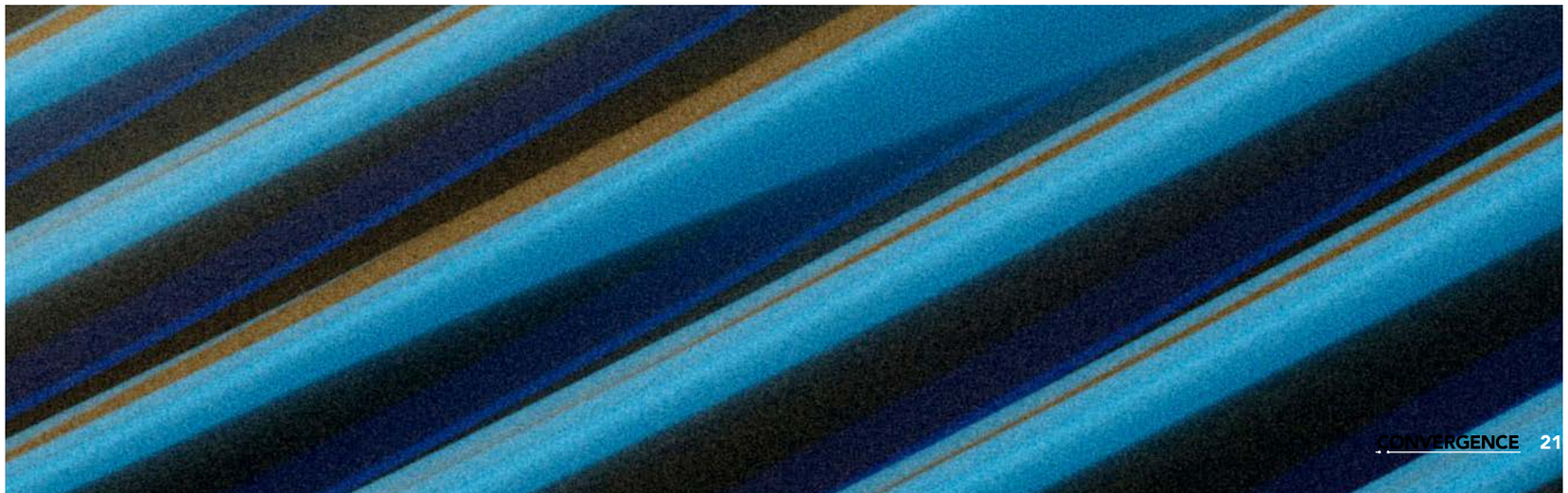
"In principle, if you can get rid of those defects, then that ceramic membrane — or other solid-state electrolyte — is physically hard enough, has adequate conductivity, and is stable enough to flatten the dendrites," Sakamoto says. This would enable uniform, dendrite-free plating and stripping of lithium metal, an improvement that would dramatically extend battery life.

> **"If there is one thing he knew, and that others who work on ceramics know, it is that they are inherently brittle....That has been the Achilles heel for ceramic solid-state battery technologies."**

Another key challenge of making a ceramic electrolyte is evidenced by what happens if you drop your coffee cup onto the kitchen floor: it shatters. The late UCSB materials professor **Tony Evans,** who wrote the proposal for the first of seven rounds of NSF funding for the MRL at UCSB, the latest commencing in 2023, did a lot of work on ceramic coatings used in extreme environments. "If there is one thing he knew, and that others who work on ceramics know, it is that they are inherently brittle," says Sakamoto, who has spent fifteen years studying ceramics as a possible solid-state battery electrolyte. That has been the Achilles heel for ceramic solid-state battery technologies, because to prevent fracture, they have to be thick, and that makes them heavy — not an option for, say, the batteries in an EV or an aircraft.

In the 1980s Evans, UCSB computational materials scientist **Robert McMeeking,** who is able to model the growth of dendrites in lithium-ion liquid and solid-state batteries, and other colleagues made a great deal of progress on that problem, which, says Van der Ven, "is exactly the same problem that arises in trying to make a ceramic electrolyte."

In batteries, the brittleness of ceramics creates a challenge related not to performance, but to making the battery at scale. "If you have an intrinsically brittle material, how do you get it into batteries without it breaking during the manufacturing process?" Sakamoto says.



Faculty Q&A

JEFF SAKAMOTO

Materials professor and Mehrabian Chancellor's Chair **Jeff Sakamoto,** who also has a partial appointment in mechanical engineering, came to UCSB last November with a reputation as a world expert on batteries, and focuses ranging from fundamental research through manufacturing. Having grown up in Silicon Valley when fruit trees dominated the pre-microprocessor landscape, Sakamoto earned his bachelor of engineering degree at Cal Poly San Luis Obispo and his PhD at UC Los Angeles. An expert in high-performance ceramics, he worked at the Jet Propulsion Laboratory in Pasadena before spending ten years at the University of Michigan, where he engaged with auto makers to develop new battery technologies. We caught up with him in February. His expertise is reflected throughout the main article as well.

What brought you to UCSB?

I was born and raised in California, and it has always been home for me. It's great to be back where I'm close to my extended family. With my kids finishing high school in Ann Arbor, I thought it was a good time to consider transitioning to a university that has a history in advanced ceramic research and, more broadly, strong fundamental materials research and materials characterization. Advanced ceramic research has been part of the UCSB Materials Department DNA since it was founded. Moreover, the College of Engineering at UCSB is recognized as a world leader in engineering studies. When I considered how well aligned my career goals and personal connections were with the opportunity, I accepted the position immediately. I also need to emphasize that the people and the collaborative environment equally contributed to my excitement at becoming a part of UCSB. This is a dream come true!

What are some of the main considerations when you think about manufacturing and commercialization of batteries?

That's the area of techno-economic analysis, and it involves big-picture thinking: before lifting a finger in the laboratory, you have to figure out if it's viable at scale, because if you're going to make a battery for EVs, you will eventually need billions of them. If we're considering using a certain material, we have to think about whether there is enough of it in the Earth's crust, where it will come from, and whether the material extraction and processing are sustainable. Public policy and environmental and social studies are integral to that kind of analysis, so it can attract the interest and contributions of faculty from across campus.

Looking at the possible trajectory for battery research at UCSB, would you like to do something here similar to the battery lab you started at the University of Michigan?

Yes, but it would be different. One mission could be to make state-of-the-art lithium-ion batteries. The students — and especially graduate students — could complement their course work by learning how to design, fabricate, and test batteries, do post mortem analyses, and so on. That would prepare them to hit the ground running when they graduate. Companies need battery experts, and companies that can benefit from this program will likely want to invest in fellowships or buy a piece of equipment that they're interested in using and that also grows our capabilities. That's a way to bring in industry, connecting its needs with the students we graduate. We would be advancing battery research while focusing on workforce development.

There's great value in fundamental research at UCSB, as well as a broad and deep technology pool. I will endeavor to bring these strengths to bear in our collaborative efforts to commercialize technologies that will help create a sustainable energy future.

"Ceramic electrolytes can be promising in prototype cells made in the laboratory, where they are handled very gingerly, but can we make them tougher and stronger, so that they can survive a high-speed manufacturing process? That's another branch of research that this [materials] department is well poised to examine."

The brittleness of ceramics derives from the nature of their bonding and how they are made. Some (usually small-scale) materials systems are fabricated from the bottom up by depositing atoms via processes such as chemical or physical vapor deposition, but, Sakamoto says, "For more of the recently discovered breakthroughs in ceramic electrolytes, you take a batch of powders and squish them together. That more-scalable process also produces microstructural defects, little pores that, in a battery, cause pressure build-up from localized deposits of Li metal, which crack the ceramic [as mentioned above]. The defects are the enemy, and we need either to get rid of them or discover ways to enable tougher ceramics."

A further challenge in solid-state batteries results from having a solid interface between both of the electrodes and the electrolyte. For example, if a Li-metal electrode is used, each charge and discharge of the battery causes a thirty-percent change in volume as a result of deposition and dissolution of lithium. "Depending on the battery-pack design, this can change the cell pressure during operation, which may change the battery behavior," Sakamoto explains. "On the other side of the cell, the cathode particles may also expand and contract during cycling, causing stress at the cathode-electrolyte interface. Whether at the cathode or the anode, these pressure changes during operation result in mechano-electrochemical phenomena that are still not fully understood. If these knowledge gaps could be closed, solid-state battery technology would advance significantly toward commercialization."

Many battery scientists, including Clément, also think a lot about the "tremendous amount of pressure that must be applied during solid-state battery fabrication to create good interfacial contact between the components." Beyond fabrication, solid-state batteries work well only if pressure is also applied *during* electrochemical cycling; i.e. during charge and discharge. "That is possible by packaging the cell in a very thick casing, but by doing that, you're defeating the purpose of a high-energy-density battery, which must be lightweight, because a casing that can contain so much pressure will be heavy," Clément notes, making it impractical for use in a car, a plane, or a cellphone we carry in our pocket, where weight matters.

Further, she adds, "We also don't know how applying so much pressure to these materials might affect their properties or how they behave. What does the pressure do to the materials at the interfaces of different components? There are still a lot of unanswered fundamental questions."

> **"We don't know how applying so much pressure to these materials might affect their properties or how they behave. There are still a lot of unanswered fundamental questions."**

Clément's research on materials for a sodium (Na) battery are driven, to some degree, by the fact that sodium is about 1,200 times more plentiful in the world and much cheaper than lithium. "Once we get it working," Sakamoto says, "it is probably the answer to enable batteries for low-cost, sustainable grid or long-duration energy storage." But even for large, heavy batteries that can be stored underground, Sakamoto says, circling back to a point of constant focus, "Once a suitable electrolyte or materials for electrolytes are identified for a sodium battery, you then have to think about *manufacturing.* If you get to the point of having new chemistry to move sodium ions through a ceramic electrolyte, and new water-based liquid electrodes, then you have to figure out how to make it affordably, safely, and at scale. So, our sodium-battery team includes a cathode team, an anode team, an electrolyte team, a cell-characterization team, and a manufacturing team."

As with so much about batteries, however, "getting it working" is the trick. The deployment of Na-ion batteries has been hampered by a lack of cathode materials that are capable of storing large amounts of charge reversibly, as occurs in a Li-ion battery. "Viable sodium alternatives to current lithium-based batteries have proven elusive," says Clément, who is studying a class of candidate Na-ion cathode materials called *weberites.* "We are curious as to whether we can make new chemistries for sodium-ion cathodes that are different from those used for lithium. A lot of research is being done on swapping out lithium for sodium and using the same

Raphäele Clément prepares an NMR rotor sample holder, which is rotated at high speed in the instrument to provide views of the material's atomic structure.

chemistry, but sodium has problems that lithium doesn't have, so we're looking at completely different structures.

"The weberite are fluorides — highly electronically insulating materials," she notes, "but the composite electrode we prepare must be reasonably conductive. We are currently optimizing the electrode formulation to achieve that."

The Polymer Picture

Chemical engineering professor **Rachel Segalman** and chemistry professor **Javier Read de Alaniz**, in collaboration with Clément and materials and chemical engineering professor **Glenn Fredrickson,** an expert on simulating polymers, are collaborating to develop a polymer electrolyte for a solid-state battery. Segalman, an expert in ion and electron conductivity in polymers, and Read de Alaniz, a synthesis expert, design and synthesize new polymer electrolytes. Clément's expertise in NMR plays a major role in helping them to understand how the lithium and its counterion (produced when an ion is) move through devices.

Fredrickson conducts multiscale modeling studies of zwitterionic polymers — polymers that bear a pair of oppositely charged groups in their repeating units — which Segalman, Read de Alaniz, and Clément are investigating. His work encompasses atomistic molecular dynamics (MD), coarse-grained MD, and field-theoretic simulations to probe the dissociation, structure, and dynamics

> **"In an ideal world, before any new battery material or component was produced it would be modeled computationally to indicate promising directions."**

of dissolved lithium salts within the solid-matrix polymer. His findings are being used to guide the design of next-generation of polyzwitterions, the aim being to optimize ionic conductivity while maintaining desirable mechanical properties, such as processability, and ignition (fire) resistance.

Segalman describes their work as developing organic molecules that both help to dissolve the lithium salts (separating the positively charged lithium from its negatively charged counterion) in the system and also enable the lithium to move through the device quickly. This is difficult, because the lithium generally ends up coordinated (stuck) to the polymer, but only the lithium (not its counterion) matters in terms of battery performance.

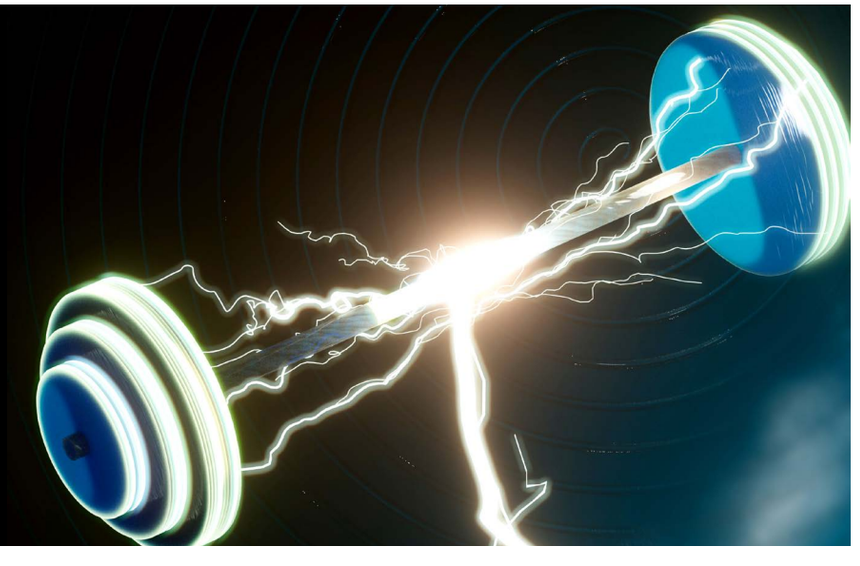
Read de Alaniz describes the research from the synthesis side as addressing a delicate balance in terms of bonding the polymer to lithium. "If you're thinking about selective lithium-ion transport, you need molecules that can interact with the lithium-ion dynamically."

On the other hand, if the binding with the polymer isn't strong enough, all the ions [lithium and its counterion] will re-cluster (aggregate) and no longer be useful in the battery. "Solubilizing the Li by coordinating with units on the polymer makes it less likely that the Li will aggregate and helps to increase the total amount of Li in the polymeric system," he says. "The goal is to separate the lithium ion from its counterion so that only lithium moves but does not aggregate."

Thus, the question of balance. "That process must also be dynamic — i.e. intermittent — enough to promote movement of lithium through the battery," Read de Alaniz adds. "That is not easy, because binding often is designed to be more long-term and persistent."

He and Segalman rely on Clément to verify the results of experiments designed to understand how lithium interacts with the polymer matrix. "Raphäele is able to say, 'Oh, you have two types of lithium, one that is free-flowing and conducting, and one that's serving as a stationary point binding the materials together,'" Segalman says. "That's what we want to have happen. It's amazingly complicated, but we are making great progress."

> **"That's what we want to have happen. It's amazingly complicated, but we are making great progress."**



Theory First

In an ideal world, before any new battery material or component was produced, says Van der Ven, it would be modeled computationally to indicate promising directions for research and rule out likely dead ends. Mostly, however, that is not what happens.

"A long-term dream of computational materials scientists is that our theories and algorithms are able to model the behavior of a new material before it is ever synthesized," Van der Ven explains. "We can do this to some extent, and there are many examples where modeling has provided useful directions for experimental researchers. Even before we fully achieve that, however, an important role of computational materials science is to generate a deeper, mechanistic understanding of how battery materials behave and how that behavior depends on the underlying chemistry of the material."

Materials assistant professor **Ananya Balakrishna** performs computational modeling that complements Van der Ven's work, but at a larger scale and in a more predictive way. "Anton's group works from first principles — the material properties, and those findings feed into our model," Balakrishna says. "When we're thinking of battery materials, we're thinking of one part of it, so let's say it's the cathode. We take a slice of it and visualize how the microstructures appear as the battery is charged and discharged, and how certain microstructural design changes could have a big impact on reducing either volume changes or interfacial stresses, both of which can damage and degrade the battery. A distinguishing feature of our method is that it allows us to predict how microstructures evolve in situ and how these microstructures collectively govern material cyclability. One can use such insights to design materials so as to mitigate some of the challenges that manifest on the large scale."

Related Efforts

Assistant chemistry professor **Lior Sepunaru** is currently focusing his research efforts on what is called a *redox flow* battery. Appropriate for long-term energy storage, it works much as a liquid-ion battery does except that the transport of ions and electrons occurs between "huge tanks of liquids that carry energy in chemical form," Sepunaru says. Such batteries incorporate a membrane that prevents the liquids on either side of it from contacting each other and short-circuiting the battery. In a recent advance, researchers in Sepunaru's lab developed a concept design for such a battery using liquids that don't mix — much as water and oil don't — eliminating the need for a membrane and cutting the cost of the battery by thirty percent.

New COE chemical engineering assistant professor **Tyler Mefford** also researches electrochemical materials and devices that can provide long-term grid-scale stationary storage of renewable electricity at a fraction of the cost of Li-ion batteries. Candidate technologies include aqueous batteries, which utilize earth-abundant elements for the electrodes and water for the electrolyte, and liquid fuels that can be electrochemically charged and discharged. Elsewhere, UCSB mechanical engineering assistant professor **Yangying Zhu** is studying how batteries hold up through repeated cycling between extreme high and low temperatures, an area of study relevant to both space travel and, perhaps, EVs, which can suffer poor battery performance in very cold temperatures on Earth. "We know a lot about batteries at room temperature, but we know very little about battery behavior outside that room-temperature window, and that might be important for space applications, such as on the moon." (Zhu was recently the PI on a study of water-droplet behavior aboard the International Space Station.)

"The battery may be close to room temperature during the lunar day, but at night, the temperature ranges from 280 to 360 degrees below zero Fahrenheit," Zhu adds. "You cannot charge or discharge a battery at those temperatures, because the liquid electrolyte will freeze, rendering the battery unusable. We want to know whether the battery will be damaged by repeatedly cycling through freezing and thawing processes, and whether freezing might damage its structural integrity."

To find out, Zhu uses two types of spectroscopy. For one, she shines a laser light into the cell and then obtains information from the back-scattered light. In the other, she works with UCSB mechanical engineering associate professor **Bolin Lao,** who uses a laser to excite the sample, which provides an acoustic response. If there is a crack in a battery component, the acoustic signature is affected.

Silver Buckshot

The current state of battery research and the complexity of the related challenges can be understood in those associated with batteries for EVs and grid storage. The key requirements of EV batteries are high performance (low weight and small size), low cost, sustainability, and safety. Because lithium-based chemistries are a proven technology that, by and large, exhibit the highest performance, they are the most attractive in that setting and, accordingly, leading the path toward an electrified future. If, however, new technologies beyond Li-ion batteries are commercialized, such as solid-state batteries that are safer and provide double the performance, they could dramatically accelerate the widespread adoption of EVs.

For grid storage and light-duty vehicles that don't require the same high performance, the challenges are guided more by cost, the abundance of materials, and their sustainability and safety. Sodium or other non-lithium chemistries that use water-based electrochemistry are attractive batteries for grid storage, but, most such "beyond-Li-ion" technologies, such as sodium batteries, are nascent and, while promising, require more technological development before they can be widely implemented.

"Regardless of the battery type, it is becoming increasingly apparent that there is no silver bullet or universal battery chemistry or energy technology that will enable the transition to a sustainable energy future," Sakamoto says. "Instead, an electrified future will likely require 'silver buckshot' — multiple chemistries and types of batteries, with each filling a role."

While the possibilities for new battery materials and chemistries may not be endless, they can seem to be, as evidenced by the multiple interdependent variables. Finding the winners will require ample time and intensive coordinated efforts, both to narrow down the field of candidates and also to build up, in some cases, atom by atom or monomer by monomer, materials for batteries that will, one day, release society from its reliance on fossil fuels. As is often the case, UCSB researchers are at the forefront of that world-wide effort.