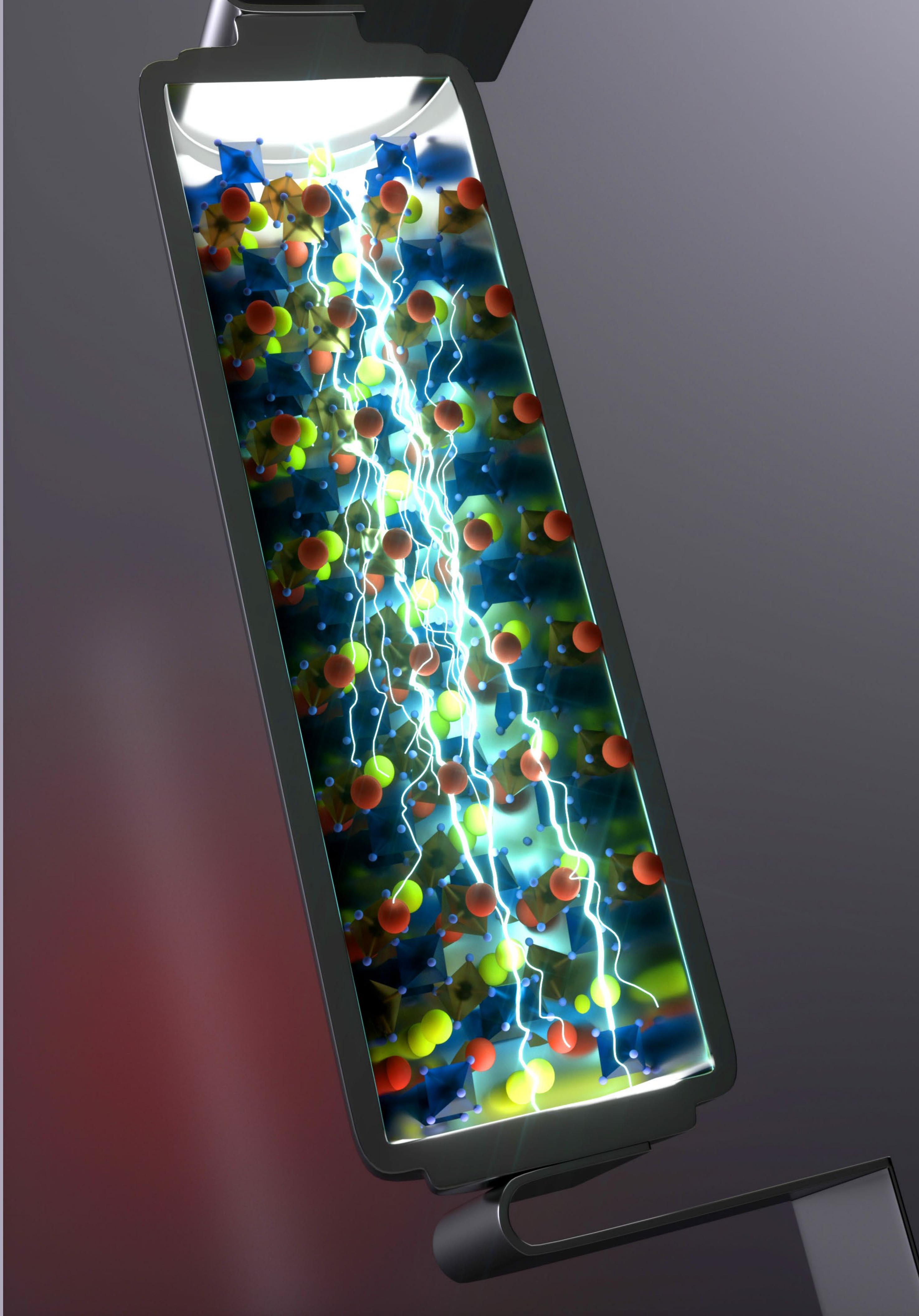

Concept illustration of ions and electrons migrating in a sodium-ion battery. Raphaële Clément seeks to develop the battery and improve the "suitability of nuclear magnetic resonance for looking at more complex systems."

the SODIUM SOLUTION

Raphaële Clément pursues a novel alternative to lithium-ion batteries

Raphaële Clément aims to develop a sodium-ion battery and new NMR techniques.

Lithium (Li) is the active ingredient in rechargeable batteries that power today's smart phones, laptops, and electric vehicles, but lithium's increasing scarcity and associated high price have led researchers to search for other, more abundant elements to replace it. Many researchers have turned to sodium (Na), which is below lithium in the periodic table and, accordingly, shares many of its properties. Sodium is also nearly 1,200 times more available in the world than lithium, making it far more affordable to extract and purify.

The deployment of sodium-ion batteries, which function through shuttling of sodium ions and electrons back and forth between the battery's electrodes upon charge and discharge, has been hampered by a lack of cathode materials that are capable of storing large amounts of charge reversibly, that is, taking up sodium ions and electrons during discharge of the battery and releasing them, so that they can be returned to the anode material, as the battery is recharged.

"Viable sodium alternatives to current lithium-based batteries have proven elusive, partly because a limited number of sodium-ion cathode materials have been tested to date," says **Raphaële Clément,** an assistant professor in UC Santa Barbara's Materials Department. She recently received an Early CAREER Award, the most prestigious prize given by the National Science Foundation (NSF) to support early-career faculty, providing her lab with more than $700,000 over five years to pursue research and educational activities related to developing a sodium-ion battery.

To find the missing cathode materials, Clément, who joined the UCSB Materials Department in 2018 after earning her PhD in chemistry from the University of Cambridge, proposes to study a new class of *transition metal fluorides* that hold promise for use in high-energy-density sodium-ion cathodes. These compounds — derivatives of Na_2MgAlF_7, a mineral known as *weberite* and named after the nineteenth-century Danish merchant who discovered it — radically depart from systems that have been explored previously for lithium. Clément will focus her search on weberite-like materials containing Earth-abundant elements, including fluorine, sodium, magnesium, aluminum, manganese, and iron.

As part of the project, titled "High-Resolution NMR for Paramagnetic Sodium Electrodes," researchers in Clément's lab will explore the new materials at a fundamental level, seeking to understand the links between their chemistry, atomic structure, and electrochemical performance. They plan to achieve this by using nuclear magnetic resonance (NMR) spectroscopy, a powerful technique that makes it possible to analyze the atomic structure of a material by tracking interactions between nuclear and electronic *spins* — tiny bar magnets associated with atomic nuclei and electrons — when the material is placed in a powerful magnetic field. NMR allows scientists to study the charge-discharge processes in battery materials.

"When a battery is operating, you have two materials [one in the anode and the other in the cathode] that can store sodium ions. On discharge, sodium ions are extracted from the anode material and then travel through a liquid electrolyte to be inserted into the cathode material. The opposite happens when charging the battery," Clément says. "When you extract a sodium ion from the anode, you're extracting a positive ion, so you also have to extract an electron at the same time from that material to make its charge neutral and, therefore, stable. That electron has to come from another metal in the material itself.

"The particular mineral we're starting from, Na_2MgAlF_7, does not contain any of what we call *redox active* transition metals, which actively give up electrons," she adds. "Na_2MgAlF_7 contains magnesium and aluminum, neither of which will give up an electron. So, we need to alter the chemistry of the weberite mineral and substitute magnesium and/or aluminum with a transition metal that *will* give up an electron. Manganese and iron are the metals we're interested in that will do that."

An initial obstacle to the research is that the compound Clément has chosen is difficult to make. Normally, she explains, "You would start with reagents in powder form and heat them to high temperatures, around one thousand degrees Celsius, and then cool them to form crystals. But these materials are very hard to make in that way, so we are using what's called *mechanochemical synthesis.* Basically, you place the powdered reagents in a metal jar, add metal spheres, and shake the jar at a very high speed for a couple of days to a week, inducing a chemical reaction between the reagent powders."

The process, however, yields a material that is not very crystalline, so, Clément says, "Typically, you use a quick annealing step in which you compress the powder into a pellet and then heat it in a furnace for a half hour to a few hours, to around five hundred degrees, and then cool it to get a more crystalline material."

There are good reasons why lithium, and not sodium, became the go-to element in the battery industry, Clément says: "Lithium is a smaller ion than sodium, so it is typically easier to insert and extract from materials [with a concurrent electron flow], which is why lithium-ion batteries work so well. It is also lighter than sodium, providing good energy density and making batteries lighter.

Finally, lithium metal has a lower voltage than sodium metal. This is important because in batteries you have to maximize the *potential difference* [in voltage] between the anode and cathode materials, because the energy density of a battery is equal to the potential difference between the two electrodes *times* the amount of charge that can be stored in these electrode materials. "So, if you maximize the potential difference and/or the charge storage capacity, you increase the energy density of your battery, and typically, lithium offers a greater potential difference than sodium does," Clément says. "Overall, sodium can work as well as lithium, but it's tricky to find the right materials that will reversibly allow the insertion and extraction of sodium from the crystal structure. That's what we are looking at with these materials.

"We're interested in these materials, because they have an open crystal structure that may allow them to hold a lot of sodium," she continues. "They also contain fluorine, which is important in this composition, because it typically leads to high sodium insertion and extraction voltages. That would make the working potential of the cathode quite high, which is good, because then you can improve the energy density of your sodium-ion battery."

Clément describes the research as "highly exploratory," because, she says, "While these are some of the more exciting cathode materials out there, they're very difficult to make and are not well understood, having been studied hardly at all for battery applications. We're first going to make some of the proposed materials, determine their atomic structure and their behavior as cathode materials, and then optimize their chemical composition to improve their performance."

Another important part of her CAREER Award–funded research, Clément says, is "pushing the boundary of the NMR technique [her area of expertise] that we use to study the materials. We plan to establish a novel NMR method to gain atomic-level insights into the working principles of these battery electrodes. We can then use that understanding to design new materials and chemistries having enhanced properties."

Using NMR to study the cathode materials of interest to this work can be challenging, because the redox active transition metals, such as the manganese and iron being investigated here, contain unpaired electrons (the very electrons that are released or taken up by the electrodes during charge-discharge). "You have many of these electrons coming from the manganese and iron atoms in your cathode, so you'll have a lot of interactions between spins, leading to very broad NMR spectra," she says. "NMR provides a lot of information on the structure of these materials, but because the spectra are so broad, the data can be difficult to interpret. The new technique that we're developing will allow us to simulate the NMR properties of complex systems, like the weberite cathodes of interest to us, in a more accurate and, more importantly, a more efficient manner. In broad terms, we are looking at developing not just materials, but ways to improve the suitability of NMR for looking at more complex systems."

Clément is one of eleven junior faculty from the COE who have received a CAREER award since April 2020. UCSB ranked first among public universities in the percentage of eligible-junior faculty who received the awards from 2016-'21.

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