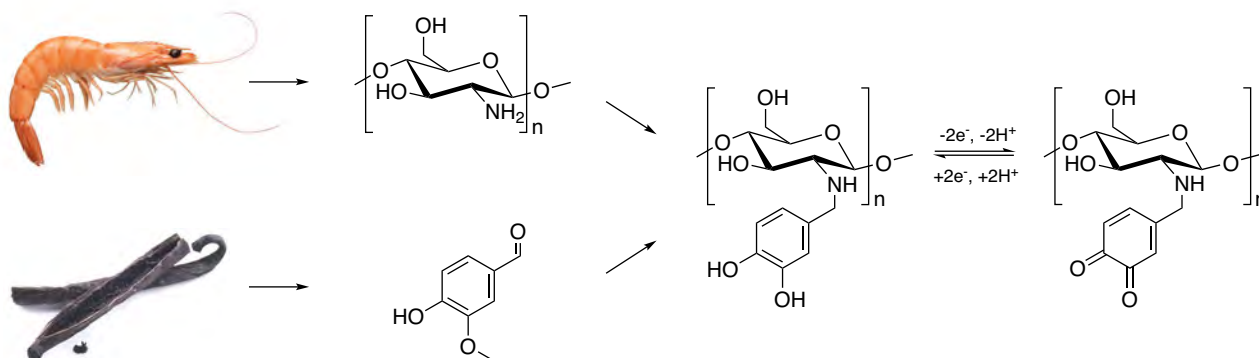


Testing sustainable battery components: researchers in Potsdam use a potentiostat to test how well the cells work with, for example, electrodes or an electrolyte made from renewable raw materials. To do this, they charge and discharge the test systems multiple times, taking measurements of the current and voltage between the poles.

The beginnings of the biobattery

The energy supply of the future has a storage problem. The ability to store surplus power from wind turbines and solar panels for times when it is in short supply relies on powerful batteries and capacitors, which should be made of materials that are as non-toxic and sustainable as possible. This is the focus of work by **Clemens Liedel** and **Martin Oschatz** at the **Max Planck Institute of Colloids and Interfaces** in Potsdam.

TEXT **KARL HÜBNER**



A recipe for an organic cathode: Max Planck chemists combine chitosan from shrimp shells with vanillin, the aroma of vanilla, which can also be produced from wood. By doing so, they hope to be able to replace substances such as lithium cobalt oxide, which is currently used for the cathodes in lithium batteries and whose use is questionable for political and environmental reasons.

There's a hint of vanilla in the air. It's not necessarily what you expect to encounter in a chemistry lab, let alone in one used for research in the field of battery materials. "That's from the vanillin," smiles Clemens Liedel. But anyone looking forward to some leftover Christmas cookies or freshly baked birthday cake is in for a disap-

pointment. There are no baked goods anywhere to be seen. In Liedel's lab, vanillin is currently being used as a starting material for a potential electrode material of the future.

Clemens Liedel is a researcher at the Max Planck Institute of Colloids and Interfaces in Potsdam, where he leads the "Sustainable Energy Storage Materials" working group. The name says it

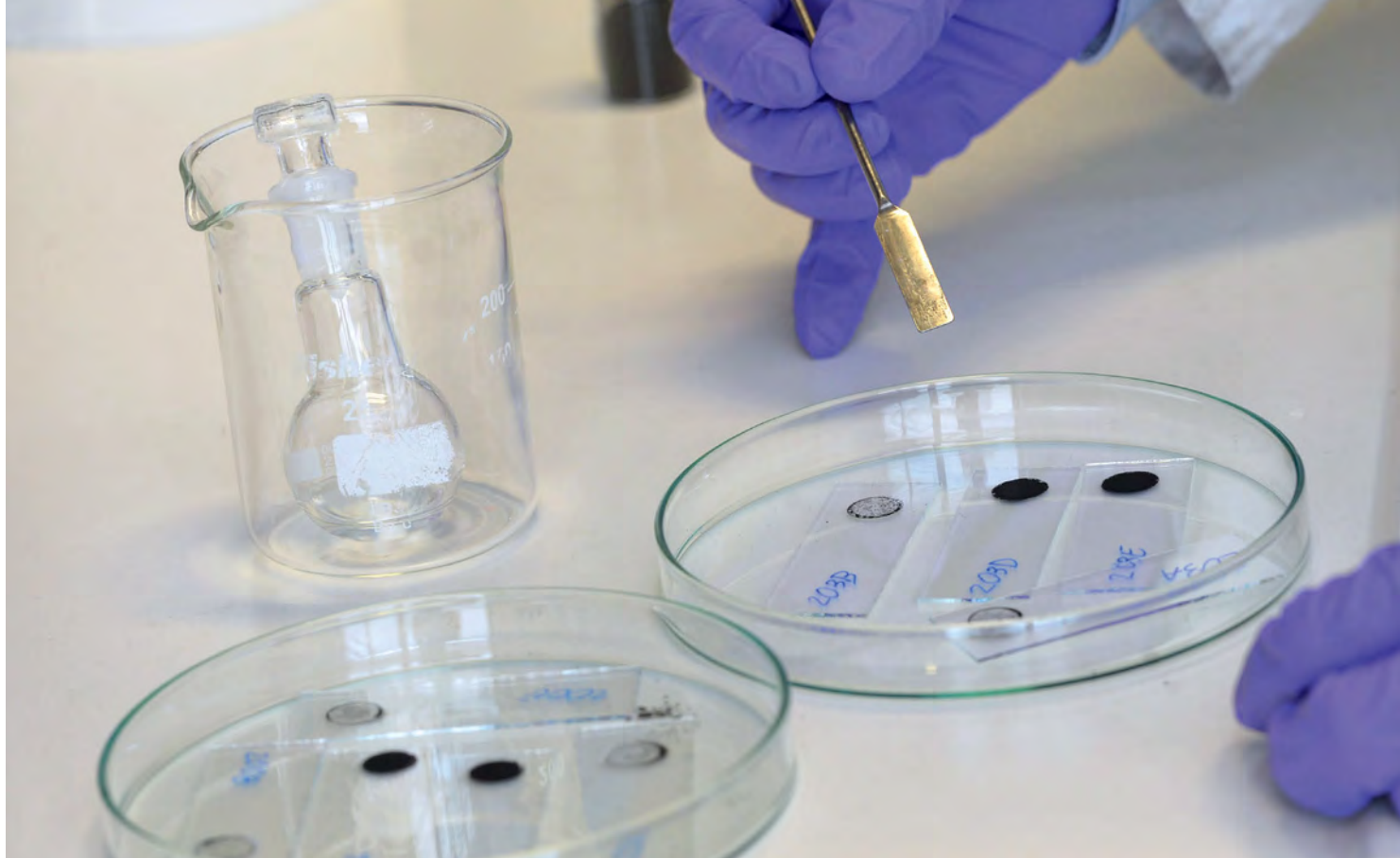
all: ideally, the new battery materials should be made from renewable raw materials and thus ensure almost unlimited availability. That is certainly not the case with today's lithium batteries. Lithium itself is quite a rare metal and is found in only a limited number of deposits around the world. Some two-thirds of lithium batteries also contain cobalt, a metal whose extraction is often accompanied by social and environmental problems in the exporting countries. Other components include electrolytes, which are sometimes toxic or even flammable. Given the rapidly rising demand for storage capacity, these conditions are still anything but ideal.

Clemens Liedel believes that the approach using vanillin could offer a significantly more sustainable alternative, as this substance can be prepared from one of the most common materials of all – from lignin, a principal component of wood. Every year, nature produces many billions of tonnes of lignin.

But how can an organic molecule be used as a material for batteries? After all,



A good mixture: working in glass flasks, the Potsdam-based chemists convert chitosan and vanillin into a sustainable electrode material.



when it comes to batteries, we typically think of metals such as lead, cadmium, or indeed lithium. “In very general terms, what you need are substances that can release electrons and then absorb them again,” explains Liedel. “These might be metals, which are then converted into metal ions, but they can also be organic substances.”

Specifically, the researchers in Potsdam envisage using vanillin for the cathode – that is, for the positive pole of lithium batteries – instead of substances containing heavy metals, such as lithium cobalt oxide. But that’s easier said than done – a brittle powder like oxidized vanillin cannot readily be used as an electrode material. “Normally, you mix the substance with a binding agent to create a compact paste and make it conductive by adding carbon,” explains Liedel. Although this approach proved successful, it was not sustainable enough for the chemist – he was still concerned about the binder, a fluorinated polymer.

At present, therefore, the researchers in Potsdam chemically bond their vanillin to the biobased polymer chitosan before mixing the combined substance with particles of soot – completely without binders. Chitosan is a sugar-like polymer that can be obtained

from the shells of shrimp, for example. Soot is still obtained from petrochemical resources, but could also be produced from biomass. At present, the Potsdam-based researchers are testing a pure vanillin/carbon mixture that works without a binder or chitosan, provided the vanillin first undergoes a chemical modification.

A MORE SUSTAINABLE SOLUTION FOR ELECTROLYTES

To test the electrode material, a member of the team applies an extremely thin layer of the mixture of substances to a sheet of carbon paper, from which they punch out a small, circular section. This is then inserted into a plastic housing, followed by a separating membrane, an electrolyte, and a counter-electrode – and the battery is complete. It is now possible to measure the battery’s voltage between two stainless-steel cylinders protruding from the plastic housing. Today, it is 3.1 volts.

But that’s not the only thing the scientists test. “In addition, we always carry out long-term tests involving a series of alternating charging and discharging processes,” says Liedel. “In this way, we can see whether our electrode is actually suitable for frequent

charging cycles.” That, of course, is an essential prerequisite for rechargeable batteries – and the researchers say that the latest vanillin-based approach has already proven successful.

Getting an overview: to investigate the properties of sustainable electrode materials, the researchers apply them to microscope slides with carbon paper.

However, Clemens Liedel’s group is also putting a great deal of thought into future electrolytes. The electrolyte is the component in a battery that contains the mobile charge carriers (the ions), which are responsible for balancing out the electrical charge between the two poles. Electrolytes usually consist of a conductive salt that is adapted to the electrodes, as well as a solvent. “Currently, these are typically solutions of toxic lithium salts in flammable organic carbonates,” explains Liedel. But the chemist has a more sustainable – and safer – solution in mind.

Here, too, the team has enjoyed some initial successes. Clemens Liedel walks into another of his labs, reaches for a round-bottomed flask, and briefly swirls it around in the air. A colorless mixture can be seen sloshing around inside. “That’s an ionic liquid,” says Liedel. The term is used to describe salts

that are liquid at temperatures below 100 degrees centigrade. Like all salts, the liquid is made up of positively charged cations and negatively charged anions. The researcher explains why this group of substances makes good solvents for electrolytes: “As well as being good conductors of other ions, ionic liquids are barely volatile and therefore offer excellent fire resistance.”

1 Silica mold with starting materials



2 Carbon material in the mold



3 Porous carbon



Baked storage battery: to create a material for powerful supercapacitors, the Potsdam-based chemists fill a mold made of quartz (silica, 1) with a highly concentrated aqueous solution of the starting materials sugar and salt. Heating this in the absence of air converts the sugar into carbon, which contains pores left behind by the evaporating salt (2). The researchers etch away the silica mold so that only the porous carbon material remains (3).

Moreover, some ionic liquids are also purely organic and, ideally, can therefore be derived from renewable raw materials. For Liedel, they also have another important feature: “It’s easy to fine-tune their chemical properties.” For example, researchers can readily configure not only the ion conductivity of the molecules, but also the temperature range in which they are liquids. His group has now identified a suitable ionic liquid for which half of the raw materials are already renewable.

A MARRIAGE BETWEEN BATTERY COMPONENTS

In commercial batteries, the two poles are usually very close together and separated by a fine-pored membrane to avoid an electrical short-circuit. This separator is typically made of an oil-based plastic and is permeable to the ions of the electrolyte in order to allow charge balancing, which is necessary when electrons migrate from the negative to the positive pole through an electrical load or while the battery is being charged. Here too, Liedel’s group can already offer an alternative – one which they stumbled across entirely by accident during their work involving chitosan. The researchers simply linked up the chitosan chains by adding additional substances to create a network of macromolecules with small pores. Experiments with this material have reportedly been successful. “The anions in particular migrate readily through the pores,” says Liedel.

After extensive basic research into individual battery components, the group is now looking to the next big step. “We now want to experiment with bringing all of these approaches together,” says Liedel – in other words, combining the organic cathode material with the ionic liquid, the chitosan

membrane, and a sodium- or magnesium-based anode. “But we still have a few details to clear up.” One such question is how chemically compatible the ionic liquid is with a biobased electrode material, such as oxidized vanillin.

The fact that polymer-based battery materials are currently seen as a promising and sustainable alternative is also demonstrated by the launch of a Priority Program by the German Research Foundation (DFG) in April 2019. Over a six-year period, the DFG will provide a total of EUR 12 million for a corresponding research network that also includes Clemens Liedel’s group.

So far, the only battery component for which Liedel doesn’t do his own materials research is the negative pole. At present, this anode usually comprises a combination of lithium and graphite. Although other metals such as sodium or magnesium are already being discussed and would offer significantly better availability, as well as being more sustainable, a number of technical questions must still be resolved before they can be put to practical use.

Another of the researchers working on this is Martin Oschatz, a colleague of Liedel’s at the Institute. Oschatz has his laboratories just a few steps away from those of Liedel’s team. He leads the working group on “Energy and Environmental Utilization of Carbon Nanomaterials,” which studies applications including the use of such materials in storage batteries. Oschatz experiments with carbon materials featuring pores of a precisely defined size. In principle, the aim is to provide the largest possible surface area with the maximum number of binding sites for metal atoms. This would also be instrumental in improving the specific energy of anodes.

While a battery is discharging, it is the anode that supplies the electrons. These are typically released by a metal,



which then becomes a positively charged ion – that is, a cation. The simplest thing would therefore be to make the electrodes from that metal, but that is hard to do with certain metals. Lithium is therefore usually combined with graphite, intercalating the lithium atoms between the graphene layers.

POROUS CARBON FOR SUPERCAPACITORS

Martin Oschatz is working on a similar solution for sodium. “The method involving intercalation in graphite doesn’t work with sodium,” he says. But the carbon chemist has already found another solution in the form of a carbon-based polymer with two important special features: the flat macromolecule forms sieve-like pores of its own accord, and the chemists have carefully selected the parent compounds in order to incorporate nitrogen atoms at the edge of the pores. “These ensure the stable storage of metal atoms,” Oschatz explains.

However, the researchers first had another obstacle to overcome. Although the high nitrogen content increases the binding strength for sodium, it also reduces the conductivity for the elec-

trons released by the sodium during the discharging process. Echoing Liedel’s approach with his organic cathode materials, Oschatz therefore had to combine his polymer with soot in order to obtain a suitable electrode material. Specifically, the researchers in Potsdam do this by coating extremely thin carbon threads with their carbon/nitrogen polymer. Following initial testing, Oschatz says that the storage capacity of their material is already relatively good for sodium.

Unlike Liedel, however, Oschatz doesn’t just have batteries in his sights. The porous, nitrogen-rich carbon polymer has apparently also proven to be an effective catalyst material for the energy-efficient synthesis of ammonia. With regard to other environmental applications, Oschatz says that, because the pores are good at capturing carbon dioxide molecules in particular, the material also makes an effective CO₂ filter for processes such as flue gas scrubbing.

Even in terms of electricity storage, biobatteries are not the only application that the chemist envisages. Oschatz also wants to use highly porous carbon as an electrode material in supercapacitors, which provide very fast access to



Top No superficial matter: Milena Perovic and Martin Oschatz prepare for a measuring procedure that allows them to determine the surface area of carbon materials. The device determines how much gas can be absorbed by four samples held in cooling vessels.

Above A tidy job: before the surface area is measured, the samples are heated in a vacuum to remove volatile substances that would distort the analysis results.



Food for thought: Clemens Liedel and Martin Oschatz discuss new ideas with a view to developing more sustainable materials for energy storage devices.

the energy they store. In addition, capacitors generally have a much longer service life than batteries, although the amount of energy they can store was also much smaller until now. Supercapacitors are already found in applications where large quantities of electricity are required at short notice – for example, when starting up a streetcar. Some automobiles also use supercapacitors for energy recovery during braking.

The capacitors that Martin Oschatz deals with store electrical energy in the form of an electric field – that is, by loading up two electrodes with opposite charges. To balance out the charge, oppositely charged ions from an electrolyte accumulate at the respective electrodes. How much charge a capacitor stores, and how quickly it charges or discharges, depends on how many ions the electrodes adsorb and release and how quickly they can do so.

The activated carbon typically used in many current supercapacitors already has plenty of contact with the outside world, providing a specific surface area of around 1,500 square meters per gram. But Oschatz wasn't going to settle for that. "Because of the manu-

facturing process, the porosity of activated carbon is quite random and completely disordered," says the chemist. He wants a material whose surface structure is clearly defined down to the nanometer level – that is, to within a few millionths of a millimeter. Moreover, this structure should ensure that, when a voltage is applied, the material can adsorb and release as many ions as possible, as quickly as possible.

A PARKING GARAGE FOR IONS

Martin Oschatz therefore uses an almost pure carbon material with a large surface area and an ingenious pore structure. This proves to be a particularly effective electrode material for energy storage devices. The material can bind to many more ions – and release them again – faster than the nitrogen-containing carbon that Oschatz's group developed for sodium batteries.

The reason why the electrode material is so effective is that it has enough pores along its contact surfaces with the electrolyte to adsorb ions without subsequently blocking others. Oschatz likes to think of it as a sort of parking

garage: "We need lots of streets that serve as access roads, which need to be lined with a sufficient number of parking bays."

To build these nanoscale parking garages, Martin Oschatz's team first uses a special silicate material to create a sort of tiny baking tin with cavities precisely matching the desired structure of the parking garage. The model essentially consists of countless parallel tubes separated from one another by a gap of a few nanometers. The researchers fill the baking tins with a mixture of sugar and salt and then put the whole thing in the oven at about 800 degrees centigrade.

In the absence of air, the sugar is pyrolyzed to leave behind a carbon material, whereas the salt evaporates in the oven to leave behind cavities – that is, the parking bays for the ions. By varying the quantity of salt, the chemists can control the pore size and create parking spaces with dimensions in the order of one nanometer or less. The researchers then chemically dissolve the baking tin, leaving behind a vast number of carbon rods connected to one another by small bridges. "The empty

spaces between the rods are then our streets,” says Oschatz. It is through these streets that the ions reach their parking spaces.

LOWER COSTS PER STORED KILOWATT HOUR

With this specially designed porous structure, the researchers can now achieve specific surface areas of up to 3,000 square meters per gram – the equivalent of half a football field in a few granules of carbon. To determine the surface area, they use an instrument that measures how many particles of a gas bind to a specific quantity of their materials. From this, they can derive the specific surface area of their substances.

Of course, they have already taken measurements to determine how quickly their material charges and discharges again. “We’ve had some samples that we could charge and discharge ten times faster than activated carbon,” says Oschatz, adding that the storage capacity also exceeded that of previous electrode materials.


Sebastian Pohlmann is also observing these attempts with interest. Pohlmann is in charge of material and cell development at Skeleton Technologies, the only manufacturer of supercapacitors in Europe, and is working on electrodes with improved properties at the company’s Grossroehrsdorf location. “In this context, it’s very important to bring greater order to the structure of the porosity,” he says.

And what about sustainability? On first inspection, sucrose – one of the essential starting materials – appears to offer a similar degree of renewability to the lignin that Clemens Liedel used to prepare vanillin. “Of course, sucrose is a foodstuff first and foremost,” Oschatz admits, but he is keen to emphasize that, “as a raw material for electrodes, the substance is still much more sus-

tainable than, say, lithium or cobalt.” He believes that the environment also stands to benefit from the development of materials with especially high specific energy and long service lives.

Markus Antonietti is also enthusiastic about the results obtained so far. He leads the Department of Colloid Chemistry – where Clemens Liedel and Martin Oschatz are also researchers – at the Max Planck Institute of Colloids and Interfaces in Potsdam. Antonietti believes that the new materials for supercapacitors will one day pave the way for a significant reduction in the cost per stored kilowatt hour of electricity. In his view, the objective must now be to boost the storage capacity to the extent that these energy storage devices might one day take on the role of existing batteries.

Antonietti also has another vision: “At some point, every household will need a storage battery of its own, and each summer they’ll charge it up with the energy they need for the next winter.” This would involve quantities of energy that simply couldn’t be stored sustainably with today’s batteries. “We therefore need materials that are free of metals – and ideally renewable,” says Antonietti. He’s therefore also pleased to detect a hint of vanilla drifting over from Liedel’s labs from time to time. Of course, future users of these storage batteries wouldn’t get the chance to enjoy this aroma. Once incorporated into a battery, the vanillin would be chemically bound – and therefore odorless. ◀

 www.mpg.de/podcasts/energie (in German)

SUMMARY

- **Current battery systems are based on raw materials that are incompatible with the sustainable expansion of storage capacities.**
- **Max Planck researchers are therefore investigating battery components – such as electrodes, electrolytes, or separators – made from renewable raw materials like vanillin, chitosan, and appropriate ionic liquids.**
- **They are also attempting to increase the specific energy and charging and discharging speed of supercapacitors by developing corresponding electrode materials with a larger surface area and a structure that is as precisely defined as possible.**

GLOSSARY

Anode: Together with the cathode, this is one of the electrodes at which electrical energy is stored as chemical energy and converted back into electrical energy within a battery or an electrolytic or fuel cell. When a battery is discharged, anions – that is, negatively charged particles from the electrolytes – or neutral metal atoms of the electrode material release electrons, which flow to the cathode via an external circuit.

Electrolyte: The conductive medium between two electrodes. It contains ions that ensure the flow of current between the electrodes and that are also involved in the electrochemical processes taking place at the electrodes, such as in batteries.

Cathode: This takes up electrons from the external circuit and transfers them to the electrolyte. It is where metal cations, for example, are converted into uncharged metal atoms.

Separator: A membrane, usually made of a porous plastic, that separates the anode and cathode compartments. It prevents short-circuiting between the two electrodes but is permeable to ions so that a current can flow through the electrolyte.