

Pioneers between the Poles

Batteries have been around for more than 200 years, but their potential is still far from exhausted. **Joachim Maier** and his colleagues at the **Max Planck Institute for Solid State Research** are investigating how nanotechnology can be used to optimize rechargeable lithium batteries.

TEXT **REINHARD LÖSER**

In order to make better use of scarce energy resources, energy must be stored and converted more efficiently. Electrochemistry, which has provided us with batteries and fuel cells, can be of help here, as it allows chemical energy to be converted into electrical energy and vice versa with a high degree of efficiency. In addition, day-to-day life requires small, light, yet powerful rechargeable batteries, for instance in cell phones, notebooks, digital cameras and camcorders. And the challenges are growing: in the future, electrochemical cells will also provide environmentally friendly hybrid or electric vehicles with electricity for hundreds of kilometers.

Rechargeable lithium batteries are currently considered to be promising candidates for this – particularly if they become even more powerful. This is a topic that Joachim Maier, Director at the Max Planck Institute for Solid State Research in Stuttgart, and his colleagues are concerned with. They have

already made quite a bit of progress. Notwithstanding the fact that “the main focus is basic research,” as Maier stresses, they have already made quite a bit of progress on the applied side, as evidenced by a number of patents that are of interest to industry. In the long term, they could possibly even contribute to replacing gas tanks in cars with batteries.

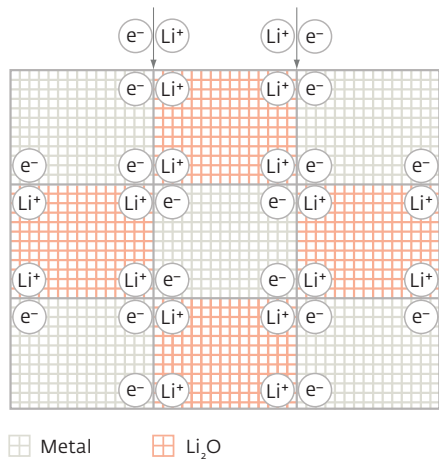
If one wanted to power a standard-range battery-operated car with a lead-acid battery, the battery would weigh about a ton. Lead has a very high specific weight and can thus store only very little energy per kilogram. A metal hydride rechargeable battery is better in this respect, but even it isn't powerful enough for purely electric propulsion. Nickel and cadmium are often used, but they also have a high specific weight. Nevertheless, such a battery already supports the combustion engine of the Toyota Prius hybrid car. However, with only a metal hydride battery, the vehicle wouldn't get very far.



Photo: Corbis

A source of lithium: The Salar de Atacama salt lake in Chile's Atacama Desert yields a salt of the lightest of the alkaline metals, which makes for especially powerful batteries.





Charge separation at close quarters: In an electrode consisting of nanoscopic grains of lithium oxide and a metal, the lithium ions (Li⁺) settle on the surface of the lithium oxide, while the electrons (e⁻) gather at the edges of the metal particles. This accelerates the charging and discharging process.

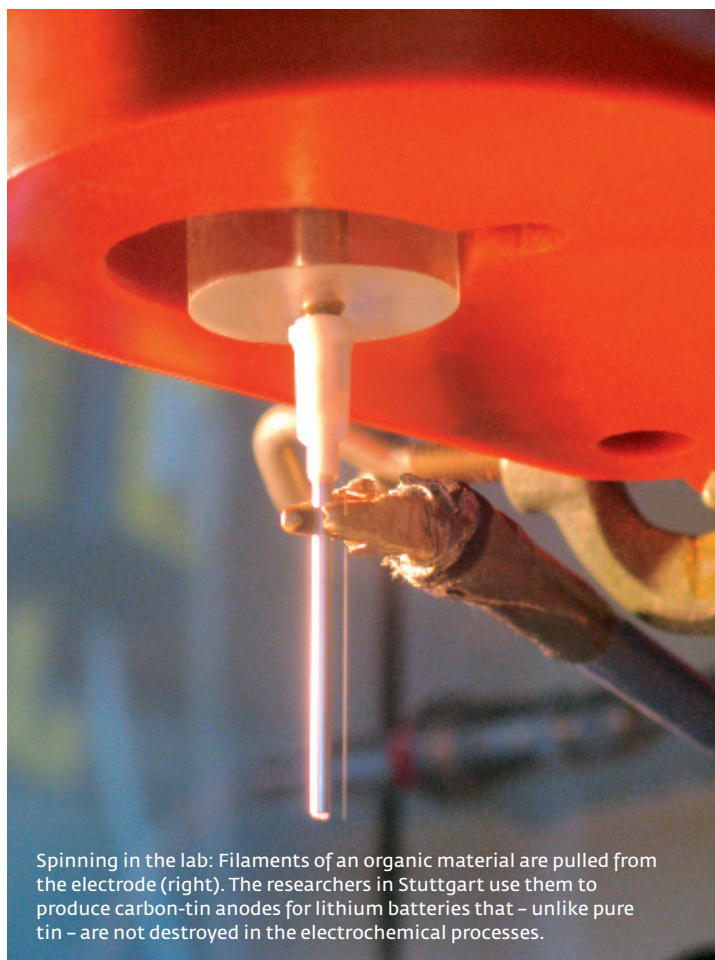
But alternatives are scarce: “From an electrochemical point of view, the molecular mass and other specific characteristics limit the selection of the elements and compounds for electrolytes and electrodes, as do toxicity, availability and costs,” explains Joachim Maier, describing the challenges.

Lithium lends itself well as the main component of a battery because it promises very high cell voltages, as well as high energy and power densities per mass. Why this is so can be seen from the periodic table of the elements: the small atoms of the lightest alkali metal – with an atomic number of three, it comes right after hydrogen and helium in the periodic system – are particularly mobile and can be accommodated in solids in large amounts.

The special position of the element in the periodic system means that lithium likes to donate electrons. If it is connected to a partner that readily accepts electrons in a galvanic cell, a high voltage – three, four or even five volts – is generated in the cell. But even five volts are nowhere near enough to power an automobile – several hundred volts are needed. This can be achieved with a battery consisting of many galvanic cells connected in series.

IONS MOVE IN ROCKING-CHAIR MODE

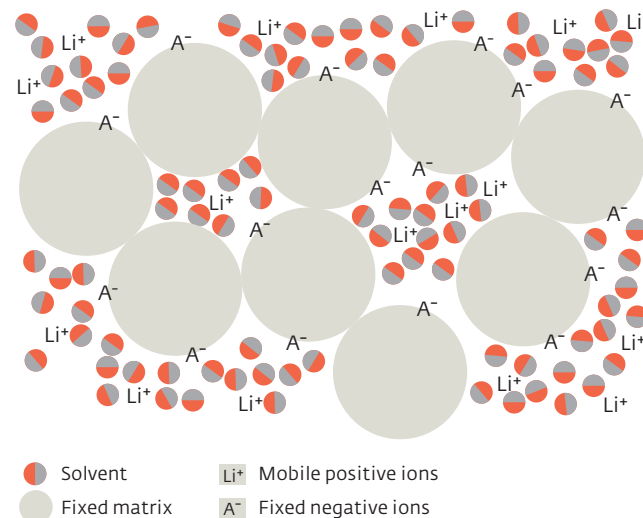
Maier and his team have been working on batteries for almost twenty years and have applied for a dozen patents for their work. They have clarified im-



Spinning in the lab: Filaments of an organic material are pulled from the electrode (right). The researchers in Stuttgart use them to produce carbon-tin anodes for lithium batteries that – unlike pure tin – are not destroyed in the electrochemical processes.

SAND AS AN ELECTRICAL LUBRICANT

Silicon dioxide insulates against electric current, but it can, as an additive to liquid electrolytes, increase the electrical conductivity in rechargeable lithium batteries. The electrolyte usually consists of a solution of lithium salts in an organic solvent. Only solvents that, unlike water or alcohols, do not release protons are an option here – as the latter would react violently with the elemental lithium in the battery. In these solvents, however, only a limited fraction of the positive lithium ions separate from their negative counterparts, which reduces the conductivity. But Joachim Maier and his co-workers discovered that nanoparticles made from silicon dioxide, the main component in sand, can put things right. They mix the nanoparticles with the electrolyte to form “soggy sands.” The silicon dioxide particle adsorbs the negative ions of the lithium salts on its surface. The countless nanoparticles together have a very large surface, thus depriving the electrolyte of a large number of negative ions. This means that, in soggy sand, many more ion pairs are separated compared with a conventional electrolyte. Thus, more lithium ions are available in the electrolyte to transport the current, and the conductivity increases.



In soggy sands, the negative ions are bound to the surface of the silicon dioxide; the number of mobile positive ions is therefore higher.

portant fundamentals for the electrodes – the battery terminals – as well as for electrolytes, the conductive materials that electrically connect the electrodes inside the cell, and have thus created the conditions for technical improvements.

In modern rechargeable lithium batteries, which are also called lithium ion batteries, the lithium ions move, on charging and discharging, in a kind of rocking-chair mode between the two terminal electrodes, accept one electron each, and are stored as neutral lithium. During discharging, the lithium atoms donate these electrons, which can then, for example, supply an electric motor with power. During charging the ions move through the electrolyte back to the negative electrode.

Materials made of carbon or tin, in which lithium readily dissolves, usually serve as the negative electrode, while the positive electrode consists of transition metal oxides, such as lithium cobalt oxide. During charging, lithium from the oxide is pumped into the carbon; during discharge, the process is reversed, releasing the pump en-

ergy again. The electrolytes are predominantly liquid organic solvents containing lithium salts. Crystalline electrolytes, in contrast, have higher mechanical stability and can be shaped. This can be advantageous for technical applications, but they do not possess the necessary conductivity.

SAND IN THE BATTERY BRINGS NUMEROUS BENEFITS

Joachim Maier and his co-workers have now found a way to improve liquid electrolytes. They mix the liquids with very small particles of solid, surface-active ceramic oxides, such as silicon oxide – the main component of sand – or titanium dioxide. The researchers call the mixtures thus produced “soggy sand electrolytes” – almost solid, moldable materials that are easy to process. In addition, the ceramic oxide particles even improve conductivity. “When we predicted this theoretically, many colleagues were fairly surprised,” says Joachim Maier. “We are now able to produce a large number of such materials.”

The soggy sand electrolytes that the Stuttgart researchers have found combine many useful properties. They reduce the internal resistance of the cells, keep the electrodes at a distance, and are less flammable. They can be shaped like solid electrolytes, but their liquid component allows perfect contact with the electrodes.

The scientists were able to improve the electrodes not least due to a fundamental insight: the properties of materials can be improved not only via their chemical composition, but also via their morphology. Morphology is the term materials scientists use to refer to the external appearance of a material. It is characterized by the typical diameters and by the nature of the surfaces. The properties of a material thus also strongly depend on whether it is processed in bulk, as a thin layer or in the form of nanoparticles. “New compounds and structures open the door to a world of new properties,” says Joachim Maier, “and with the right ingredients and clever tricks, we can then optimize these properties.” >



In this context, the Stuttgart-based scientists have researched a new storage mechanism that combines the advantages of electrostatic storage in the capacitor with electrochemical storage in the battery. The capacitor – in its simplest form, two oppositely charged metal plates – quickly releases its charge, but its capacity is exhausted just as quickly. A battery, in contrast, has a high capacity to store charge, but is sluggish when charging and discharging.

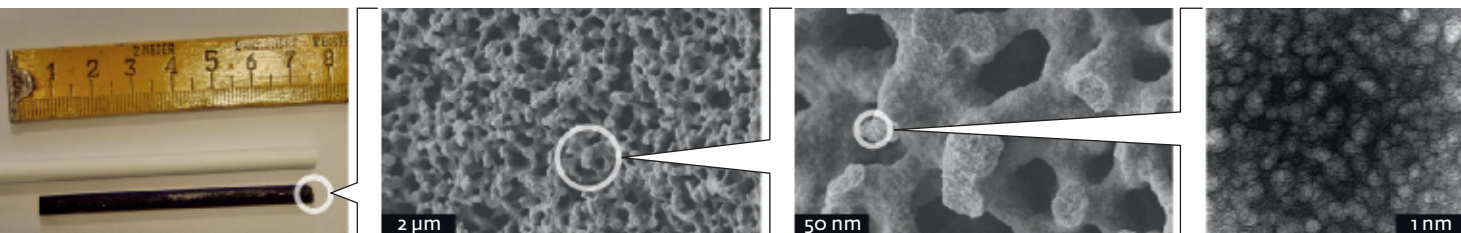
CAPACITOR IN NANOFORMAT

Combining speed and large storage capacity sounds like squaring the circle, because large capacities usually require long transport paths and thus long charging periods. From theoretical investigations, however, the researchers in Stuttgart concluded that a new type of mechanism can solve this problem. Lithium, namely, can be stored in the interface between two materials, neither of which would be able to store it by itself.

The researchers use lithium oxide and ruthenium to produce a nanoscopic powder mixture that acts as the negative terminal of a battery. Ruthenium can accept only electrons, and lithium oxide only lithium ions. Elemental lithium cannot penetrate into either of the two substances. The ions, however, can accumulate on the lithium oxide side of the interface with the metal, and the electrons collect on the ruthenium side.



Joachim Maier presents a product of basic research: The particularly conductive soggy sand. It looks like a gel and it is a gel – a mixture of nanoparticles in a liquid.



The hierarchy of pores: In an electrode of mesoporous carbon, the cavities become ever more finely branched. The lithium ions quickly penetrate them as a result.

The charge is then stored in a separated state as in a capacitor, and it can discharge as quickly as from a capacitor. The same mechanism accelerates the charging process, but the nanostructured electrodes can store a substantial amount of charge, like conventional battery electrodes.

SHORT DISTANCES FOR IONS

The charging and discharging process can also be accelerated with mesoporous carbon electrodes. Since their pores are constructed hierarchically, the transport paths of ions and electrons are shortened: just like air through the bronchial tubes, the ions and electrons travel through a finer and finer branching system of cavities. Joachim Maier is researching materials such as these in collaboration with Markus Antonietti, Director at the Max Planck Institute for Colloids and Interfaces in Potsdam.

In order to investigate the chemical foundations of the energy supply of tomorrow, their institutes have combined with three further Max Planck Institutes to form the EnerChem research association. One result of their combined activities is that the researchers have made use of the mesoporous carbon electrodes to drastically reduce the charging time of rechargeable lithium batteries, allowing rapid charging. Mesoporous car-

bon also has a large capacity, meaning that it can store many lithium ions.

Joachim Maier and his team have recently extended the hierarchical principle to solids, which are poor conductors of not only ions, but also electrons. By providing the material with ever more finely branching nanopores and filling them with electrolytes, they again increase ion availability. This does not, however, improve electron conduction. The researchers in Stuttgart solve this problem with metallization: they superimpose on the tiny pores a metallic transport network through which the electrons readily flow.

Thanks to these advances, the chances are increasing that insulating materials are going to become the future cathodes in lithium batteries. Lithium iron phosphate is the secret favorite of manufacturers because, theoretically, it allows a high energy density to be achieved, and it is low in cost, safe and environmentally friendly. So far, however, the material has one key disadvantage: it is a very poor conductor of electricity, which makes applications in a battery difficult. The fundamental findings that Joachim Maier and his colleagues have gained could change this. "Modern electrochemistry is so fascinating," says Maier, "because basic knowledge of physical chemistry and its technical application are so close to each other."

MI 1201-4090-BC-JK ◀

GLOSSARY

Rechargeable metal hydride battery

Rechargeable battery with a metal hydride as the negative electrode and nickel oxide hydroxide as the positive electrode.

Electrode

In electrochemistry, they either only supply or drain off electrons, or they participate in a cell reaction themselves. At the anode, a substance releases electrons; during battery discharging, this is the negative pole. At the cathode, electrons are taken up. During battery discharging, this is the positive pole.

Electrolyte

Ionically conducting medium between the electrodes; it prevents chemical short-circuiting and maintains the current flow in a battery by means of ion conduction.

Galvanic cell

Combination of electrodes and electrolyte that serve as a DC voltage source. Named after the Italian physician Luigi Galvani who, in 1780, discovered that a frog's leg twitches when it comes into contact with iron and copper. The reason for this – the electric current that flows between the metals through the leg – was not yet known to him at the time.

Capacity

The electric capacity indicates how much charge a system can store per voltage. It is measured in farads, named after the English scientist Michael Faraday. For rechargeable batteries, the capacity is generally identified with the charge itself.