The authors team of the Department of Functional Materials

Process technologies for new solid electrolytes

Innovations for the lithium-ion battery of the future

Constructing the cell of a lithium-ion battery and testing it (Photo: Christian Wißler).

These days, primary batteries and accumulators – the latter can be recharged and are also called secondary batteries – are ubiquitous. The spectrum of applications ranges from simple devices such as watches, remote controls, and battery-powered tools, to smartphones, tablets, e-bikes, and electric vehicles, to off-grid decentralised power supply units.

Depending on the application in which they are later to be used, batteries have different characteristics which largely determine their suitability. First and foremost, however, safe operation is essential for all battery types. Here, the prevention of spontaneous combustion and the toxicity of the materials are two important parameters. In addition, batteries must also meet the requirements of their respective applications with regard to the following parameters:

- Energy density:
  gravimetric: the ratio of storable energy to battery weight
  volumetric: the ratio of storable energy to battery volume

- Power density:
  gravimetric: the ratio of the retrievable power to the weight of the battery
  volumetric: the ratio of the retrievable power to the battery volume

Accumulators in smartphones, for example, ideally contain sufficient energy to ensure long periods of operation while taking up as little space as possible. Accumulators for electric cars, on the other hand, not only require a high energy density but also a high power density so that energy can be quickly stored or retrieved. In addition, accumulators must have a long service life – both in terms of storage (calendar service life) and of frequent charging and discharging (cyclic service life). Because the numbers of electric vehicles are constantly increasing, it is assumed that demand for battery storage capacity will increase sharply in the medium term (Fig. 1).

In order to be able to meet future requirements in terms of energy and power density as well as high demand, many fundamental innovations and major improvements will be necessary. In the first place, these will concern the material systems used, then the design of the battery cells, and finally the level of the overall system.[1] After all, the finished battery is competing with other energy storage devices on the market. Costs for the consumer will therefore remain a decisive factor. These in turn depend directly on processing costs, availability, recyclability and above all on the prices of the materials used.

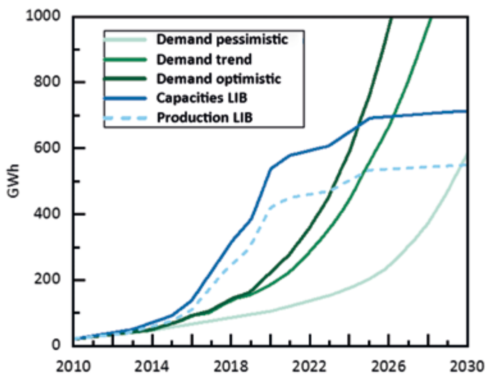


Fig. 1: Forecast development of global demand, capacities and production of lithium-ion batteries up to 2030.[2] (Illustration: Dominik Hanft).

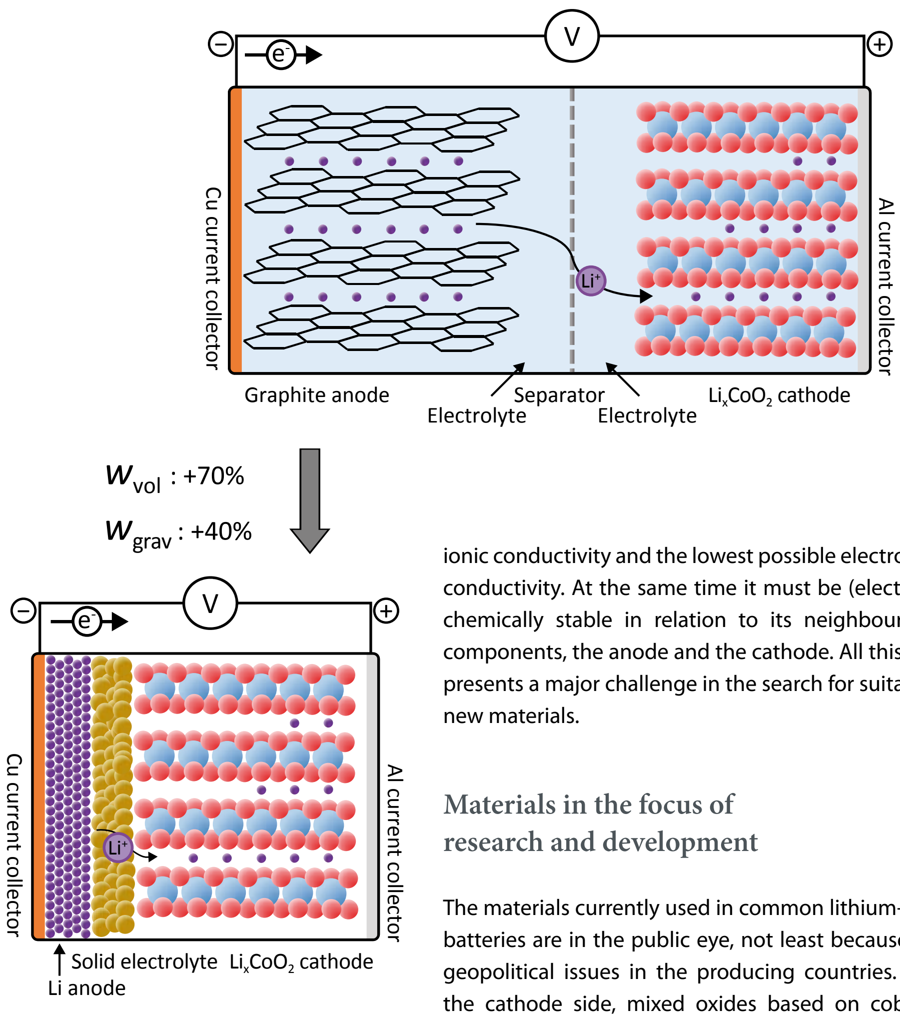
„Ceramic solid electrolytes often have a very wide range of electrochemical stability.“

Lithium-ion batteries

A conventional lithium-ion battery (LIB) contains – in simplified terms – four components: The two electrodes, the cathode on the one hand and the anode on the other, consist of two different energy-storing materials. Between them there is a liquid electrolyte and a separator. The latter ensures that the electrodes have no direct contact with each other, which would lead to an internal short-circuit. To discharge the battery, a contact is established between the electrodes via electronic current collectors so that electrical current flows from the anode to the cathode. At the same time, an ionic current flows inside the battery from the anode to the cathode. Besides the electrode materials, the electrolyte also has a special role to play: it must have the highest possible

AUTHORS

The authors team of the Department of Functional Materials: Prof. Dr.-Ing. Ralf Moos, Dipl.-Ing. Tobias Nazarenus, Yannick Jännsch M.Sc., Dr. Martin Hämmerle, Dr.-Ing. Jaroslaw Kita, and Dipl.-Ing. Dominik Hanft (from left to right).



■ *Fig. 2: Schematic representation of the structure of different battery concepts. Above: Commercial lithium ion cell with $LiCoO_2$ cathode, liquid electrolyte, and graphite anode. Below: Concept of a solid battery with $LiCoO_2$ cathode, solid electrolyte and Li-Metal anode. Compared to conventional cells, solid batteries have significantly higher energy gravimetric and volumetric densities (W_{grav} and W_{vol}) (Illustration: Yannick Jännsch / Tobias Nazarenus, edited by Christian Göppner).*

ionic conductivity and the lowest possible electronic conductivity. At the same time it must be (electro-) chemically stable in relation to its neighbouring components, the anode and the cathode. All this represents a major challenge in the search for suitable new materials.

Materials in the focus of research and development

The materials currently used in common lithium-ion batteries are in the public eye, not least because of geopolitical issues in the producing countries. On the cathode side, mixed oxides based on cobalt, nickel and manganese oxide are frequently used as active materials. The reason for choosing the mixed oxide compound is the high cell voltages that can be achieved with these components, and material prices. Further advantages of mixed oxides are the comparatively large gravimetric and volumetric capacity for rapid reversible storage of lithium ions, high cycle stability and high Coulomb efficiency.

This type of active material is an intercalation material, which, similar to a sponge, can absorb lithium ions when the accumulator is discharged and release lithium ions when it is charging. During the charge-discharge cycles, the skeleton remains intact, and free spaces in the crystal lattice can be filled similarly to the pores of a sponge.

On the anode side, graphite is chosen as state-of-the-art intercalation material. In order to further increase storage capacity on the anode side, silicon particles are added in small quantities during the production of the anode. Silicon has a very high storage capacity, but is associated with a particular challenge: Charging and discharging is accompanied by an extreme change in the volume of the silicon particles. This leads to mechanical stresses and consequently to loss of contact. As a consequence, the more often an accumulator is cyclically charged and discharged, the lower is its energy density and thus also its service life.

A possible alternative to the use of graphite and silicon particles currently being discussed is to use metallic lithium as anode material. In this way, cell voltage could be raised, and the capacity increased significantly. During cyclic operation, the anode would be constantly eroding and reforming. A surplus of lithium can be used there to improve the connection to the current collector.

Meanwhile, solid electrolytes based on polymers or (glass) ceramics are considered to be a promising technology that can enable the commercial realization of metallic lithium as an electrode material. Ceramic solid electrolytes in particular often exhibit a very wide electrochemical stability range, so that decomposition of the electrolyte material at the electrodes will not occur – as is usual with liquid electrolytes. In addition, the use of a ceramic ionic conductor can increase operational safety, since it neither leaks out nor is flammable. Although ceramics have a higher specific weight than liquid electrolytes, this disadvantage can be countered by adapting cell design. In fact, the mechanical stability of ceramics promises to counteract the risk of short circuits. Furthermore, if solid electrolytes were used, self-discharge would no longer be an issue.

New directions in Bayreuth: Powder aerosol-based deposition at room temperature

Although research activities in the field of materials have increased significantly in recent years and although it has been possible to demonstrate the technical functionality of solid-state batteries on a laboratory scale, there is still a lack of process technologies for mass production of lithium-ion batteries with the aforementioned (glass) ceramic solid electrolytes. Indeed, the production of dense ceramic solid electrolyte layers, which are only a few micrometres thick, represents a major challenge for process technology. The aim is to create layers that are less than half as thick as a human hair, which is typically around 60 micrometres in diameter. Conventional ceramic process technology is characterized by high

1 Cf.. T. Placke et al.: Lithium ion, lithium metal, and alternative rechargeable battery technologies: the odyssey for high energy density. J. Solid State Electrochem. (2017), 21, 1939-1964. DOI: 10.1007/s10008-017-3610-7; J. Janek, W.G. Zeier: A solid future for battery development. Nat. Energy (2016), 1, 16141. DOI: 10.1038/nenergy.2016.141.

2 Data according to A. Thielmann et al: Energiespeicher-Roadmap (Update 2017): Hochenergie-Batterien 2030+ und Perspektiven zukünftiger Batterietechnologien. Karlsruhe 2017.

processing temperatures and correspondingly high plant and operating costs.

The Department of Functional Materials at the University of Bayreuth is therefore breaking new ground with a novel ceramic coating process. Powder aerosol-based deposition at room temperature (Aerosol Deposition Method, ADM) makes it possible for the first time to produce thick films at room temperature directly from the ceramic starting powders. This spray coating process stands out for enabling the cost-effective production of layers ranging from a few micrometres to several hundred micrometres in thickness. The ceramic particles are accelerated to almost the speed of sound and directed onto the surface to be coated. Here, the particles form a dense nanocrystalline layer. The process is also characterized by excellent bonding to a wide variety of base materials. A unique feature of the process is that, in addition to ceramic and metallic materials, glasses and even plastics can be coated.

This points to some highly interesting applications in the field of battery development: The strong bonding of the ceramic coatings creates the prerequisite for the build-up of the electrolyte layer on the cathode substrate. Furthermore, the almost free choice of process gases and the low process temperatures involved make inert processing of moisture-sensitive and reactive materials highly feasible. This applies to most common solid electrolytes for future lithium-ion batteries. What is particularly promising for the construction of an „All-Solid State Battery" is that a direct connection of electrolyte and cathode is possible without having to consider the coefficients of thermal expansion or the limits of chemical stability at elevated temperatures of the two components.

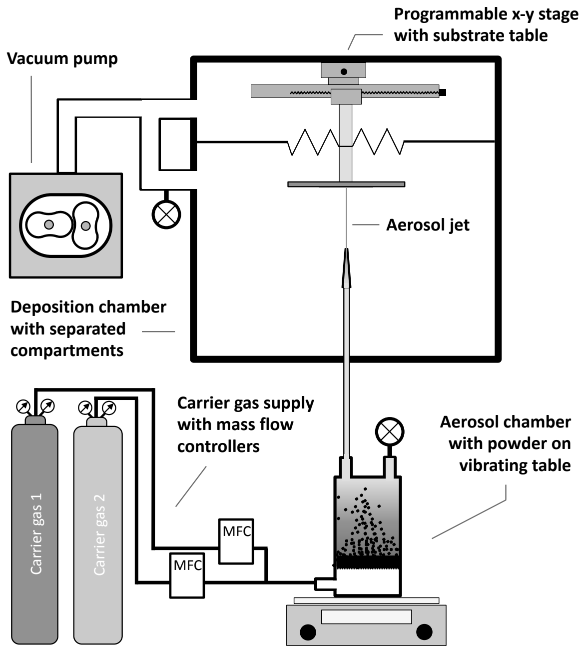


Fig. 3: Schematic representation of an apparatus for powder aerosol deposition (Illustration: LS for functional materials).

Outlook

In addition to research into materials and process technology for novel accumulators, research at the Department of Functional Materials extends to other areas of energy storage and conversion. Materials for thermoelectric generators are being researched that can convert thermal energy directly into electrical energy. In electrochemical CO_2 reduction, electrical energy – for example as excess energy from renewable energy sources such as wind or photovoltaics – is used to produce hydrocarbons from CO_2 in an electrolysis process. In this field, the Department of Functional Materials is researching catalyst materials (electrode materials) and suitable process management to improve yields, selectivity and process stability.

RECOMMENDED READING

D. Hanft et al.: An Overview of the Aerosol Deposition Method: Process Fundamentals and New Trends in Materials Applications, J. Ceram. Sci. Technol. (2015), 6, 147-182. DOI: 10.4416/JCST2015-00018.

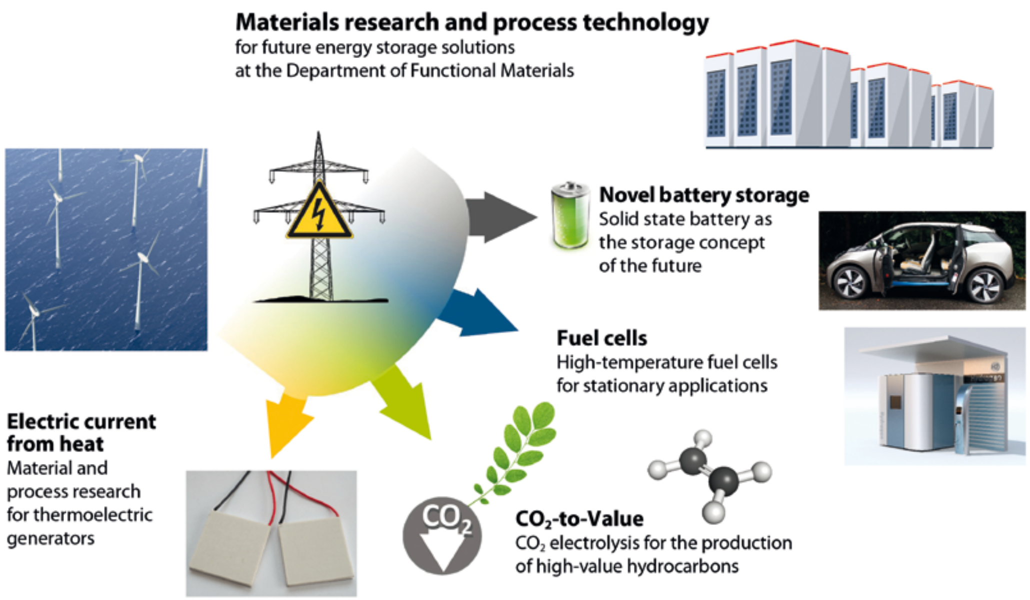


Fig. 4: Spectrum of research at the Department of Functional Materials in the field of energy technology (Illustration: Dominik Hanft, Images: sst).