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FRAUNHOFER INSTITUTE FOR CERAMIC TECHNOLOGIES AND SYSTEMS IKTS

INDUSTRIAL SOLUTIONS

LITHIUM-ION BATTERIES

COVER *Electrode coils.*

1 *IKTS test cell and electrode coils.*

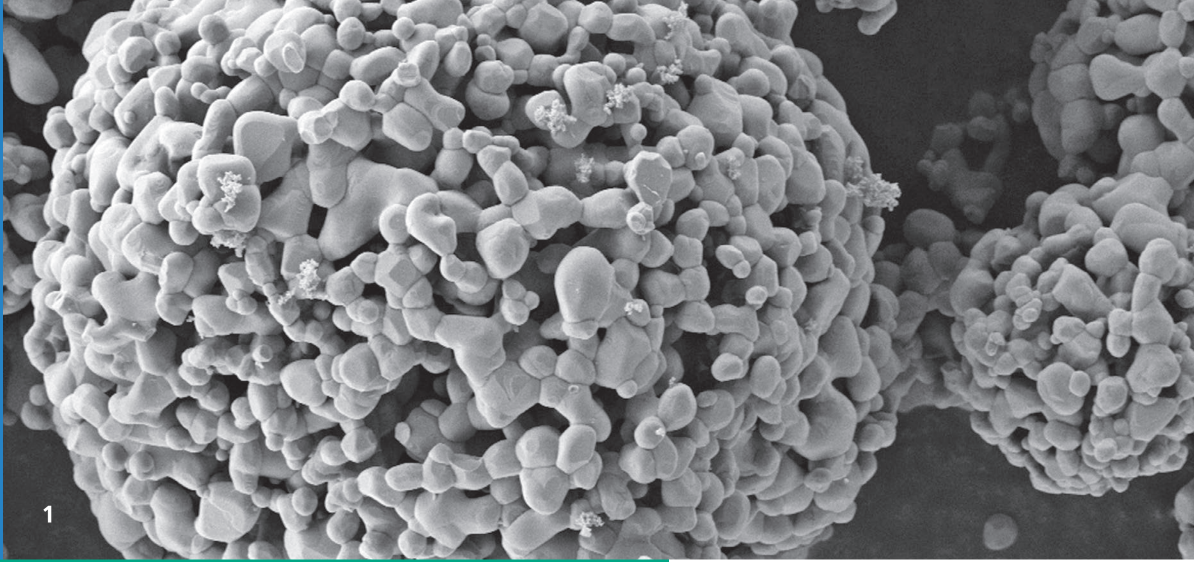
LITHIUM-ION BATTERIES

Ceramic materials and technologies are essential components of today's lithium-ion batteries and will continue to play a key role in the future. At Fraunhofer IKTS, development work is aimed at the pilot scale to ensure a fast transfer of the results from fundamental laboratory research to industrial process development.

Fraunhofer IKTS applies its ceramics expertise towards synthesizing and preparing active materials and separator components, and processing them to form battery electrodes. A variety of methods is available for characterization of the electrode structure, electrochemical behavior, and aging during battery operation. As a result, a thorough understanding of the relationship between production conditions and battery reliability has been gained.

Decades of know-how in development of ceramic materials and technologies as well as in materials analysis and electrochemical characterization ensure that new cost-effective strategies can be established. This involves materials, process, and systems development as well as supply of groundbreaking cell concepts for mobile and stationary applications.

Battery competencies at Fraunhofer IKTS: from material to system



MATERIALS DEVELOPMENT

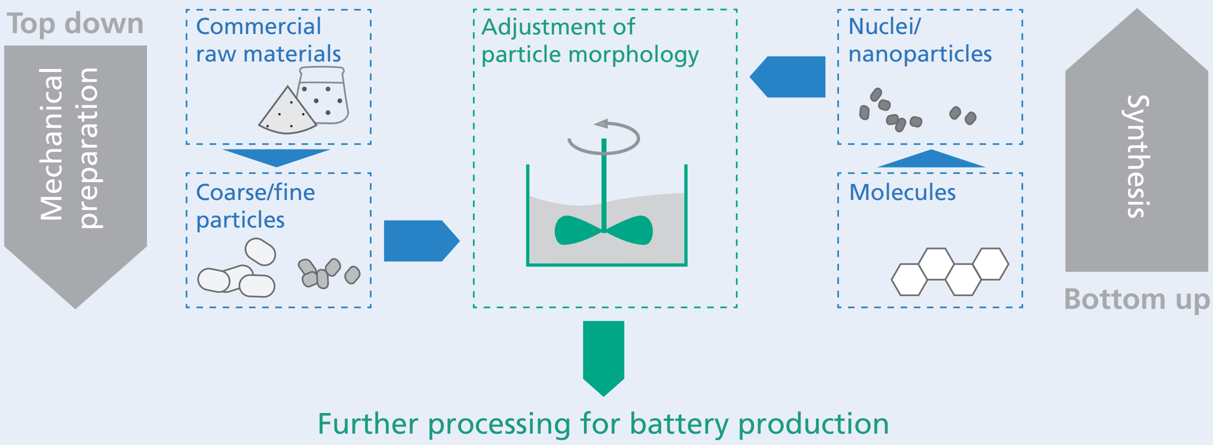
POWDER SYNTHESIS AND PREPARATION

Development of competitive lithium-ion batteries starts with the synthesis and preparation of tailored powders (active materials, ceramic electrolyte and separator materials). As cathode costs constitute around a third of the overall cell material costs in the current generation of lithium-ion batteries, demand-specific, scalable synthesis routes are essential for lowering costs. In addition, the production methods are key to achieving further increases in specific storage capacity, cell voltage, power density, and service life. This in turn requires precise control of particle size and morphology.

At Fraunhofer IKTS, two process routes are taken. With the top-down approach, commercial powders are reduced to the desired size using mechanical preparation processes and are then classified. In the bottom-up approach, particle size, distribution, and morphology are already adjusted to the appropriate levels during synthesis of the primary particles (0.1–50 µm).

Besides the classic solid-state reactions and spray drying-based methods utilizing precursor compounds, sol-gel methods under normal pressure as well as hydrosyntheses and solvothermal syntheses with microwave-assisted reactors are employed. High purities and inert process conditions are required for the resultant primary particles to be processed to yield homogeneous powders with well-defined functionalities. For the production of active mixtures, powders with precisely defined granule morphologies, sizes, and compositions as dictated by the respective applications, e.g., for high-power and high-energy electrodes or for solid-electrolyte cell concepts, are needed.

Process steps for powder synthesis and preparation



ACCOMPANYING ANALYTICS

Fraunhofer IKTS offers all processes for modification, tailoring, and characterization of the properties of battery powders (5–100 µm) and their chemical precursors. With the equipment and experience available at Fraunhofer IKTS, small quantities of up to one kilogram to pilot-scale quantities of several hundreds of kilograms can be handled.

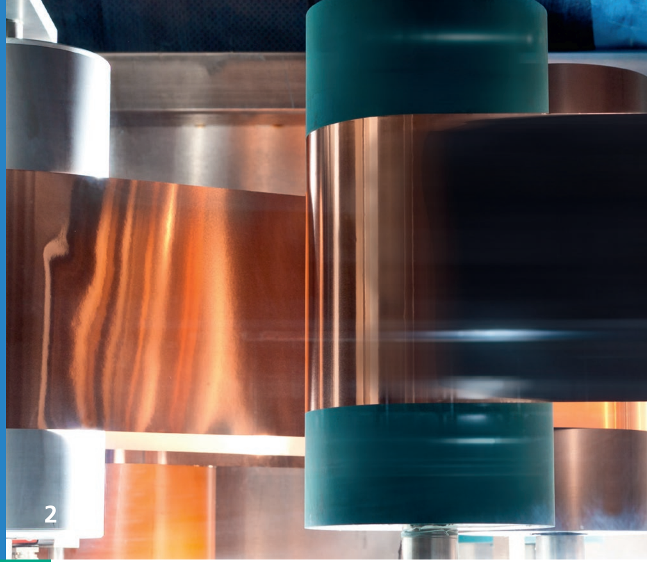
Microscopic materials behavior, aging, and degradation as well as the influence of the production technologies exhibit mutual dependencies throughout the entire battery development and production process. Hence, measurement-assisted evaluation of the powder-based battery components over the course of the process delivers useful information for targeted process analysis, monitoring, and optimization.

At Fraunhofer IKTS, state-of-the-art equipment and a comprehensive portfolio of highly modern analysis methods are available. Apart from standard analysis methods, such as FESEM, TEM, XRD, EDX, Raman spectroscopy, and IR spectroscopy, a number of special techniques can be used. In the last few years, Fraunhofer IKTS has established ion beam-based preparation methods (FIB/BIB) that enable delicate samples, such as granules, electrodes, or pre-sintered components, to be prepared in such a way that the internal structures and the microstructure can be imaged with high resolution and no artifacts. Thus, it is possible to visualize the distribution of solid materials and organic components like binder over the sample cross section. With this information, process technologies can be optimized and degradation mechanisms investigated.

Direct transfer of samples in a protective gas atmosphere from the glove box to a scanning electron microscope or an X-ray diffractometer for subsequent analysis is also possible at Fraunhofer IKTS. Reaction of the materials with air and the resultant changes of material properties are thus prevented.

1 *Tailored cathode powders produced at Fraunhofer IKTS.*

2 *Analysis of the battery materials at the scanning electron microscope.*



TECHNOLOGY DEVELOPMENT

SLURRY PREPARATION

In the conversion of the starting powders to a homogeneous slurry, all components must be adapted to the applied coating process and the desired electrode properties. In doing so, Fraunhofer IKTS draws on its expertise in ceramic technologies. The active materials define the capacity, while the conductive additives are decisive for the electrode resistance. In addition, the organic binder materials used essentially determine the later mechanical stability of the electrodes, the processability, and the cycling stability.

Fraunhofer IKTS utilizes various mixing units, such as dissolvers, planetary mixers, and kneaders, for tailored slurry preparation. During processing, parameters such as energy input, temperature control, particle stability, atmosphere, and mixing duration determine the degree of dispersion. At the end of the mixing process, coordinated process routes ensure a homogeneous particle distribution in the slurry and they prevent reagglomeration.

Fraunhofer IKTS focuses on substituting organic solvents with water-based solvents and reducing the solvent content to maximize the environmental friendliness of the production process.

ELECTRODE PRODUCTION

Doctor blade, comma bar, and slot die casting as well as various drying methods are used in the development of electrode coating processes. Batch processes, such as screen printing and mask extrusion, enable a flexible design of electrode geometry.

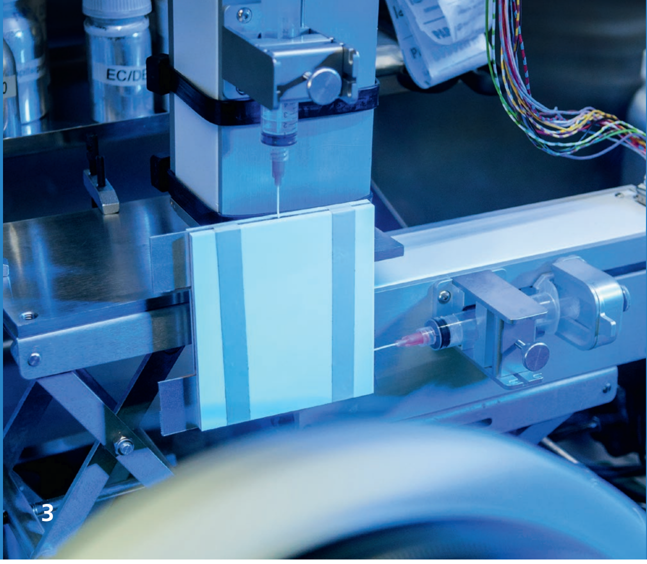
Selection of suitable process parameters during electrode manufacturing can dramatically improve long-term stability and performance, and it can yield advantages with respect to cost-effectiveness, quality, and speed. Focus is on the following:

- Optimum adhesion and binder distribution after drying
- High coating speeds
- Surface quality (no blowholes or particles)
- Prevention of gas pockets
- Minimal fluctuations in layer thickness

Significant cost-saving potential can be realized through optimization of temperature profiles in the drying zones and monitoring of the electrode drying process. However, these energy savings should not have an impact on adhesion, morphological properties, electrode quality, and process speeds. The final electrode porosity is defined through the subsequent calendering process.

1 *Mixing and strip coating.*

2 *Electrode coating.*



ELECTROLYTE FILLING

The process times for the elaborate filling process used for lithium-ion battery cells and the long times required for penetration of the electrolyte into the separator and the electrodes still represent a huge cost factor in battery production and are closely related to the design of the electrodes and to the electrode-separator assembly. Homogeneous distribution of the electrolyte in the cell is also a prerequisite for reliable formation and cell life.

Penetration behavior of the electrolyte in the cell is controlled by numerous factors, the most important of which are the wettability of the electrodes and the separator as well as the capillary forces in the separator membrane and at the interface between the separator and the electrodes. An electrochemical method for determining the correlations between the structure and the properties in separator-electrode systems was developed based on extensive knowledge of the viscosities, surface tension, and pore structures of the electrode and separator materials. The method also allows monitoring of the penetration progress, which enables the penetration behavior of separators, electrodes, and assemblies made up of separators and electrodes with electrolytes to be described in a systematic, quantitative manner.

TEST CELLS AND CELL DESIGN

Both coin and laboratory pouch cells are used at Fraunhofer IKTS for preliminary characterization of developed materials and processes. The manufactured electrodes are stamped out according to the later cell format, tailored, and dried to a minimal residual moisture level. Subsequent cell assembly and electrolyte filling are performed in glove boxes in an argon atmosphere.

After functional testing and formation, the cells are subjected to various tests. Pouch cells up to 5 Ah can also be manufactured in cooperation with thyssenkrupp System Engineering GmbH in a joint pilot-scale facility.

Apart from assembly of test cells, conceptual design is performed for developing cell designs adapted to specific application requirements through coordinated development of materials and processes.

Development work centers around bipolar lithium-ion batteries, with emphasis on such aspects as the properties of the bipolar electrodes, interactions with downstream processes, or adjustment to the electrolyte or other components.

3 *Electrolyte filling investigations in lab-scale.*

4 *IKTS test cell from the pilot-scale battery facility.*

CELL-LEVEL CHARACTERIZATION

ELECTROCHEMICAL CHARACTERIZATION

Electrochemical materials characterization forms the basis for achieving a comprehensive understanding of the electrochemical processes taking place inside a lithium-ion battery. Fraunhofer IKTS has an broad repertoire of electrochemical methods and supplementary measurement procedures for determining the capacity, cycling stability, cell voltage, and impedance of electrode materials for batteries.

One main focus of development work at Fraunhofer IKTS is on methods for complementary measurements during operation. Electrochemical investigations are coupled with spectroscopic, gravimetric, or temperature measurement methods in order to gain detailed information about the processes taking place during charging and discharging of the storage materials.

It is precisely these complementary investigations that allow to establish correlations between the electrochemical behavior of the materials and the material properties of the individual battery components. With a detailed understanding of kinetic and thermodynamic processes as a function of charge state, cycle number, and temperature, it is possible to identify concrete optimization routes. This in turn opens numerous possibilities for targeted materials development and design optimization.

CELL PERFORMANCE AND SERVICE LIFE

Developed materials and technologies can be suitably evaluated via characterization of the cell performance (performance data) and the service life (cycle life and calendar life) of laboratory battery cells. The information gained can also be applied towards evaluation or comparison of performance and applicability of various cell types in connection with post-mortem analyses or for determination of simulation parameters. Fraunhofer IKTS conducts targeted performance tests to investigate the charging and discharging behavior under fluctuating temperatures and to optimize the internal cell resistance.

Lifetime testing is performed with a wide range of defined load cycles in conjunction with aging tests at different temperatures. This yields information on cycling stability as well as long-term stability of the batteries.

Modern battery test stands at Fraunhofer IKTS enable testing and characterization of complete cells up to a capacity of 40 Ah by means of current/voltage measurements and impedance spectroscopy as well as application-specific load cycles.

1 *Cell design for investigation of battery materials by in-situ Raman spectroscopy.*

POST-MORTEM ANALYSIS OF BATTERY CELLS

In the so-called post-mortem analysis, exhausted or defective battery cells are opened carefully in a protective atmosphere and investigated with respect to aging effects, degradation, and failure mechanisms.

This allows the effects of developed materials and technologies or specific operating conditions on aging to be researched. Samples can also be taken in a protective atmosphere for subsequent analytical structural characterization. By means of these samples, the individual electrodes can also be assembled to form button cells and special electrochemical characterization can be performed, e.g., for determination of the lithium loss in the storage material.

Another main application field for post-mortem analysis is investigation of failure mechanisms in defective cells. Manufacturing defects and causes of battery failure can be analyzed on behalf of customers. Information about interactions between cell design, system integration, and operating mode can be derived and thermal battery management optimized.

SIMULATION

Because of the strong interactions between thermal and electrochemical processes, fine-tuned thermal management is the key to the safe and long-lasting operation of lithium-ion batteries. One important aspect of this is the avoidance of local thermal loading inside the battery.

For this, state-of-the-art simulation tools are used for detailed analysis of the effects of structural elements (coil, housing, contact structures) and material-specific parameters on the thermal behavior inside a lithium-ion cell during operation. Thus, they provide a unique in-situ insight into the battery cell conditions, which would hardly be able to be observed directly in real operation.

Possible applications for these simulation models are battery design optimization as well as, e.g., virtual battery labs, specification of cell operating limits in high-performance battery applications, and calibration of rough, real time-capable lithium-ion battery models.

2 *Battery test stand for characterization of IKTS laboratory cells.*

PILOT-SCALE BATTERY FACILITY

FROM LAB TO FAB

For lithium-ion batteries to find widespread use in electromobility and stationary energy storage applications, manufacturing costs must be lowered. Pilot-scale technology development represents a key link between fundamental laboratory investigations and industrial process development.

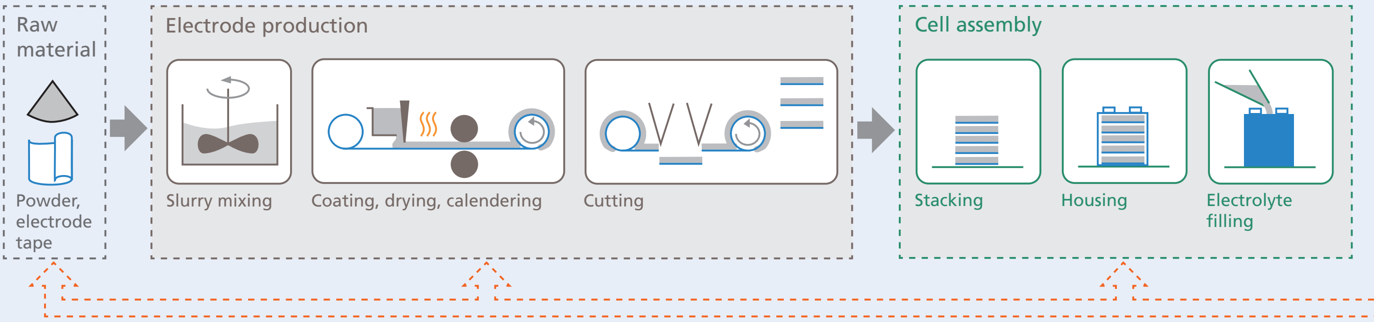
In 2012, thyssenkrupp System Engineering GmbH and Fraunhofer IKTS opened a new 350-m² joint pilot-scale facility at Pleissa, near Chemnitz, Germany. The pilot line is used for connecting research activities and industry value added. The complete production chain, encompassing slurry preparation and characterization, electrode coating, and calendering, cutting of the coated electrode tapes, assembly of the battery, electrolyte filling, and cell formation, is mapped and optimized in a collaborative process.

One core activity is the scale-up and optimization of coating and production technologies for efficient, resource-saving, reproducible mass production of lithium-ion batteries. In addition to existing technological approaches, new methods are considered and adapted for accelerating transfer to industry.

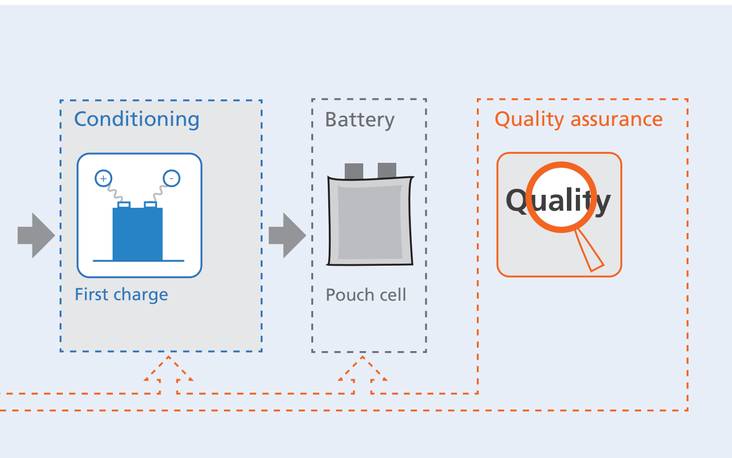
Research partners also address topics, such as in-process tape handling, design of the manufacturing environment, and realization of efficient process monitoring. Efficient process monitoring is crucial for rapidly achieving industrial-scale production capabilities and thus keeping system costs at a competitive level. The partners can draw on their mechanical engineering expertise to adapt production equipment to customer requirements.

Besides being used to conduct publicly funded joint projects, the pilot facility is available to interested industry customers from all stages of the value chain. The joint service offer includes the following:

Process steps for battery production



- Materials testing
- Testing and optimization of established as well as new material and technology concepts
- Development, testing, and optimization of integrated manufacturing concepts
- Scale-up and technology transfer
- Feasibility studies and consulting



IN-LINE PROCESS MONITORING

In addition to performing a comprehensive range of analysis and characterization tasks, Fraunhofer IKTS develops methods for integrated quality assurance for all relevant steps in the manufacturing process. Long-standing experience in the application of non-destructive test technologies is applied towards requirements-based adaptation and integration of optical, acoustic, and electromagnetic methods for individual production steps.

Focus is on critical parameters in the process steps:

- Electrode production (adhesion, strip formation, cut edges, homogeneity, and crack formation)
- Electrolyte filling (filling degree)
- Cell assembly (damage, stacking precision, and welded joints)

A non-contact, thermography-based in-line inspection method for electrode defect analysis during production was developed. With it, pores, cracks, and surface effects can be visualized.

1 *Pilot-scale electrode production for lithium-ion batteries.*
2 *Electrode coils.*

PRELIMINARY RESEARCH

TEMPERATURE MEASUREMENT DURING OPERATION

Current challenges concerning heat generation in lithium-ion batteries can only be met with a comprehensive understanding of the heat-generating processes and mechanisms on a microscopic scale. A special measurement setup was developed to allow for localized temperature measurement across the anode-separator-cathode interfaces in a model lithium-ion battery cell during battery operation with very high lateral resolution. The three-dimensional temperature distribution for defined charge and discharge currents can be reconstructed with the additional detection of the axial temperature gradient.

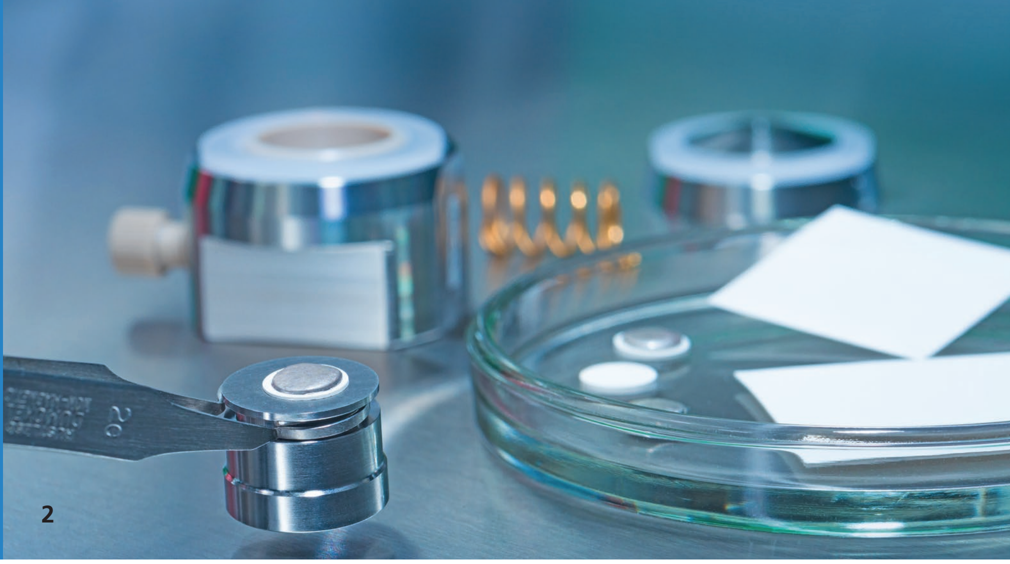
Unlike the usual integral measurements used for commercial battery systems, this allows heat sources and sinks in the electrochemical system to be located, identified, and differentiated between. With localized temperature measurements during operation in combination with advanced electrochemical techniques, light is shed on the complex relationships between the kinetics and the thermodynamics of the individual cell components and the resultant localized heat generation. Based on these findings, mechanistic models are developed and put into the modeling and simulation of the thermoelectrochemical behavior of lithium-ion batteries to form the basis for optimization of the materials with respect to thermal safety aspects.

HIGH-ENERGY CATHODE

One of the central goals of current development efforts is to increase the energy storage density of lithium-ion battery cells, mainly to satisfy the requirements for use in automotive applications. The primary approach taken to achieve this is to optimize the cathode structure and, because it serves as the lithium supplier to the cell, its storage capacity. Optimized cells currently have a capacity per unit area of about 4 mAh/cm^2. This is achieved by using active materials of high storage density combined with increased electrode packing densities. Mass per unit area and electrode density are hence the levers with which storage density-optimized electrode designs are realized. However, restrictions are coming from the processability in downstream cell manufacturing processes (mechanical requirements, electrolyte filling duration) and cell performance during operation (especially rate capability limitations due to limitations in lithium-ion diffusion).

The work of Fraunhofer IKTS deals with laboratory- and pilot-scale extrusion-based deposition techniques, whereby both classic extrusion processes with solids contents of 90 % from ceramics technology and slot die coating with solids contents of 50–70 % show great technological potential.

1 *Micrograph of an LTO-LFP bipolar electrode.*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EMBATT BIPOLAR BATTERY

With the EMBATT battery, Fraunhofer IKTS and partners are pursuing a new approach to achieving system-level energy densities of more than 450 Wh/l and hence making the range of electric vehicles suitable for everyday use. The EMBATT bipolar battery consists of cells stacked in such a way that the deflector on the negative electrode side of one cell serves as the contact to the positive electrode of the adjacent cell. Thus, two electrochemical cells connected in series share the deflectors – one side of the bipolar electrode serves as the anode in one cell and the other side serves as the cathode in the next cell.

The stack design of the bipolar battery concept eliminates the need for elaborate cell packaging. Advantages of the EMBATT battery are the low internal resistance of the stack, the potentially very large electrode surface areas, and a highly simplified joining technology in the battery system. The EMBATT concept hence transfers the high energy density at the cell level directly to the battery system.

A consortium develops the large-format bipolar lithium-ion battery, coordinated manufacturing technologies, and concepts for direct integration into the vehicle chassis. Fraunhofer IKTS has the task of designing the bipolar electrode and efficient manufacturing processes.

SOLID-STATE BATTERY

Lithium-ion batteries with solid-state conductors and lithium-metal anodes are treated as promising next-generation storage technologies due to their higher specific energies as well as their favorable safety aspects.

For many years now, Fraunhofer IKTS has been striving to develop lithium-conducting glasses and solid electrolytes and to integrate these components into the cell assembly. The aim is to derive suitable process technologies for the production of all-ceramic solid-state batteries (in particular composite cathodes and solid electrolyte separators).

The core elements of this are realization of a defect-free, stable electrolyte separator (avoidance of dendrite growth on the lithium-metal anode), compensation for thermomechanical stresses in the composite cathode and in the electrolyte (volume compensation by active material, adjustment of thermal expansion coefficients), and production of a composite cathode with a low residual porosity and with simultaneous avoidance of damaging secondary reactions between the active material and the ionic conductor. To that end, development of manufacturing processes and investigation of suitable combinations of active materials and ionic conductors as well as optimization of grain structures, surface structures, and microstructures are necessary.

2 *Components and characterization of ceramic solid-state batteries.*

SPECIAL TECHNICAL EQUIPMENT

Powder synthesis

- Glove boxes
- Schlenk line
- Spray dryers for precursors (air or inert gas)
- Flame spray pyrolysis
- Pyrolysis furnaces
- Rotary kiln

Powder preparation

- Preparation equipment (milling and homogenization) and peripheral equipment (dispersion containers with heating and cooling)
- Screen units for conditioning
- Laboratory- and pilot-scale spray dryers (air, inert gas, and explosion-proof versions)
- Fluidized bed system
- Spray-freeze granulation unit

Materials characterization

- Mechanical and ion beam-based preparation techniques (broad and focused ion beam)
- Microscopic methods (optical microscopy, confocal 3D laser scanning microscopy, analytical field-emission scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and ultrasonic microscopy)
- 3D characterization (computed and FIB tomography)
- Qualitative and quantitative X-ray diffractometry, including line profile analysis
- High-temperature X-ray diffractometry up to 1200 °C
- X-ray fluorescence analysis
- Micro-Raman and IR spectroscopy

Electrode production

- Coating units (doctor blade, doctor blade against backing roll, and slot die and triple slot die in continuous and intermittent operation)
- Dryer units (passive drying, contact drying, flotation drying, UV curing, and convection)

Electrochemical characterization

- Glove boxes, climate cabinet (-40 °C to 120 °C), and multi-channel potentiostat
- Measuring cells (two- and three-electrode setups) for electrochemical, thermo- and spectroelectrochemical investigations
- FTIR/Raman spectrometers
- Karl Fischer titration for water content determination in solids and liquids

Cell testing

- Battery test containers

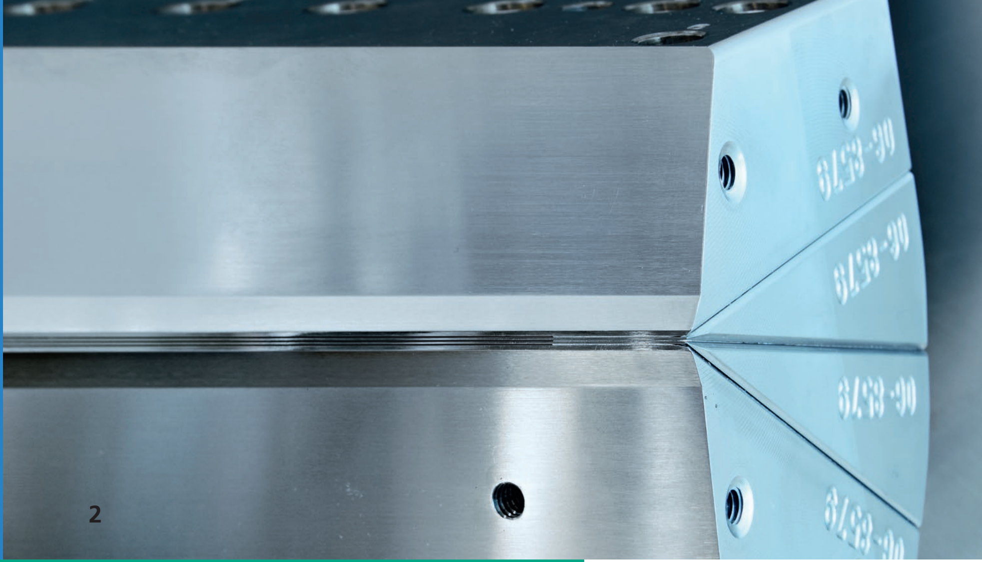
Simulation

- FE codes: ANSYS, COMSOL, and FlexPDE
- CFD codes: Fluent and ANYSY-CFX
- System simulation: Modelica/SimulationX

Quality assurance

- Demonstrator for active thermography on running tape casting belts
- Air-coupled ultrasonic layer thickness gauge for monitoring of tape basis weight

1 *Coater for electrode production.*



COOPERATION MODELS

Innovation and development are the cornerstones of a promising corporate future. In order to create a competitive edge, Fraunhofer offers tailored options for cooperation, so that small and medium-sized companies can work together in the best possible way. This also allows to utilize development skills at short notice and as needed.

One-off contracts

The classic cooperation model is the one-off contract. A company perceives a need for research or development. A discussion with Fraunhofer IKTS identifies possible solutions and clarifies the form the partnership could take and the estimated cost.

Large-scale projects

Some challenges are so complex that they require multiple partners to develop a solution. Clients in this situation have access to the full range of Fraunhofer Institutes. It is possible to incorporate external partners and additional companies.

Strategic partnerships and innovation clusters

Pre-competitive research which starts off without any ties to specific development contracts often results in long-term partnerships with companies on a regional and international level.

Spin-offs

Fraunhofer researchers often take the step towards independence by founding their own company. Fraunhofer itself only participates in these kinds of start-ups up to a certain extent. Sometimes the customer who commissioned the new development is interested in taking a stake in the spin-off company.

Licensing models

Licenses grant third parties the right to use industrial property rights under defined conditions. They provide an option for making use of an innovation in cases where in-house development is prohibitively expensive, capacities are not sufficient for market introduction, or the innovation does not fit into the company's existing range. Fraunhofer IKTS offers flexible licensing models for companywide use, supplementation of the range of offers, or marketing to end customers.

2 *Die on a triple slot die coater.*

FRAUNHOFER IKTS IN PROFILE

The Fraunhofer Institute for Ceramic Technologies and Systems IKTS conducts applied research on high-performance ceramics. The institute's three sites in Dresden (Saxony) and Hermsdorf (Thuringia) represent Europe's largest R&D institution dedicated to ceramics.

As a research and technology service provider, Fraunhofer IKTS develops modern ceramic high-performance materials, customized industrial manufacturing processes and creates prototype components and systems in complete production lines from laboratory to pilot-plant scale. Furthermore, the institute has expertise in diagnostics and testing of materials and processes. Test procedures in the fields of acoustics, electromagnetics, optics, microscopy and laser technology contribute substantially to the quality assurance of products and plants.

The institute operates in eight market-oriented business divisions to demonstrate and qualify ceramic technologies and components as well as non-destructive test methods for new industries, product concepts and markets beyond the established fields of application. Industries addressed include ceramic materials and processes, mechanical and automotive engineering, electronics and microsystems, energy, environmental and process engineering, bio- and medical technology, optics as well as materials and process analysis.

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Industrial solutions
Lithium-ion batteries

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