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FEP

Fraunhofer Institute for
Organic Electronics, Electron Beam
and Plasma Technology FEP

Thin film technology for energy storage media

Vacuum thin film processes for the future of energy storage media

Research on lithium and post-lithium technologies

Electrical energy storage systems are everywhere. Whether in transport systems, electromobility, portable communication electronics or medical aids – powerful, reliable and cost-effective accumulators are indispensable. In most cases, lithium-ion batteries are used.

However, there is still a great need for improvement an optimization, e. g. with regard to:

- Long service life
- Short charging times
- High energy densities
- Increase of safety.

Vacuum thin film processes, a core competence of Fraunhofer FEP, offer a variety of innovative approaches for improving and optimizing a lithium-ion cell over the entire system structure.

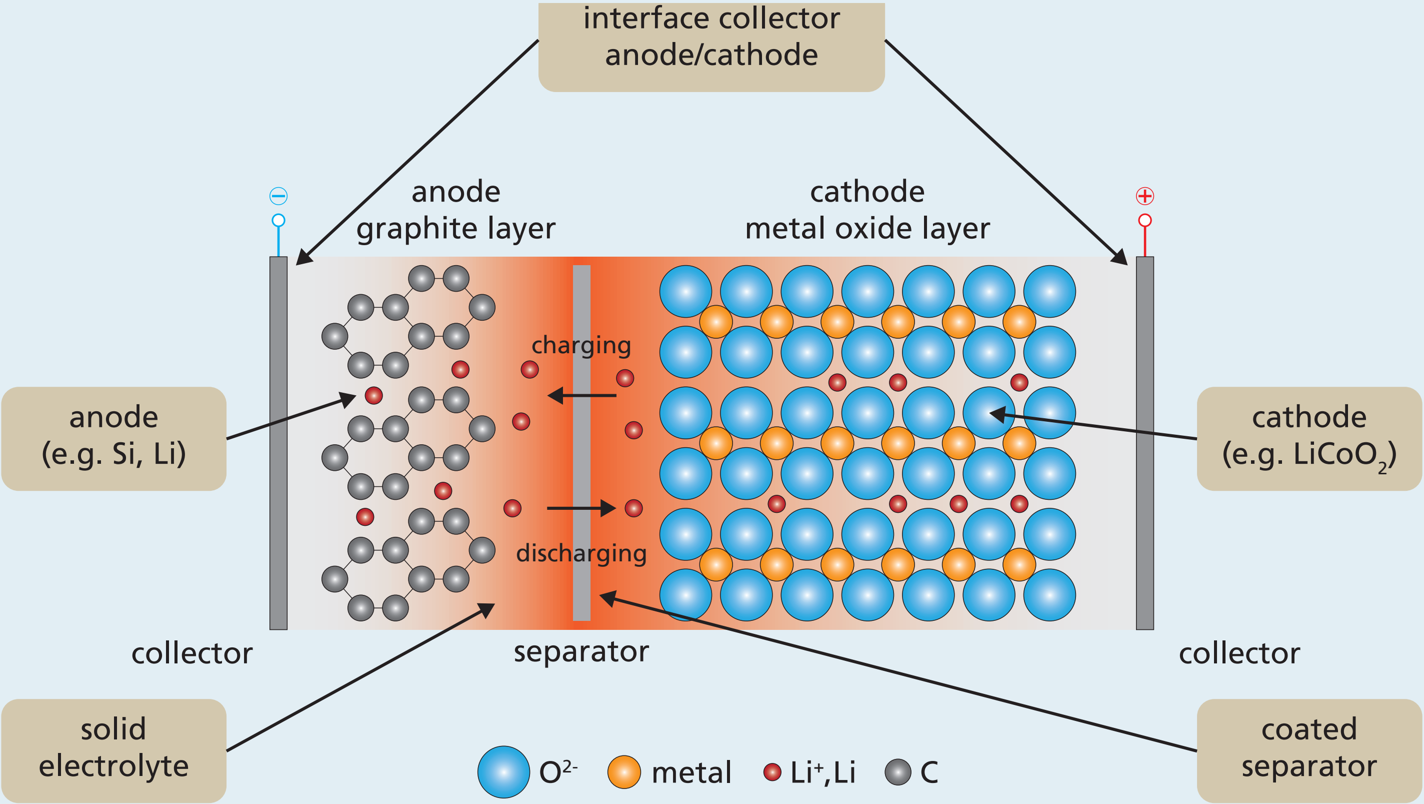
For instance:

- Diffusion barrier coatings
- Anti-corrosion coatings
- Coatings of complex chemical compounds for the realization of active cathode materials
- Metallization of thin polymer films to replace metal films in the field of current conductors
- Deposition of metallic lithium for pre-lithiation or as metallic cathode

The individual approaches, innovative technologies and processes along the construction of a lithium-ion cell are described on the following pages. In addition, we are already researching tomorrow’s technologies for energy storage media beyond lithium.

> »
>
> Our vision is low-cost, high-performance batteries to promote electromobility and support the global energy transmission. We are developing vacuum thin-film processes that make low-cost production of high performance components for batteries possible.«
>
> **Dr. Nicolas Schiller**
> Division Director Plasma Technology, Fraunhofer FEP

Schematic setup of a lithium-ion battery and potential applications for vacuum thin-film processes



Interfaces

APPLICATION

- Interface between current collector and electrolyte or active material and electrolyte.
- Prevent / avoid / reduce corrosion damage to aluminum current collector used by surface coating
- Influence the formation of irreversible boundary layers (SEI – solid electrolyte interface) between active material and electrolyte
- Control internal contact resistances

DEVELOPMENT PARAMETERS

- Coating process for anti-corrosion coating
  - substrate: aluminum foil as cathode contact in a lithium metal polymer (LMP) cell
  - substrate thickness: 30 µm, layer material: e.g. titanium nitride (TiN)
  - Layer thickness of approx. 100 nm, high deposition rate
- Development of coating processes for "artificial" SEI formation between active material and electrolyte.

TECHNOLOGY

- Development of a plasma-assisted high-rate process:
  - HAD (Hollow cathode arc-activated deposition)
  - SAD (Spotless arc-activated deposition)
- Electron beam evaporation of titanium in our in-line vacuum coating line for sheets and metal strips
- Reactive deposition of TiN on foil by additionally introduced nitrogen
- Hollow cathode arc discharge by means of plasma
  - to increase the reactivity of the process
  - to densify the layer structure
- Coating of e.g. $LiCoO_2$ with other oxidic materials (Al_2O_3, TiO_2, SiO_2) or carbon

ADVANTAGES

- Wide variety of materials
- Higher layer quality with very low thickness at the same time

Drops on fleece

Metallized polymer films as current collector

APPLICATION

Metallized polymer films as current collectors represent interesting opportunities to increase both gravimetric and volumetric energy density while improving battery safety aspects and saving scarce resources compared to previously used metal films.

- Thin and lightweight current collectors to increase volumetric and gravimetric energy density
- Replacement of metal foils by metallized polymer foils

DEVELOPMENT PARAMETERS

- Film thickness (base substrate) < 8 µm
- Metal thickness > 1 µm
- Total thickness < 10 µm

TECHNOLOGY

- Roll-to-roll process for film widths > 400 mm and strip lengths > 100 m
- Double side coating with Al or Cu by means of
  - electron beam evaporation
  - cathode sputtering (magnetron sputtering)

ADVANTAGES

- Weight, thickness
- Increasing the intrinsic safety of battery cells

Metallized polymer films

Solid-state electrolyte coatings

APPLICATION

Utilization of vacuum thin film processes for the deposition of solid state electrolyte layers for use e. g. as:

- Sole electrolyte in a thin-film cell
- Ion-conductive protective layer in a conventional cell with liquid electrolyte

DEVELOPMENT PARAMETERS

- Material composition
- Morphology
- Ion conductivity
- Deposition rate

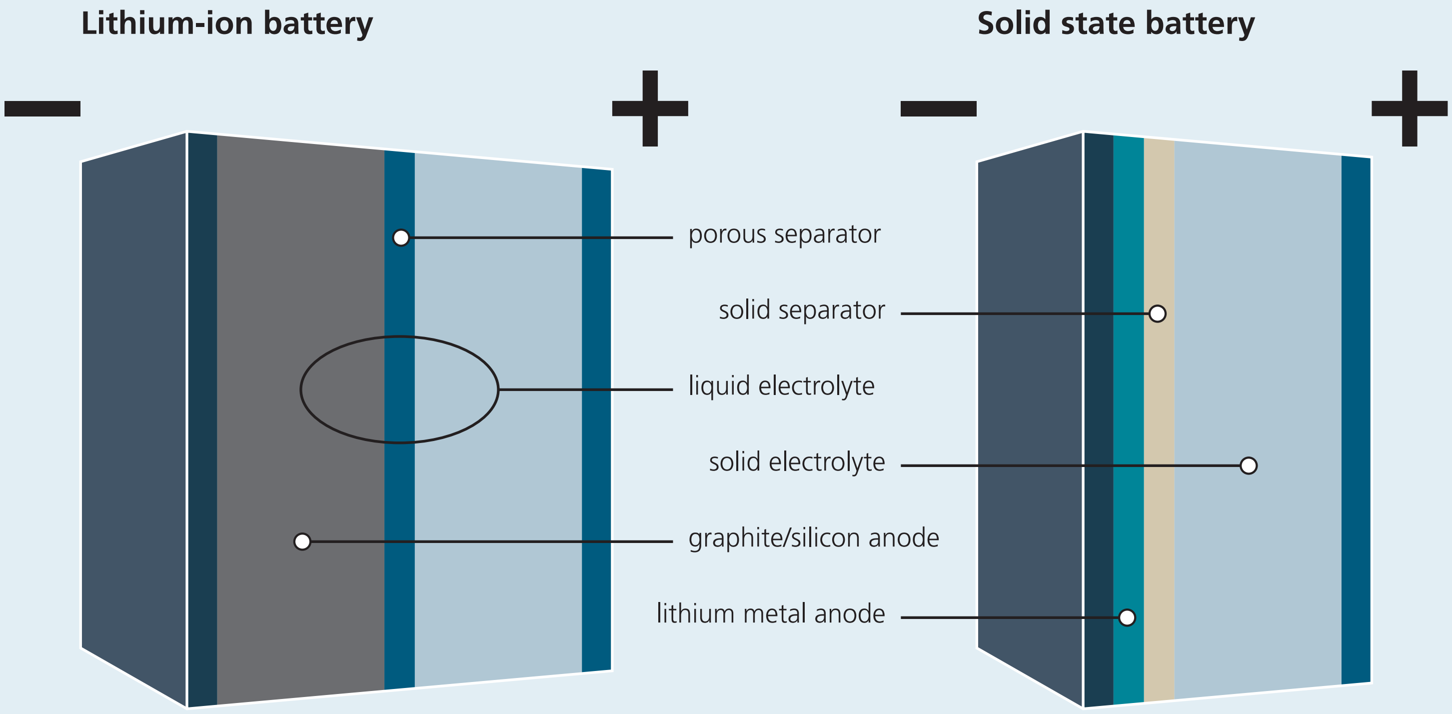
TECHNOLOGY

- Evaporation of lithium phosphate (LIPO) in induction evaporator
- Deposition of lithium phosphorus oxynitride (LIPON) by reactive process control using nitrogen
- Utilization of an intense plasma by hollow cathode plasma sources
- Achieved static deposition rates of 100 to 200 nm/min

ADVANTAGES

- Wide variety of materials
- 10× higher deposition rates compared to sputtering processes

Schematic illustration of a battery



Separators

APPLICATION

Important properties of the separator and its surface such as wettability, ion conductivity or puncture resistance can be influenced by inorganic, partly ceramic coatings. Fraunhofer FEP uses vacuum thin-film processes, for example, to coat substrate materials with SiO_x or AlO_x.

DEVELOPMENT PARAMETERS

- Base substrate: films or nonwoven materials
- Coating material
- Coating rate

TECHNOLOGY

- Roll-to-roll process for film widths > 400 mm and strip lengths > 100 m
- Coating by means of
  - electron beam evaporation
  - magnetron sputtering
  - arcPECVD

ADVANTAGES

- Wide variety of materials
- High deposition rates compared to sputtering processes

Example of a fleece separator

Deposition of active materials on metal foils

APPLICATION

Deposition of active materials using vacuum thin film technology, e. g.:

- Mixed oxides based on lithium and one or more transition metals as a cathode
- Metallic lithium as anode material for solid state cells
- Silicon as active material for the anode

to reduce the safety risk both in production and in the operation of the cell

DEVELOPMENT PARAMETERS

- Material composition
- Morphology
- High deposition rates

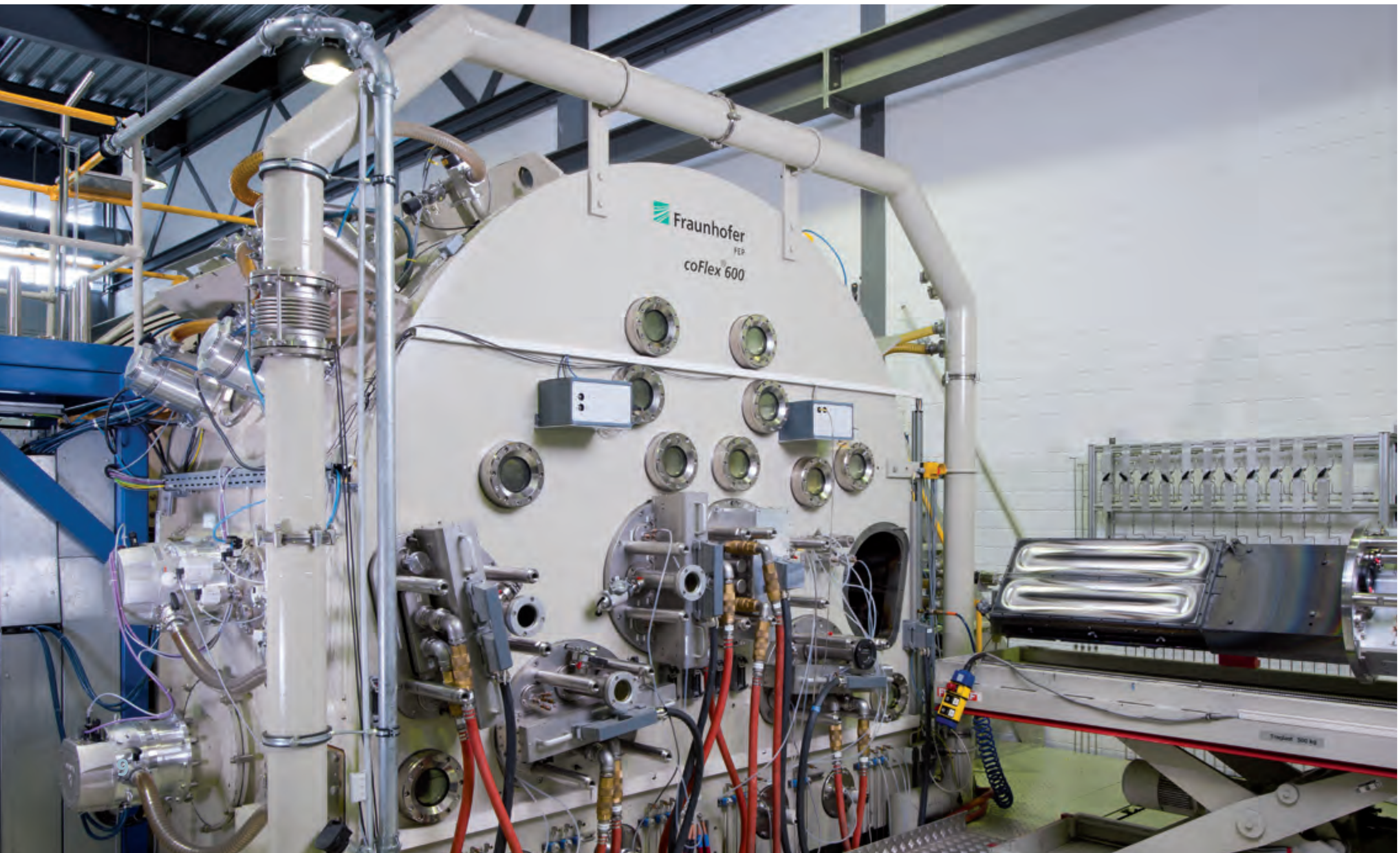
TECHNOLOGY

- Magnetron sputtering
- Thermal evaporation
- Electron beam evaporation

ADVANTAGES

- Wide variety of materials
- Solvent-free processes (dry process)
- Easy control of layer thicknesses and stoichiometries

coFlex® 600 – Roll-to-roll pilot sputter roll coater



Nodular silicon layers by roll-to-roll process

APPLICATION

Pure silicon anodes in lithium-ion cells potentially enable a dramatic increase in volumetric energy density. Porous nodular structures are required to enable high cell cycle stability.

- Growth of silicon in nodular structures to incorporate free spaces in the layer to compensate for volume expansion

DEVELOPMENT PARAMETERS

- Silicon area loading,
  e. g.: 1 ... 4 mgSi/cm² per film side. (corresponds to a geometric film thickness of approx. 5 ... 15 µm)
- Deposition rate
- Porosity

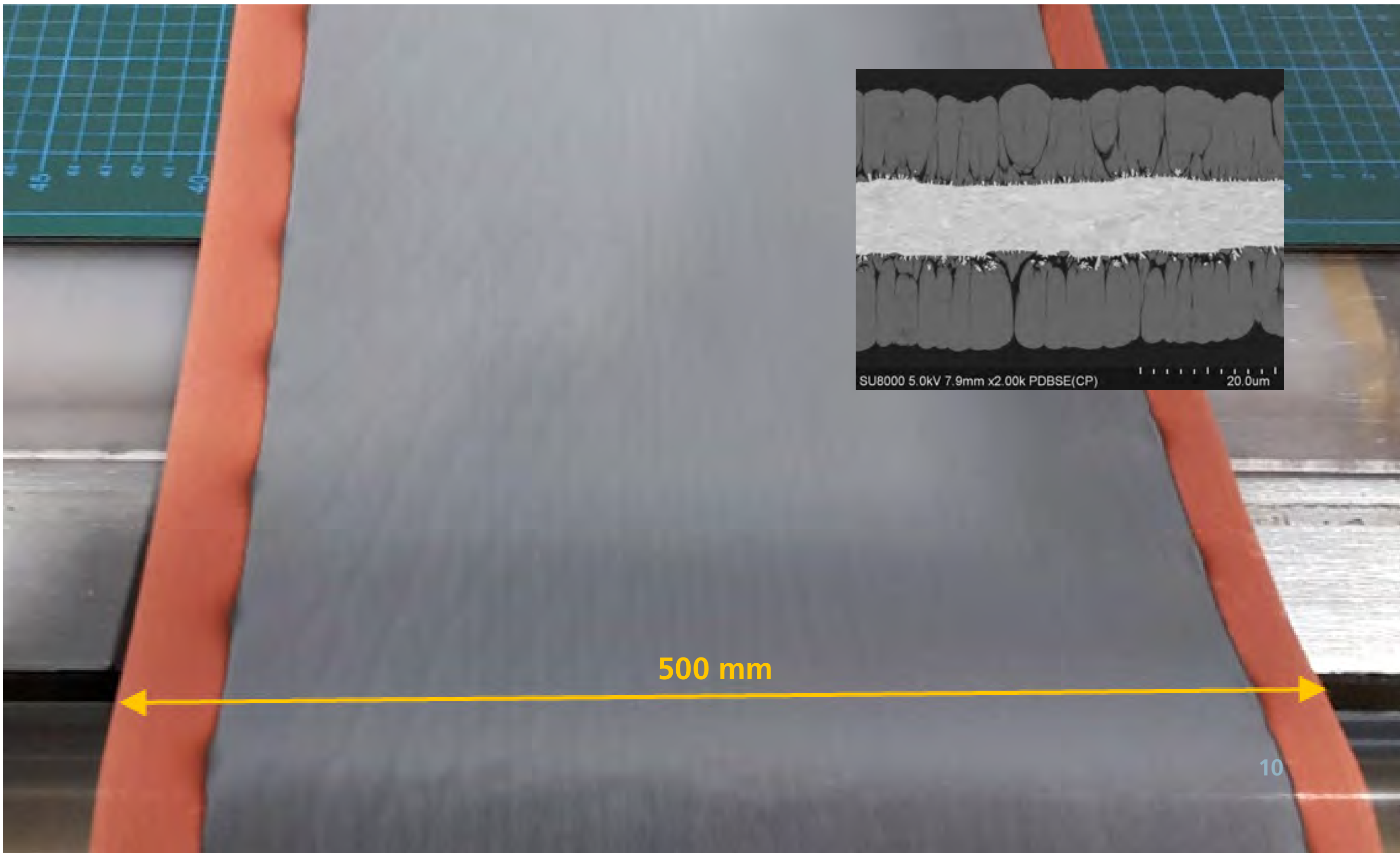
TECHNOLOGY

- Roll-to-roll process for film widths > 400 mm
- Coating by magnetron sputtering
- Electron beam process in preparation

ADVANTAGES

- High charge capacity of porous silicon layers
- Good cycle stability
- Roll-to-roll process

Nodular pure silicon anode on copper foil



Electron beam co-evaporation for porous layer structures

APPLICATION

Porous layers with adapted properties are required, for example, in microelectronics for sensors, actuators and other functional layers with low dielectric constants. In chemistry, porous layers are used for catalysts or for filtration. Due to the large internal surface area of porous materials, the focus is on energy conversion applications such as super capacitors or innovative anodes for lithium-ion batteries. Silicon is a promising material for this purpose, among others. However, a porous Si matrix is needed to compensate for mechanical stresses and volume expansion occurring during the charging process.

DEVELOPMENT PARAMETERS

- Materials used
- Porosity and morphology
- Technology transfer for roll-to-roll processes

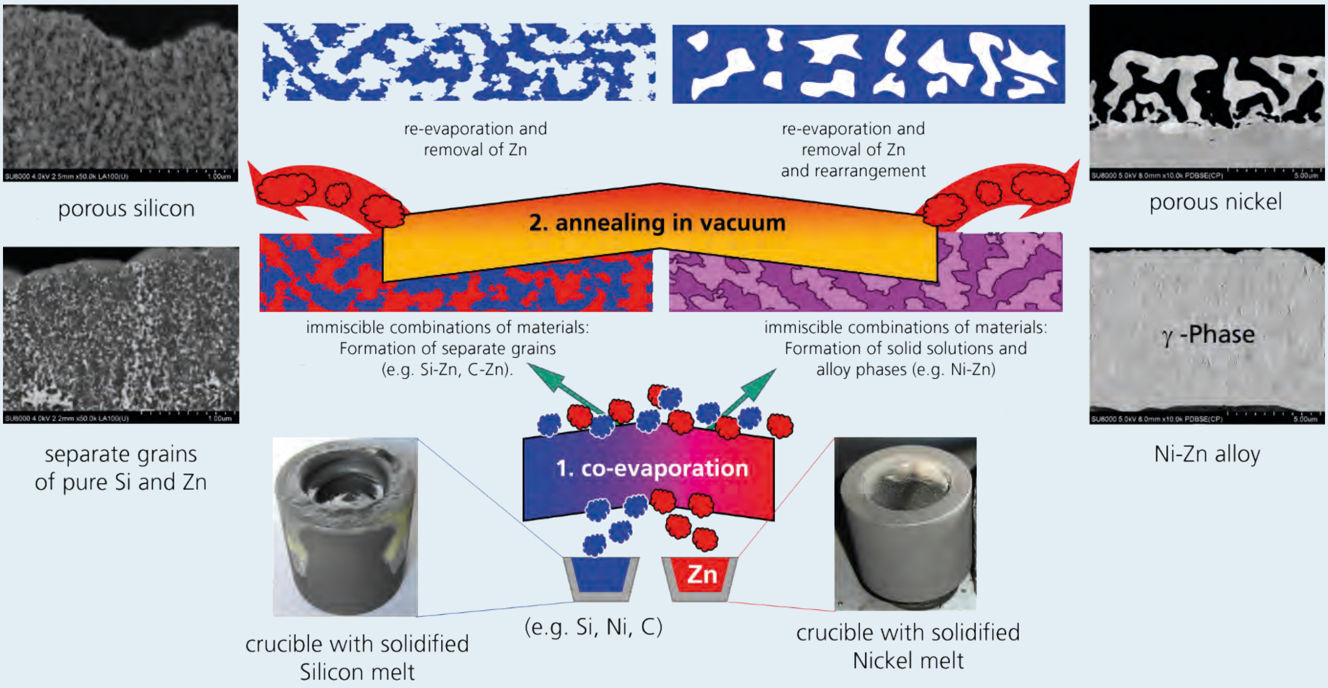
TECHNOLOGY

- Co-evaporation of silicon and zinc
- Mixing of the two elements in the vapor phase and deposition of compound layers on metal substrates
- Subsequent annealing treatment in vacuum for re-evaporation of zinc and structure formation

ADVANTAGES

- High coating rate (up to 100 nm/s demonstrated)
- Creation of a porous structure in the silicon that provides space for its expansion in the charging process and minimizes capacity loss
- Process can be adapted and optimized to specific battery requirements
- Reuse of zinc in the process possible in the long term
- Initial charge capacity of the layers over 3,000 mAh/gSi
- Comparatively good cycle stability

Concept for the synthesis of porous layers by co-evaporation and subsequent annealing in vacuum



Powder-based Si anode material and functionalization in arcPECVD process

APPLICATION

The use of small-scale Si particles as anode material is an alternative way to minimize the stresses that occur during cycling. A carbon coating on the particle surface also supports the electronic conductivity, stabilizes the silicon and prevents the loss of lithium and electrolyte through continued SEI formation. Fraunhofer FEP is pursuing the approach of coating the Si particle surface with carbon in the arcPECVD process with a high deposition rate.

DEVELOPMENT PARAMETERS

- Coating rate (≥ 35 nm/s on flat substrates already demonstrated)
- Powder delivery set up in vacuum
- Variation of coating thickness possible by manipulation of exposure time and particle distribution

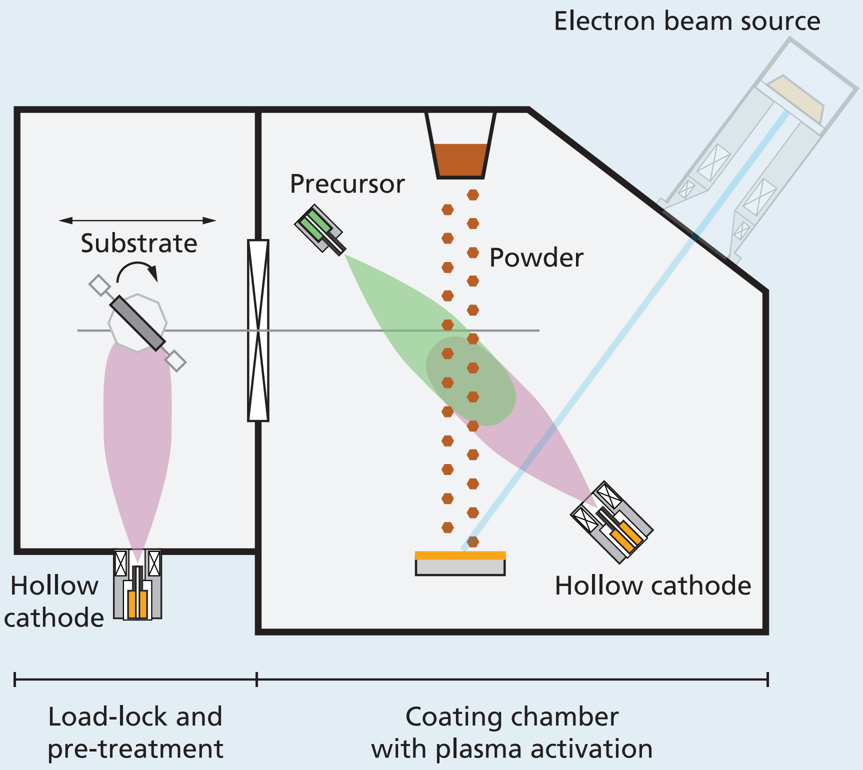
TECHNOLOGY

- Precursors (e. g. C_2H_2) are converted into compact carbon coatings by exposure to an intense hollow cathode plasma
- The powder is conveyed through the plasma's action zone by a special conveying mechanism and then collected again

ADVANTAGES

- All-sided coating of particles with high throughputs
- High degrees of freedom with regard to the size distribution of the particles
- Flexibility of the coating material by using different precursors

NOVELLA test facility, equipped with two hollow cathode arc sources for the pre-treatment of reference substrates and for arcPECVD coating



Metallic lithium and pre-lithiation

MOTIVATION

Usually, lithium layers are produced in the form of thin films by rolling processes, which also necessitate the use of lubricants. By thermal vapor deposition in a vacuum, lithium layers can be produced without contaminating additives in a thickness of 1 – 20 micrometers. This allows very pure and, above all, thin metallic lithium layers to be produced in a reproducible manner.

STATE OF RESEARCH

- Fabrication of pure lithium thin films on metal substrates
- Optimization of layer thickness and layer morphology
- Development of suitable passivation layers
- Pre-lithiation of anodes

TECHNOLOGY

- PVD of pure metallic lithium layers by thermal evaporation at deposition rates > 100 nm/s and > 1 µm m/min, respectively
- Deposition of Li compound layers by co-evaporation from separate crucibles for the production of
- Pre-lithiated layers
- Deposition of protective coatings by PVD

ADVANTAGES

- High degree of freedom for adjusting the optimum anode thickness
- Highest degree of purity
- Adaptation of the optimum layer morphology in layer growth direction possible
- High flexibility in layer composition

Lithium granules as feedstock for evaporation

Post-Lithium Technologies

MOTIVATION

New energy storage systems are needed for the electrification and thus flexibilization of energy-intensive technologies such as home storage or power-to-grid. For this purpose, research is being conducted worldwide into alternatives to lithium-based storage systems, as these have a relatively low energy density and the liquid electrolyte is problematic due to the potential fire hazard. Furthermore, the raw material lithium is considered controversial.

Alternatives are solid batteries in which a solid electrolyte is used. Compared to lithium-ion batteries, aluminum-based battery systems can have significantly higher energy densities and do not require lithium.

STATE OF RESEARCH

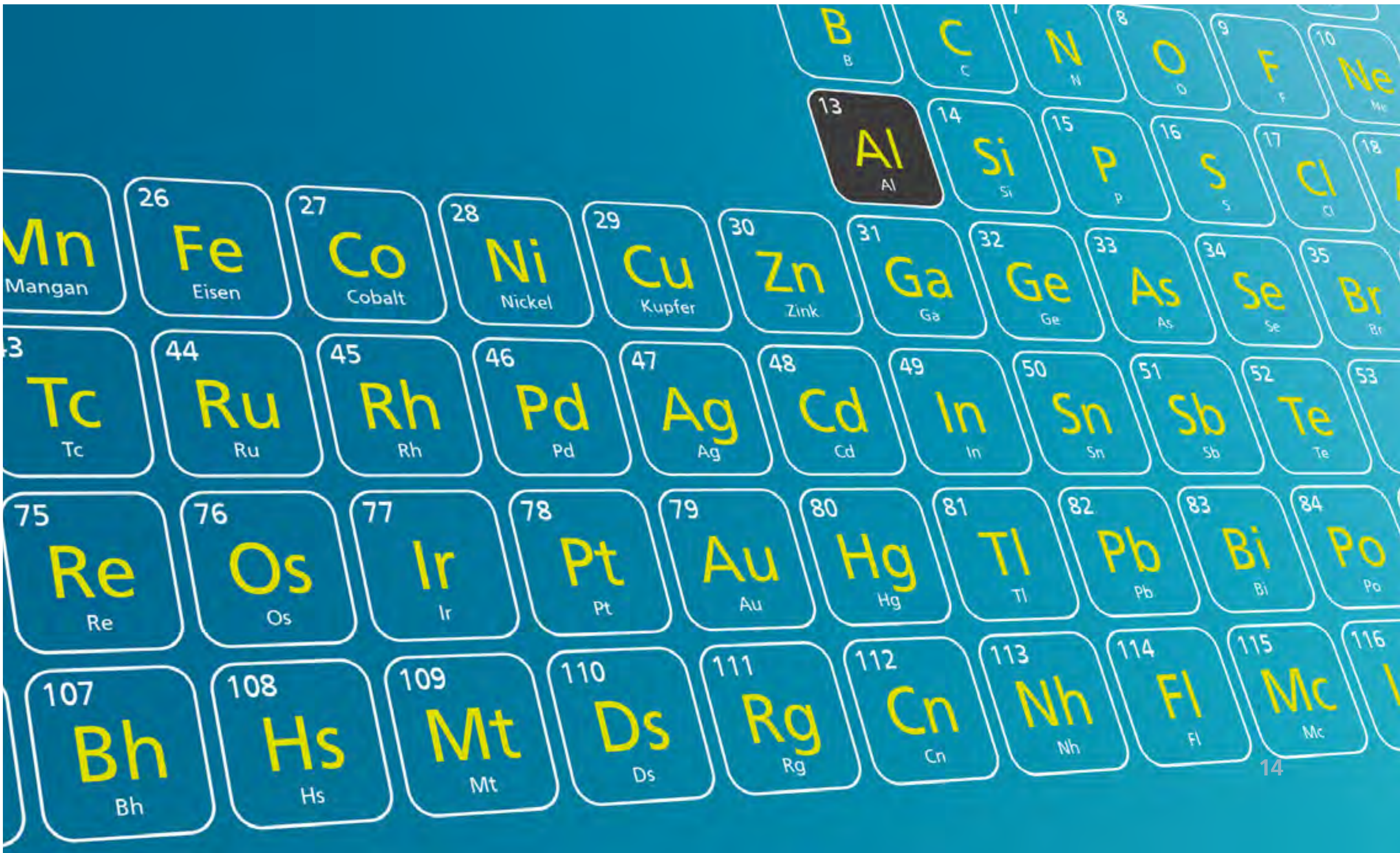
- Development of a novel technology for the production of electrochemical energy storage systems as an alternative to lithium-based battery systems ➝ Aluminum batteries
- Development of a solid-state battery for mobile high valent ions
- Development of a manufacturing technology for solid-state electrolytes and electrodes

TECHNOLOGY

- Layer deposition for electrolytes or electrode materials by magnetron sputtering or electron beam evaporation

ADVANTAGES

- High achievable volumetric energy densities, potentially double to quadruple those of commercial lithium-based battery systems
- High safety
- Extensive availability of materials
- Recyclability of systems
- Cost reduction potential of up to 20% in terms of price per kWh



Equipment

Various pilot production facilities and laboratory equipment for roll-to-roll and sheet-to-sheet coating are available at Fraunhofer FEP for research and development.

This basis is supplemented by the development of technological key components in-house..

- Coating widths up to 600 mm
- High coating rates, strip speeds 0.1 ... 100 m/min
- Roll-to-roll and sheet-to-sheet processes
- Dual magnetron sputter systems
- Single magnetron systems
- Ion sources
- Electron beam co-evaporation

Our offer

We offer extensive know-how in the field of roll-to-roll vacuum processes and high-rate electron beam evaporation technologies on large surfaces, which we apply to your requirements for research and development of new energy storage media. Processes can be tested on both laboratory and pilot plant scale.

We accompany you from the specification of the customer requirement to the technology transfer to the industry.

novoFlex® 600 – Roll-to-roll pilot web coater

Projects

ProBaSol

Federal Ministry
for Economic Affairs
and Energy

Joint project: The Aluminum battery: Challenges for industrial production
Sub-project: Development of industrial vacuum thin film technologies for deposition electrical functional layers on flexible carriers for use in Aluminum batteries

Funding reference: 03EI3014B

ProSoLitBat

VDI

Joint project: ProSaLitBat, Sub-project: Innovative roll-to-roll process for high-rate vacuum coating of metal foils with solid electrolyte layers

Funding reference: 13N13236

PolyCollect

STAATSMINISTERIUM
FÜR WIRTSCHAFT
ARBEIT UND VERKEHR

Freistaat
SACHSEN

Investigations on technologies for high-rate evaporation of thin plastic foils for battery current arresters

Funding reference: 100385882

ProSiSt

Federal Ministry
of Education
and Research

Process technologies for structured silicon layers as anodes in high-energy lithium batteries
Sub-projects: Fundamentals of thin film and etching technology and cell concepts

Funding reference: 03XP0130D

PoSiBat

Europäische Union

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EFRE
Europäischer Fonds für regionale Entwicklung

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Highly-porous silicon-zinc coatings for batteries with very high energy density

Funding reference: 3000659083

NextBatt

Federal Ministry
of Education
and Research

Resource-efficient production processes for next-generation battery anodes

Funding reference: L1FHG42421

PolySafe

Federal Ministry
of Education
and Research

Increase of safety of lithium-ion batteries using metal-polymer composite current collectors

Funding reference: 03XP0408D

Imprint

Fraunhofer Institute for Organic Electronics,
Electron Beam and Plasma Technology FEP
Winterbergstr. 28
01277 Dresden, Germany

Marketing
Ines Schedwill
Phone +49 8823 238
ines.schedwill@fep.fraunhofer.de

Scientific Contact
Dr. Nicolas Schiller
Division Director Plasma Technology
Phone +49 351 2586 131
nicolas.schiller@fep.fraunhofer.de

battery@fep.fraunhofer.de

www.fep.fraunhofer.de

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