RESSOURCENEFFIZIENTE NANOMATERIALIEN FÜR DIE ENERGIE-SPEICHERUNG – 3D-ARCHITEKTUR UND CHARAKTERISIERUNG

RESOURCE-EFFICIENT NANOMATERIALS FOR ENERGY STORAGE – 3D ARCHITECTURE AND CHARACTERIZATION

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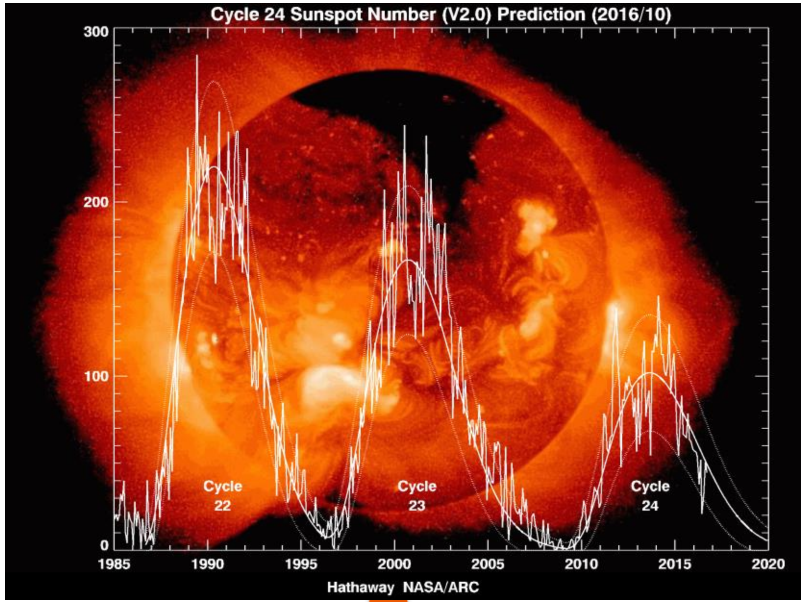
Lübeck, 13 January 2020

Fraunhofer
IKTS

Climate dynamics: Our earth does not guarantee constant climate

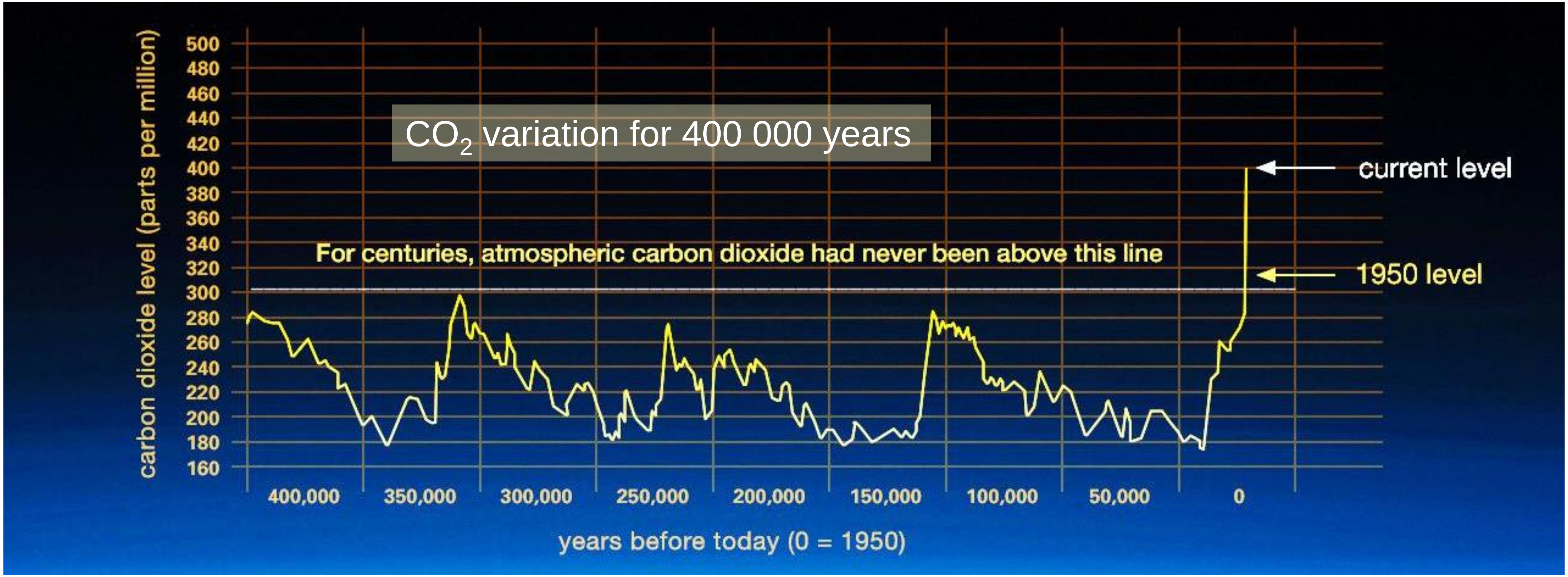
Anthropogenic factors

Natural factors



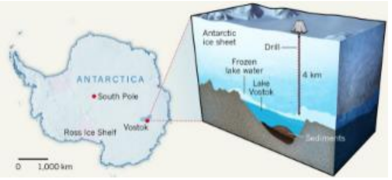
Climate change today and in future

Climate: Human factor



Increased CO_2 emission ➔ Greenhouse effect (global warming)

„Energiewende“ is essential to survive on our planet!!!



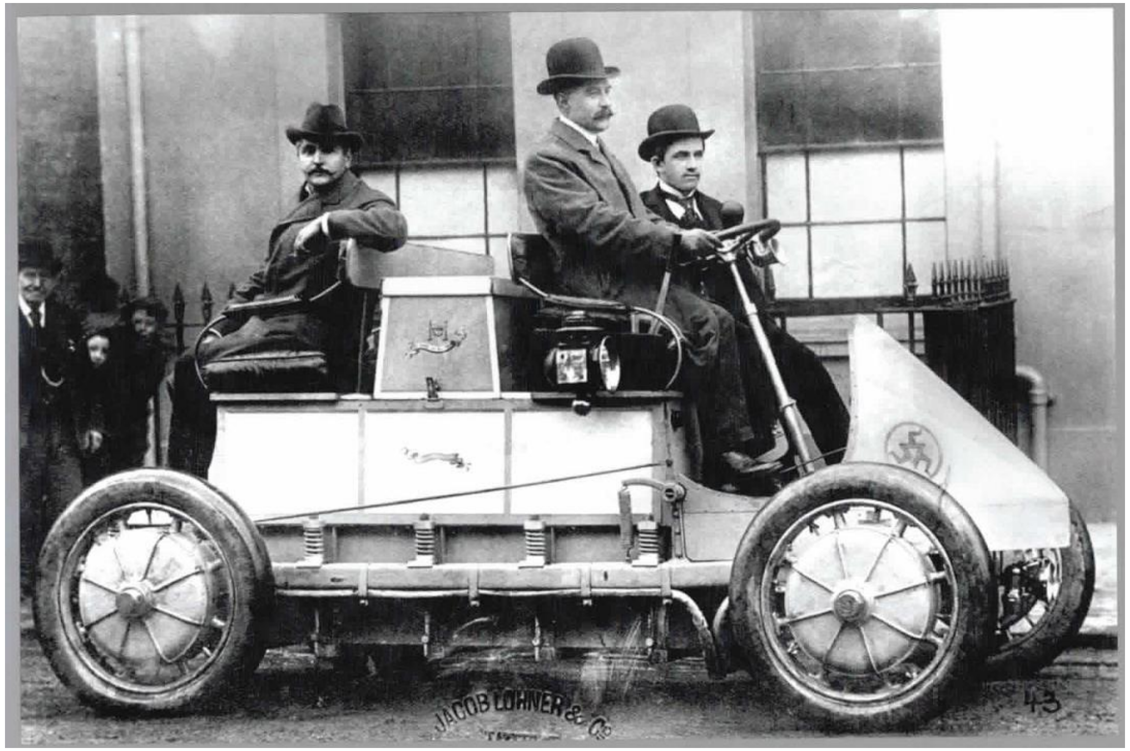
Source: NASA; Credit: Vostok ice core data/J.R. Petit et al.; NOAA Mauna Loa CO_2 record

Deutschland: Energiewende war schon immer schwierig…

Kaiser Wilhelm II.

"Ich glaube an das Pferd.
Das Automobil ist eine
vorübergehende Erscheinung."

Weltausstellung 1900:
Lohner-Porsche
4x2.5 PS Elektroantrieb
Geschwindigkeit 50km/h
Reichweite 50km



Deutschland: Ziele der Energiewende

Ausstieg aus der Kernenergie bis 2022

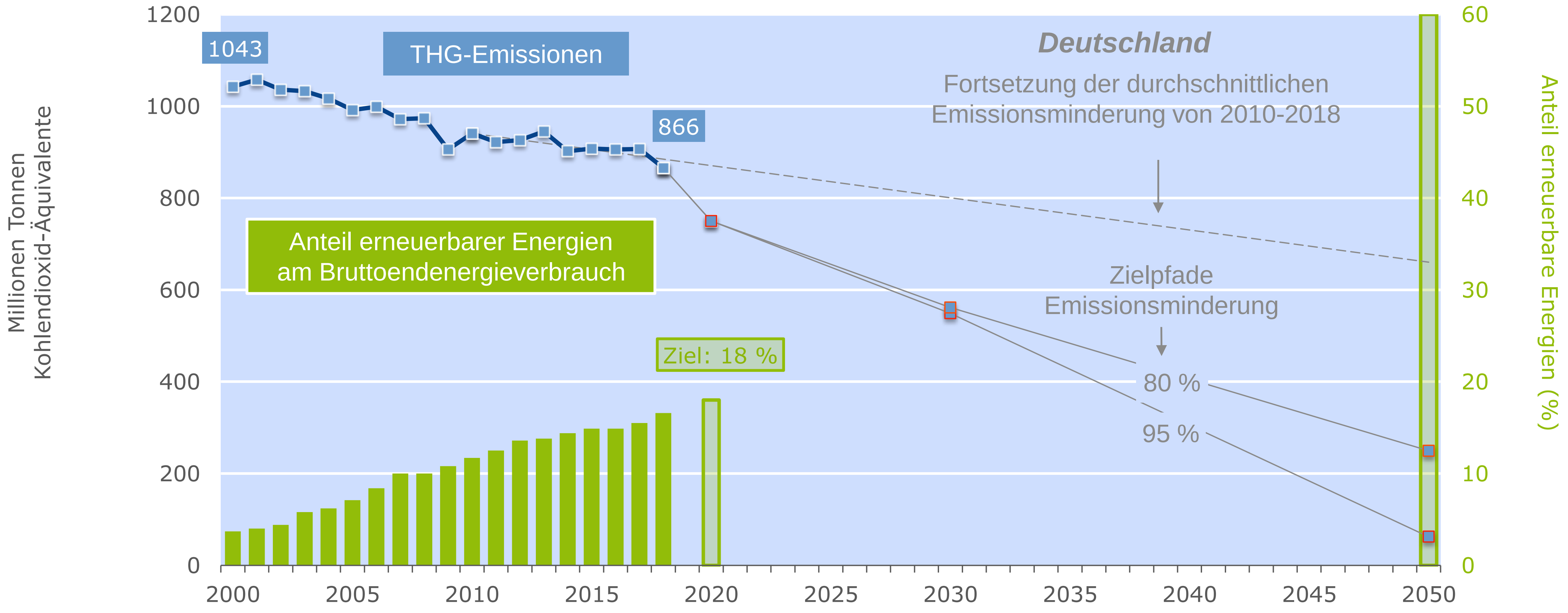
Steigerung des Anteils der erneuerbaren Energien am gesamten Energieverbrauch

Reduktion des Primärenergieverbrauchs und Steigerung der Energieeffizienz

Reduktion der Treibhausgasemissionen

THG

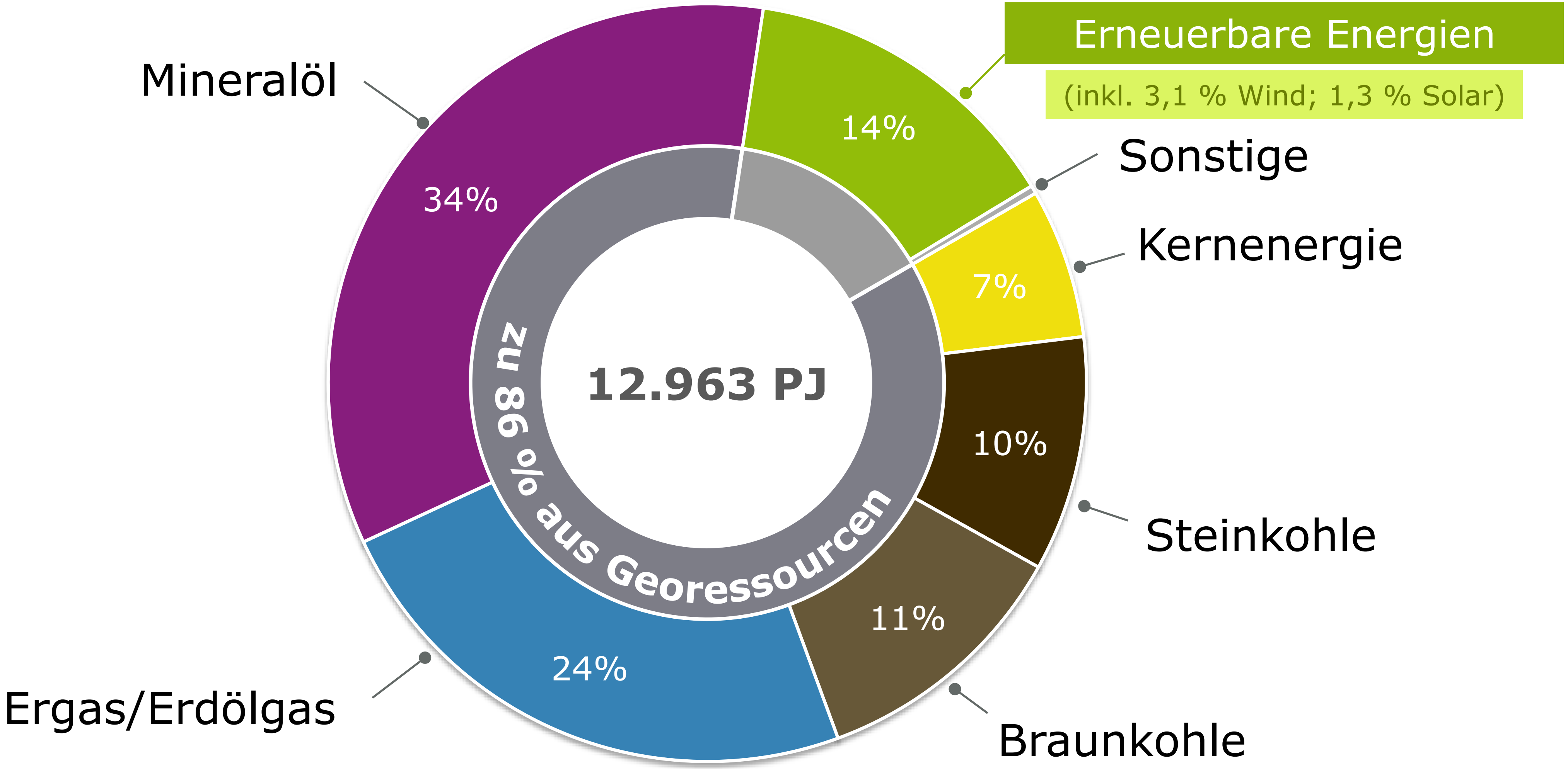
Trends und Ziele für den Ausbau erneuerbarer Energien und die Minderung von Treibhausgasemissionen



Daten: UBA/AGEE-Stat, Januar 2019

Fraunhofer IKTS

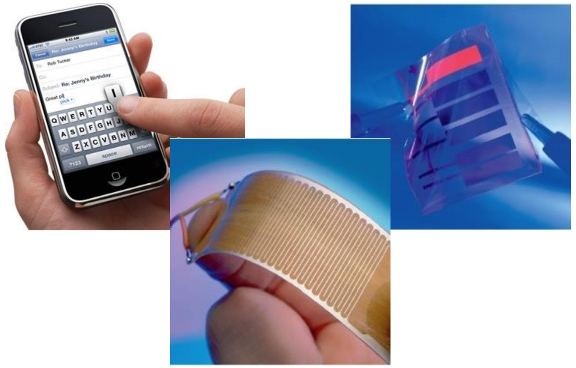
Primärenergieverbrauch nach Energieträgern in Deutschland (2018)



Daten: AGEB/BMWi, März 2019

The 21st century: 3 key technologies and technical megatrends

Energy, Mobility

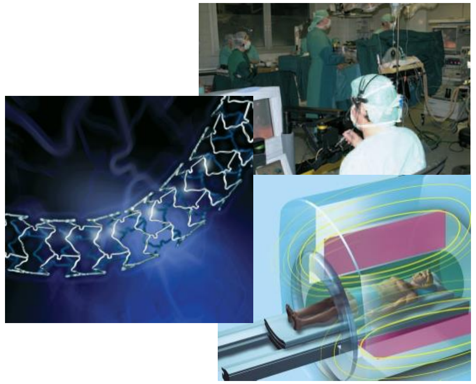


Information/Communication

„INFORMATICS“

„MATERIALS“ „BIOTECH“

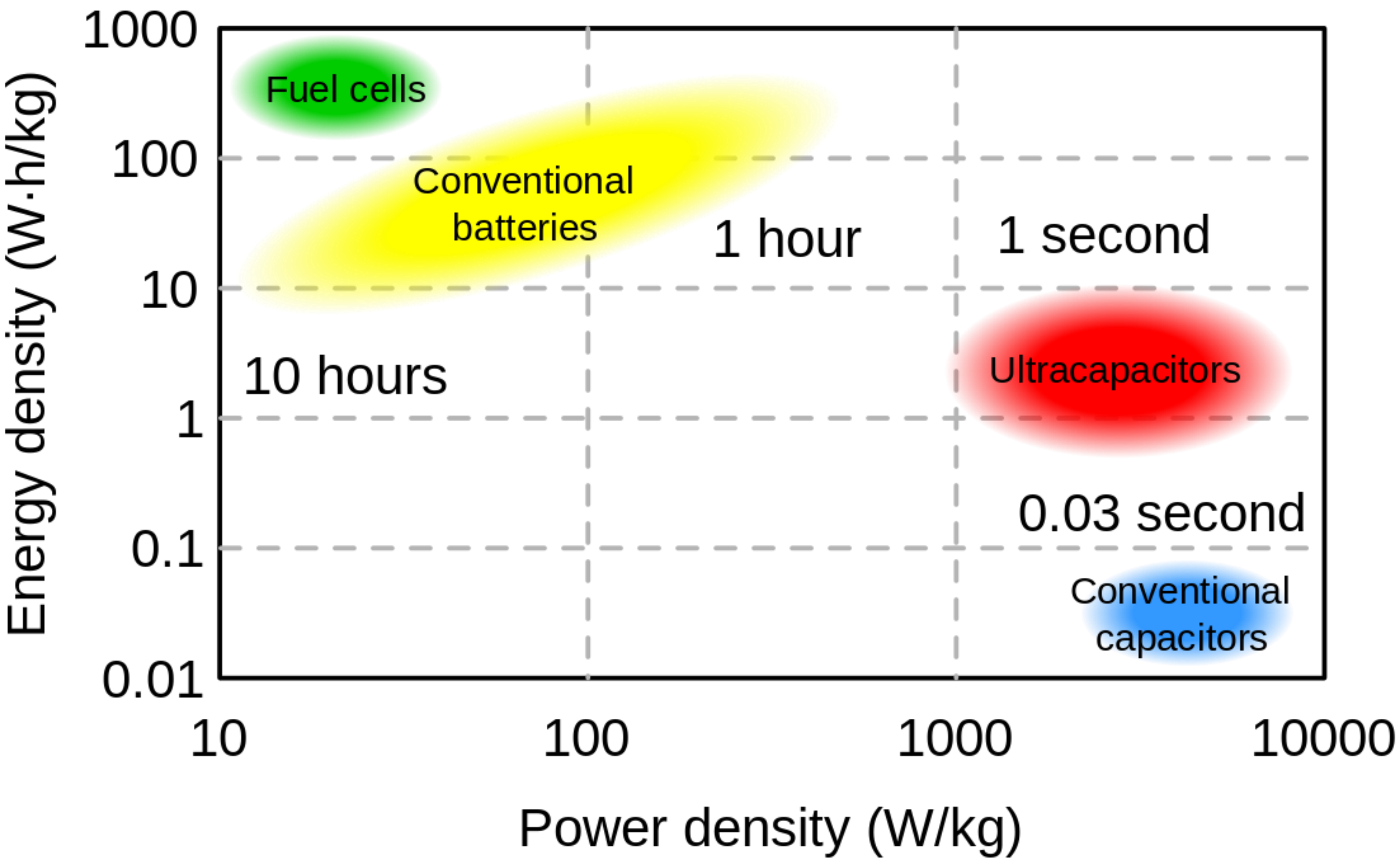
Ressources/Raw materials



BioTech, Medicine

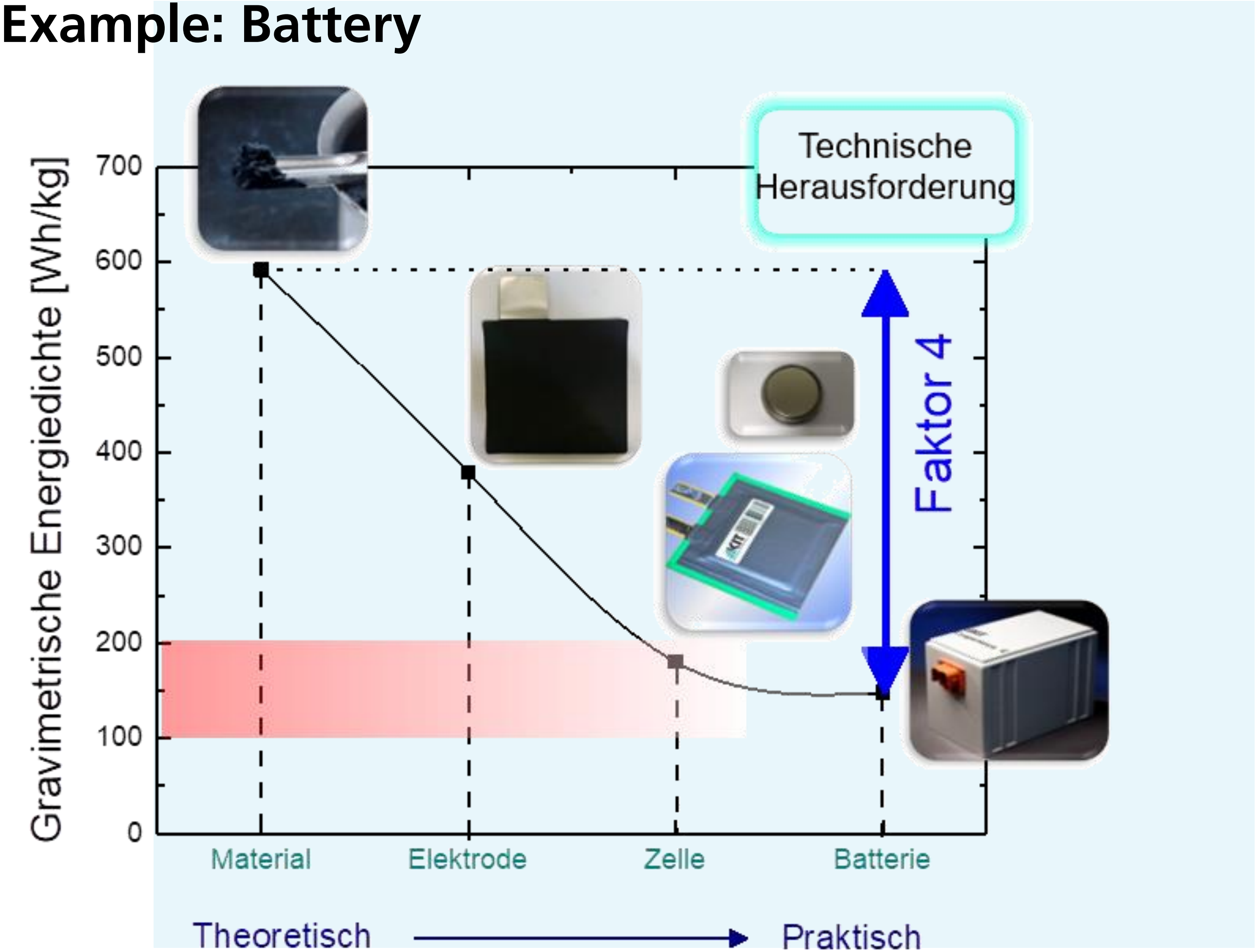
Materials is a key technology !

Energy density vs. power density of several technologies



Batteries have a higher energy density than capacitors, but a capacitor has a higher power density than a battery. This difference comes from batteries being able to store more energy, but capacitors can give off energy more quickly.

Example: Battery



Requirements for future mobility:

- **high energy density**
- **high power density**
- **short time for charging**

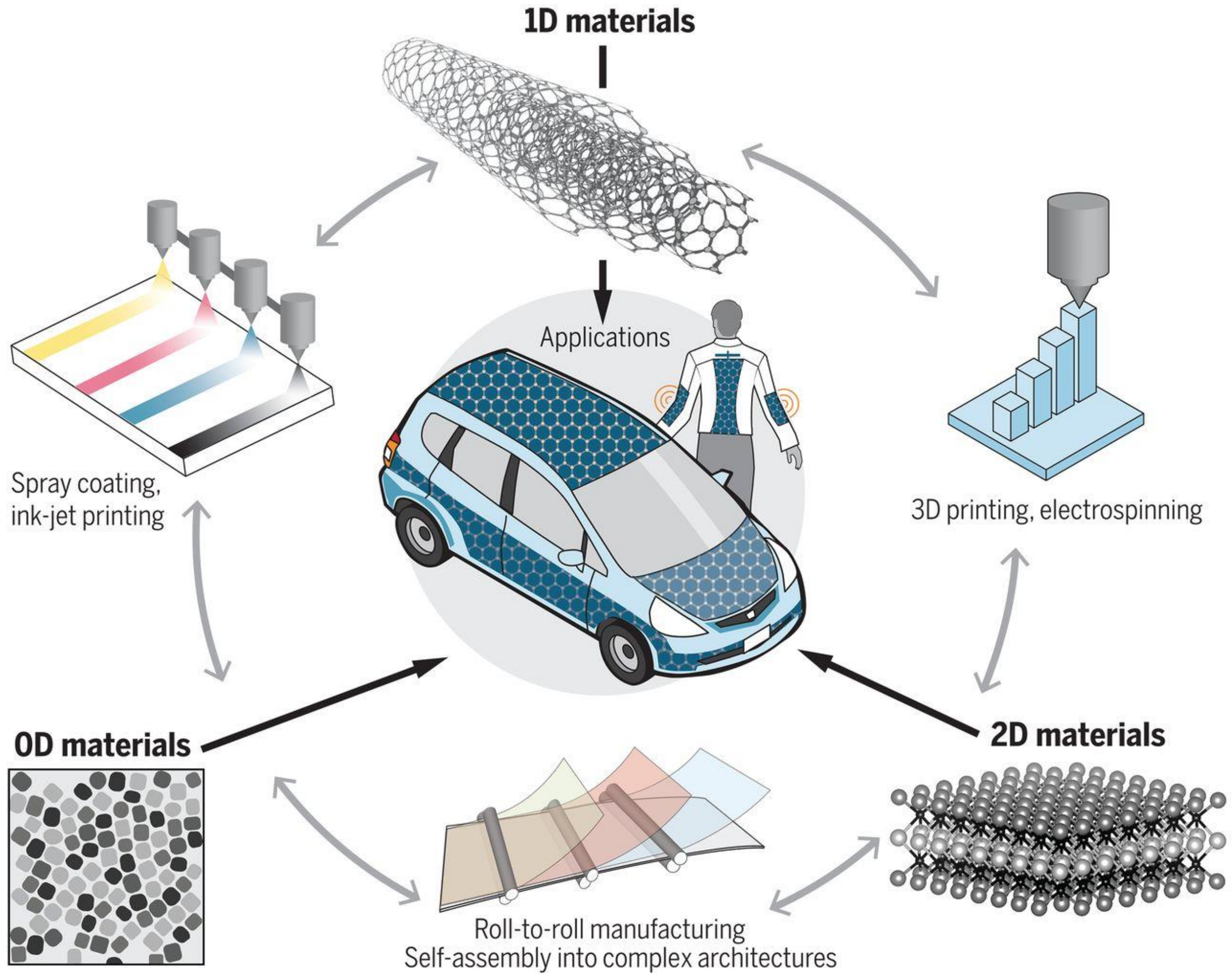
➔

Contrary requirements

„Hierarchical approach“:

New materials and new electrode architectures needed !!!

New materials:
Why nanomaterials for energy storage applications?



<u>Nanomaterials:</u>

- high surface-to-volume ratio and short diffusion pathways

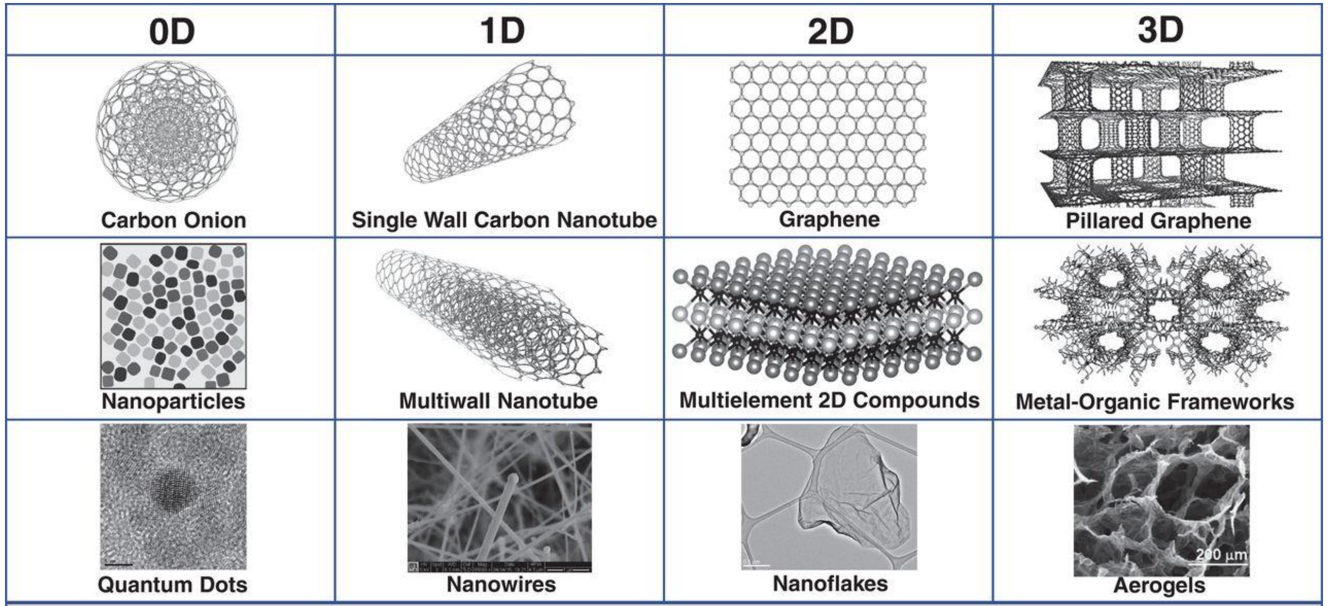
➔ provide a solution for simultaneously achieving high energy density and high power density.

- compatibility of nanomaterials with advanced manufacturing techniques - such as printing, spray coating, roll-to-roll assembly

➔ allows for the design and realization of wearable, flexible, and foldable energy storage devices.

E. Pomerantseva et al., Science 366, 969 (2019)

Overview of 0D, 1D, 2D and 3D nanomaterials



Advantages

0D	1D	2D	3D
Small in all dimensions Surfaces on all sites are accessible to electrolytes No bulk solid-state diffusion Can be integrated into multiple systems Can be used in stable inks for printing	Mechanical reliability Possibility to integrate with wearable devices Porous flexible freestanding films	Open 2D channels for ion transport; all surface is accessible enabling fast charge storage Compatible with flexible devices Small nanoflakes can be used in inks for printing	Can be used to create thick electrodes with large areal and volumetric storage properties

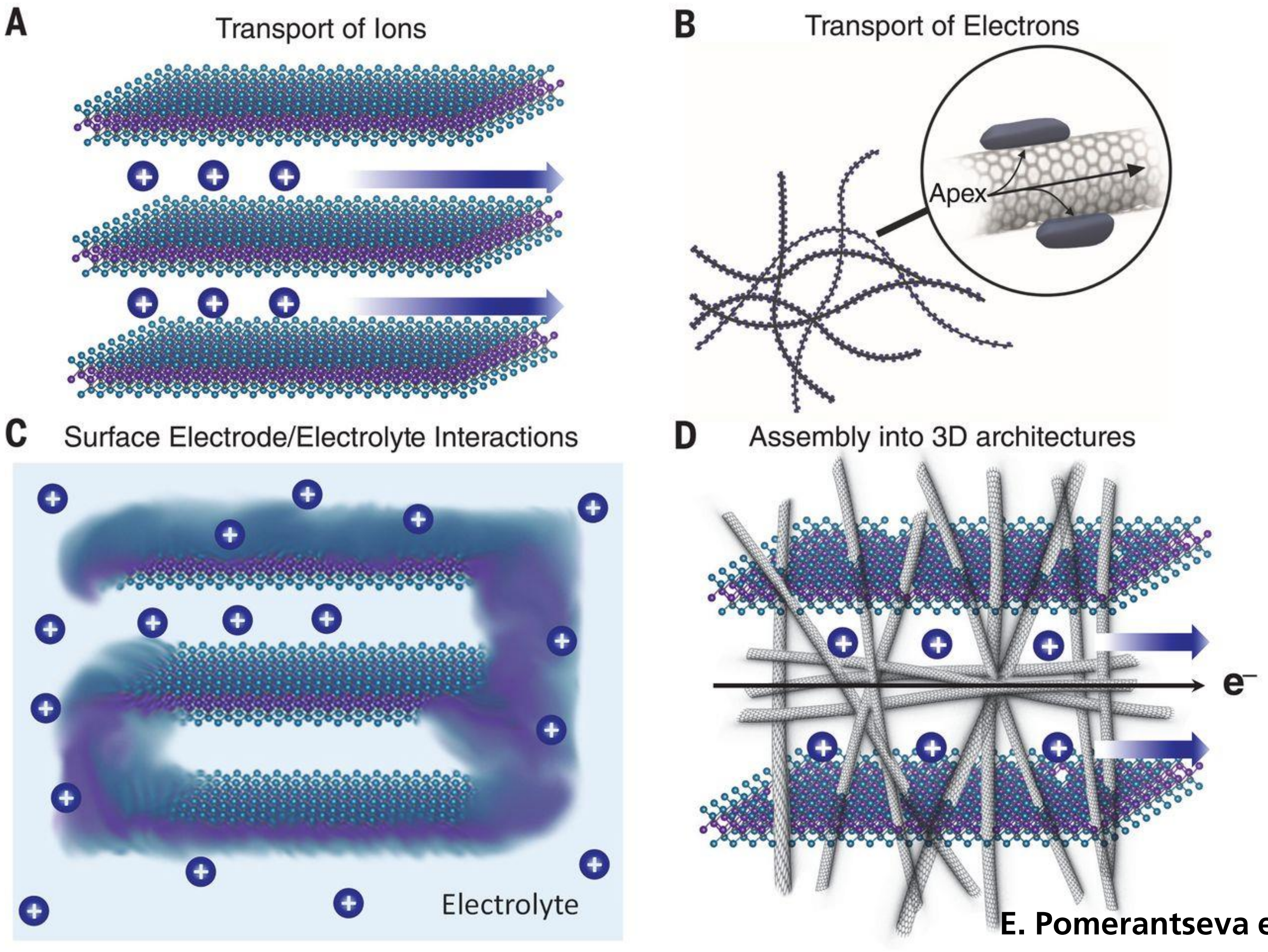
Limitations

0D	1D	2D	3D
Agglomeration Do not densify and form only low density non-uniform structures Numerous points of contact lead to high resistance Poor chemical stability	Low packing density; cannot exhibit high volumetric performance Low yield and high cost of synthesis Diffusion pathways can be relatively long	Re-stacking Low out-of-plane electronic and ionic conductivity High cost of synthesis	Design Stability Manufacturing

Chemical, structural, and morphological diversity of the *available nanoscale building blocks* that can be used to create *complex hierarchical 3D architectures* for next-generation energy storage devices with improved performance compared with the currently available ones.

E. Pomerantseva et al., Science 366, 969 (2019)

Fundamental properties governing the performance of nanomaterials for energy storage and conversion



(A)Transport of ions.

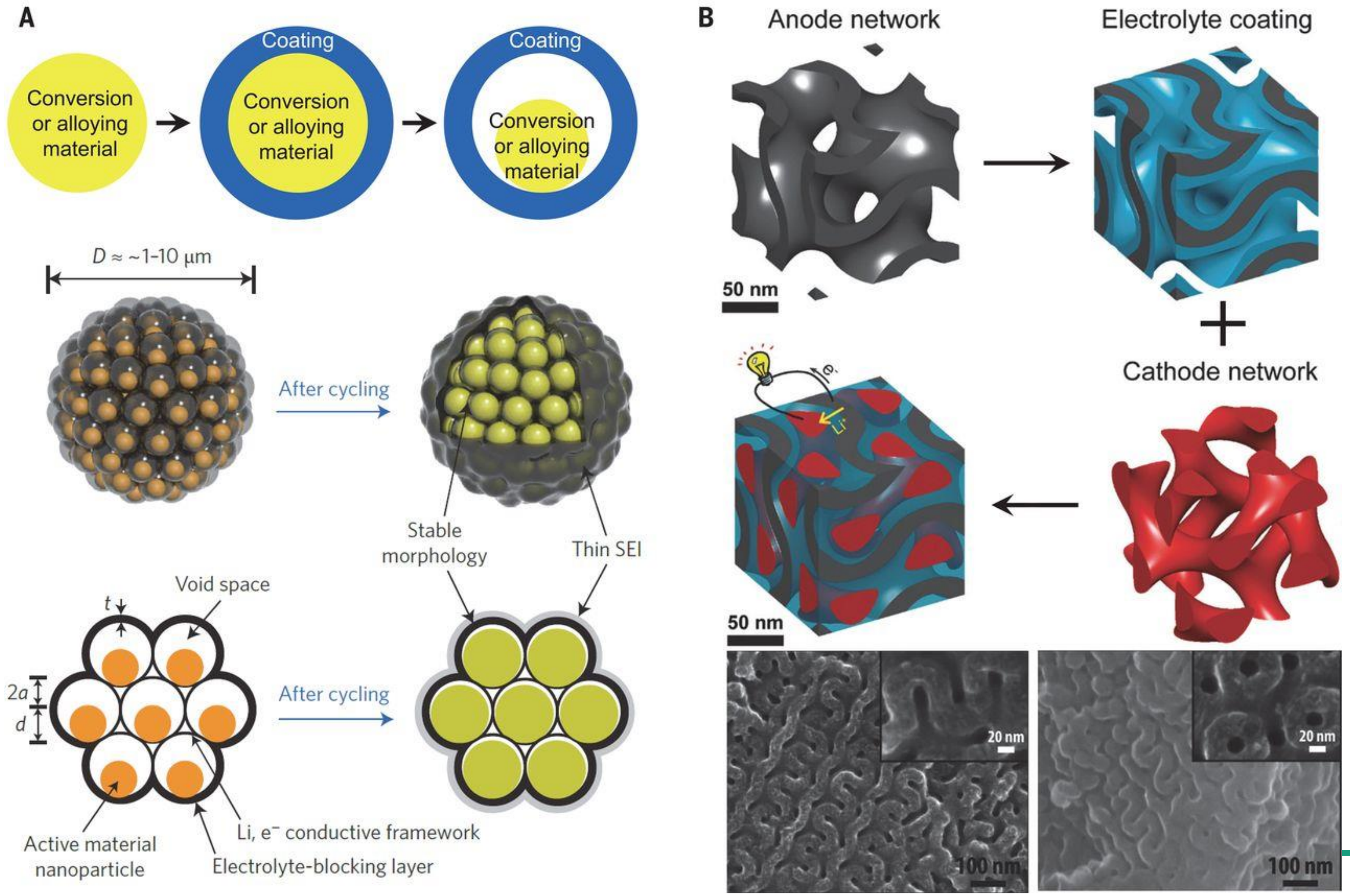
(B) Transport of electrons.

(C) SEI formation and parasitic reactions between electrode and electrolyte. Blurry areas represent reaction products, such as SEI.

(D) Connectivity and transport in 3D space.

E. Pomerantseva et al., Science 366, 969 (2019)

Strategies to overcome performance limitations of nanomaterials in energy storage and conversion applications



(A) Nanoscale coatings on the surface of conversion and alloying electrode materials need to avoid mechanical instability caused by large-volume change and loss of the surface area as a result of agglomeration

D, diameter of pomegranate microparticle; *t*, thickness of the conducting framework; 2*a*, void dimension; *d*, diameter of the active material primary particles.

(B) Nanostructured 3D electrode architecture can be realized through a scalable block-copolymer self-assembly process

E. Pomerantseva et al., Science 366, 969 (2019)

How to characterize nanoscale materials and 3D hierarchical materials systems?

How to characterize nanoscale materials and 3D hierarchical materials systems?

X-ray microscopy, based on two major inventions at the end of 19th century

1873:
Ernst Abbe:
- Theory of image generation of an ideal lense

1895:
Conrad Röntgen:
Invention of X-ray radiography

Why it took so long until X-ray microscopy became an imaging technique?

1) Arguments against X-ray microscopy

Complex refractive index > 0.999
➔ No lenses with sufficient refractive power.

$$\tilde{n} = 1 - \delta - i\beta$$

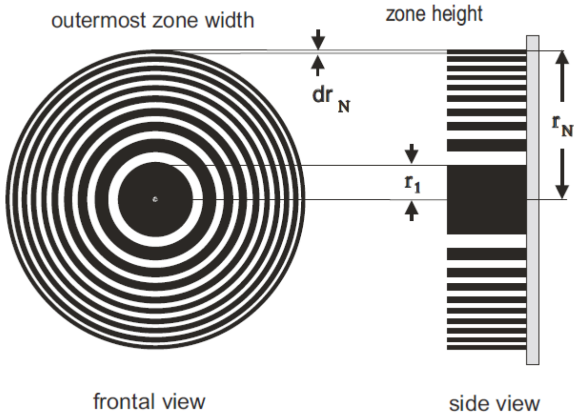
Ernst Ruska, Argument against an X-ray microscopy:

„There are no materials for the construction of X-ray lenses with sufficient refractive power – because the refractive index is close to one.“

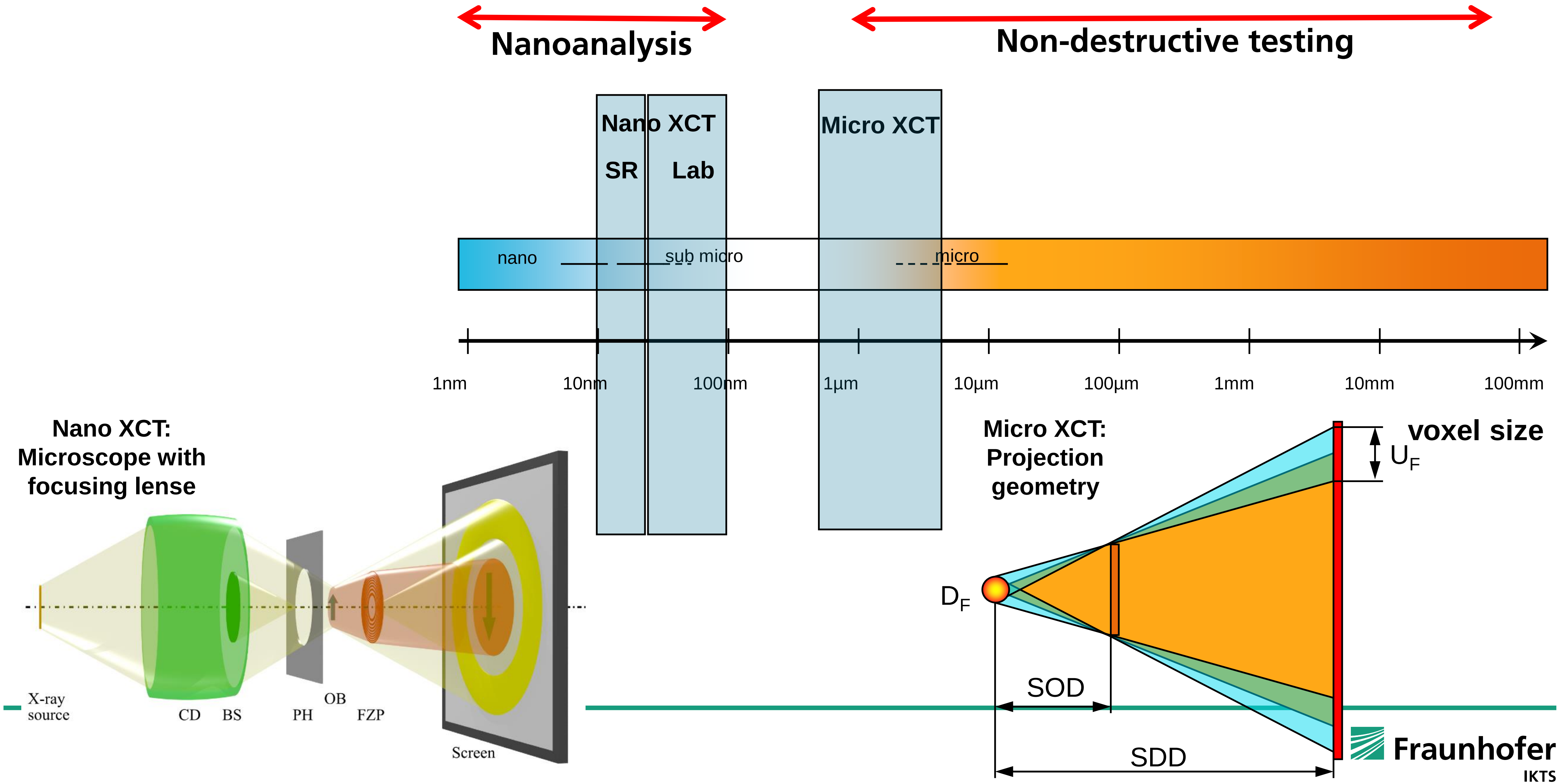
2) Technological limitations, particularly manufacturing of X-ray lenses

No technology to manufacture lenses for high resolution imaging.

Fresnel zone plate: Patterning – e-beam lithography + etching



3D characterization of defects in materials and products using laboratory X-ray computed tomography (XCT)



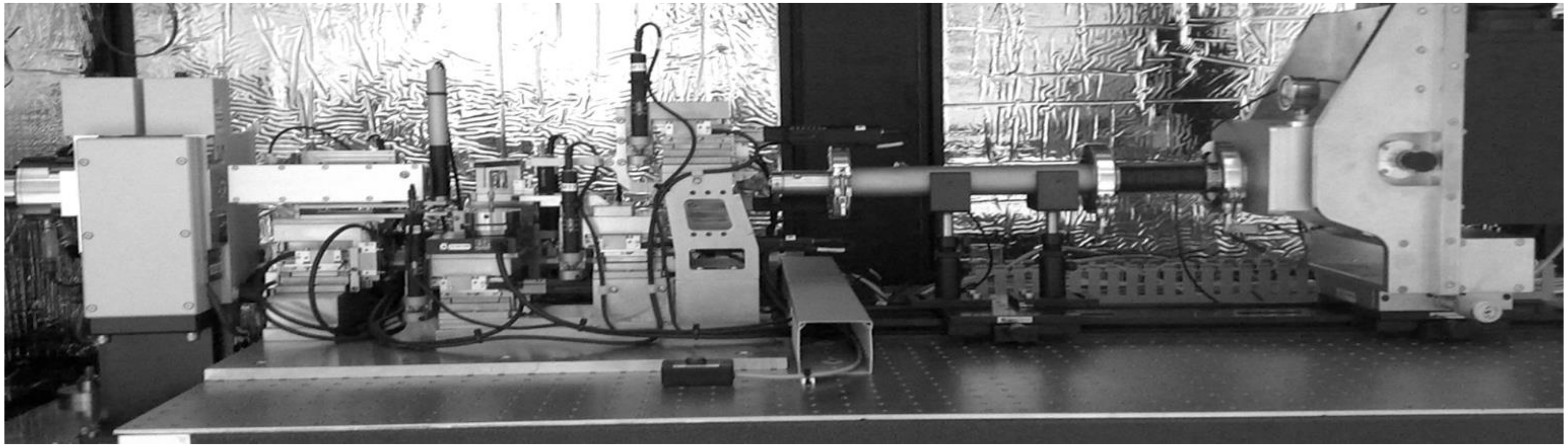
Fraunhofer IKTS

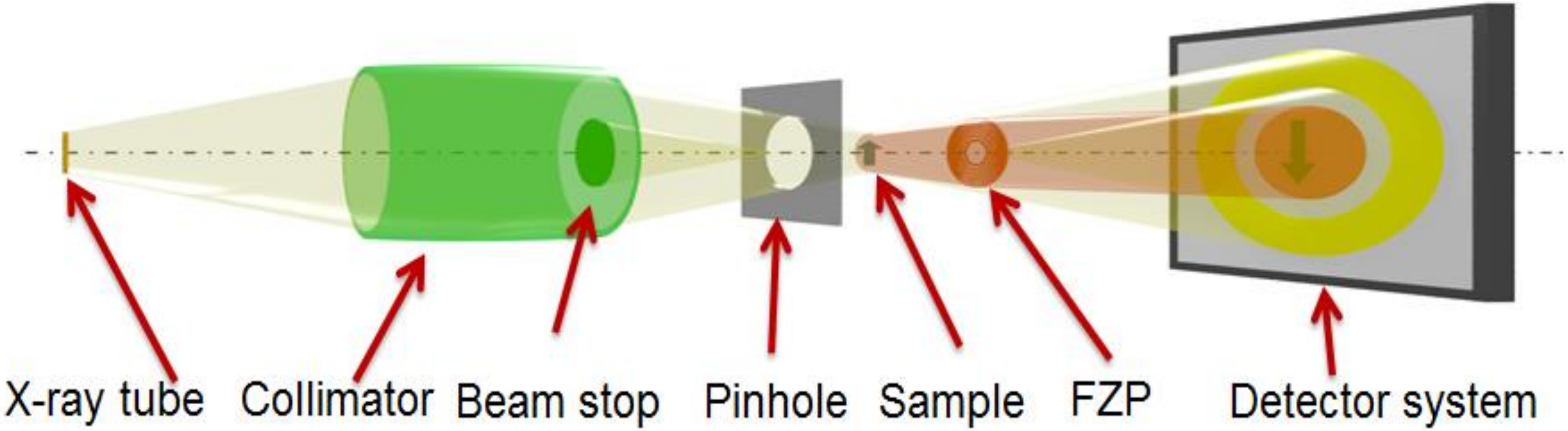
Microscopy in materials science and engineering, and biology

	light microscopy	X-ray microscopy	Electron microscopy
resolution	~ 160 nm	~ 50 nm (lab) ~10 nm (SR)	~ 0.1 nm (TEM)
object thickness	> 10 µm	~ 1…100 µm	~ 0,1 µm (TEM)
limits	wavelength	X-ray optics, X-ray sources (lab)	inelastic scattering, radiation damage
special forms	fluorescence-, …	TXM, STXM, …	TEM, STEM

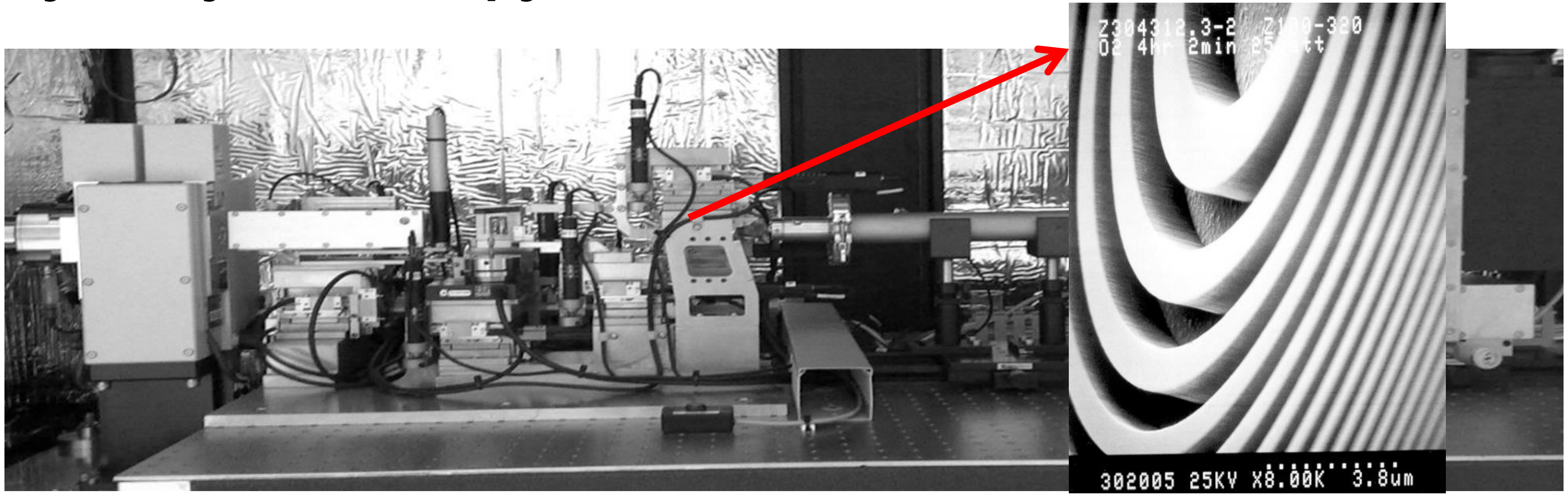
X-ray microscopy: combination of high spatial resolution and sample penetration ➔ High-res 3D volume data

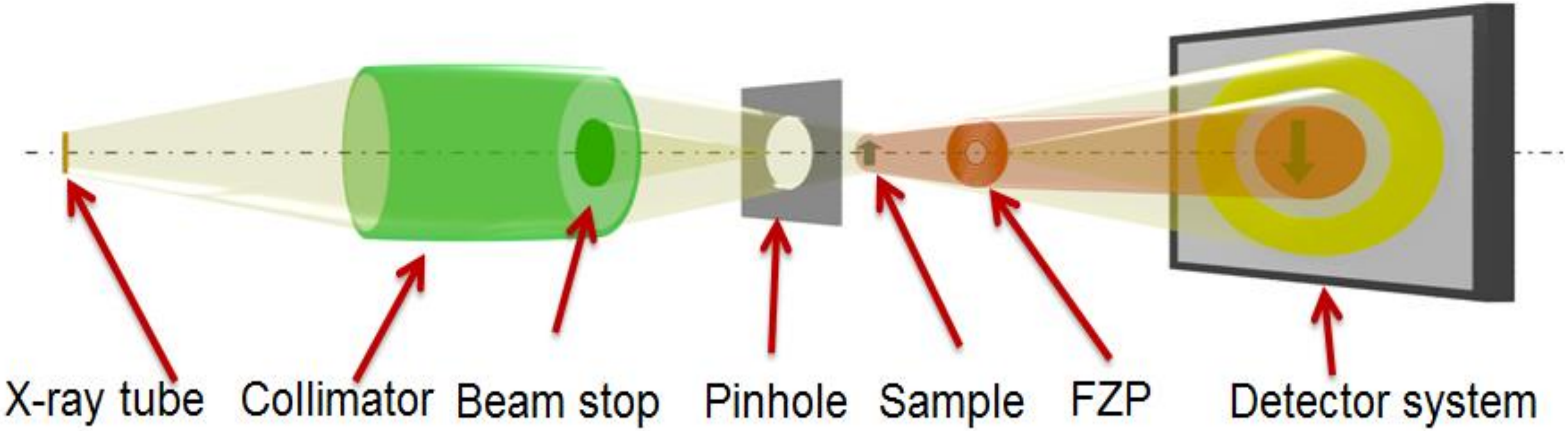
Laboratory X-ray microscopy and nano XCT



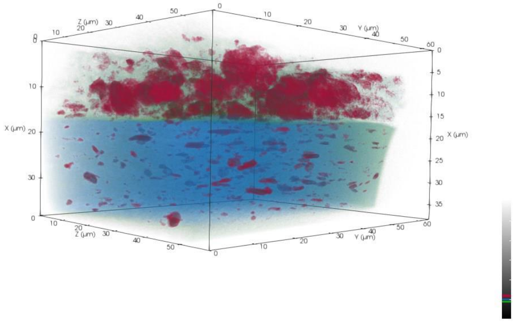


Laboratory X-ray microscopy and nano XCT

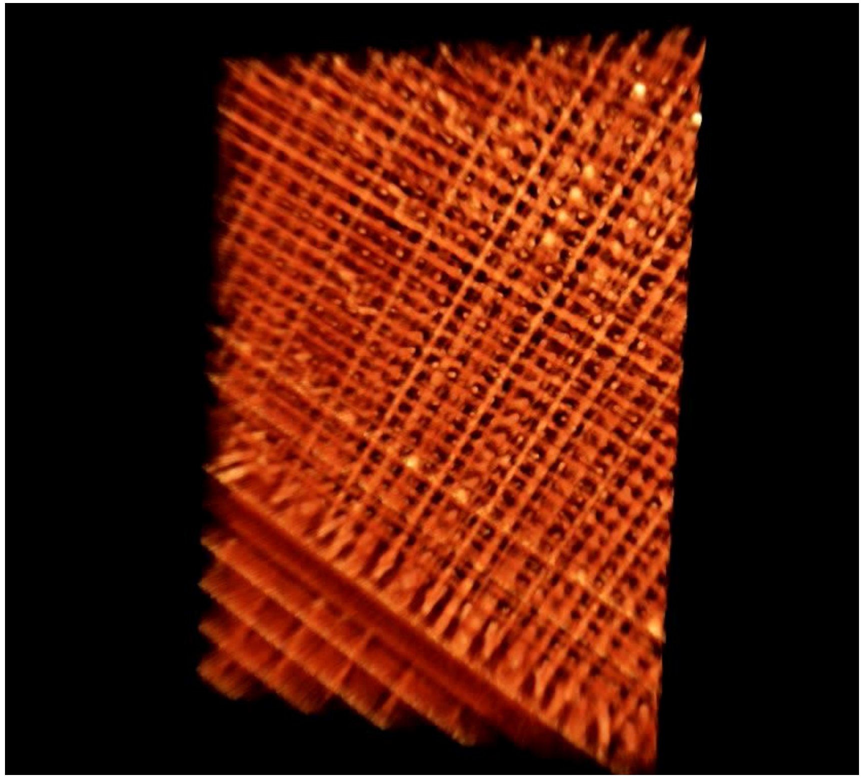




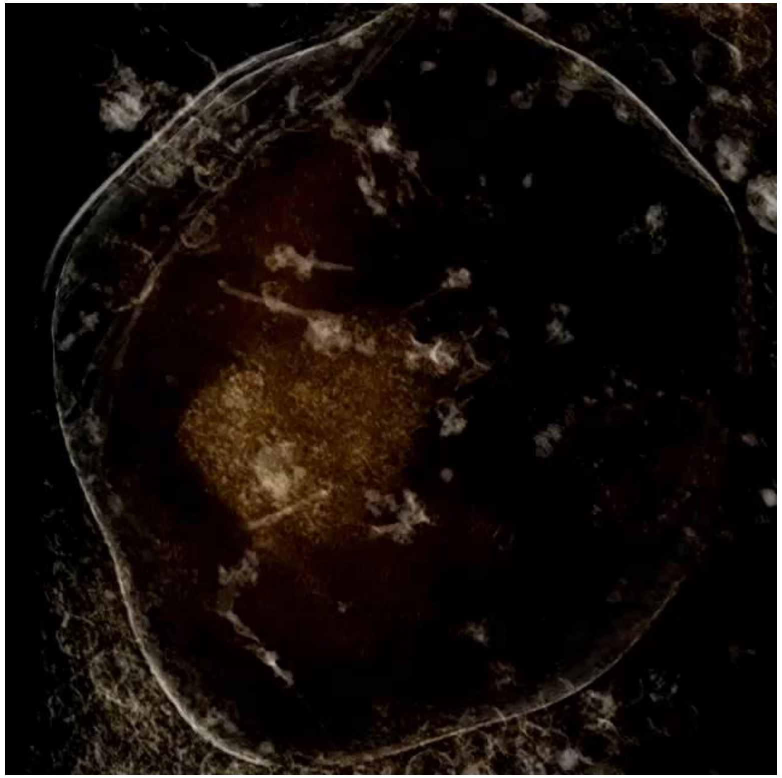
Major application fields in laboratory X-ray microscopy



Energy technologies

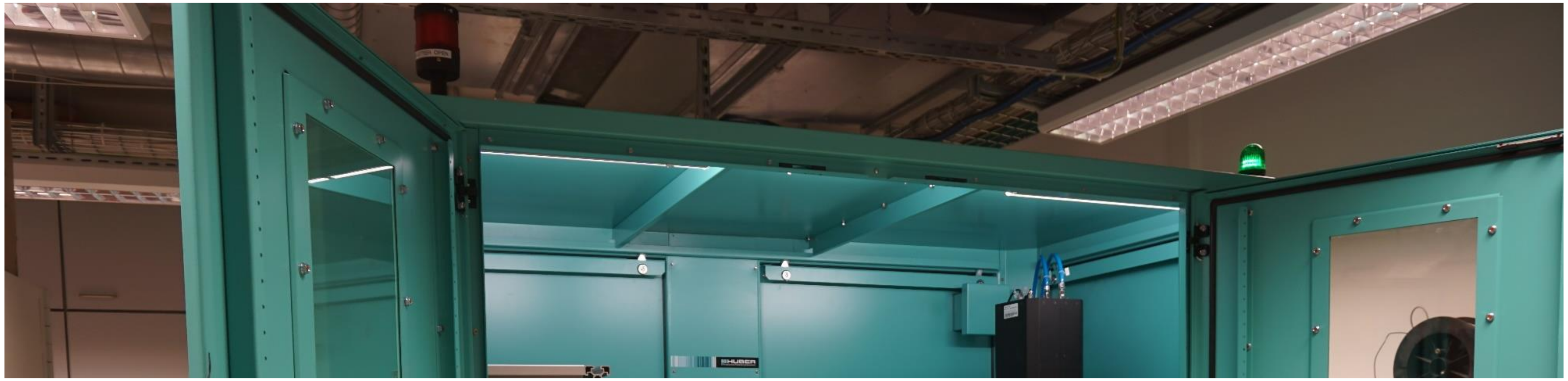


Microelectronics



Biology/Medicine

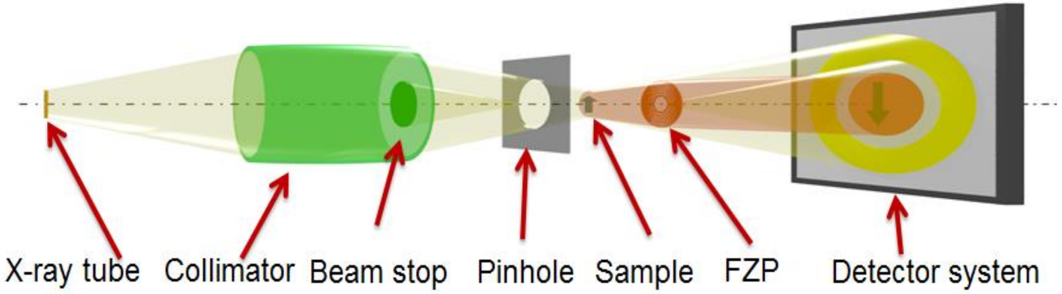
Next step in laboratory X-ray microscopy:

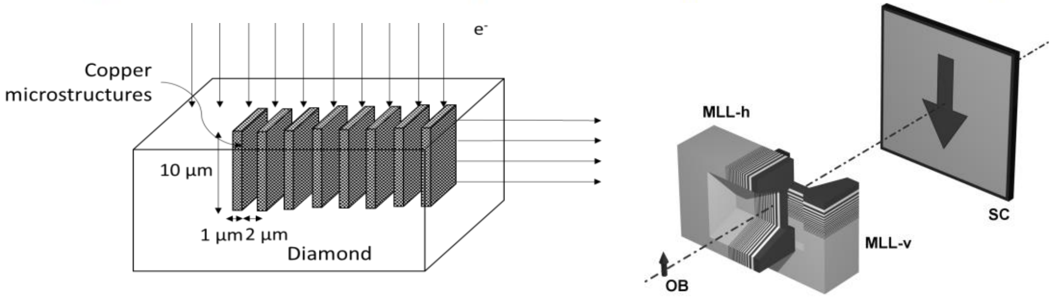


X-ray microscope for photon energies > 10 keV:
Fast and really nondestructive

Laboratory nano XCT for 3D materials and object characterization: Nondestructive & 3D, high resolution, high throughput

Parameters \ Development	Status	Target
Resolution	50 nm ⇨	10 nm
Energy range	< 10 keV ⇨	> 10 keV
Acquisition time	2 min – 10 h ⇨	40x faster
Sample thickness	50 µm ⇨	some mm





Innovations:

Novel nano X-ray tomography system with

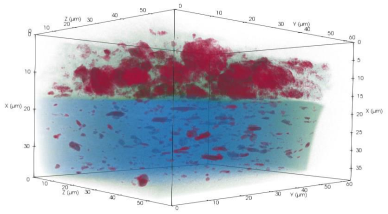
- High-flux X-ray source (Sigray Inc., Concord/CA, USA)
- Novel multilayer Laue lens X-ray optics (Fraunhofer IKTS + IWS Dresden)

Solution/Application:

Novel tool for industry (process control, quality assessment) and academia (materials science and engineering, physics, chemistry, biology)

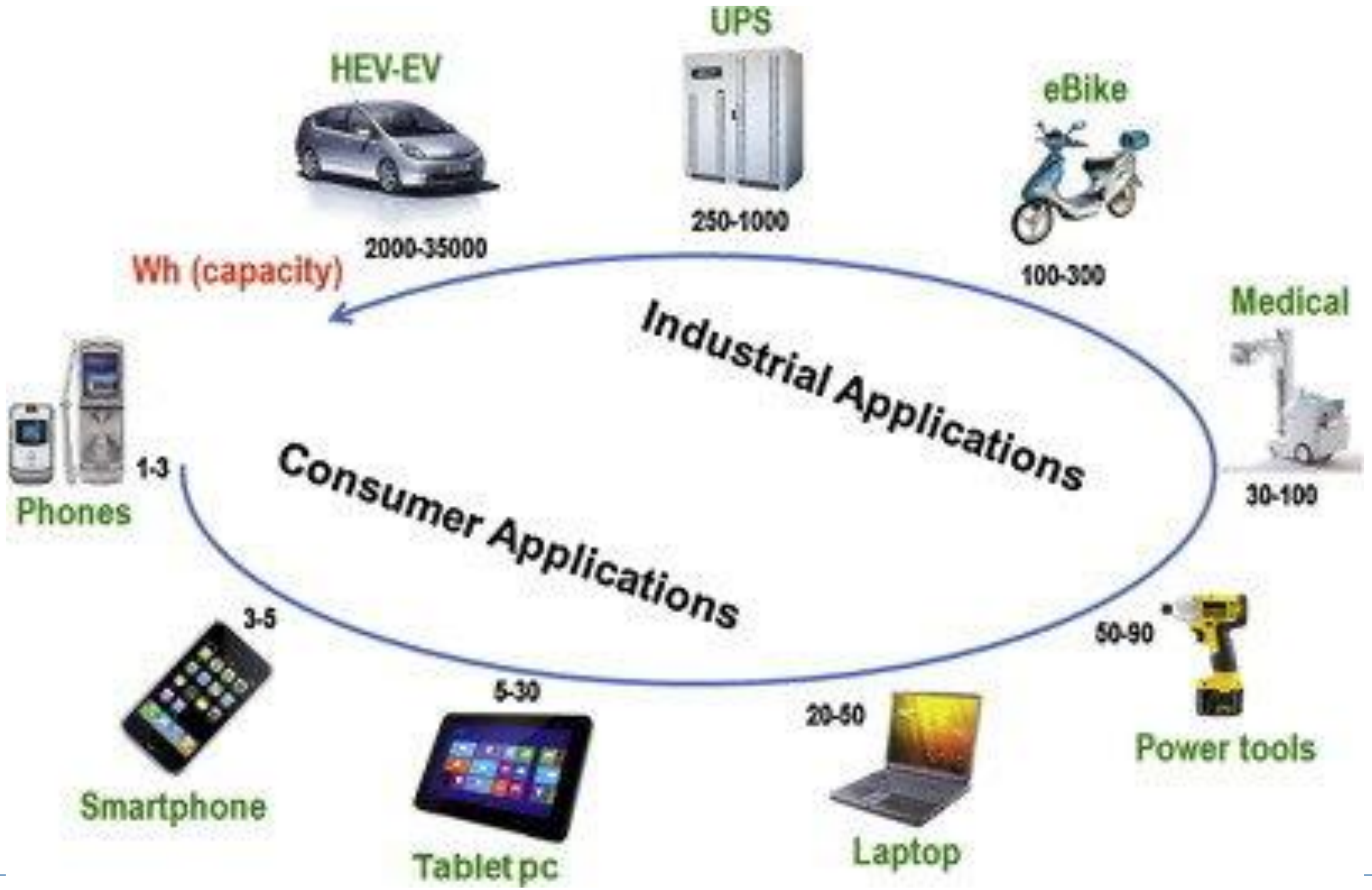
- Really non-destructive (no or low sample preparation efforts)
- High throughput: 3D data set in minutes
- Resolution down to 10 nm

3D imaging of morphology of battery electrode

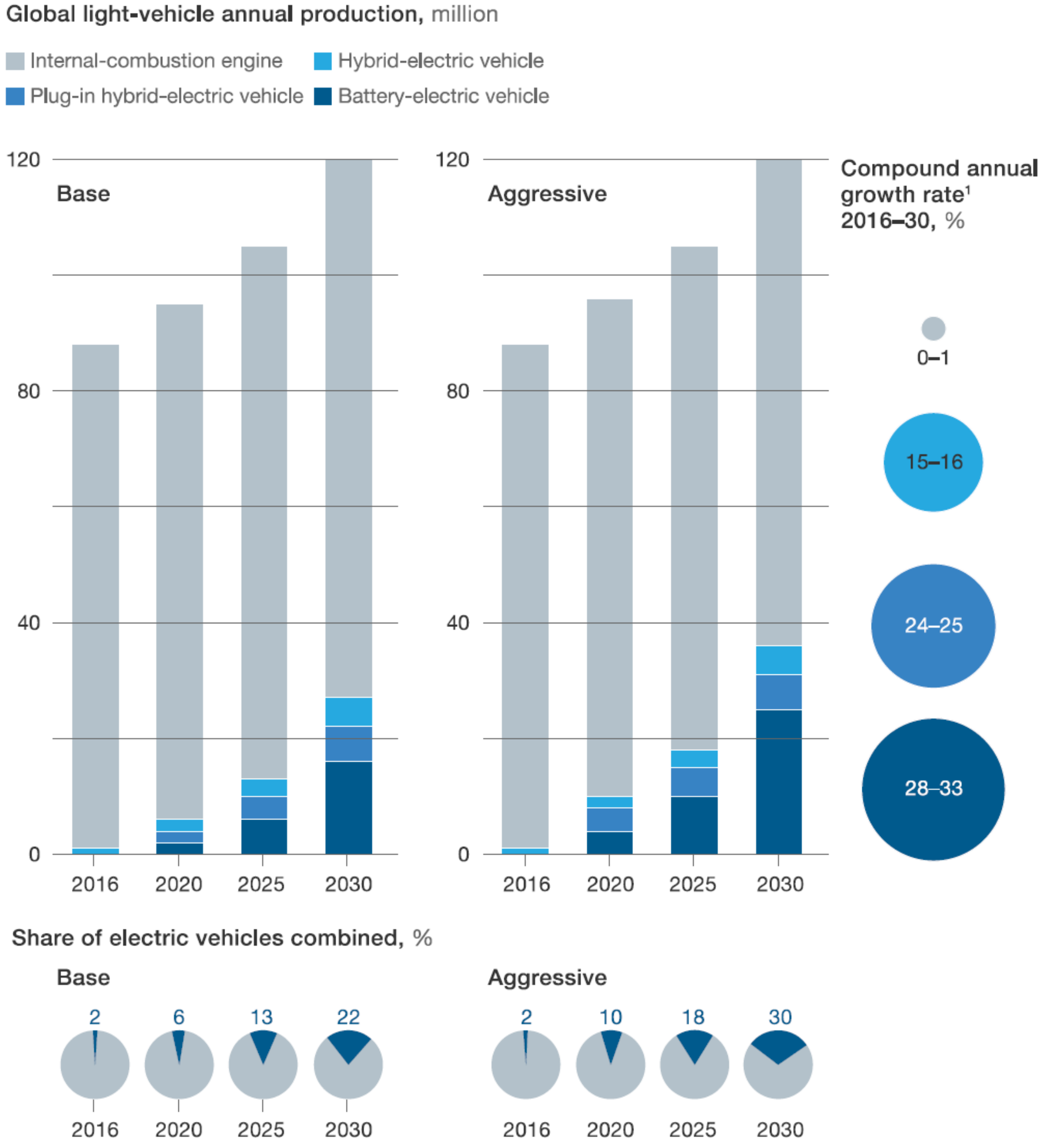


Example 1: Battery

Rechargable batteries



Electric vehicle (EV) revolution ➔ Driver for battery demand



[1]Range of base and aggressive scenarios.

McKinsey&Company | **Source:** McKinsey Sustainable Mobility Initiative

Demand for lithium and cobalt

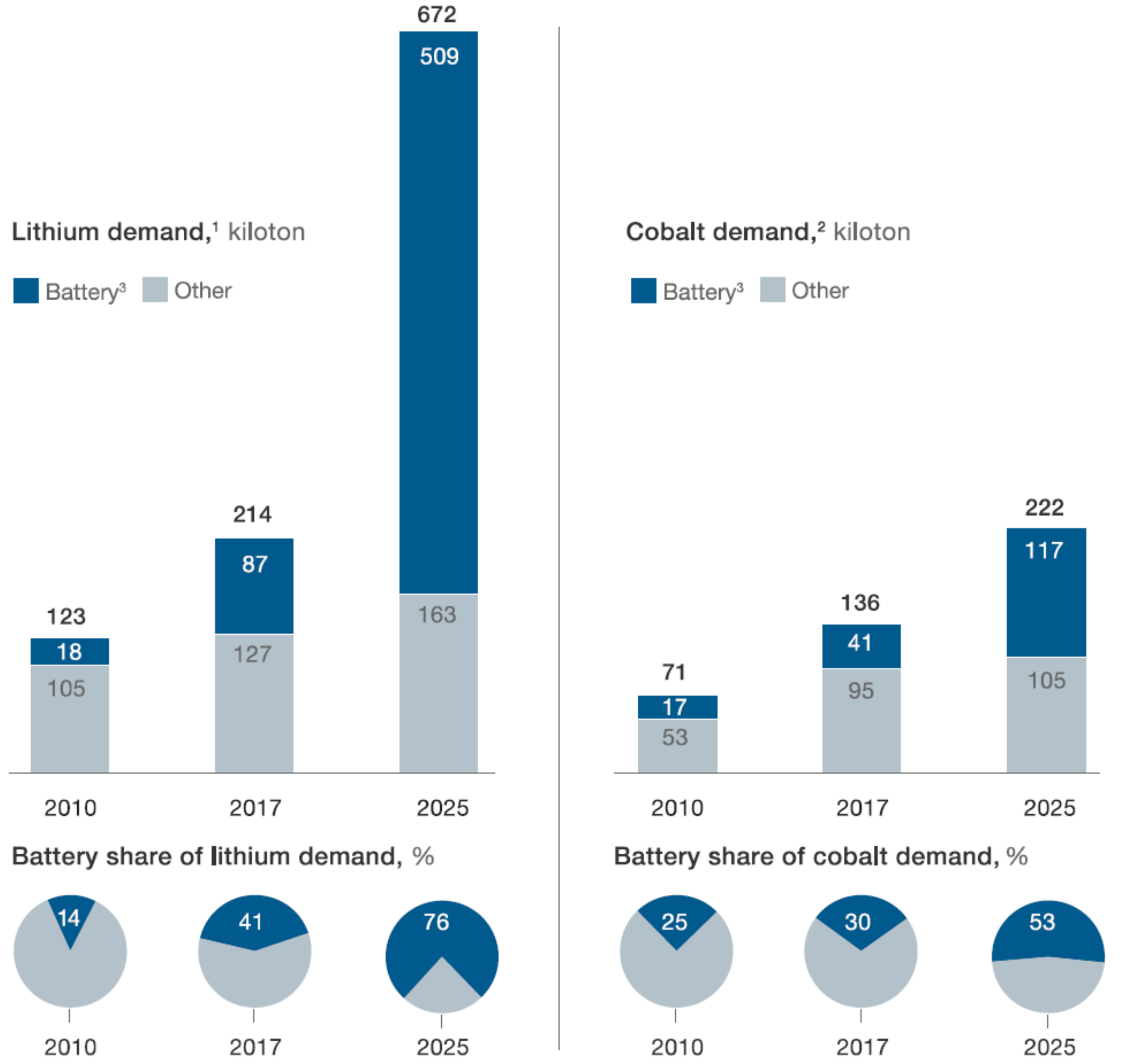
Issues:

Concerns regarding the future of the raw-material supply availability for batteries

Impact of rising commodity prices on battery production costs

➔ R&D for new materials needed, with no or low amount of critical raw materials

The growing adoption of EVs and the need for EV batteries with higher energy densities will see the demand for lithium increase more than threefold between 2017 and 2025. Cobalt will increase by 60 percent over the same period.



[1]Lithium carbonate equivalent.
[2]Refined metal equivalent.
[3]Includes automotive (hybrid-, plug-in hybrid-, and battery-electric vehicles), trucks and buses (light, medium, and heavy), two and three wheelers, machinery (forklifts and others), grid storage, and consumer electronics.
Note: Figures may not sum to listed totals, because of rounding.

McKinsey&Company | **Source:** McKinsey Basic Materials Institute

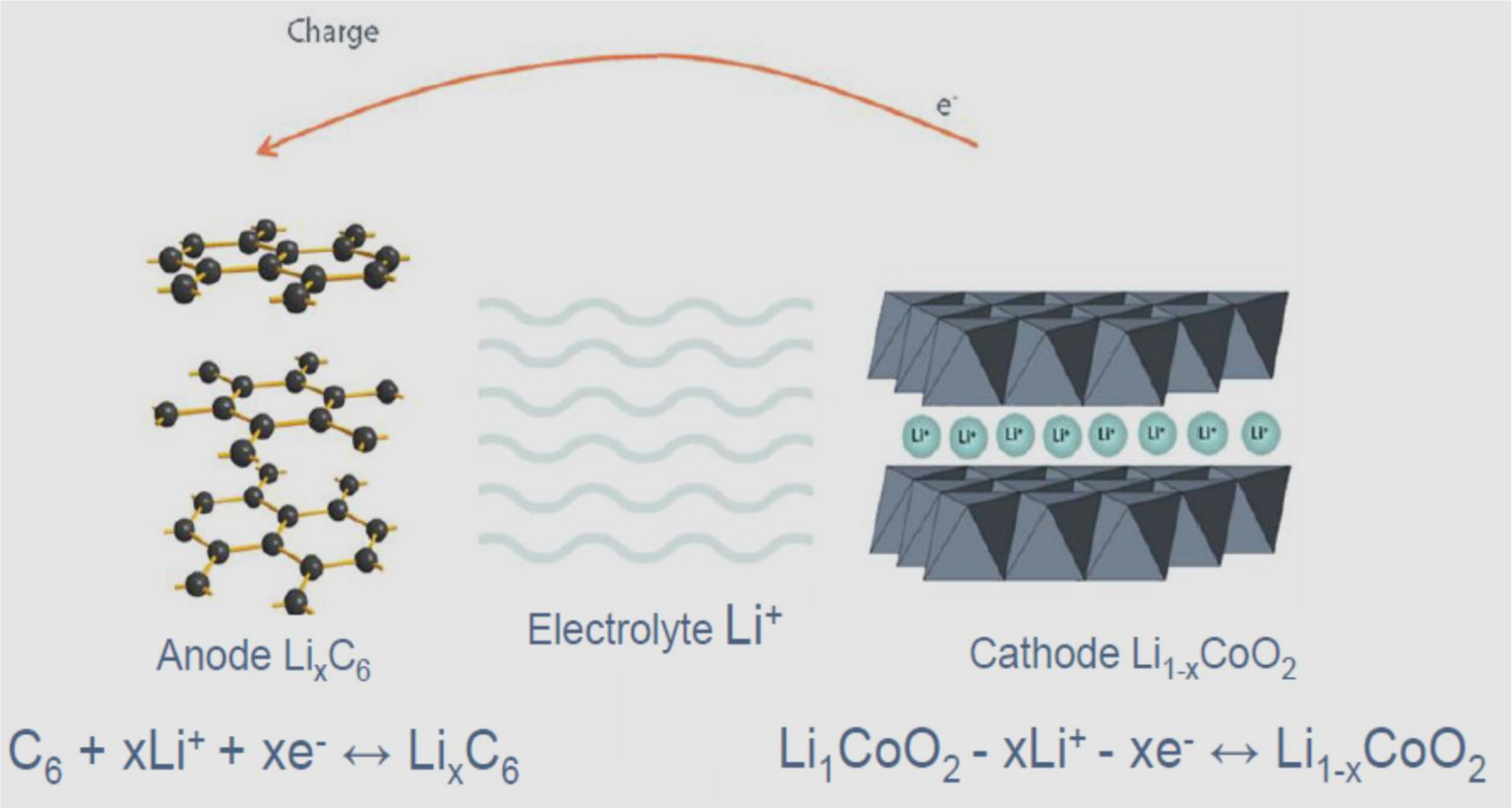
Research on Co-free and Li-free Na-ion batteries

AGH UST Kraków (PL) Fraunhofer IKTS Dresden (DE)

Co-free and Li-free Na-ion batteries have been recognized as one of **the candidates for next-generation rechargeable batteries**, because of their comparable energy density, significantly reduced costs and practically unlimited resources of sodium.

Research goal: Battery with a novel cathode material based on the low cost, earth abundant elements with $Na_2M_2(SO_4)_3$ chemical composition, green fabrication technology and with tailored microstructure.

Li-ion battery



Charging and discharging is related to a reversible „pumping" of lithium ions from one electrode to another (subsequent, reversible intercalation and deintercalation processes).

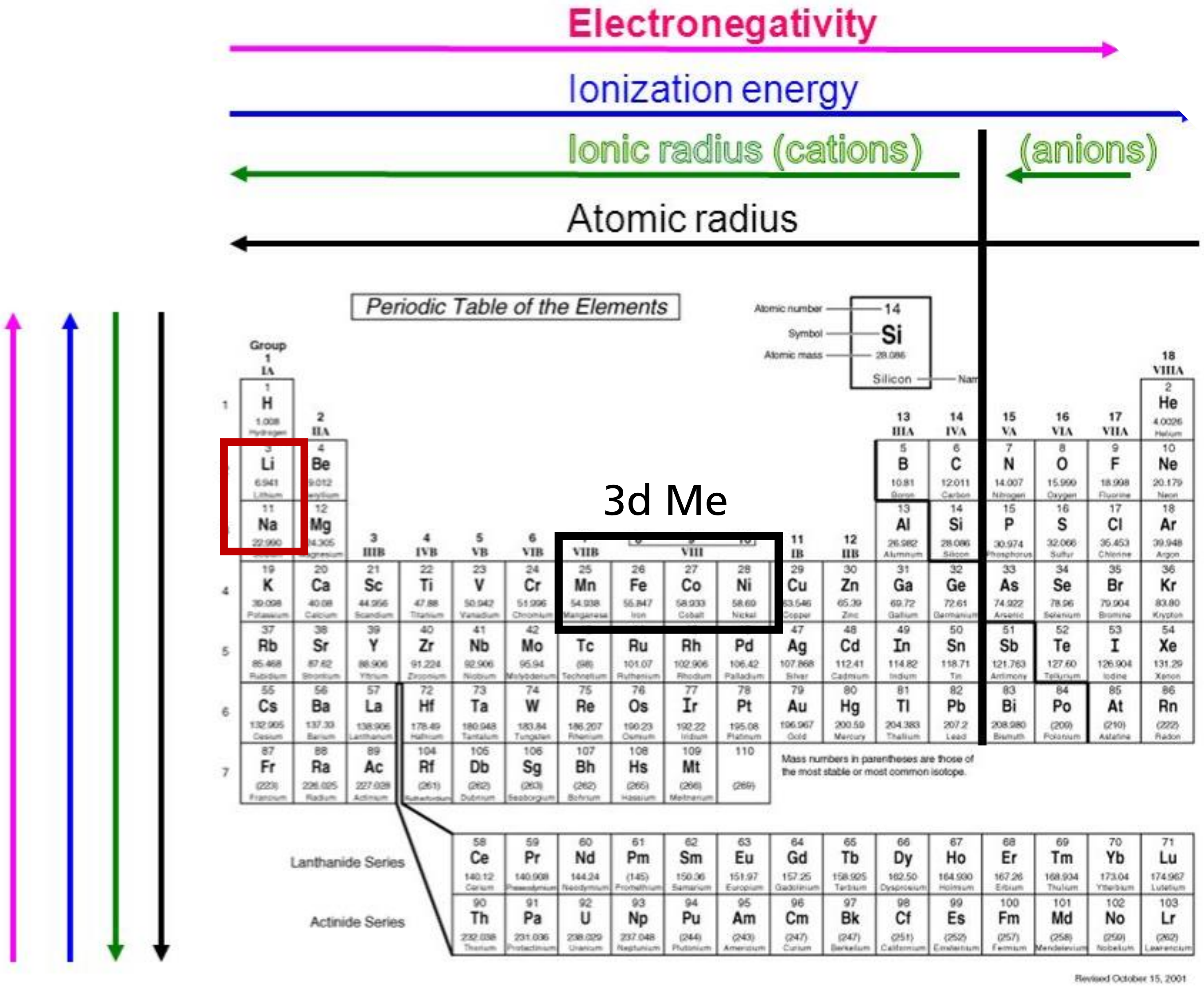
The intercalation of sodium is similar to intercalation of lithium.

Na-ion battery

- Ionic radius of Na+ is higher than of Li+ and results in a slightly lower volumetric and gravimetric energy density --> lower cell voltage and lower capacity
- $x\,Na^{+} + x\,e^{-} + M_aX_b \leftrightarrow Na_xM_aX_b$

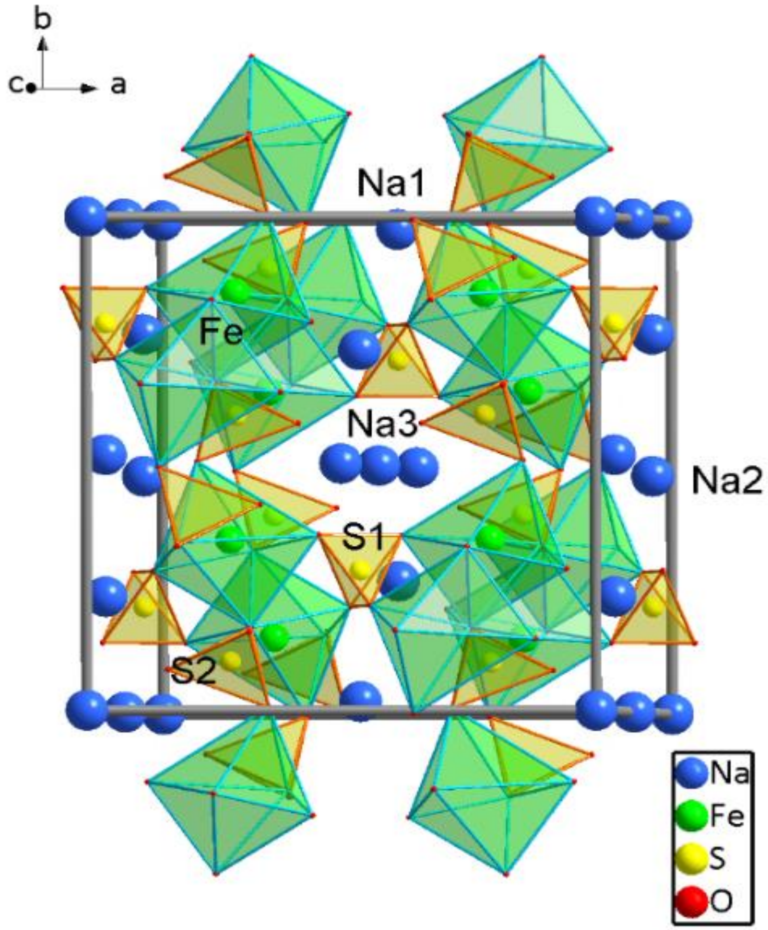
→ new approach called "electronic structure engineering" to control the electrochemical potential of $Na^{+}/Na_2M_2(SO_4)_3$ (M = Fe, Mn, Ni) cathode and its changes during sodium insertion in the battery

→ It is assumed that the chemical substitutions at the 3d metal site can modify the electronic states of the cathode material near the Fermi level.



Cathodes for Na-ion battery

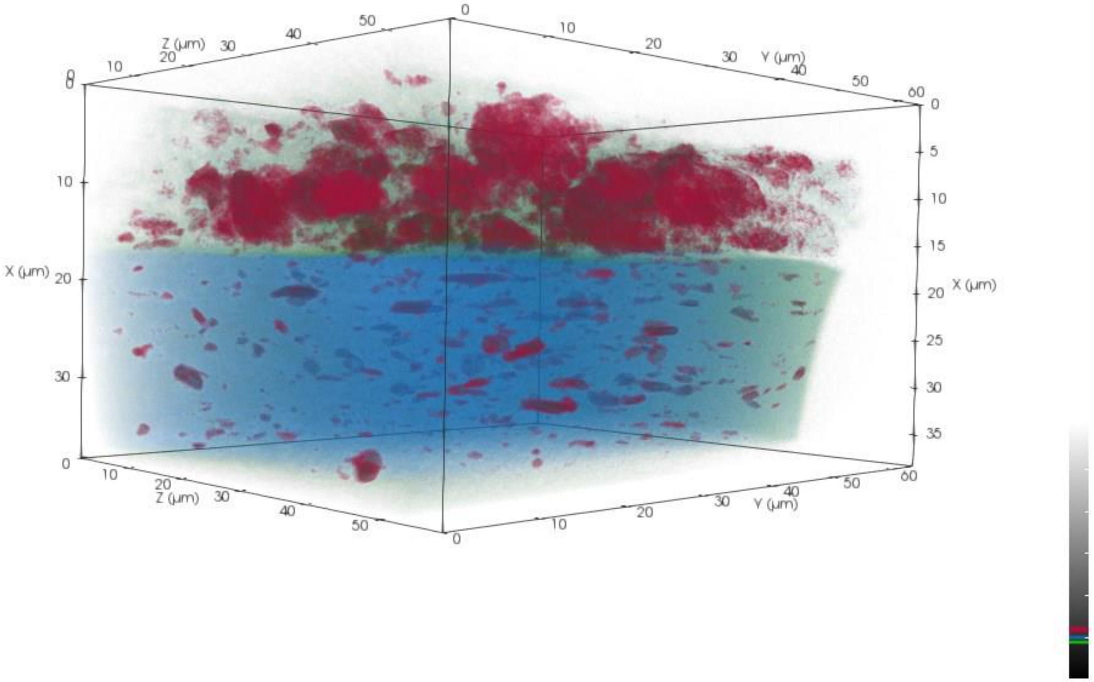
- The AGH Krakow team has developed and patented* a facile, low cost, green chemistry, low temperature synthesis method yielding nanometric $Na^+/Na_2M_2(SO_4)_3$ cathode material.
- This synthesis method material could give negligible impurity level (3 wt.%).



Crystal structure of $Na_2Fe_2(SO_4)_3$ alluaudite with sodium diffusion paths.

* Polish Patent Office, patent application 2017 no. 423612

X-ray studies at battery electrodes: Nano-XCT



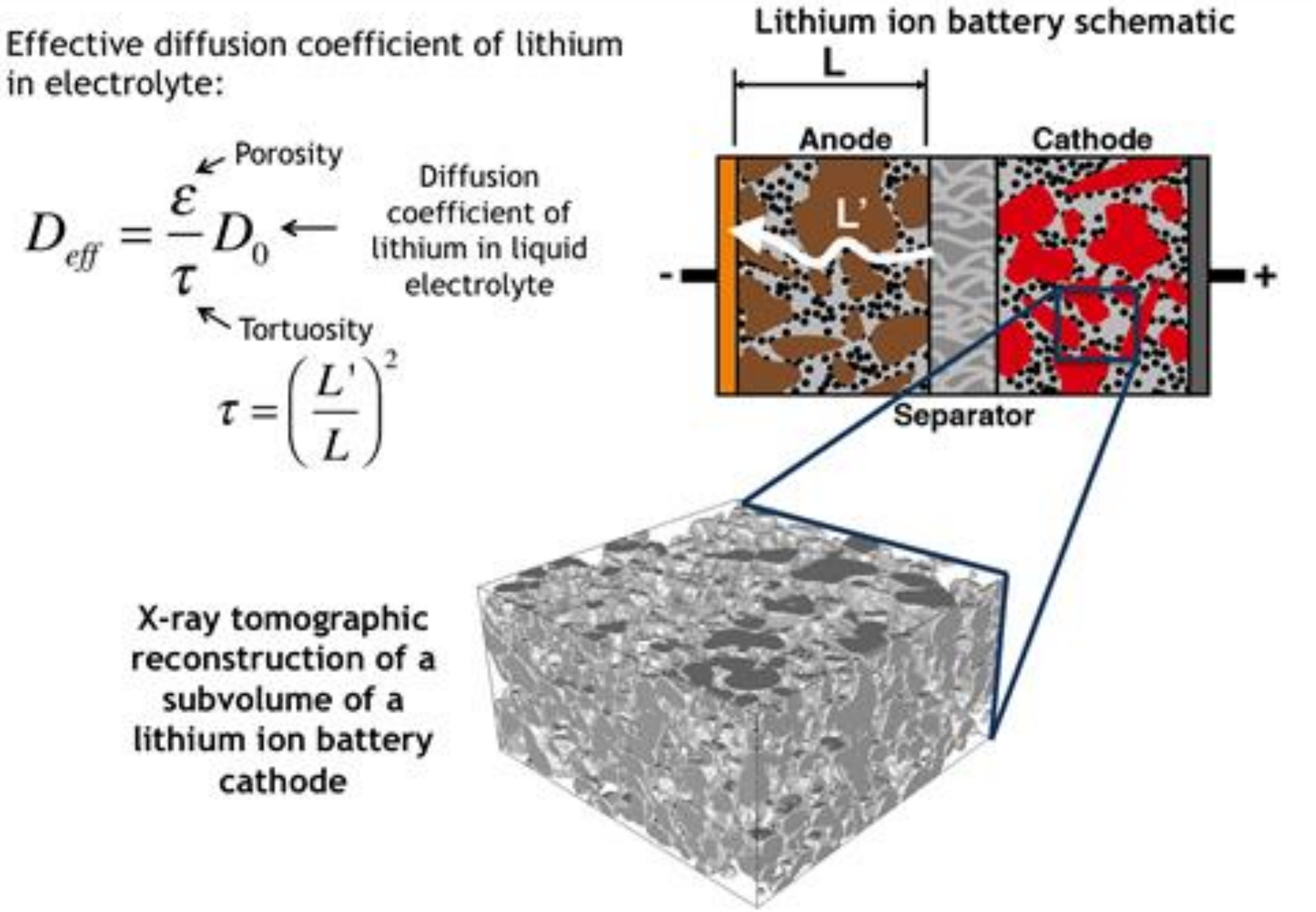
Nano XCT of cathode material (absorption contrast).

➔ Determination of 3D morphology parameters such as tortuosity.

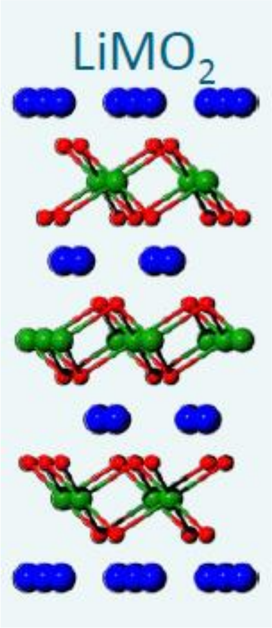
Tortuosity

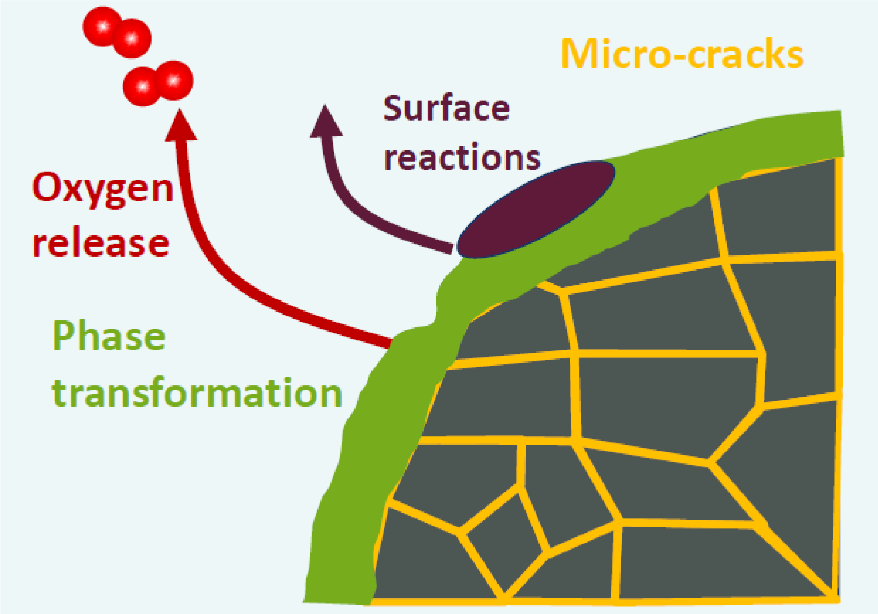
- In geometrical terms, tortuosity τ is defined as the fraction of the shortest pathway through a porous structure L ´and the Euclidean distance between the starting and end point of that pathway *L*

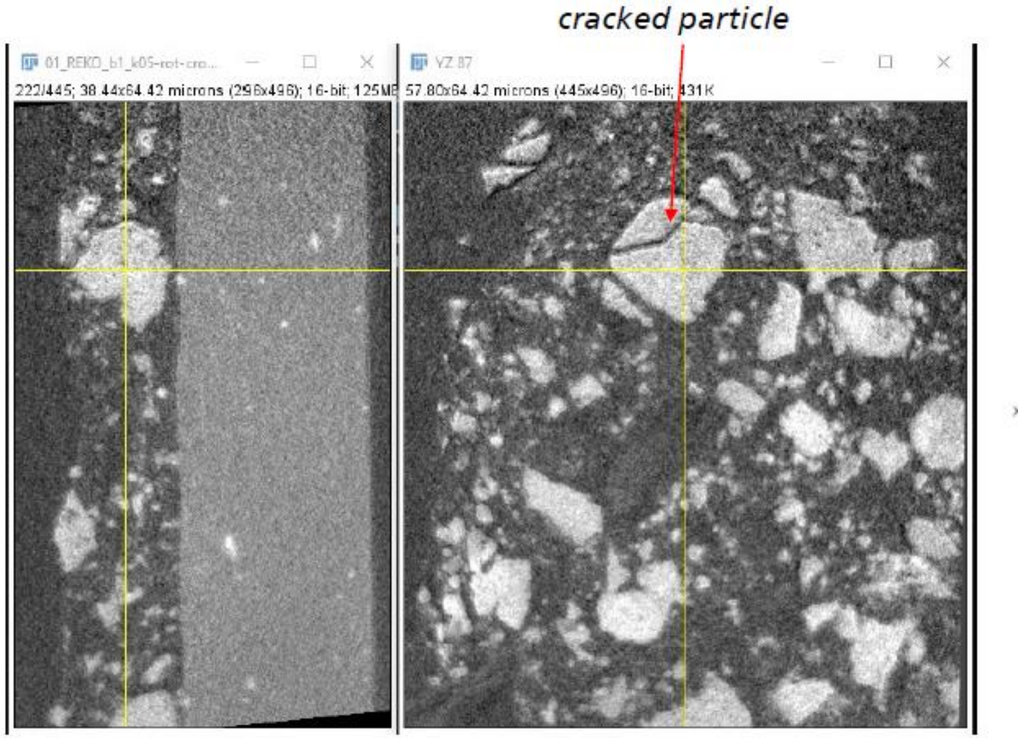
- Tortuosity describes influence of the morphology of the electrode on the effective transport properties of lithium ions in the electrolyte.



X-ray studies at battery electrodes: Micro-cracks in battery electrode materials





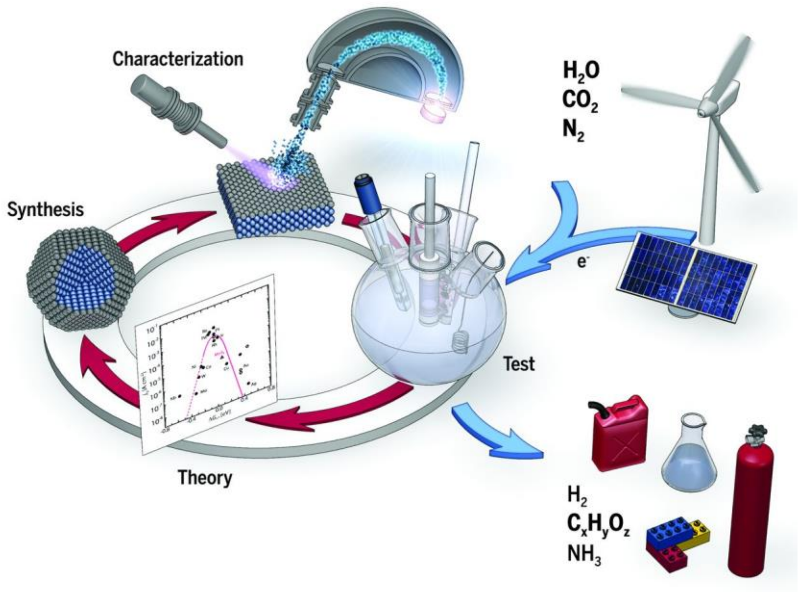


- Tomography, virtual cross section

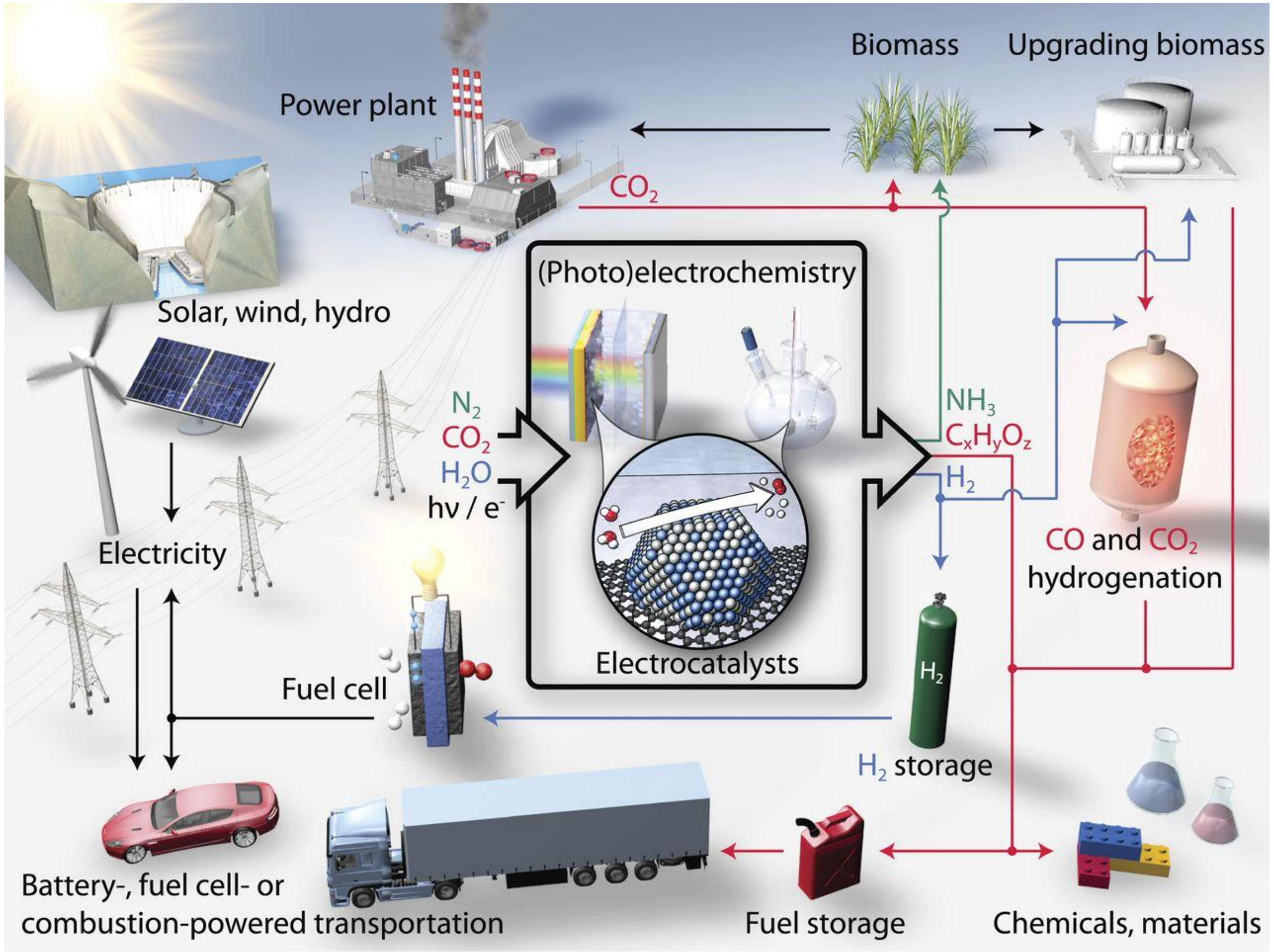
Nano XCT (absorption contrast):
Cracks in $Na_2M_2(SO_4)_3$ cathode material

Example 2: Hydrogen technologies / Water splitting

Sustainable energy future



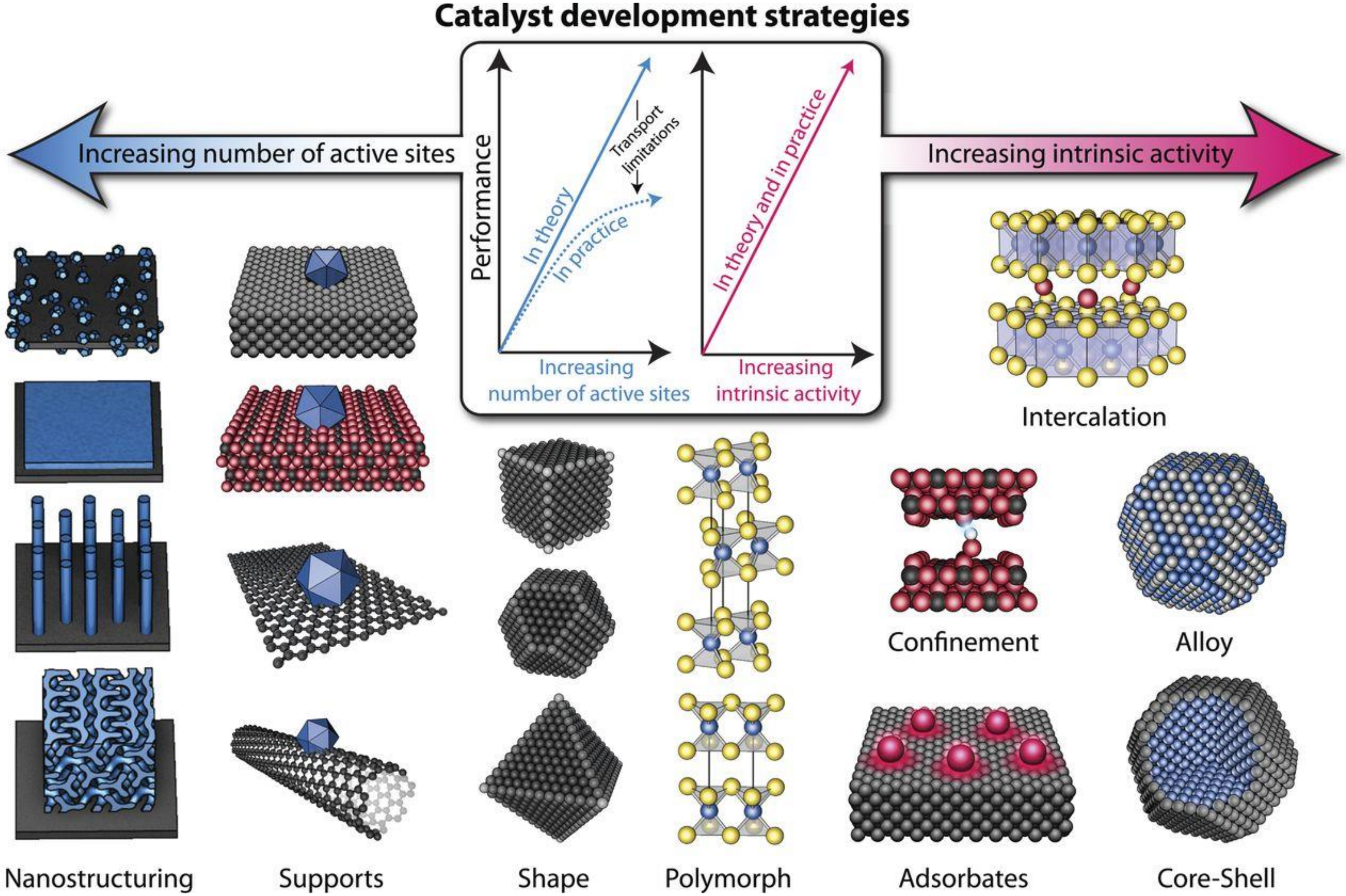
Schematic of **electrochemical conversion** of water, carbon dioxide, and nitrogen into value-added products, using energy from renewable sources.



Schematic of a **sustainable energy landscape based on electrocatalysis**

Z. W. Seh et al., Science 355, 6321 (2017)

Electrocatalyst development strategies



Schematic of various **catalyst development strategies**, which aim to increase the number of active sites and/or increase the intrinsic activity of each active site

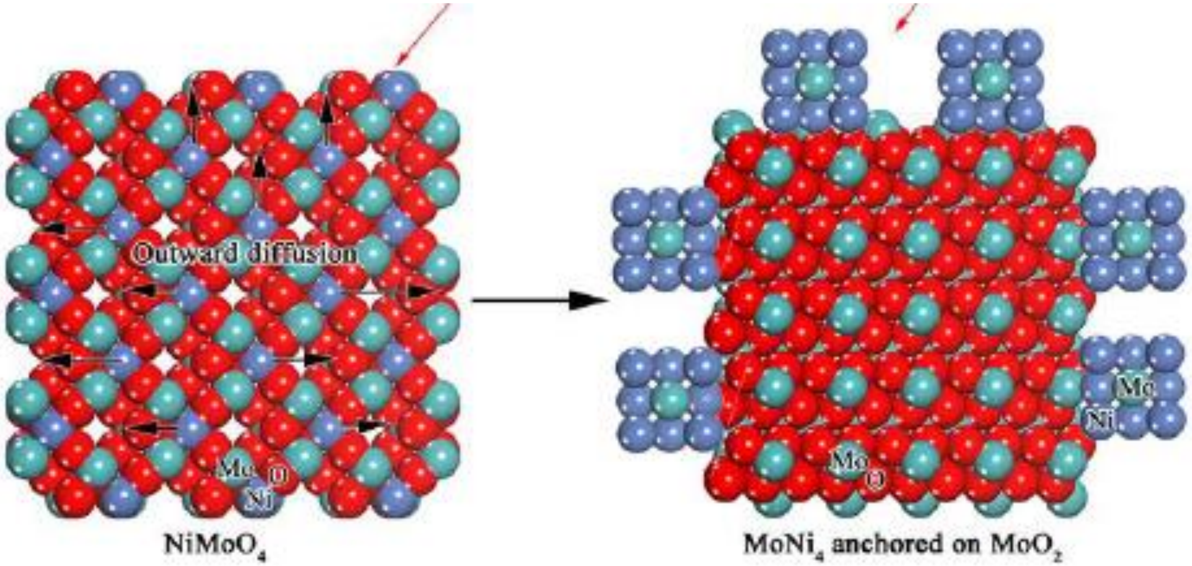
Z. W. Seh et al., Science 355, 6321 (2017)

Design and synthesis of material systems for electrochemical energy conversion

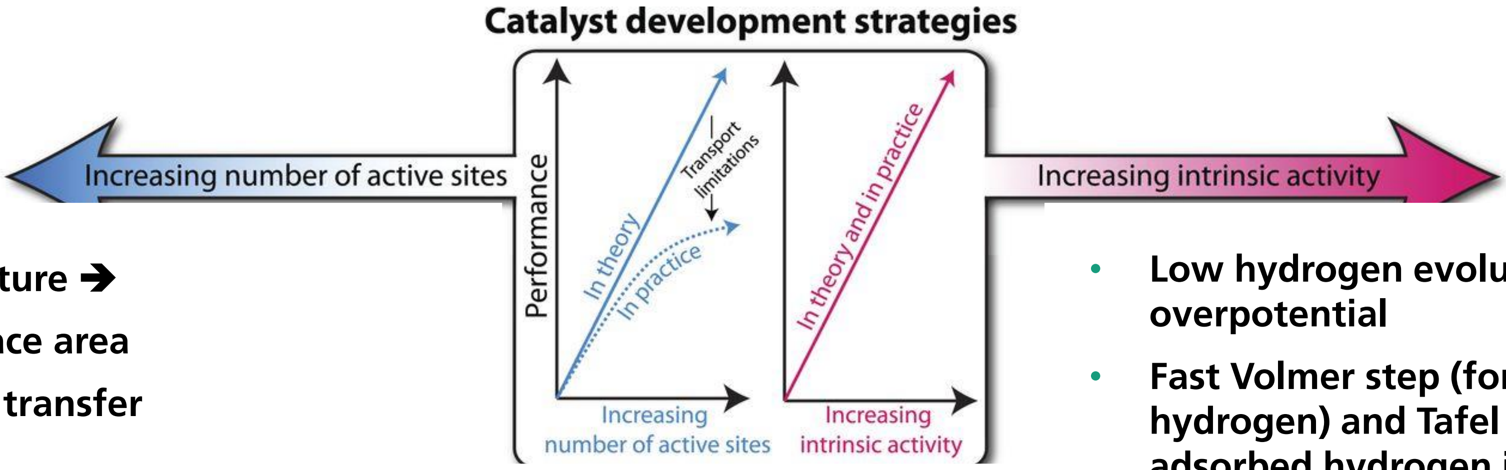
Requirements for material systems with high electrocatalytic activity (performance) and electrochemical stability (reliability):

1) Materials with **optimized intrinsic properties of the electrocatalytic active components**
   - The intrinsic properties of a component determine ist activity and conductivity.
2) Materials with **optimized morphology of hierarchically systems**.
   - Modification of the maetrial's morphology selectively exposes specific crystal faces with higher activity.
   - The 3D porous structure with high surface area can provide abundant active sites because favorable structures contribute to preventing agglomeration and can promote mass transfer.

Example: $MoNi_4$ electrocatalysts, anchored on MoO_2 cuboids, aligned on Ni foam



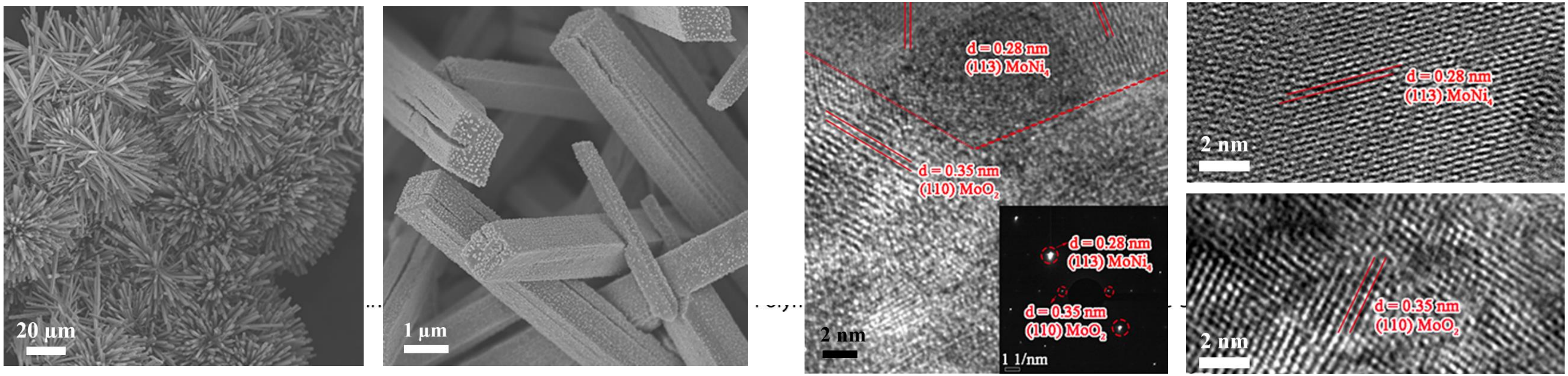
Intrinsic properties of $MoNi_4$ electrocatalyst and morphology of the system $MoNi_4/MoO_2@Ni$ for water splitting



- 3D porous structure ➔
  - large surface area
  - high mass transfer

- Low hydrogen evolution reaction (HER) overpotential
- Fast Volmer step (formation of adsorbed hydrogen) and Tafel step (combination of adsorbed hydrogen into molecular hydrogen)

Morphology and structure analysis of $MoNi_4/MoO_2@Ni$.



J. Zhang, et al., Nature Communications 8, 15437 (2017)

Morphology of the electrocatalytic system $MoNi_4/MoO_2@Ni$: Multi-scale XCT

- Multi-scale 3D information is provided
- Possible image-based quantitative analysis
- Quantitative correlation between 3D hierarchical structure and performance
- Hierarchical structure design with 3D model

Resulting data:

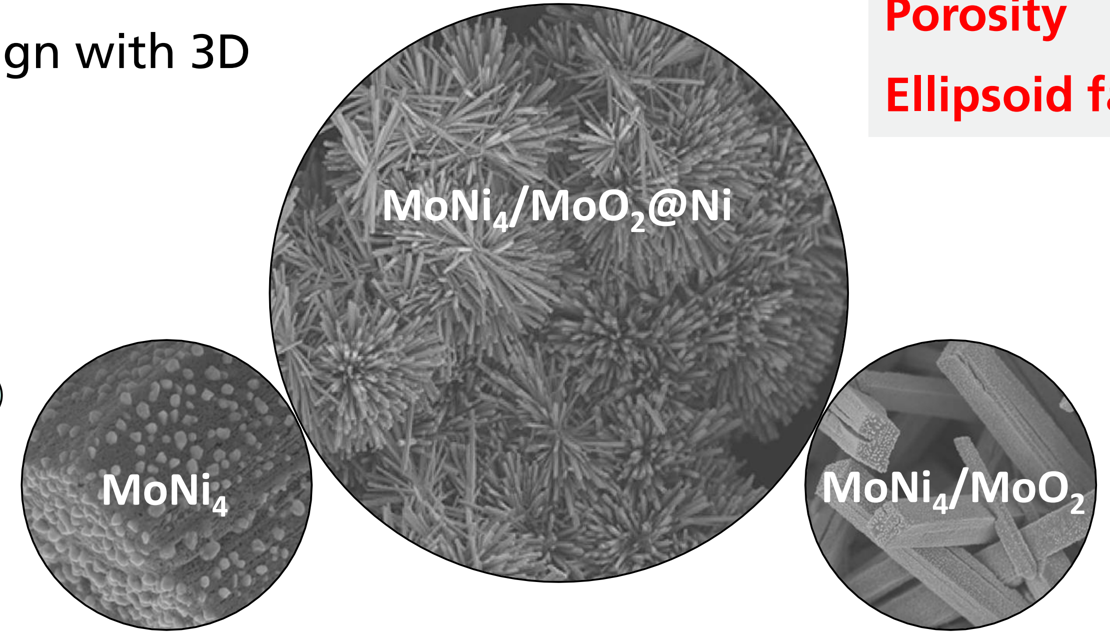
Tortuosity

Geometrical / Active surface area

Size distribution

Porosity

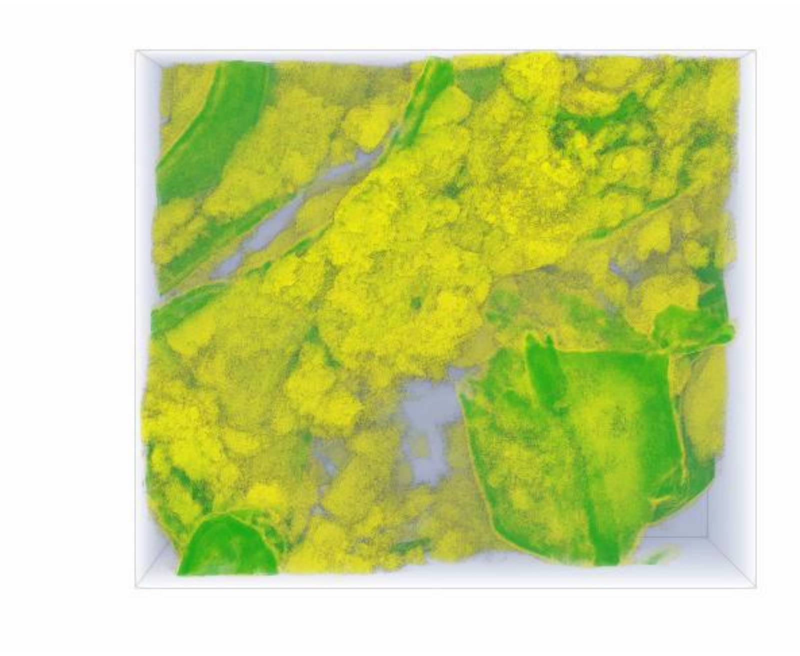
Ellipsoid factor (rod-plate geometry)



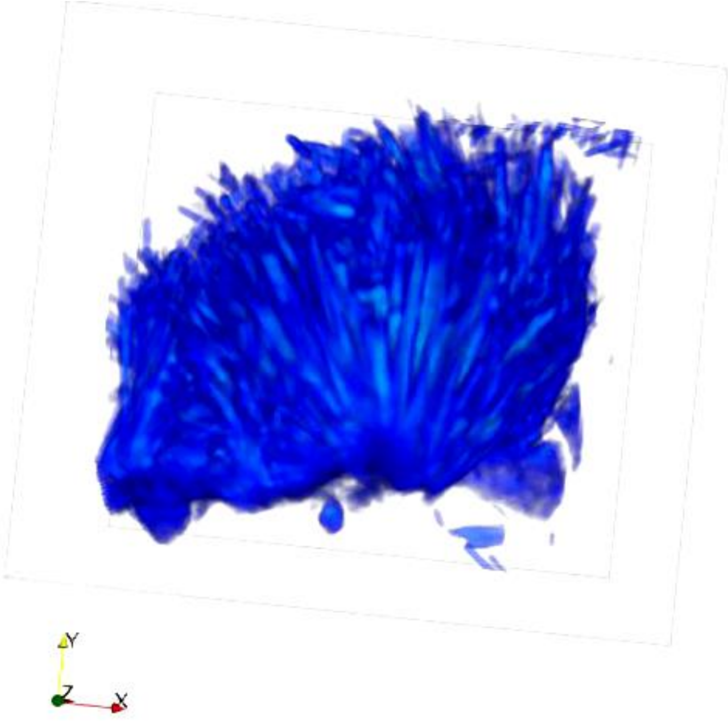
Hierarchical structure of Ni / MoO_2 / $MoNi_4$ System

Courtesy: S. Werner (HZB Berlin)

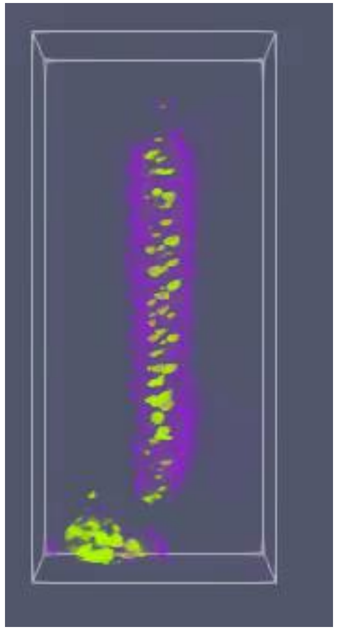
Multi-scale XCT of the electrocatalytic system $MoNi_4/MoO_2@Ni$



Micro-XCT



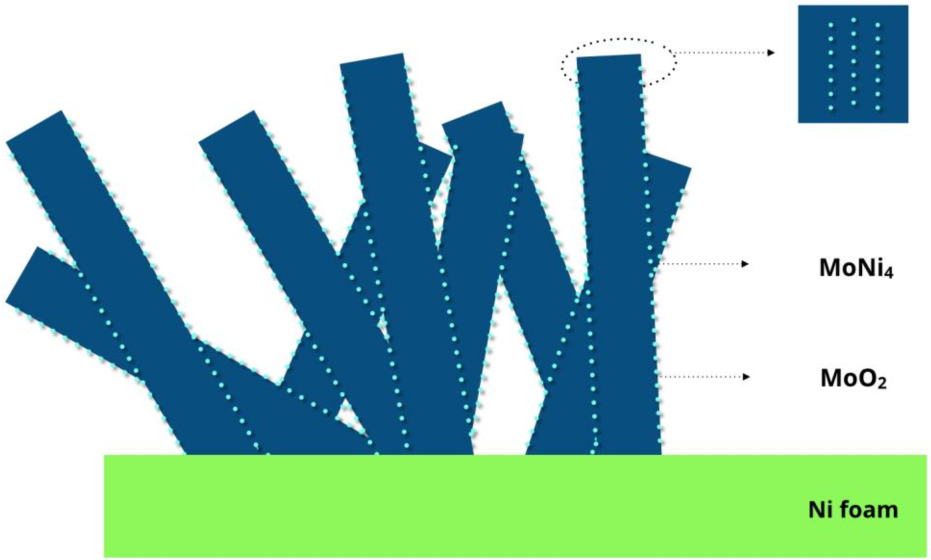
Nano-XCT (lab)



Nano-XCT (SR)

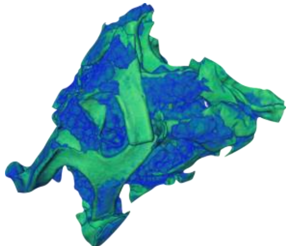
Courtesy: S. Werner (HZB Berlin)

Multi–scale XCT of hierarchically structured materials: $MoNi_4$ electrocatalysts anchored on MoO_2 cuboids aligned on Ni foam



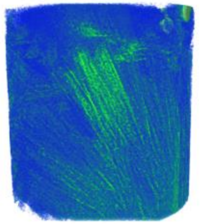
A novel transition–metal-based materials system: $MoNi_4$ electrocatalysts anchored on MoO_2 cuboids aligned on Ni foam

- **The design of high-performance and durable 3D electrocatalysts requires electrochemically active surfaces and an optimized hierarchical morphology.**
- **Multi-scale X-ray tomography:** A systematic approach to determine the 3D morphology of hierarchically structured materials with high accuracy.



MoO_2@Ni

Micro-XCT



MoO_2@Ni

Nano-XCT

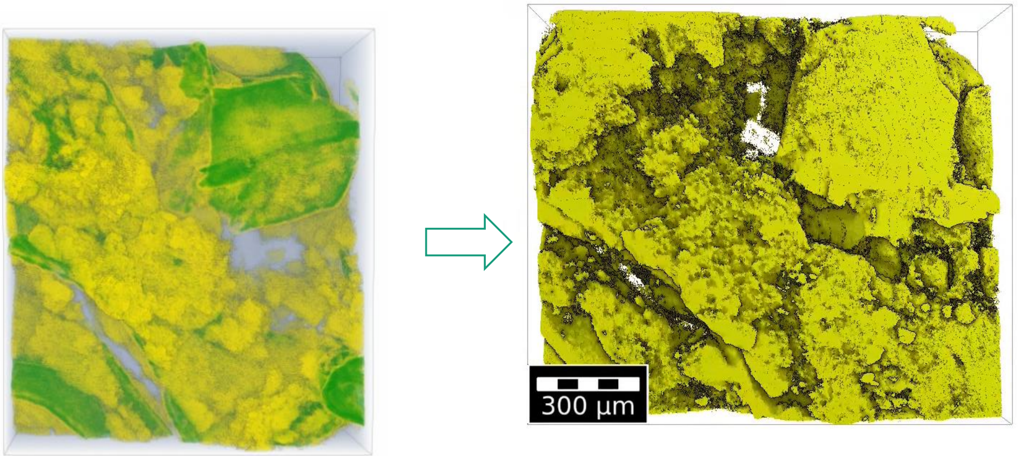
$MoNi_4$@MoO_2

Nano-XCT

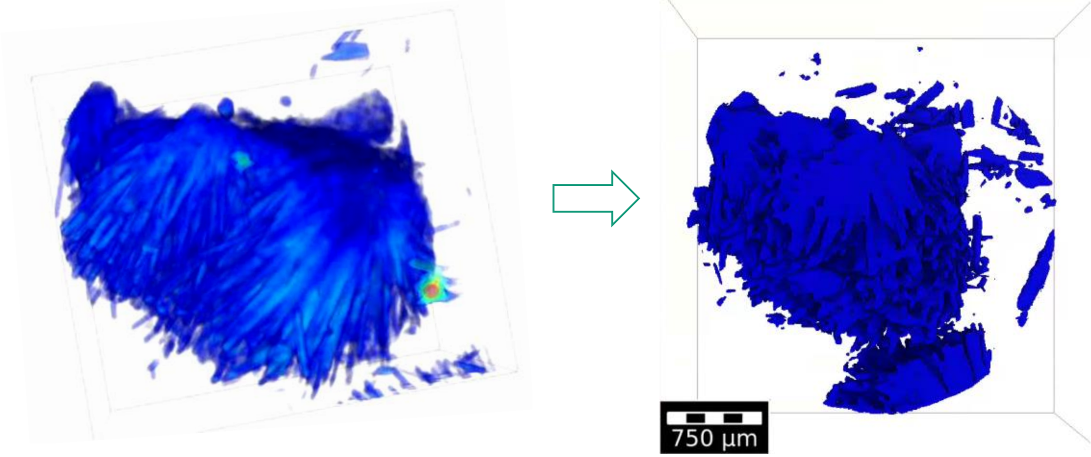
Method	FOV	Spatial resolution	Energy	Sample thickness
Micro-XCT	0.5–50 mm	0.7 µm	30–160 kV	0.5–70 mm
Laboratory nano-XCT	10–100 µm	30–100 nm	5–20 keV	50 µm–10 mm
Synchrotron radiation nano-XCT	5–100 µm	10–100 nm	0.1–20 keV	1 µm-10 mm

E. Topal et al., BMC Materials (2019, in review)

Determination of morphology parameters, model building for the electrocatalytic system $MoNi_4/MoO_2@Ni$



GeoDict software



- Model building by importing the 3D CT data into GeoDict
- Design of a 3D model with performant and durable hierarchical microstructure

Results:

Tortuosity

Geometrical / Active surface area

Size distribution

Porosity

Ellipsoid factor (rod-plate geometry)

Courtesy: Onkar Pathak (Fraunhofer IKTS)

Fraunhofer
IKTS

Take-away message

- Materials are a key technology for energy storage and conversion.

- Nanomaterials are characterized by a high surface-to-volume ratio and short diffusion pathways. They provide a solution for simultaneously achieving high energy density and high power density.

- Nano X-ray computed tomography is a novel technique to provide 3D information of the morphology of hierarchically structures materials systems, including kinetic electrochemical processes.

- R&D is needed for new materials for battery electrodes (materials substitution!) with no or low amount of critical raw materials (e.g. Co, Li).

- Advanced design and synthesis of materials for future energy storage and conversion systems is needed
  - with optimized intrinsic properties of the electrocatalytic active components *and*
  - with optimized morphology of hierarchically systems.

Thank you !

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