REGEN-Seminar

BTU Cottbus, Lehrstuhl Angewandte Physik/Sensorik

Brandenburgische Technische Universität Cottbus

New developments in the field of energy storage

0–3 composite supercapacitors

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SUPER KON

ForMaT

UNTERNEHMEN REGION

Die BMBF-Innovationsinitiative Neue Länder

gründerwerkstatt NANOSTRUKTURIERTE WERKSTOFFE

Center of Materials Science (CMAT)

Nanotechnikum Weinberg, since 2008, 1800 m^2 labs, 620 m^2 cleanroom

TGZ HALLE

Central lab units (CMAT-MLU Halle)

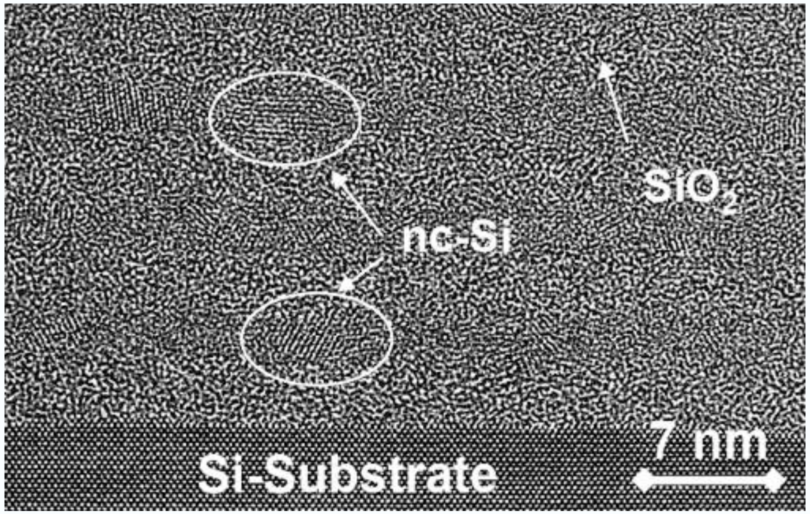
- Nanostructuring: lithography, thin film deposition, device prototyping
- Nanoanalysis: electron microscopy, optical characterization, positron annihilation

Research disposal area (Bio–Nano Center)

for physists, chemists, materials scientists, biologists, pharmacists

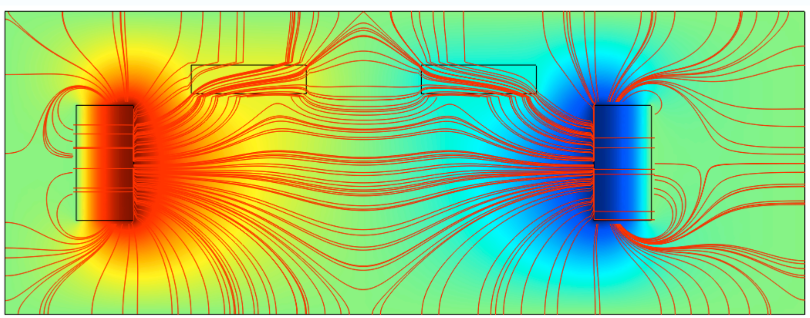
MLU, MPI, Fraunhofer, TGZ (KMU)

Renewable energy materials



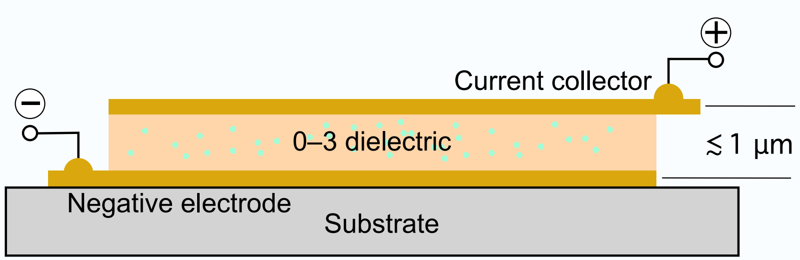
GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung

- Silicon-based nanostructured thin film materials as functional elements for next-generation solar cells



WING
Werkstoffinnovationen für Industrie und Gesellschaft

- Si and Si–Ge thin films for thermoelectric applications



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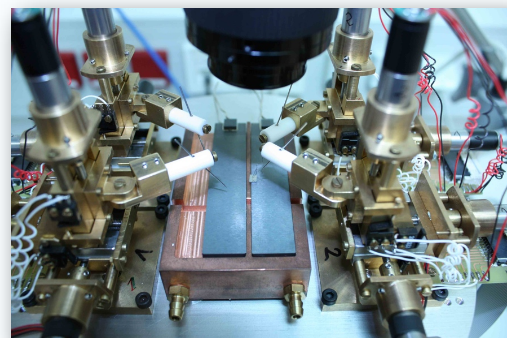
- New supercapacitors as energy storage devices

Equipment

Nanostructuring

Cleanroom class 10/100/10000

Analysis



- Various electron microscopes
- Raman microscopy, ellipsometry
- Atomic force microscopy
- Electrical/thermal transport measurements

Renewable energies = Direct energy from the sun

- Oil resources: 3 trillion barrels ($4 \cdot 10^{14}$ kg) ≙ energy of $2 \cdot 10^{22}$ J; supplied from the Sun in 1½ days
- Amount of energy humans use annually: $5 \cdot 10^{20}$ J, delivered to Earth by the Sun in 1 h
- Enormous power of the Sun continuously delivered to Earth: $1 \cdot 10^{5}$ TW; human civilization uses currently 10 TW

Values after GW Crabtree, NS Lewis: Phys today **3** (2007) 37
Video: NASA

Energy from renewable resources

- Climate discussion is about CO_2.
- Basic orientation to energies from renewable resources needed
- Grid consolidation, distributed energy supply
- Energy efficiency, saving
- Further development of renewable energies: Photovoltaics, solar thermal energy, wind, water, biofuel
- Requirement for new materials

3月11日

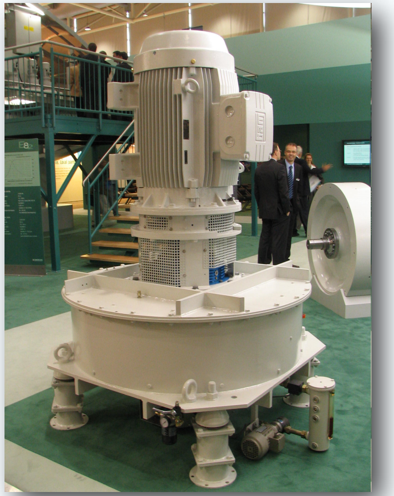
Nanostructured materials

- Better energy storage devices are needed for sustainable energy supply.
- New materials are the key for basic improvements.
- Nanoscaled materials can be precisely adopted for energy harvesting, transformation and storage
- Excellent properties for the selection of electrodes, electrolytes or dielectrics
- Nano-scaled electrolytes, nanoelectrodes for lithium ion batteries, supercapacitors, fuel cells
- Concept followed for electrochemical, as well as for electrostatic storage

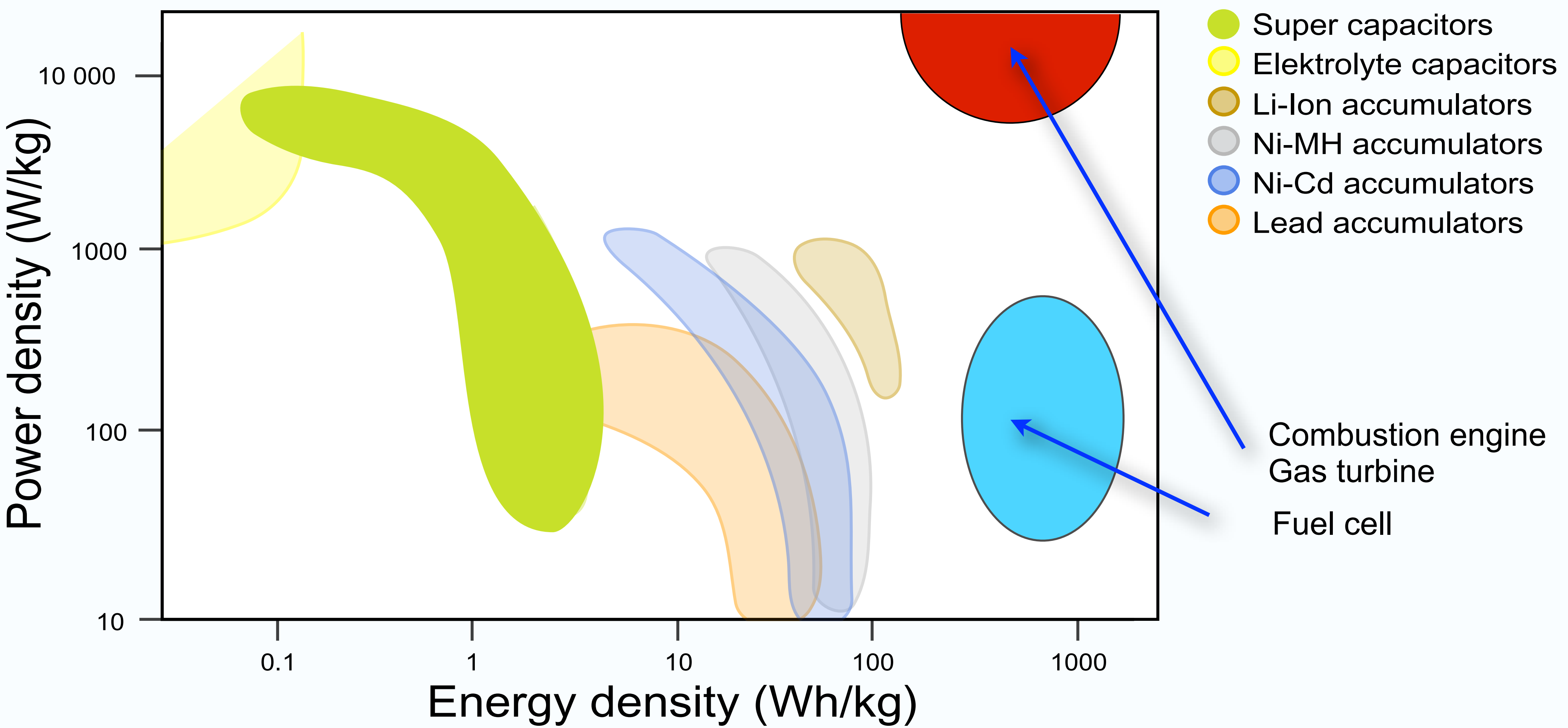
Energy storage

- Renewable energy sources: highly discontinuous
- Various energy storage concepts
  - Thermal and thermochemical storage
    (water, water–gravel, latent heat)
  - Chemical storage
    (hydrogen)
  - Mechanical storage
    (fly wheel, pump storage station, compressed air)
  - Electrochemical storage
    (lead, lithium ion, redox flow, NaS battery)
- Advantages ↔ disadvantages

  → no single solution for all applications



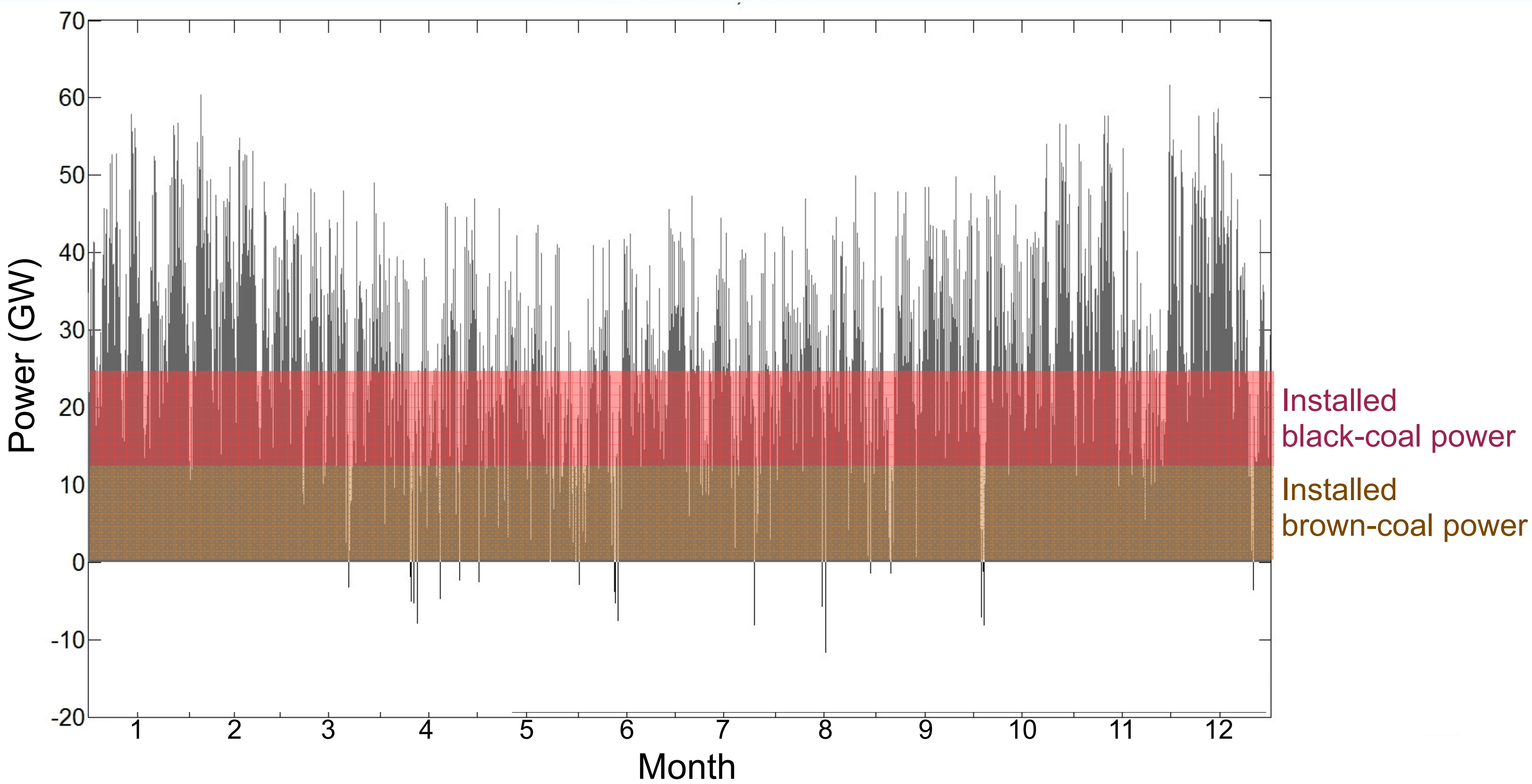
Ragone diagram



Time scales

- Large time scales (seconds to weeks)
- Short-time storage
  (fluctuations in the grid, grid management, guarantee of supply)
- Middle-range storage
  (electromobility)
- Long-time storage
  (*e. g.* longer periods without wind)

Need for energy storage



Estimated fluctuations in the residual power for 2020

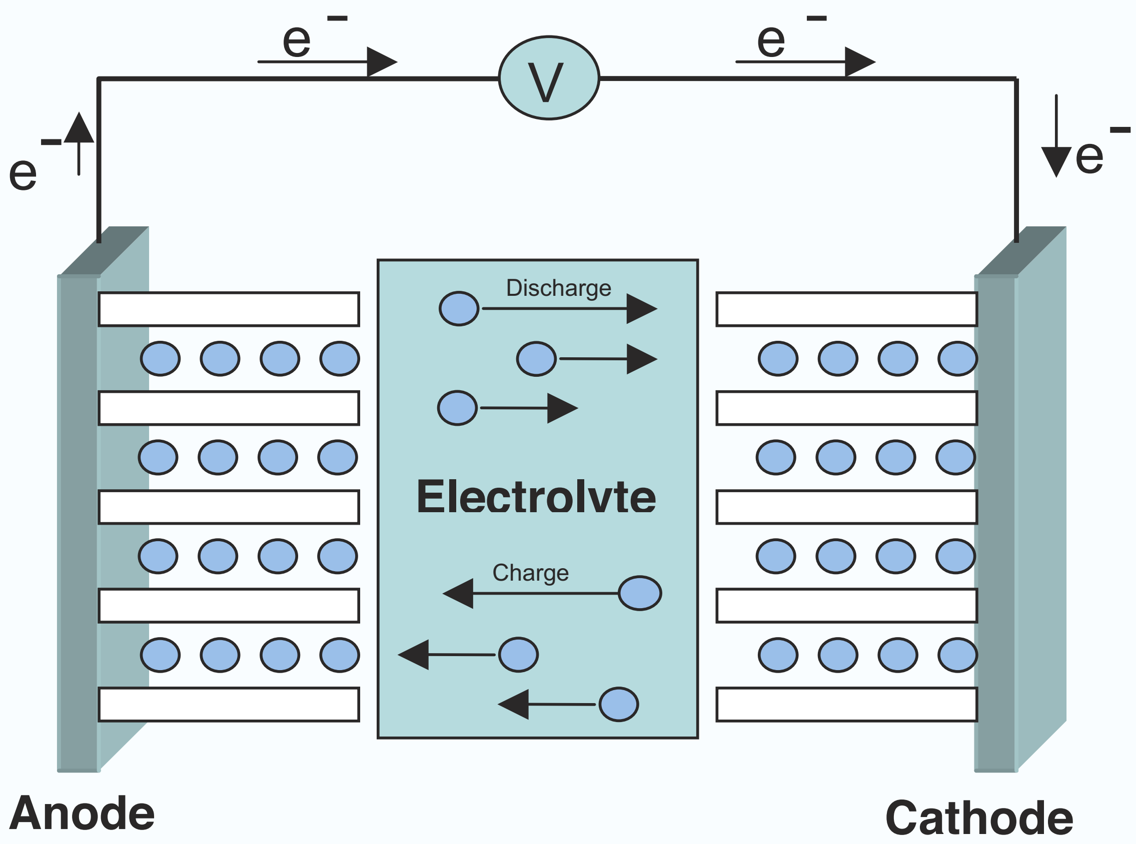
[J Quentin 2011]

Electrical storage

- Characteristics
  - Energy density, power density, storage time, voltage
  - industrial processing, prize, weight
- Electrochemical devices (batteries, accumulators) mainly used
- Disadvantages
  - Limited lifetime, temperature range
  - Memory effect
  - Problems with overloading, deep discharge
  - Low charging speeds

Selfdischarge	Battery:		1 – 5 %	per year
	Accum:	Li Ion:	2 %	per month
		Lead:	2 – 30 %	
		NiCd:	15 – 20 %	

Lithium ion battery



Scheme of a classical LIB

[Wallace 2009]

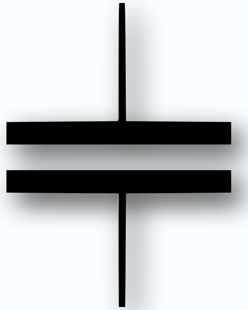
Classical electrode process

(Intercalation)

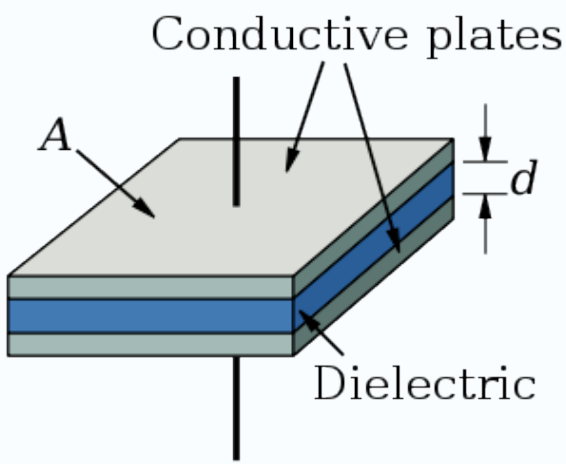
$$Li_xM \leftrightarrow M + x\, Li^+ + x\, e^-$$

(M – metal)

Capacitors



Capacitance C = Amount of charge stored per unit voltage



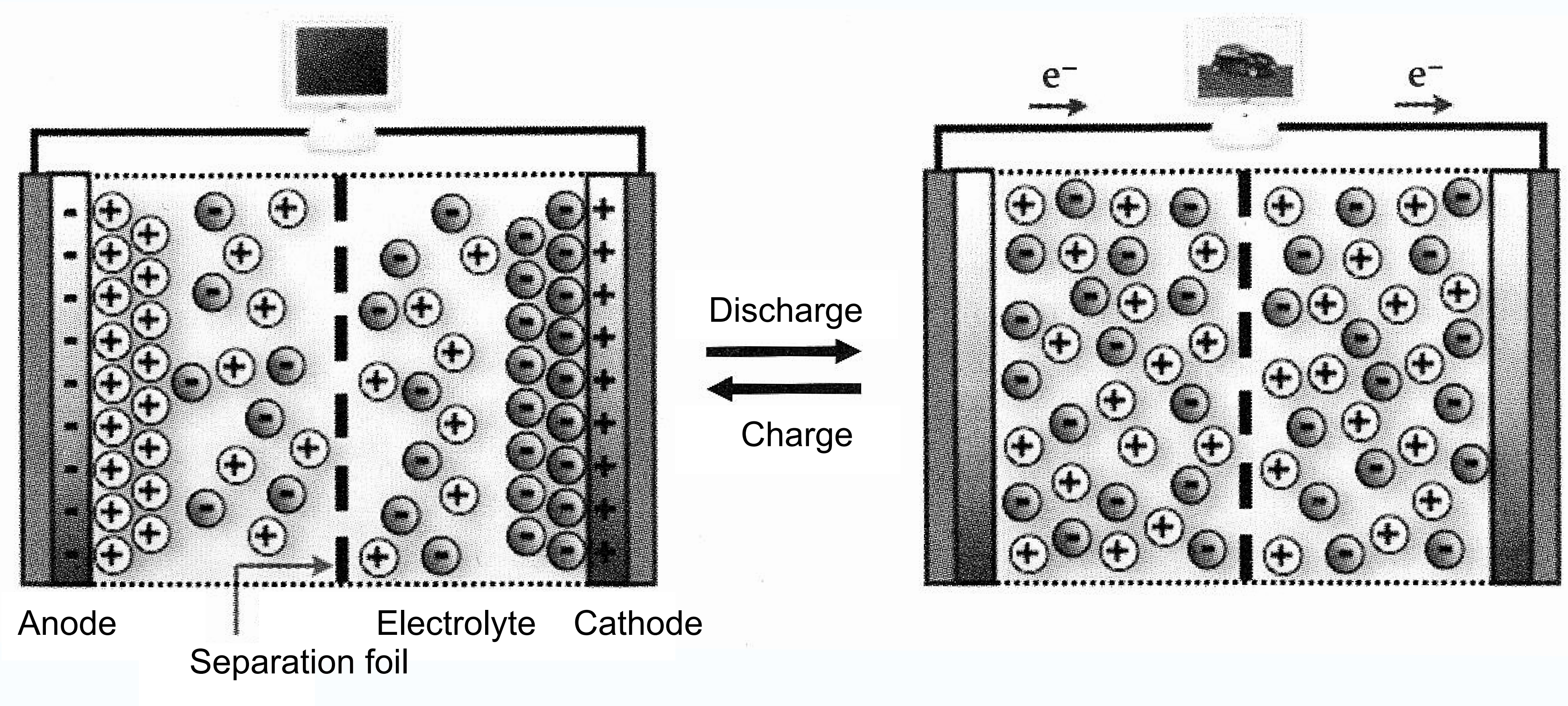
$$C = \varepsilon_r \varepsilon_0 \frac{A}{d}$$

ε_0 vacuum permittivity $\approx 9 \cdot 10^{-12}$ F/m

ε_r relative static permittivity of the dielectric (sometimes called dielectric constant)

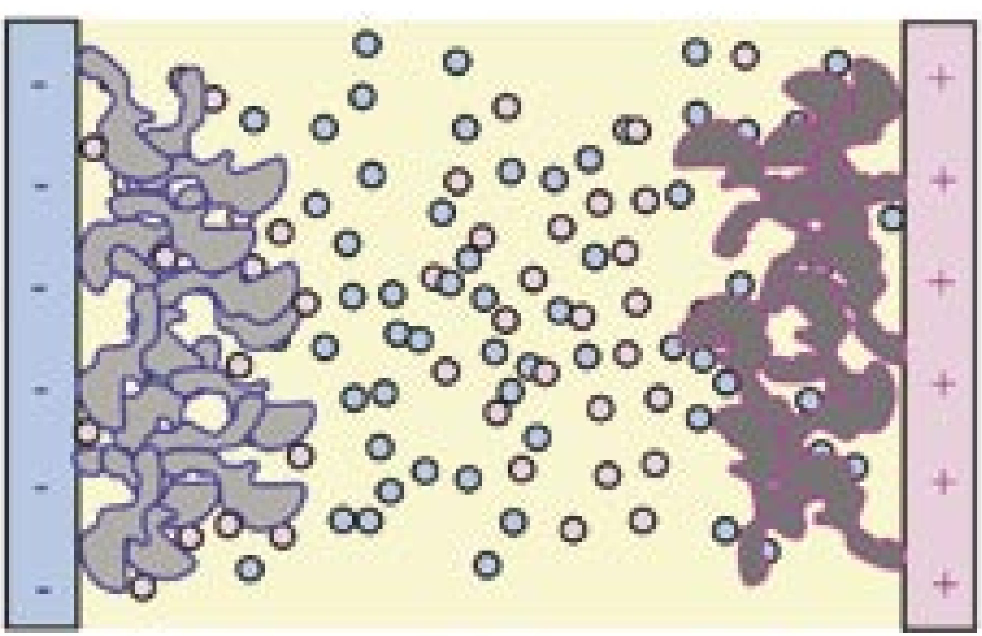
Energy stored: $$E = \frac{1}{2} C U^2 = \frac{1}{2} \varepsilon_r \varepsilon_0 \frac{A}{d} U^2$$

Double-layer capacitor



[Abruña 2008]

Capacity



$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \qquad \frac{C}{A} = \frac{\varepsilon_r \varepsilon_0}{p \ln \frac{p}{a_0}}$$

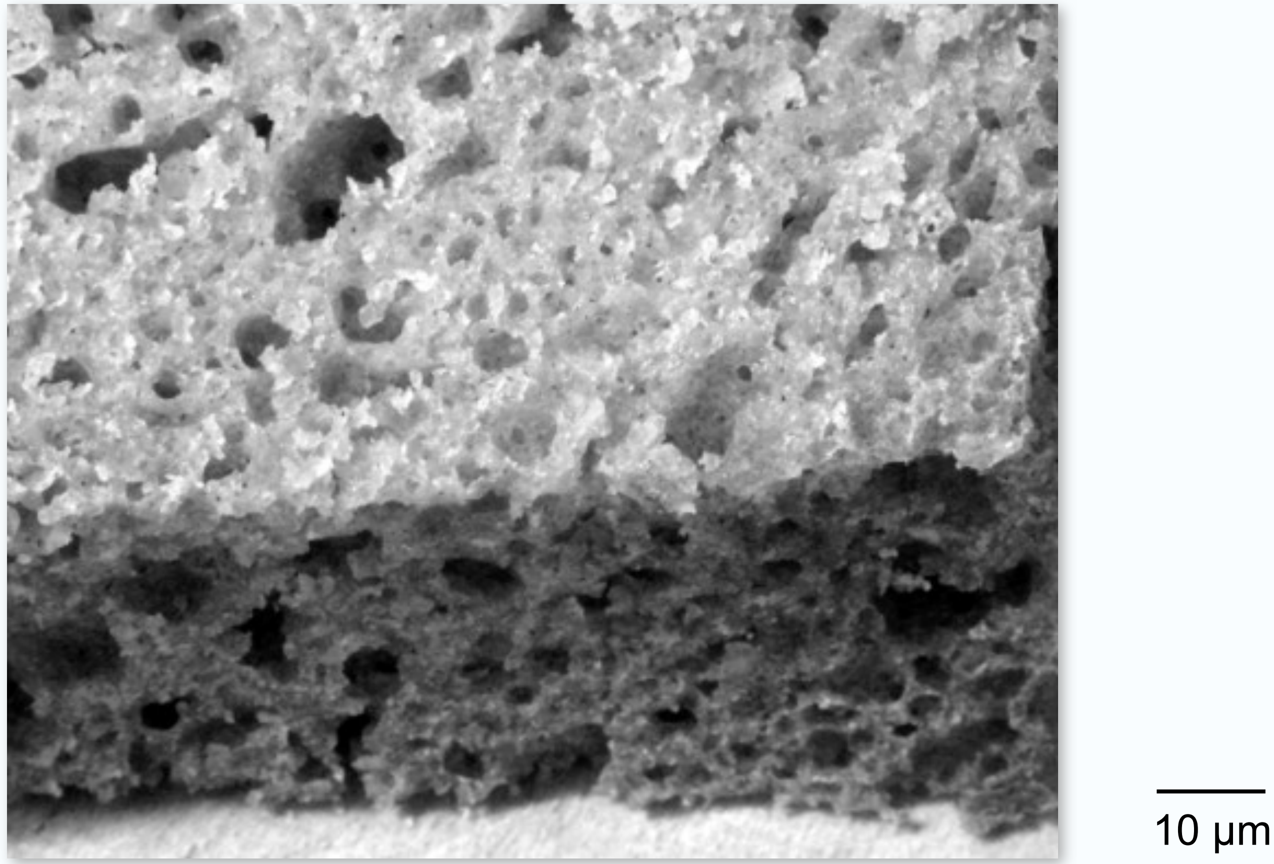
(p pore radius, a_0 effective ion size)

$$E = \frac{1}{2} C U^2$$

Charged double-layer capacitor with two double layers in series (i. e. the interfaces electrode–charged layer and charged layer–electrolyte) with a large specific surface.

[Scherson, Palenscár 2006]

Capacity



Graphite particles with a large specific surface

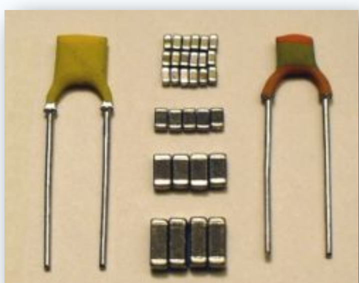
[Takamura *et al*. 2007]

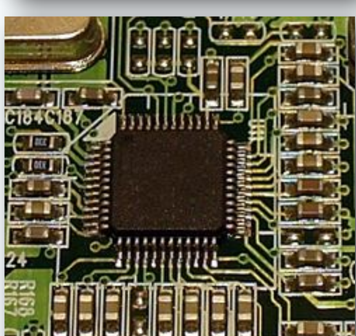
Commercially available standard capacitors

Ceramic capacitors
based *e. g.* on barium titanate

+ high permittivity
+ thermal stability
+ allow high frequencies

– brittle

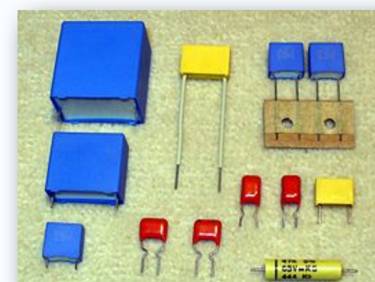




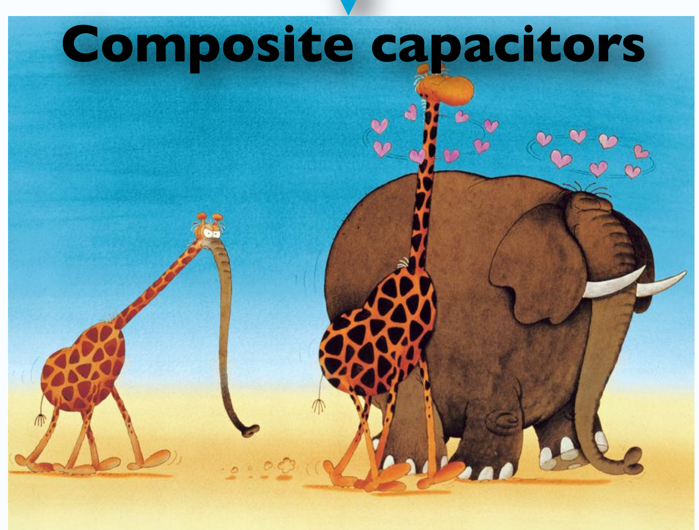
Thin-film polymer capacitors
e. g. PET, PP

+ high voltage
+ low conductivity
+ simple shapes

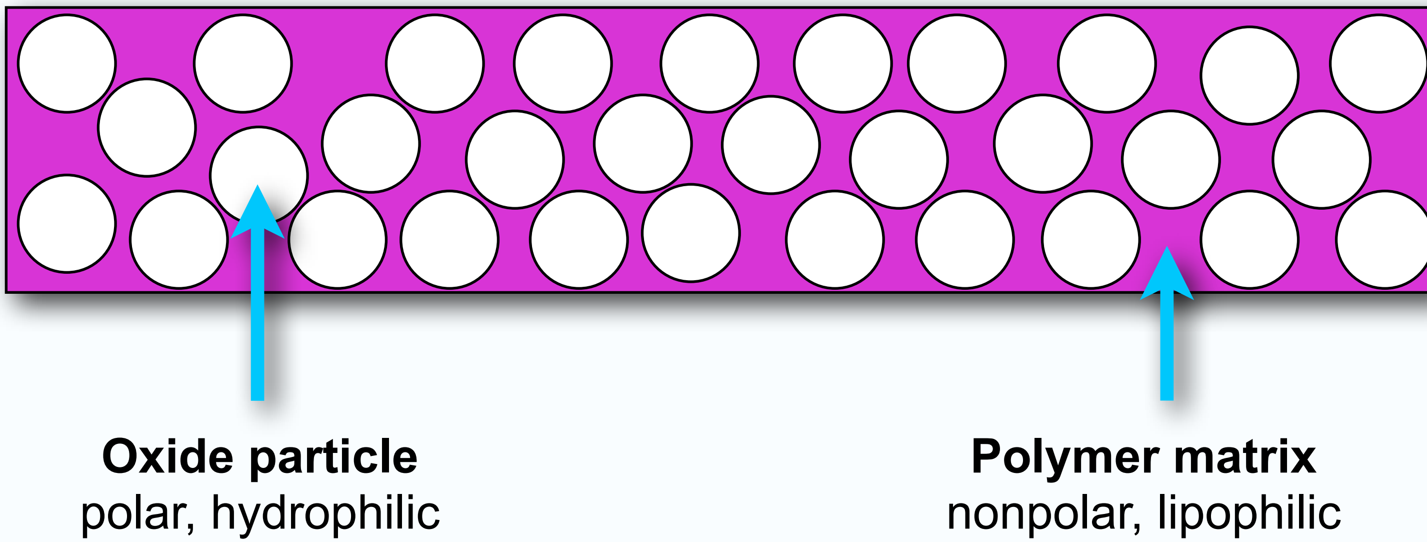
– low permittivity

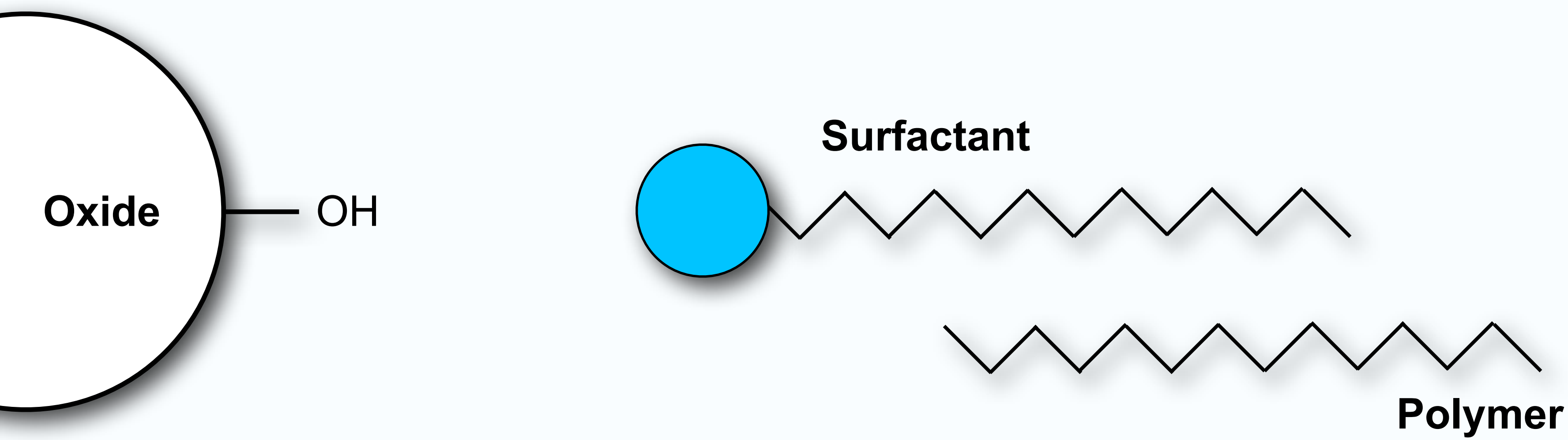


Composite capacitors



Composite dielectrics

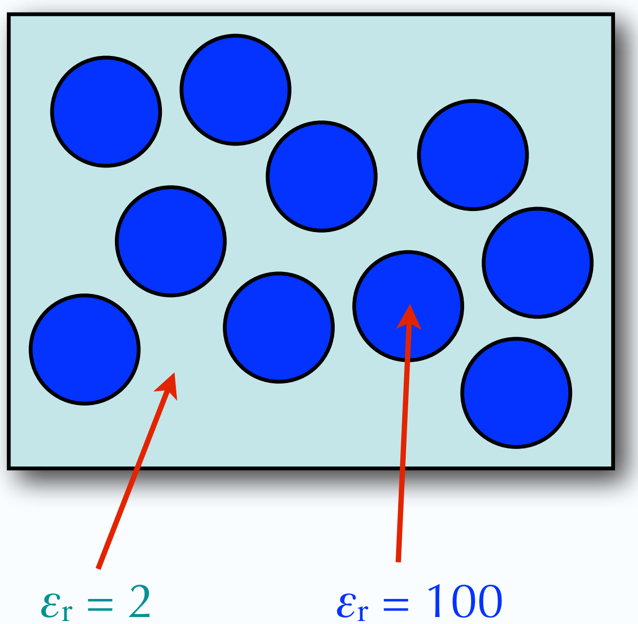


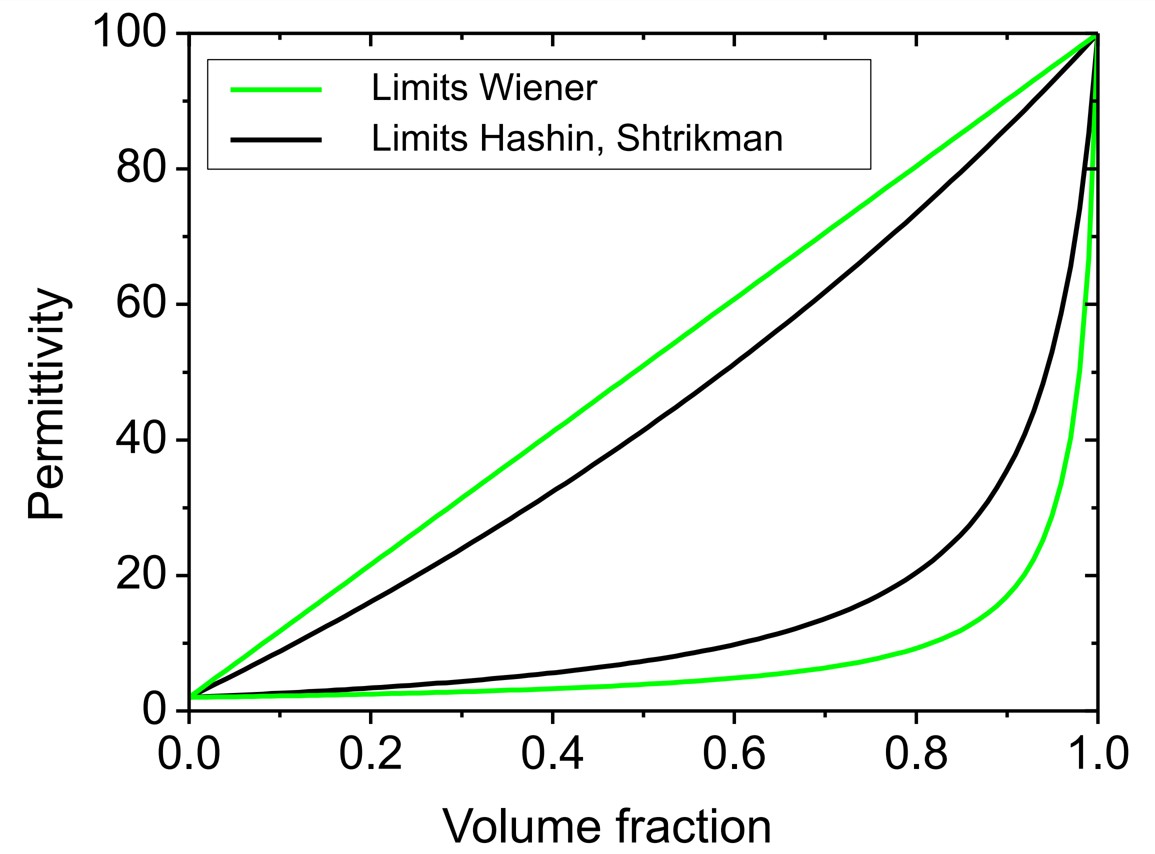


Mixing rules

Simple models

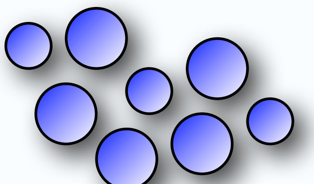
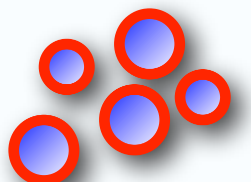
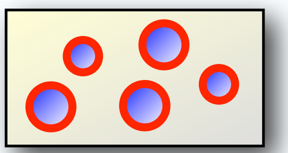
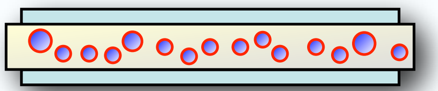
- Serial or parallel connections
- Isotropic statistic distribution of spherical particles in a homogeneous matrix



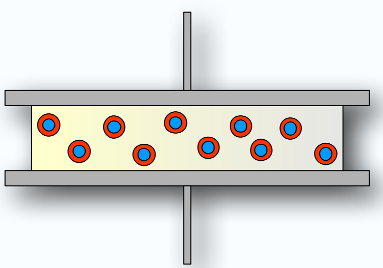


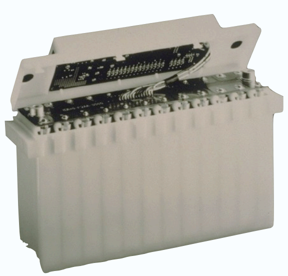
Composite capacitors

Nanoparticles of ceramic dielectrics like $BaTiO_3$ ⇨ Specific surface coating ⇨ Embedding in polymer or glassy matrix | Processing to thin films and electric contacting

Single capacitor ⇨ Multilayer capacitor ⇨ Assembly ⇨ Module



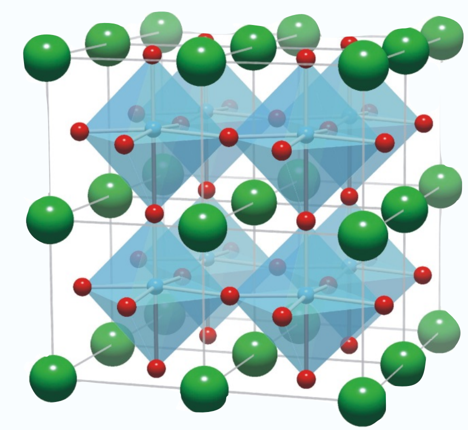



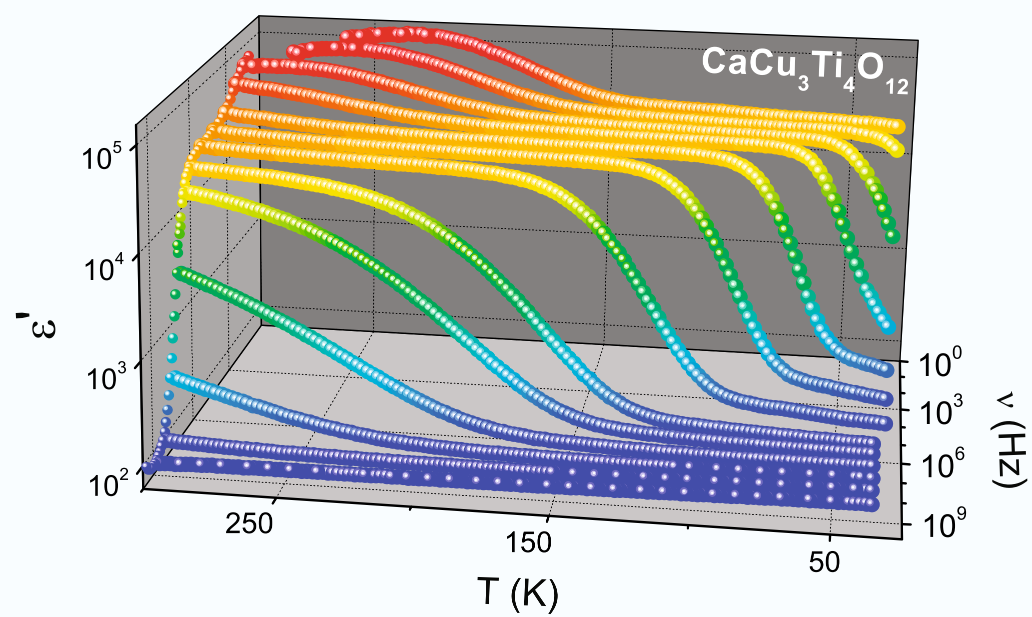
Advantages of composite supercapacitors

- Robust, negligible aging, high lifetime
- High charging voltages
- Thermal stability (operation temperatures > 60 °C possible
- No cooling
- High charging or discharging rates
- High efficiency
- Modular structure
- Environmentally friendly
- Reasonable energy and power density

Ceramic particles

- $BaTiO_3$
  - Ferroelectric, $\varepsilon_r > 2\,000$
  - Phase transitions
- $CaCu_3Ti_4O_{12}$
  - Non ferroelectric
  - Giant $\varepsilon_r > 100\,000$
- Different synthesis routes
  - Oxide mixing, Pecchini, Oxalate, Sol–Gel
  - Particle size 50…100 nm



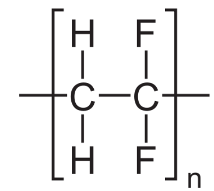


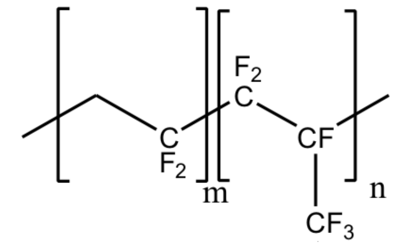
Permittivity ε' of single crystal CCTO as a function of the temperature T and the frequency ν

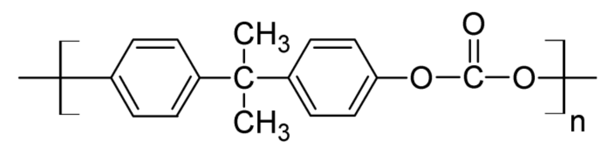
[P Lunkenheimer *et al*. (2010)]

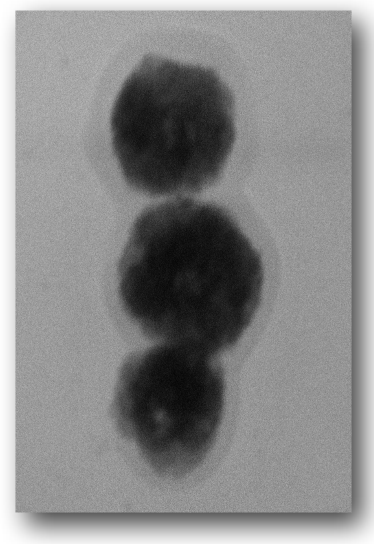
Matrix and shell components

- Polymer films
  - PVDF
  - P(VDF-HFP)
  - Poly(bisphenol A-carbonate)
- Glasses
- Preparation methods
  - sintering, spin coating, spray deposition
- Surface coating
  - passivation of the surface, block aggregation/percolation, minimum of leakage current, high breakdown voltage
  - phosphonic acids; E-glass

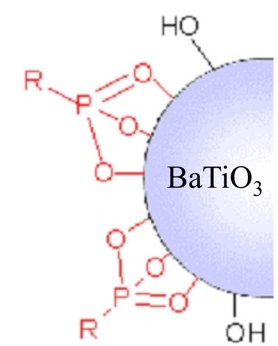






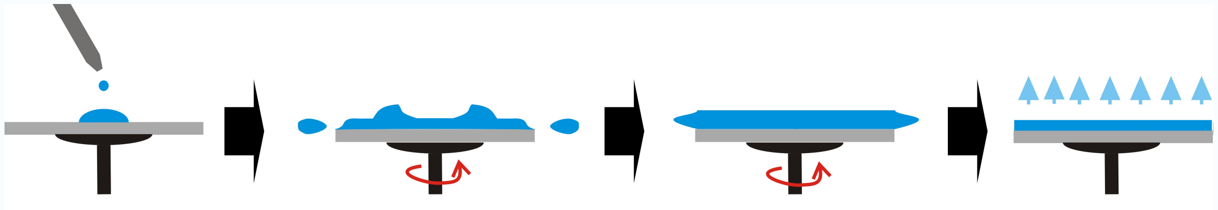


100 nm

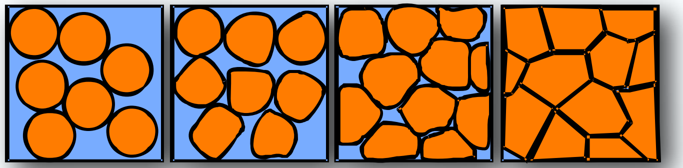


Thin film preparation

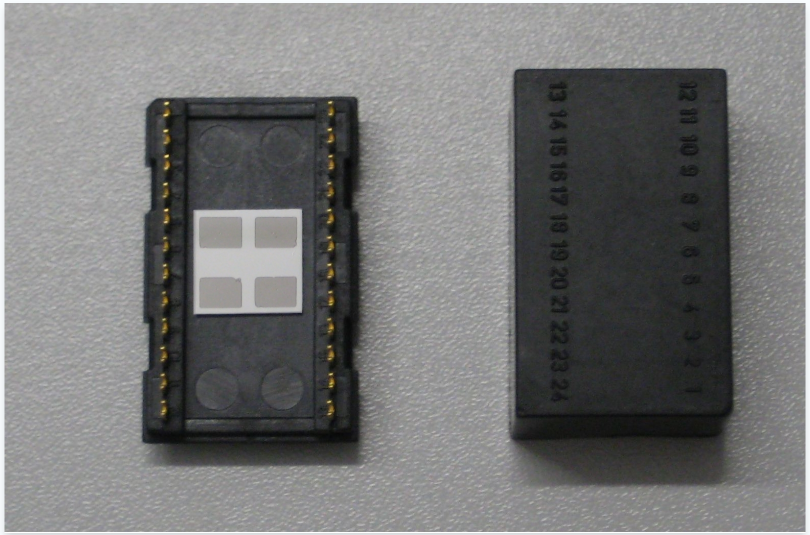
homogeneous, reproducible, scalable, cheap



- Single films, lab stage
  - Spin coating
    - Established for homogeneous solutions
    - More difficult for composites
    - Thickness profile may become inhomogeneous
    - Problems with rectangular substrates, geometry effects
  - Molding, pressing, sintering
- Large areas with linear coating, spray deposition
- Transition to multilayers

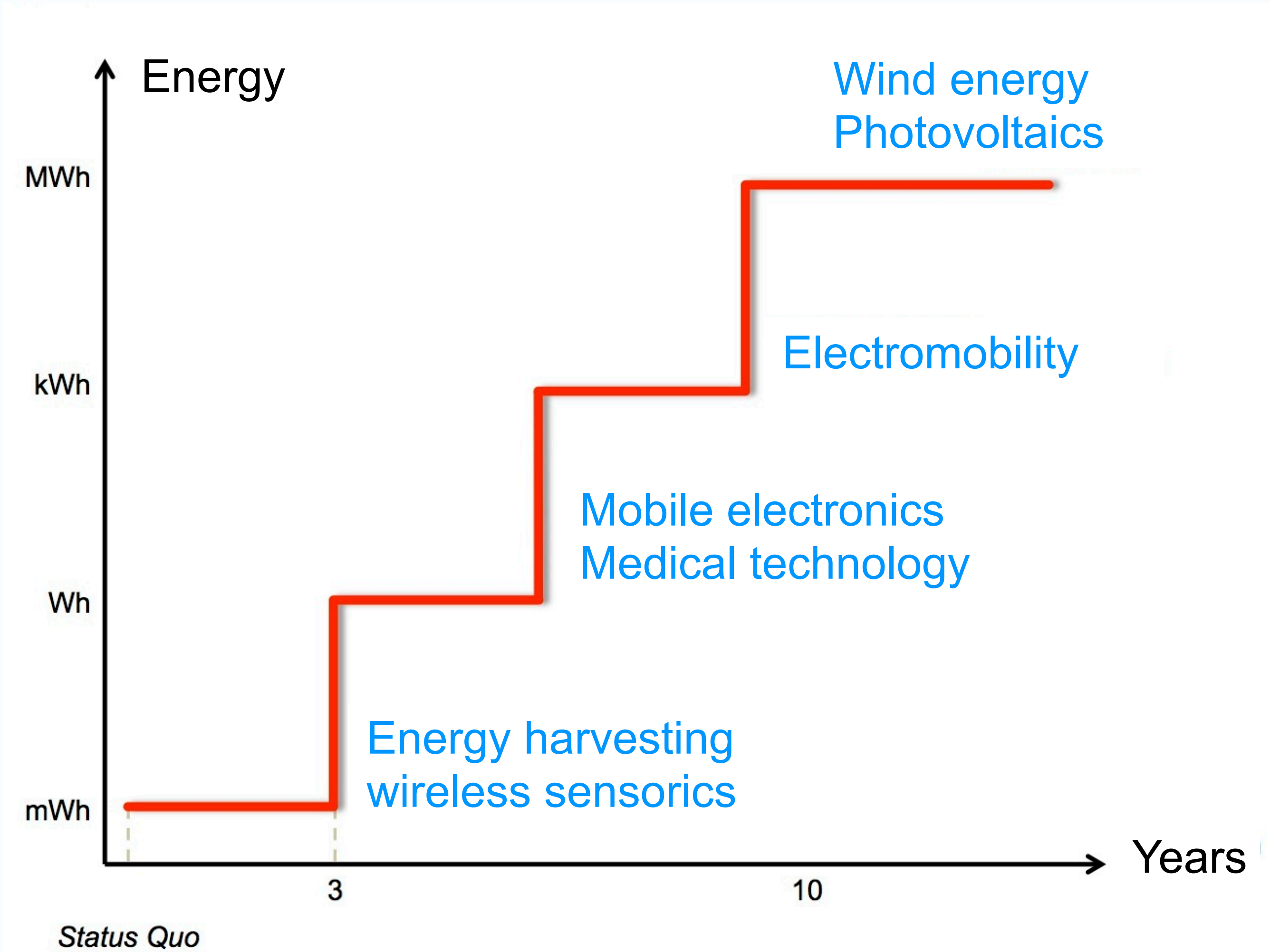


Next targets of the Super-Kon project



- Proof-of-concept → development of a demonstrator
- Application for energy harvesting purposes
- Industry-grade environmental tests
  - Influence of temperature, moisture, vibration
  - Long-time stability
  - Compliance with standards
- Local breakdown and defect analysis

Technology roadmap



Technology roadmap with the development of the amount of stored energy in nanocomposite supercapacitors and possible applications in each state of the development

"Did anyone call for high-power, infinitely rechargeable electrical energy storage?"

Thanks to the Super-Kon team:

H. Beige, A. Buchsteiner, M. Diestelhorst, S. Ebbinghaus, C. Ehrhardt, J. Glenneberg, T. Großmann, S. Lemm, W. Münchgesang, C. Pientschke, K. Suckau, G. Wagner, M. Zenkner

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