Vth International summer school of Environmental Sciences (ISU Eco 2013)

Energy storage with supercapacitors

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Interdisciplinary Center of Materials Science

Center of Materials Science (CMAT)

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

Central lab units (CMAT-MLU Halle)

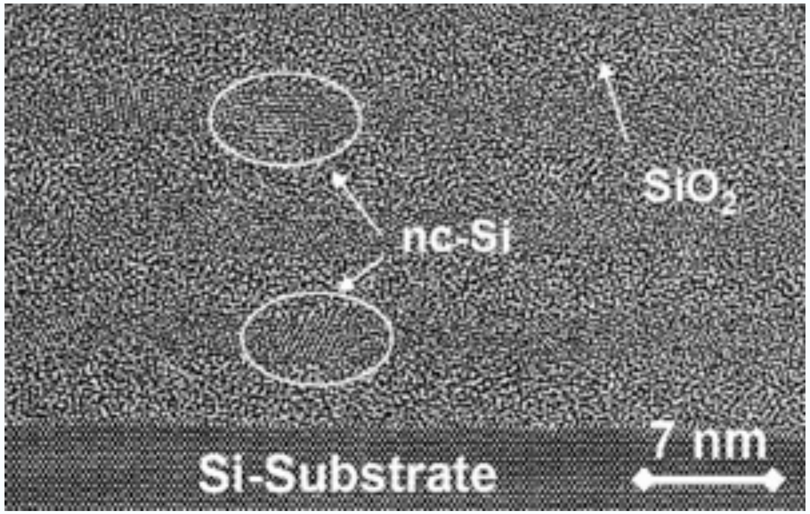
- Nanostructuring: lithography, thin film deposition, device prototyping
- Nanoanalysis: electron microscopy, optical characterization, positron annihilation

Research disposal area (Bio–Nano Center)

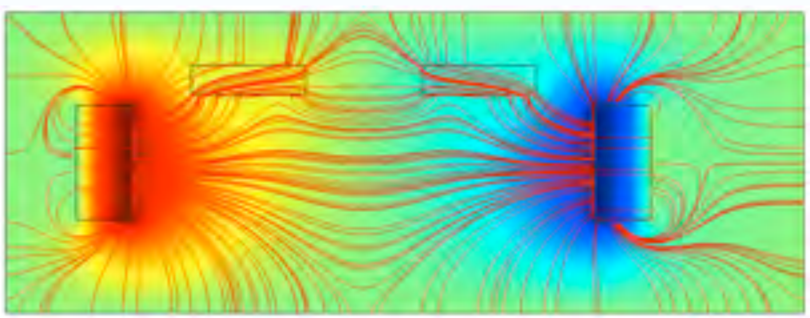
for physists, chemists, materials scientists, biologists, pharmacists

MLU, MPI, Fraunhofer, TGZ (KMU)

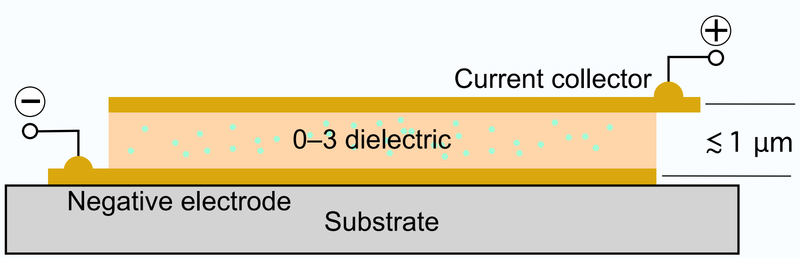
Renewable energy materials



- Nanostructured thin film materials as functional elements for next-generation solar cells



- Silicon-related materials for thermoelectric applications



- Novel supercapacitors as energy storage devices

WING
Werkstoffinnovationen für Industrie und Gesellschaft

ForMaT
UNTERNEHMEN REGION

gründerwerkstatt
NANOSTRUKTURIERTE WERKSTOFFE

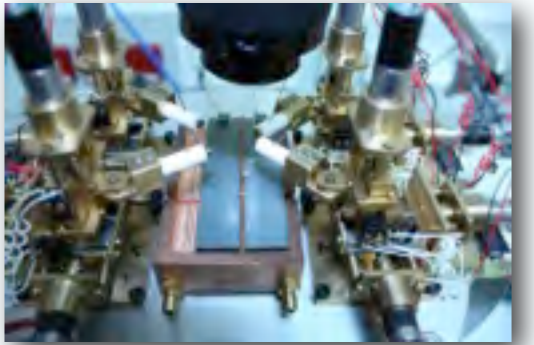
GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung

Equipment

Nanostructuring

Cleanroom class 10/100/10000

Analysis



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

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
- The same concept is followed for electrochemical, as well as for electrostatic storage devices.

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

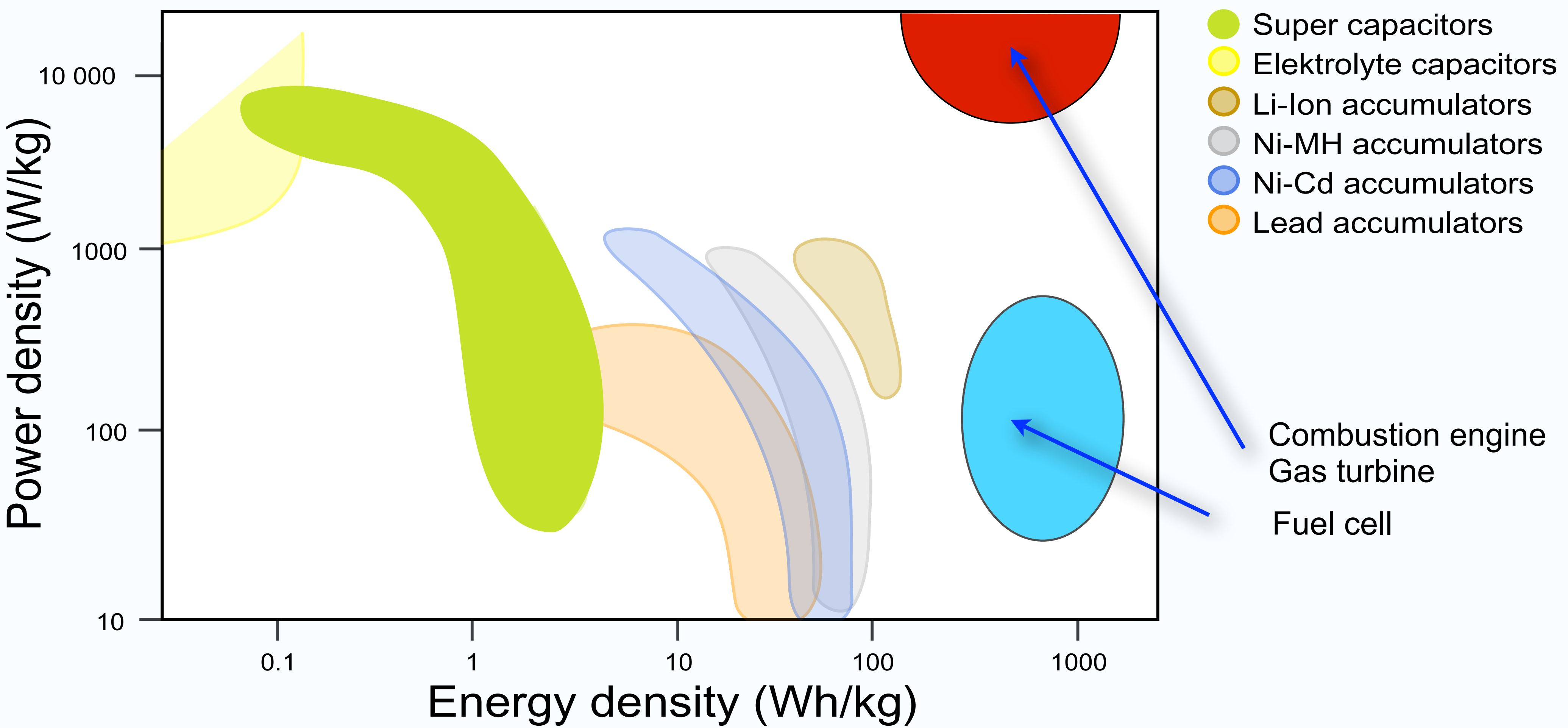
Values after GW Crabtree, NS Lewis 2007
Video: NASA

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

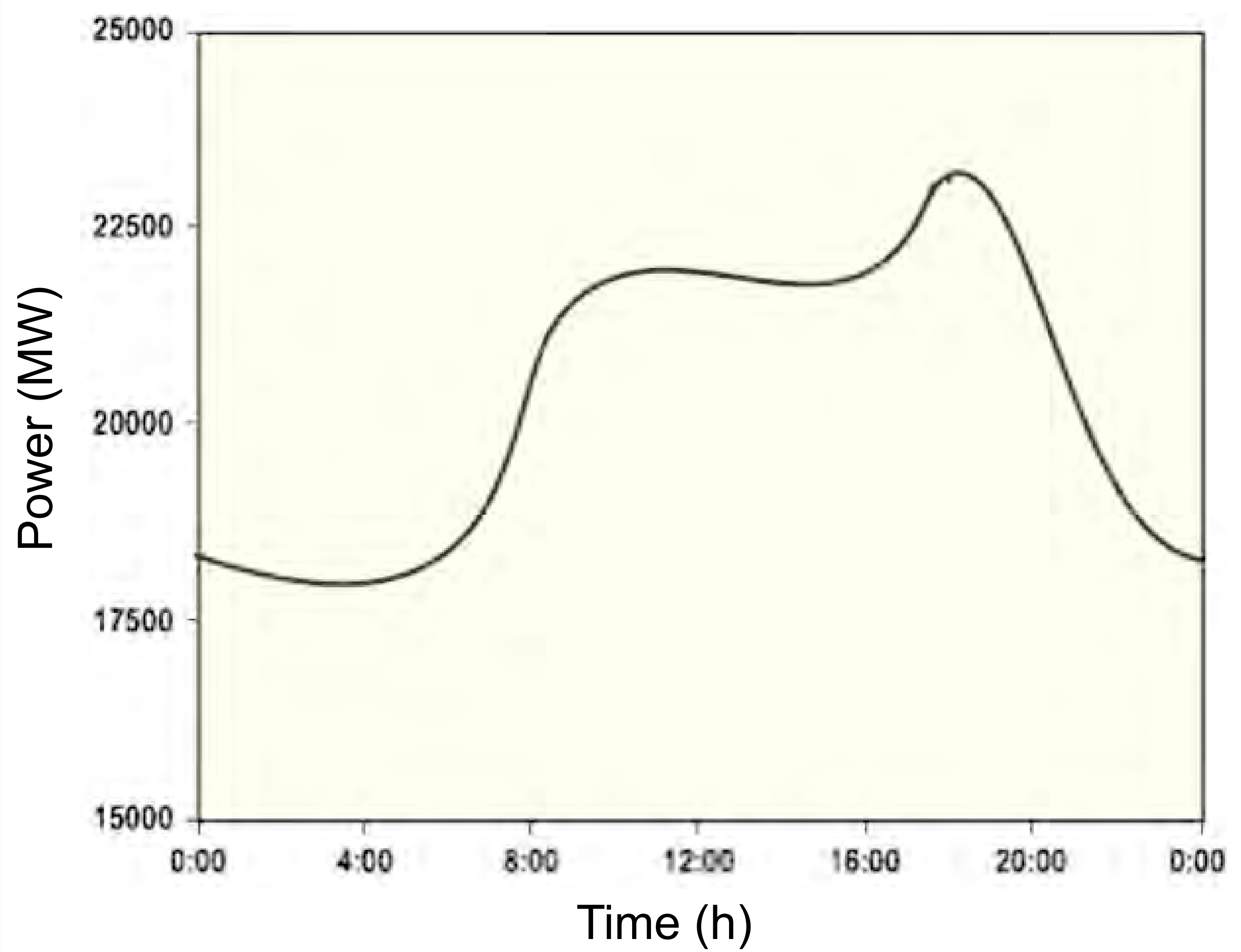
Ragone diagram



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



Example of the time dependence of the daily electrical power demand

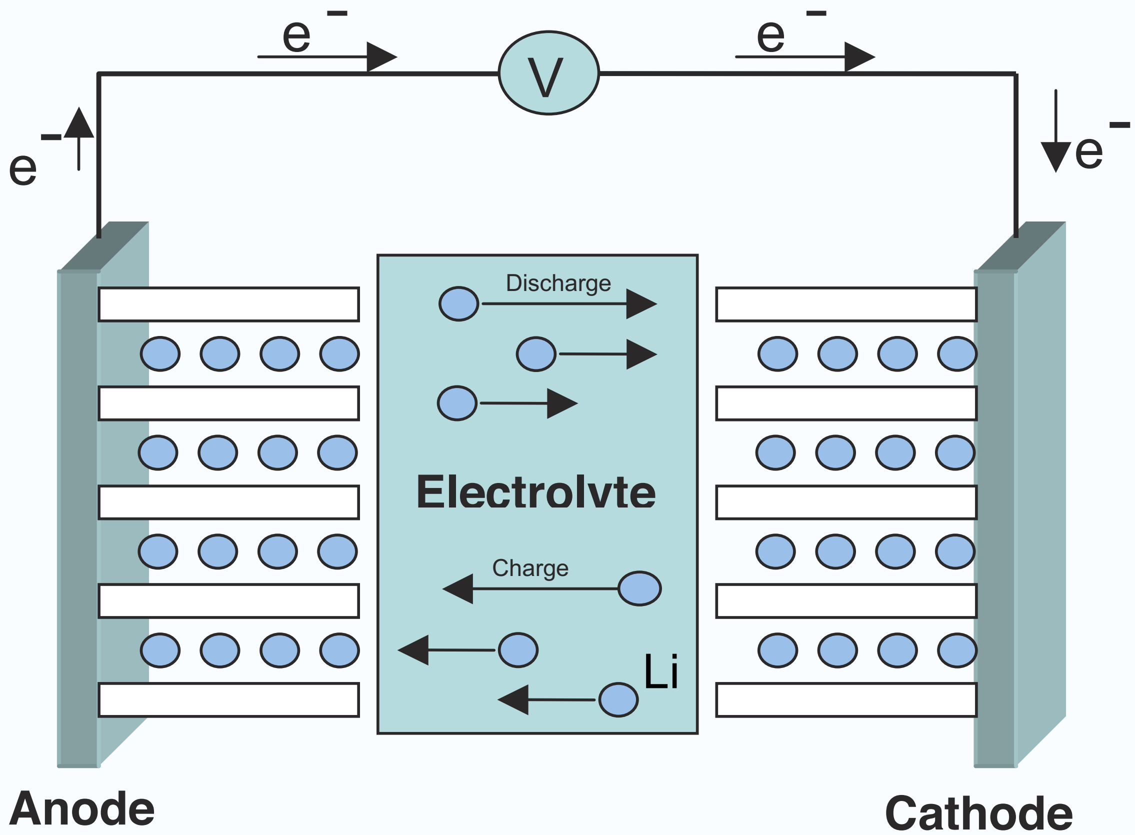
[Huggins 2010]

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

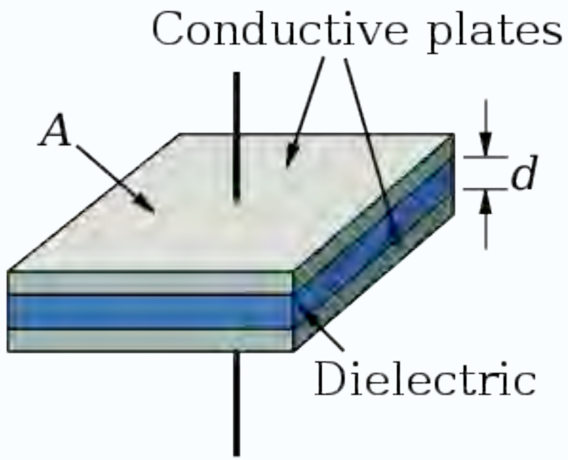
(Intercalation)

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

(M – metal)

Capacitors

Capacitance C = Amount of charge stored per unit voltage



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

ε_0 dielectric constant $\approx 9 \cdot 10^{-12}$ F/m

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

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

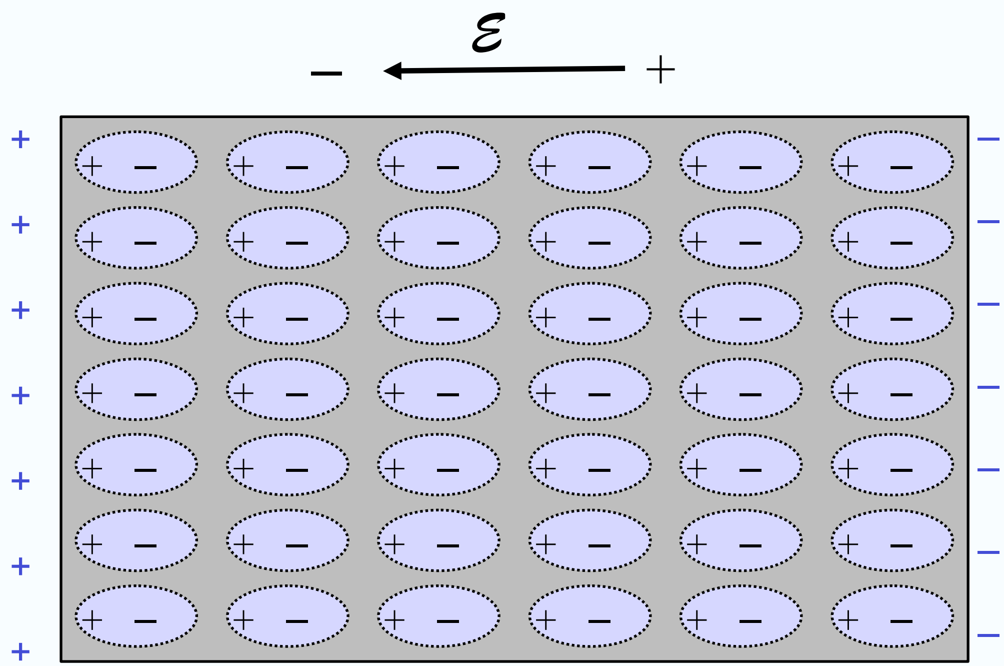
Dipole moment

- Induced dipole moment of a single atom by the external electric field

$$\mathcal{P}_{\mathrm{a}} = qd$$

- Polarisation of a dielectric crystal (dipole moment per volume)

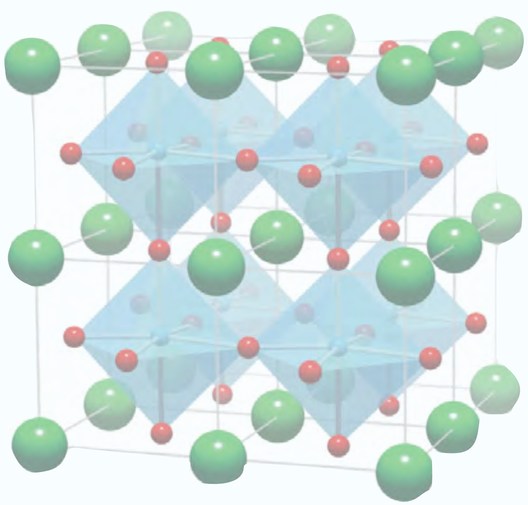
$$\mathcal{P} = Nqd$$



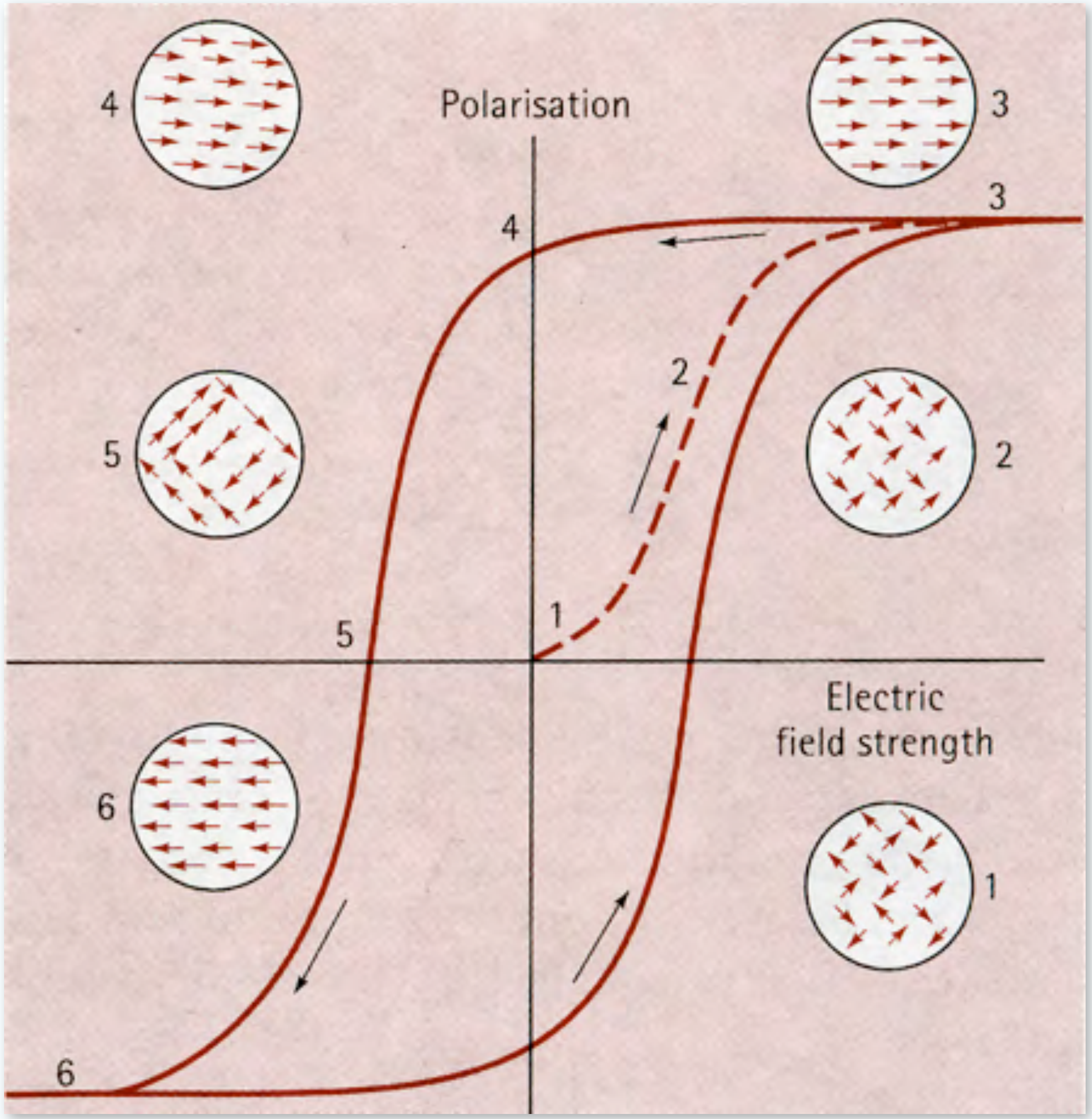
Dielectric crystal made of atomic dipoles. The result of the external field ist a surface charge on both terminals.

Ferroelectrics

- Materialials with a finite polarization, even without an external field
- Name misleading: no iron; properties resemble ferromagnetic solids
- Hysteresis in the polarization



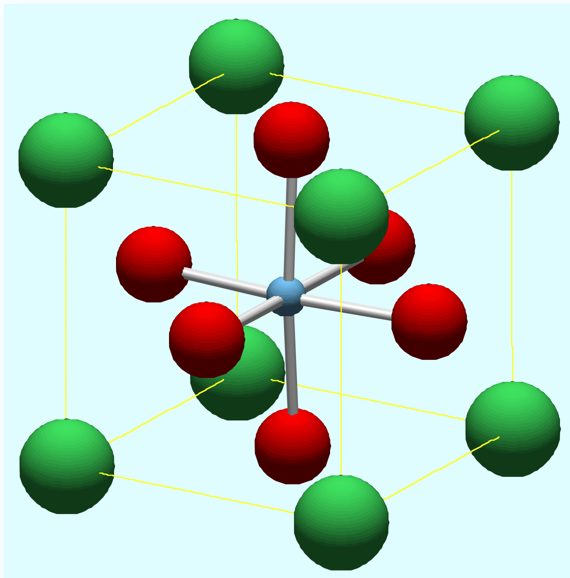
Arrangement of dipoles

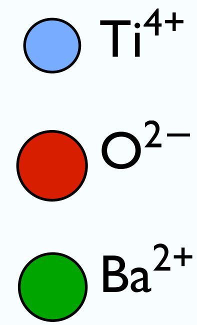


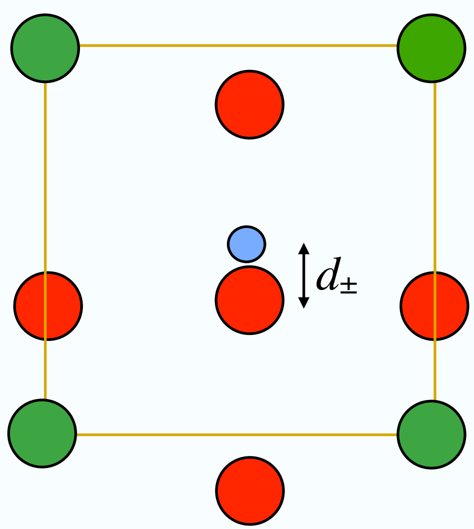
Ferroelectric hystereses with the arrangement of the dipoles

[Askeland 1996]

Structure of barium titanate

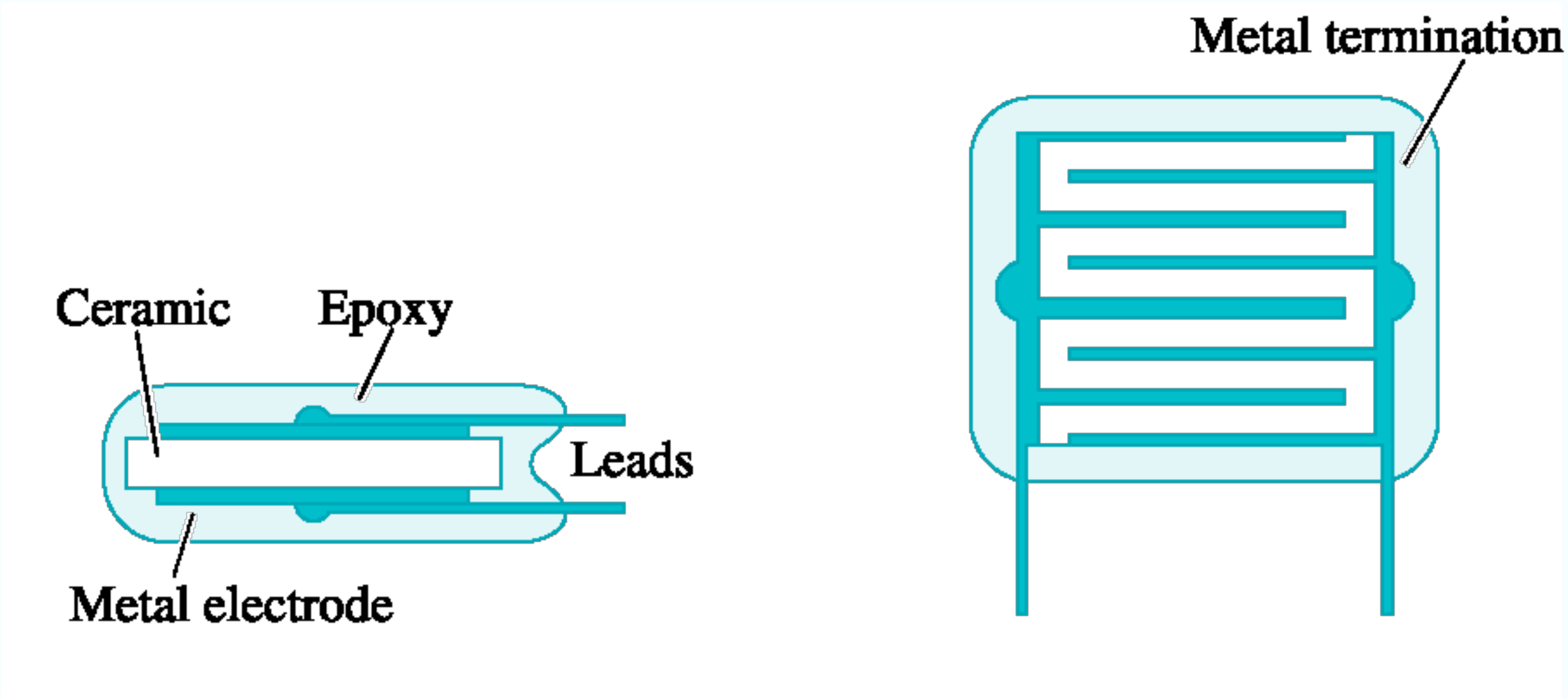






Compared to the ideal cubic arrangement, the positive and negative ions are shifted by a distance of $d_{\pm} \approx 0.01$ nm.

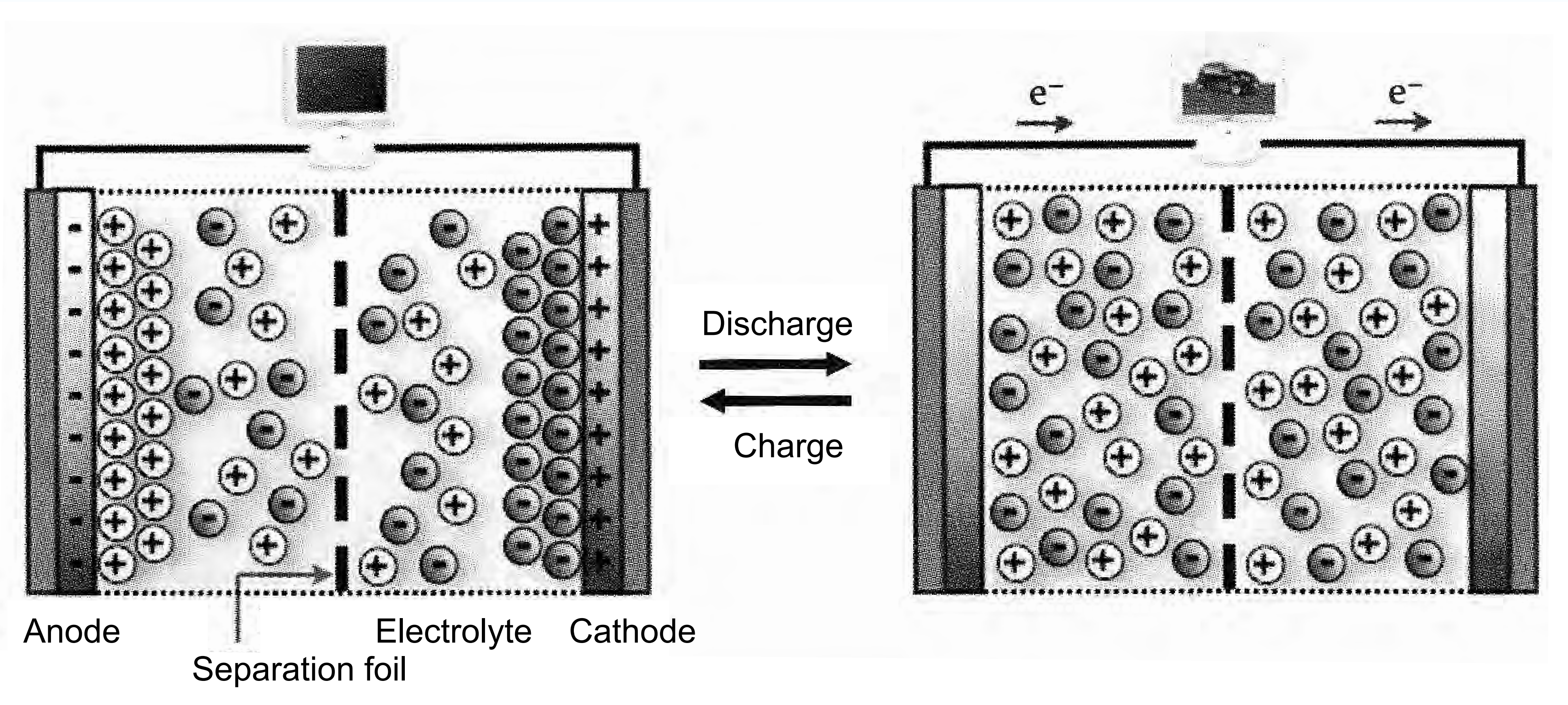
Design of a ceramic capacitor



Examples of ceramic capacitors. Single-layer ceramic capacitor (plate capacitor) and multilayer capacitor (stacked ceramic layers).

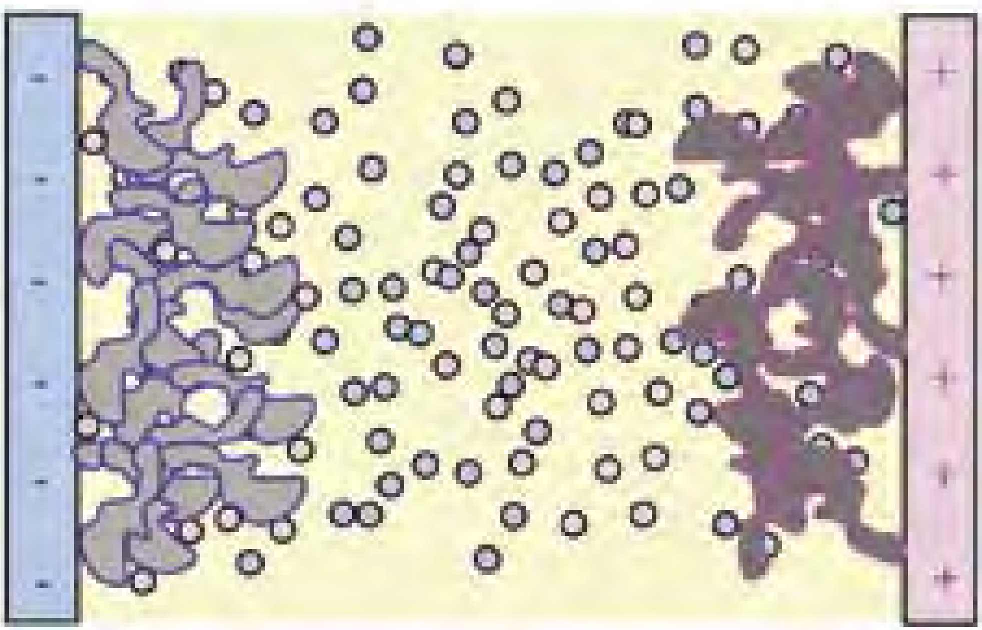
[Askeland 1996]

Double-layer capacitor



[Abruña 2008]

Capacity



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

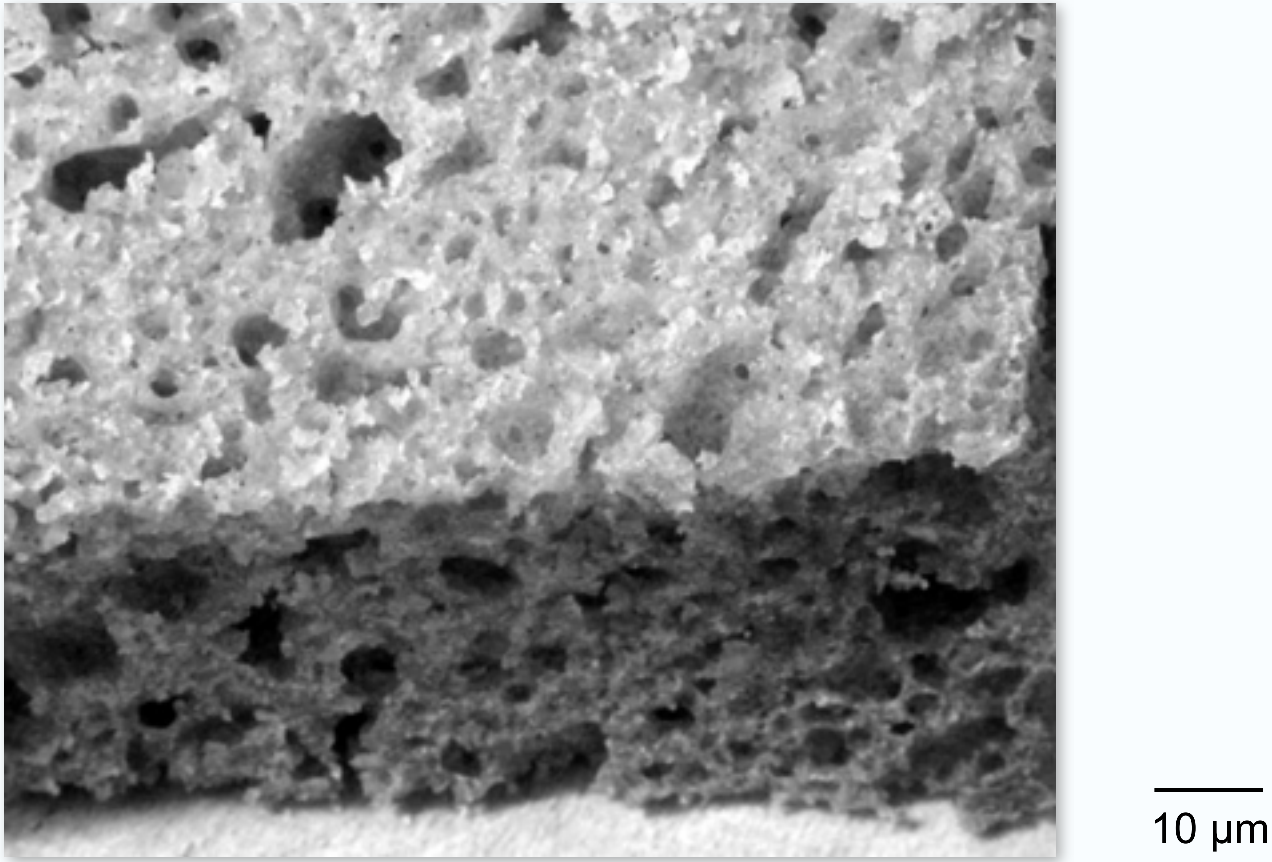
(p pore radius, a_0 effective ion size)

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

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

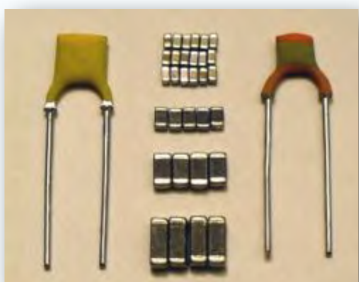
+ high permittivity
+ thermal stability
+ allow high frequencies

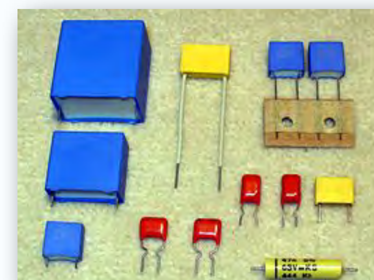
– brittle

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

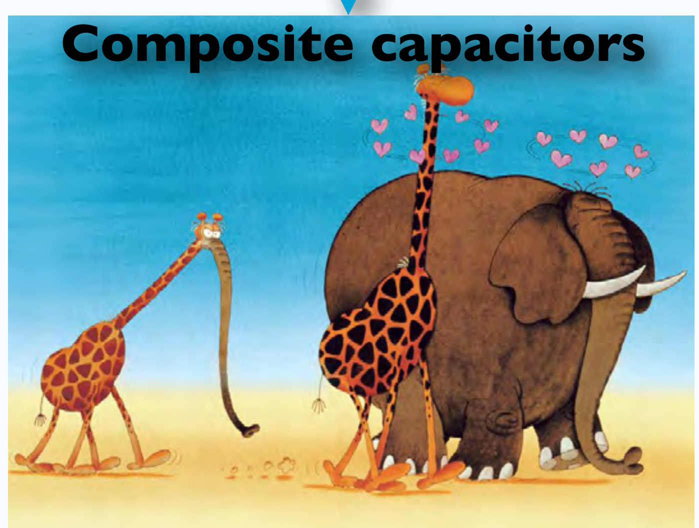
+ high voltage
+ low conductivity
+ simple shapes

– low permittivity

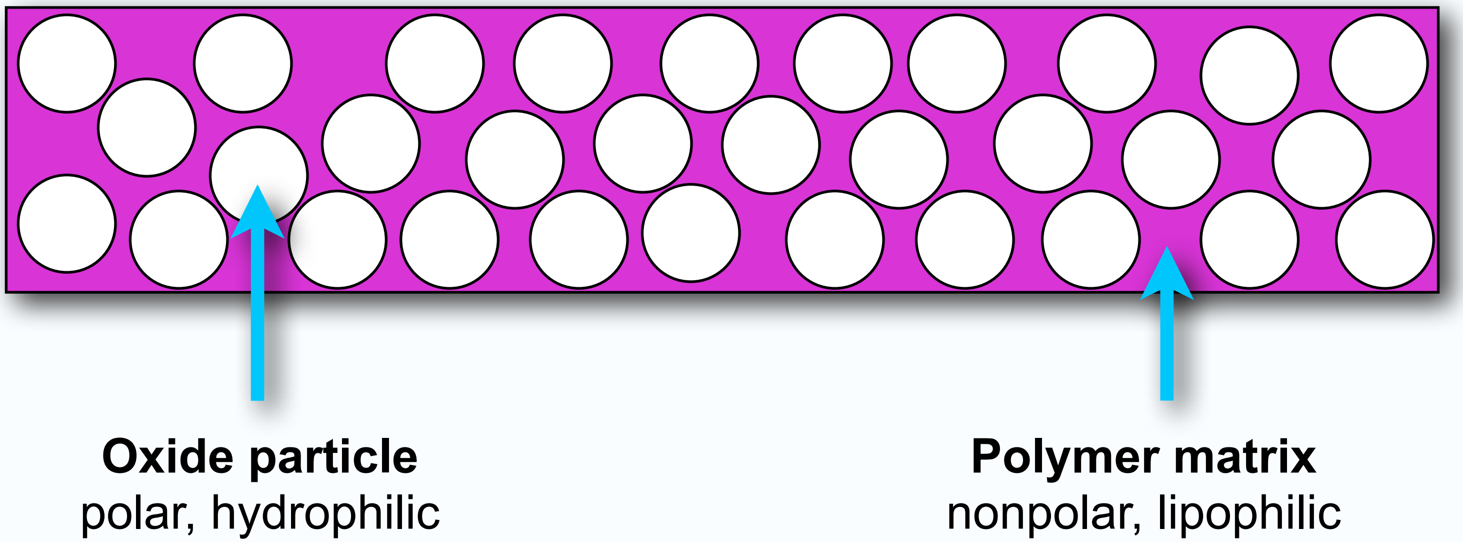


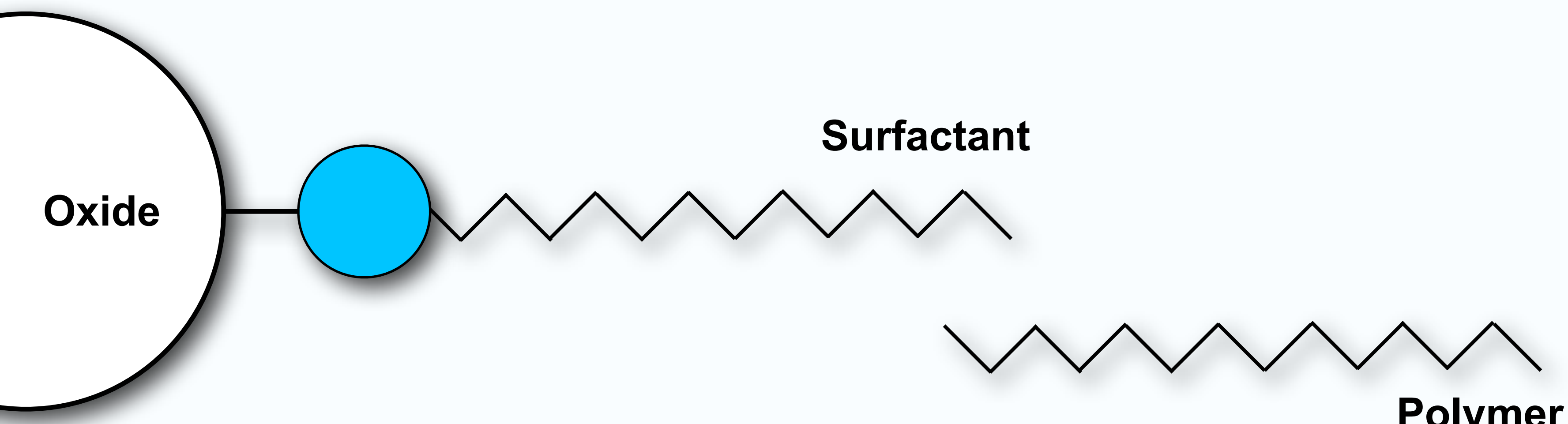


Composite capacitors



Composite dielectrics

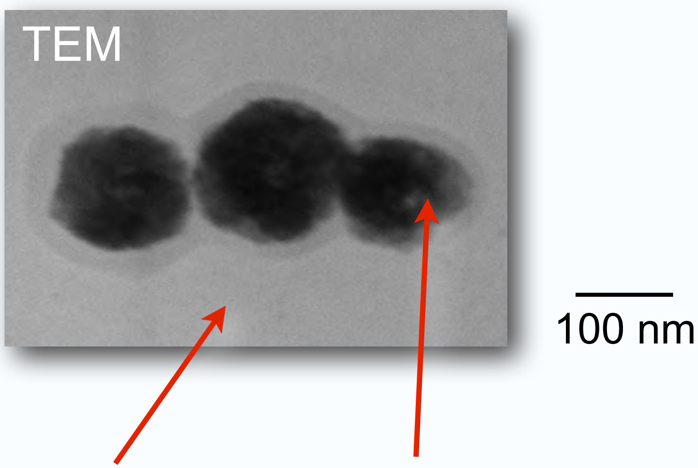




Mixing rules

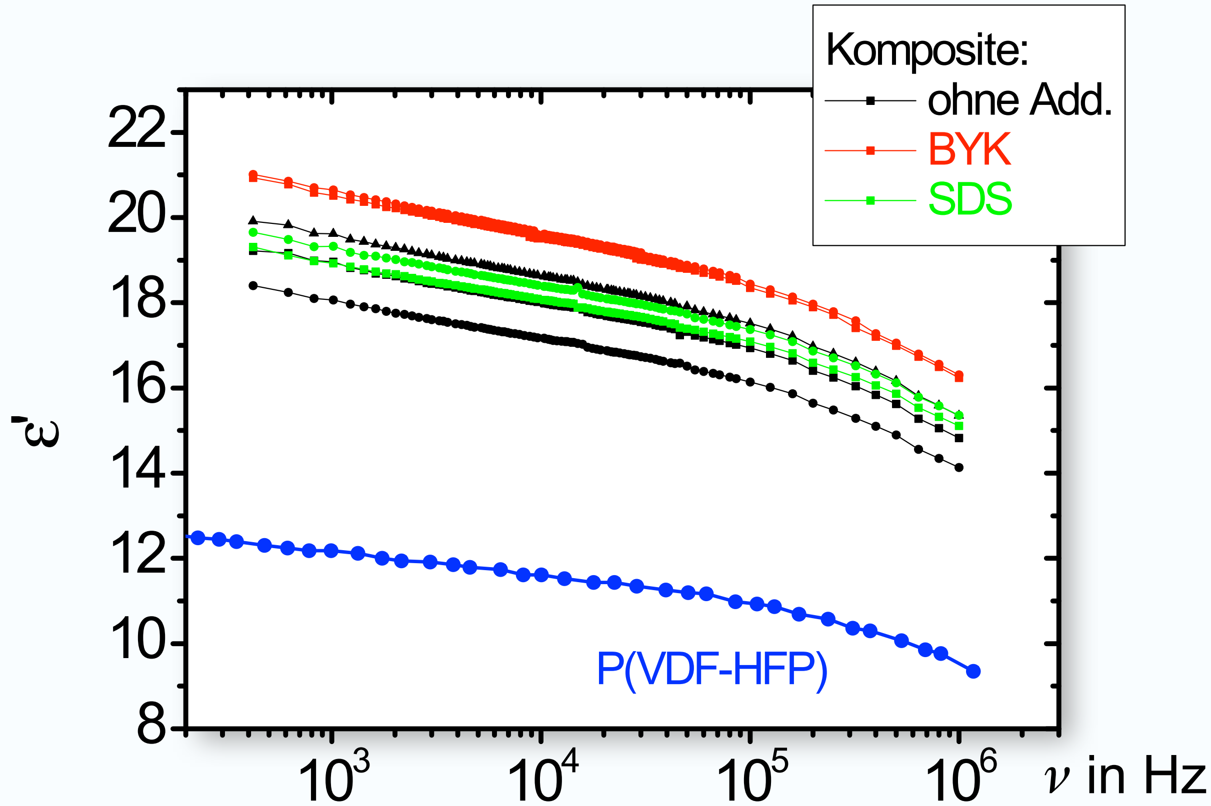
Simple models

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



ε_r Matrix ε_r Nanoparticle

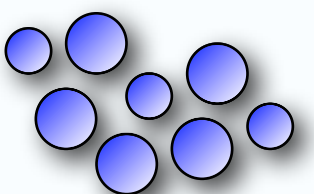
→ Permittivity of the composite ε'

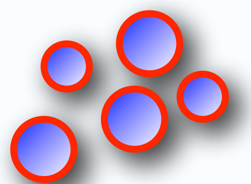


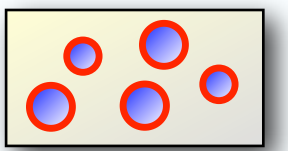
Permittivity ε' as a function of the frequency ν for different 0–3 composites

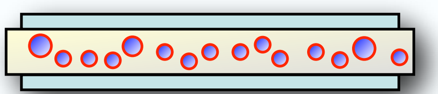
Composite capacitors

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

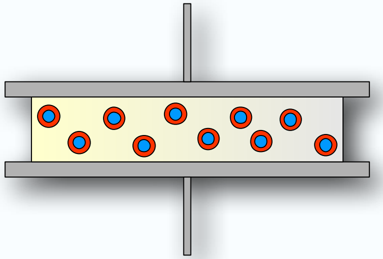


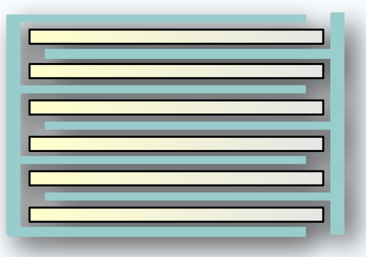






Single capacitor ⇨ Multilayer capacitor ⇨ Assembly ⇨ Module



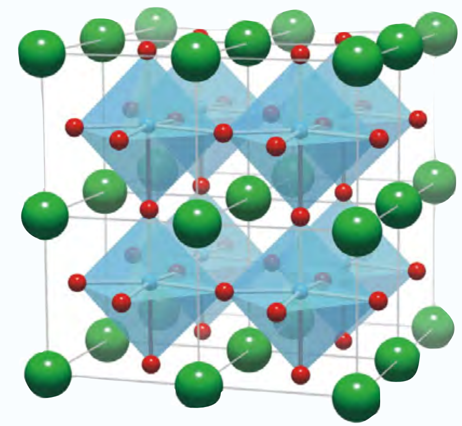


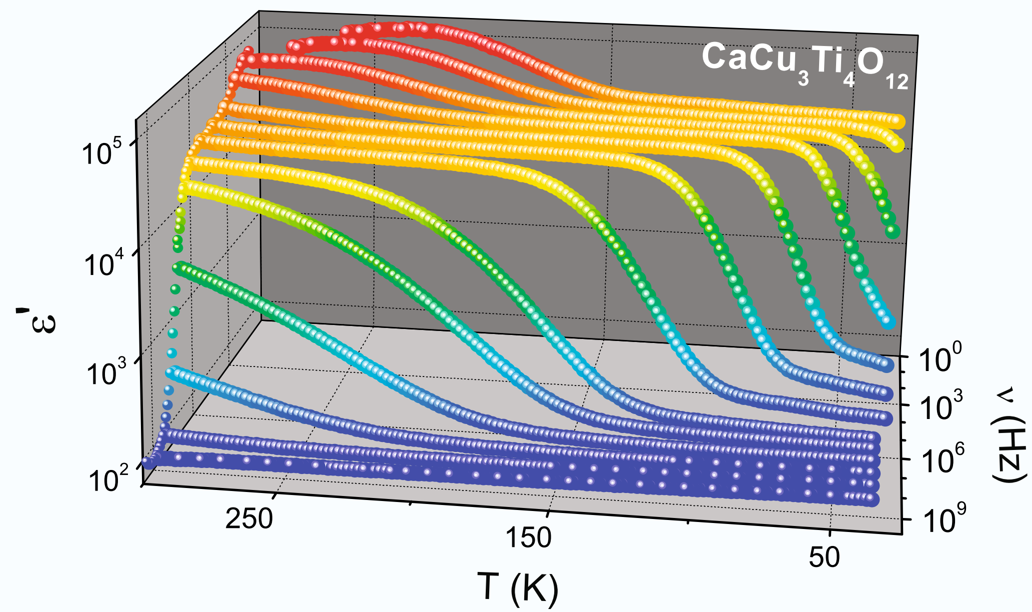
Advantages of composite supercapacitors

- 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



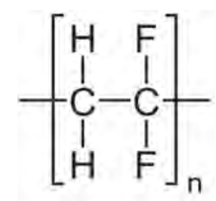


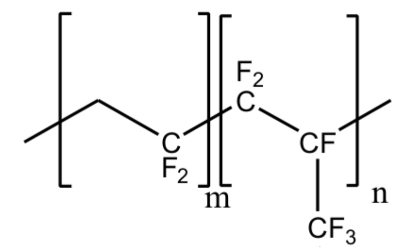
Permittivity ε' of single crystal CCTO as a function of the temperature T and the frequency ν

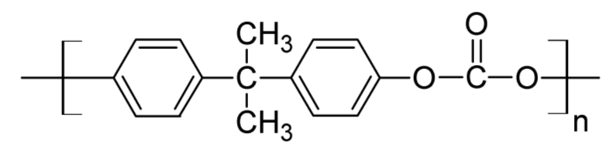
[Lunkenheimer *et al* 2010]

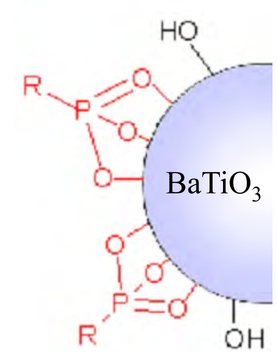
Matrix and shell components

- 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



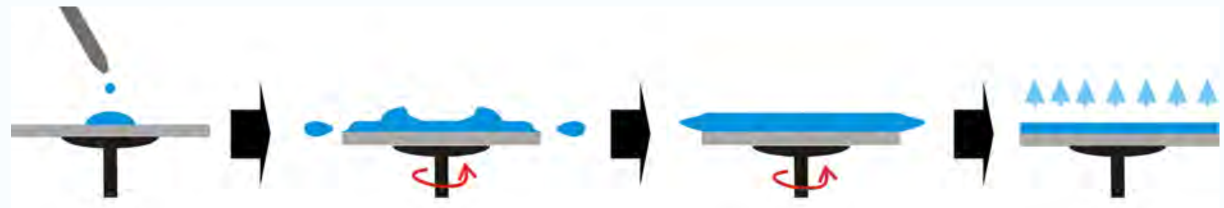




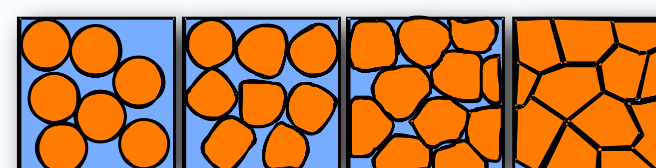


Thin film preparation

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

Energy density of a capacitor

- Max. voltage given by the break-down voltage

$$U_\mathrm{b} = \mathcal{E}_\mathrm{b} d$$

- Storage density

$$w_\mathrm{Sp} = \frac{E}{V} = \frac{\mathcal{C}}{Ad}\frac{U_\mathrm{b}^2}{2} = \varepsilon_0 \varepsilon_\mathrm{r} \frac{\mathcal{E}_\mathrm{b}^2}{2}$$

- Typical no. for a polymer dielectric: $\approx 0{,}3\ \mathrm{kWh\,m^{-3}}$
- Storage efficiency of capacitors → 1

Application of supercapacitors

- Control of the pitch angle of the rotors in wind turbines – big variation in T, independent of the grid, no maintanace
- Start of microturbines or fuel cells working as UPS requires usually some 100 kJ electrical energy within ca. 10 … 20 s
- Energy storage for photovoltaics; capacitors can supply periodic power with higher currents as coming directly from the solar modules
- Recuperation of brake energy in cars

Recuperation

- Brake which regains the electrical energy from the motor acting as a generator during braking (grid, energy storage)
- Since the 1920ies in the Swiss *Krokodil*
- Hybrid cars: electrical energy into the battery, storage capacitors or fly wheel

SBB Ce 6/8^{II} electrical locomotive "*Krokodil*", working in the Gotthard railway until the 1980ies

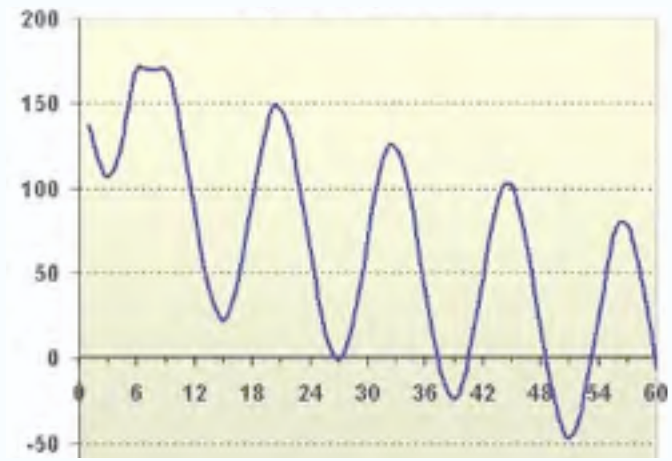
recuperare (*lat.*) = regain

Fuel saving in the car

- Regain of kinetic energy when idling or braking and feeding into the battery
- During acceleration all energy consumers which are not necessary are separated from the power train
- strong generator + electronic regulation: „dynamo" not working permanently
- Commercials: *Efficieny dynamics, brake energy regain*

Benefits of capacitors for energy storage

- Maintanance free, relative low weight
- Resistent to temperature variations
- Long lifetime
- More than 500 000 charge–discharge cycles
- No destruction by deep discharge



Conclusions

- Present energy density of capacitors low, but high power density
- Possibilities of short-term storage (*e. g.* grid stabilization, automotive applications, sensors)
- High development potential with the overcome of materials science problems

"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

SUPER KON

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