Westphalian Wilhelms University Muenster

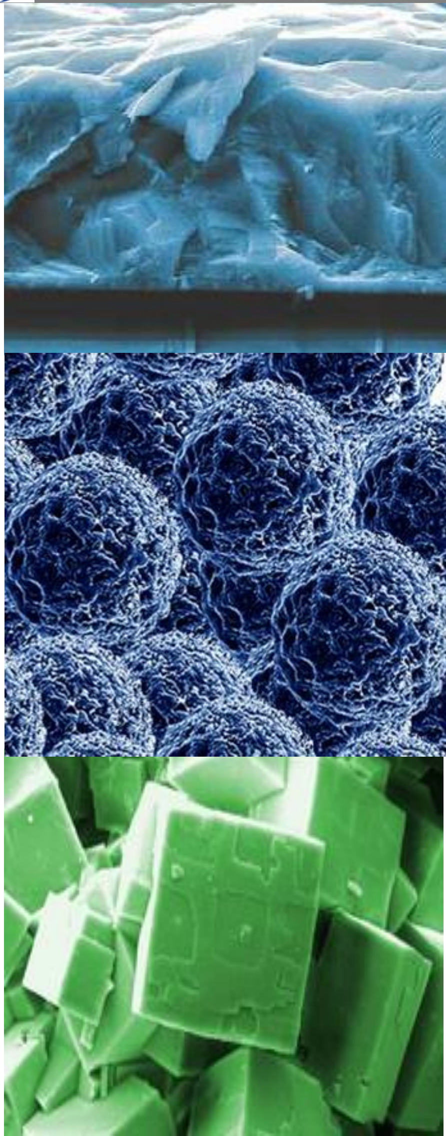
MARCOTECH

Nanomaterials for Energy

- background & examples -

German-Russian Workshop:
Russia - Germany Cooperation in Alternative Energy
September 21 - 23, 2016
Nizhny Novgorod

Lothar Heinrich
marcotech oHG & Westphalian Wilhelms University Muenster



1. Reasons for alternative energy resources and concepts for energy conversion

world population
2015/2016: 7,4 bill. people
2050: 9,7 bill. people

source: United Nation 2015

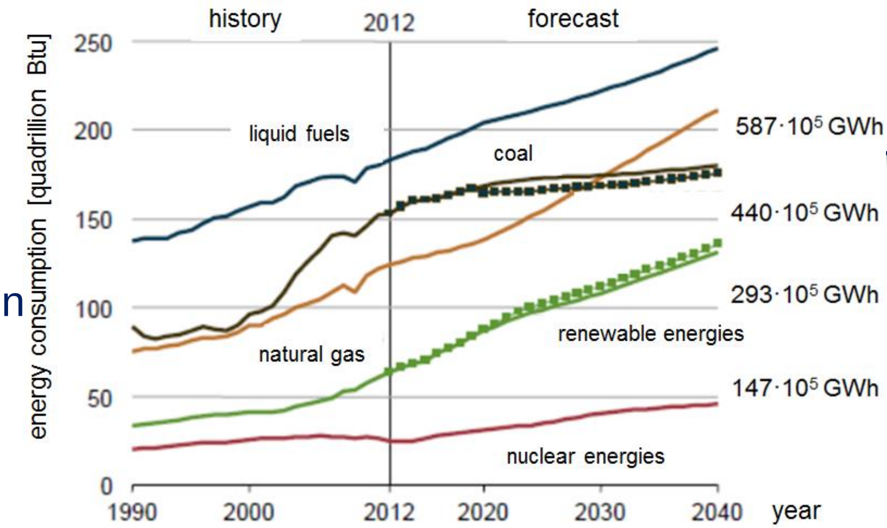
Increase & intensification of

- production of industrial and consumer goods,
- agricultural productions,
- density of settlements, urbanization,
- infrastructures,
- IT-networks

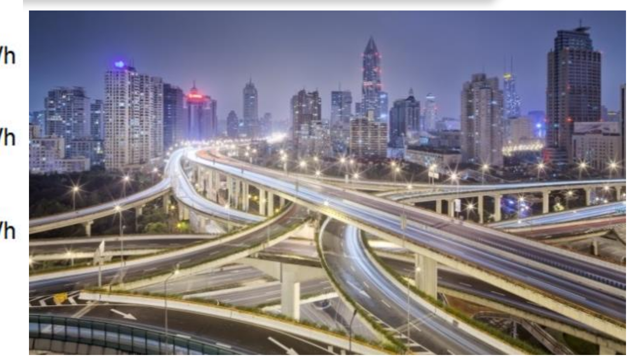
Challenges:

- Decrease of greenhouse gas emissions
- Reduction of the emission of fine dust, chemicals & toxic substances (air, water)
- Conserving resources fossil fuels and minerals
- Saving the food production
- Guarantee of adequate healthcare
- Infrastruktures for energy, transport and IT

estimated energy consumption up to 2040

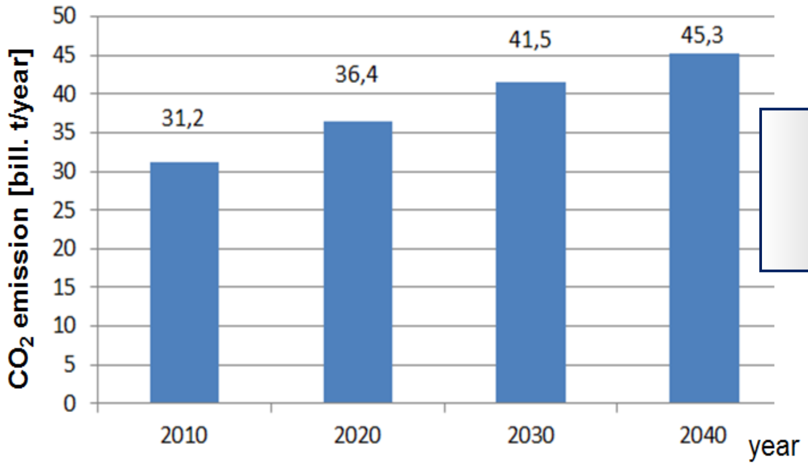


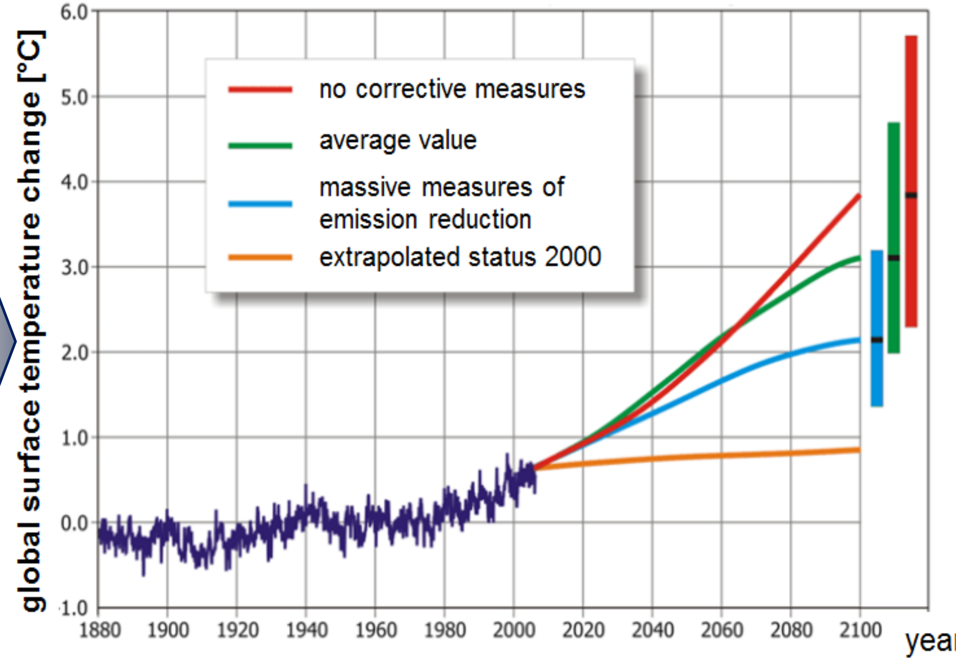
source: iea 2015



Consequences arising out of emissions woldwide up to 2040

growth of the energy demand =
increase of the environmental stress





source: National Climate Center (NOAA)

In addition to the global CO_2 load emissions of:
- SO_2, NO_X, NH_3 …
- fine dust
- mercury, lead, cadmium; As_2O_3 …
- halogenated hydrocarbons, dioxines …
- any chemicals; methane …
- and more

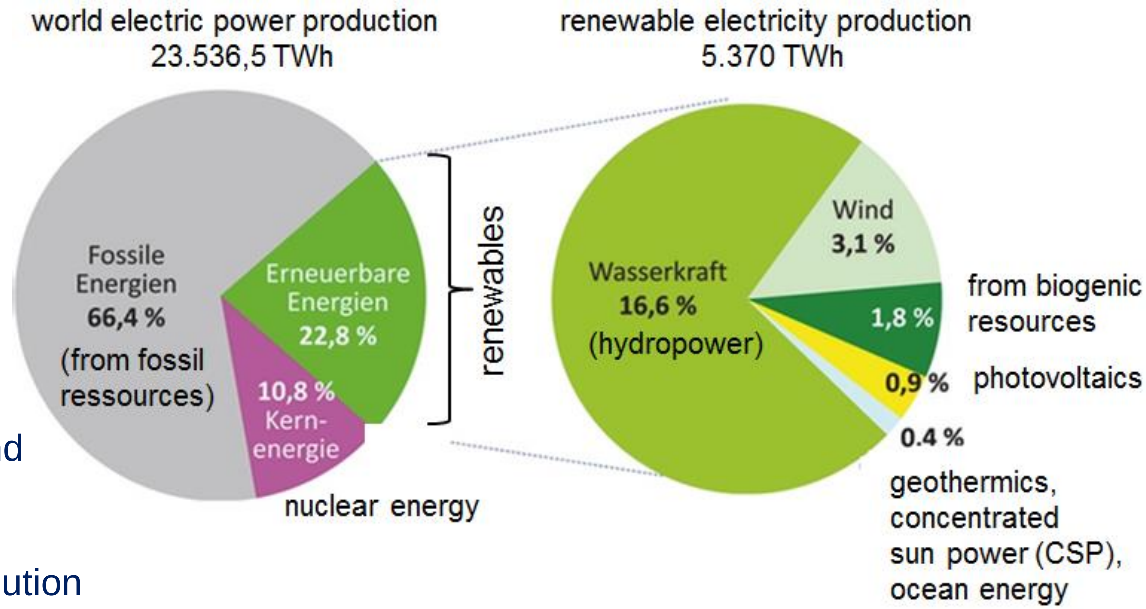
UN estimated that per year **about 3.3 Mill. people** die from air pollution

Climate policy actions of the wold community

International climate conferences:
(incomplete listing):

1972 UN conference environment & people
1979 Climate conference, Oslo
1985/87 agreement of Vienna and Montreal Protocol on the protection of the ozonosphere
1997 Kyoto Protokol on the climate convention
2002 world summit for sustainable development, Johannesburg
2009 UN climate conference, Kopenhagen
2013 UN climate conference in Poland
2015 UN clmate conference, Paris

Increasing shares of the renewable energy in the power production (status: 2014):



China and USA have agreed in the resolution of the conference in Paris (2016)

Limitation of the global warming at ≤ 2 °C

source: World Energy Council, REN 21, IHA,
PB Statiszical Review of World Energy, June 2015

2. Renewable sources vs. conversion technologies

Primary (non-fossil) energies:

Conversion technologies:

Examples of nanomaterials enhancing efficiency or durability:

sun light → **photovolatic (PV)**
collector moduls, PV windows, thin films

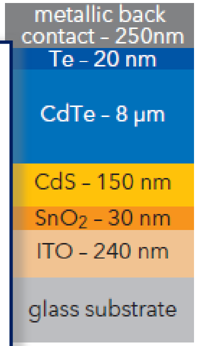
flow energy → **hydropower**
wind power plants, tidal power and hydro plants

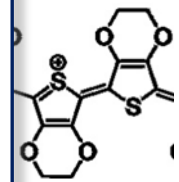
biomass → **Bio-energy conversion**
combustion, gasification, bioethanol, biofuels

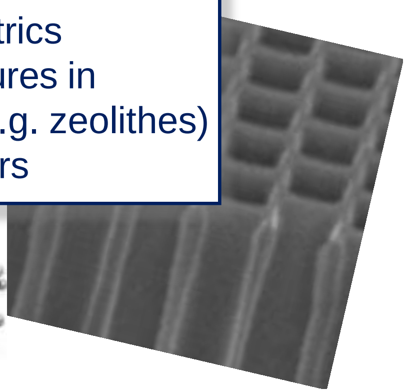
caloric energy → **heat recovery**
geothermics, solarthermics, thermoelectric conversion of waste & excess heat

secondary energies: **energy from wastes** → **waste-to-energy (WtE)**
incineration, gasification, pyrolysis, fermentation

- nanodimension SiO_2, quantum dots (InP) & nanocrystalline TiO_2, organic and polymer semi-conductors, epitactic multilayers of CdTe, CdS, $CuInSe_2$ …
- NCT to reinforce wings wind power plants,
- nano- and submicro-structured modules for thermoelectrics
- nanostructures in catalysts (e.g. zeolithes)
- nanoreactors







3. Storage of energy

Key factors: high electric energy density, fast charge-discharge cycles, lifetime, minimal energy loss (low temperature rise), reasonable price/operation costs

electric power

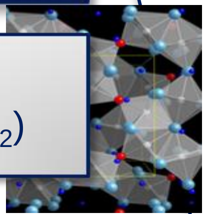
primary & secondary energy resources

storage technologies:

rechargeable batteries
Li-ion batteries: NCA; Li_xPO_4, LFP, Li-sulfur, Li-air …

supercapacitors
serially connected capacitors, nano-capacitors, superconducting magnetic energy storage (SMES)

hydrogen storage
(after electrolysis to H_2)



tanks & underground storage
of liquid & gaseous fue**ls**

Examples of nanomaterials enhancing efficiency or durability:

- carbon nanotubes, fullerenes, graphene
- nano-Si, Sn and nano-crystalline compounds
- nano-porous electrodes & separators
- Supercapacitors:
  - nanoporous NiF_2-layers on thermoplastics,
  - SWCNT, MWCNT
  - nano-porous Al_2O_3 on TiN
- Hydrogen storage: nanodimension Ammonium-boranes, CNT, metal hydrides, alloys of Ti, Fe or Ni

4. Power supply/transport of electricity

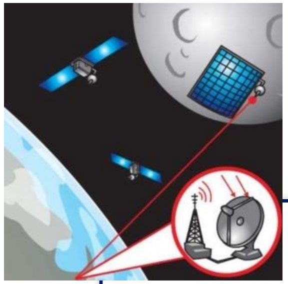
Key factors: High current transport capability at temperatures >77 K, low AC-losses, high mechanical strength (cables), availability in long length (several km), cheap production, low operation costs

technologies:

cables
engines, transformers, magnets

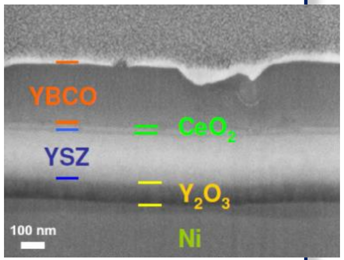
high temperature superconductors (HTSC)
supraconducting Bi-2223, YBCO …)
superconducting CNT & organic supraconductors

- high anisotropic alignment of the crystals
- nanoscaled pinning centres
- techniques for deposition of nanoscaled layers

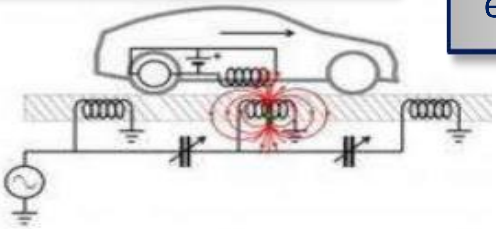


wireless energy transmission

transmission
by
laser beam, microwaves, electromagnetic resonance



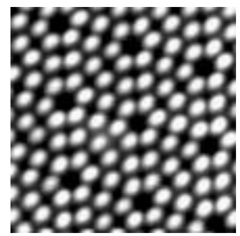
- „nano-enhanced“ components to enlarge efficiency



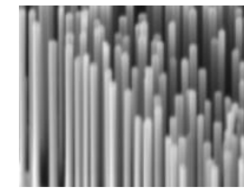
5. Reasons to apply nanodimension materials

The properties of nanoscale materials change as a function of the size such as

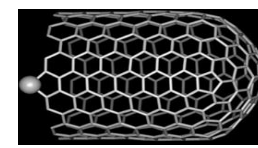
- melting point
- enhanced or reduced electrical and heat conductivity
- increased strength and tensile properties
- magnetic properties
- optical properties – color changes with size, flourescence
- chemical and catalytical reactivity
- self-assembling and reconstruction of surface

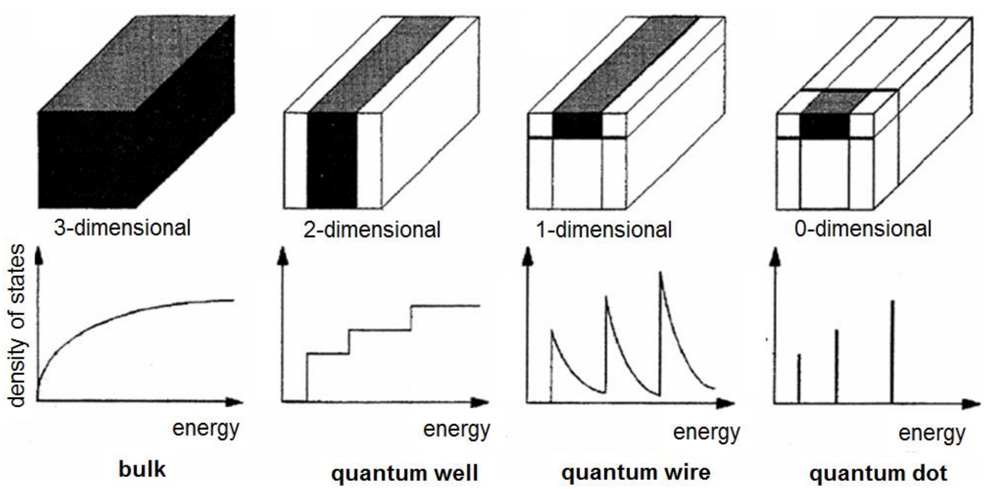


Various nanomaterials of different size and shape:



•Nanoparticles
•Nanocapsules
•Nanofibers
•Nanowires
•Fullerenes (carbon 60)
•Nanotubes (MWNCT, SWNCT)
•Nanosprings
•Nanobelts
•Quantum dots
•Nanofluidies





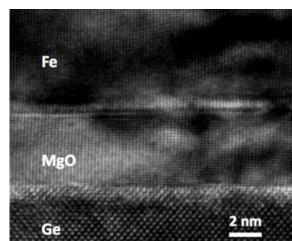
density of states (DOS = dn/dE) as a function of dimensionality; **quantum dots** = a nano-semiconductor confining the motion of the conduction band electrons, or the valence band holes, or exciton in all three spatial directions

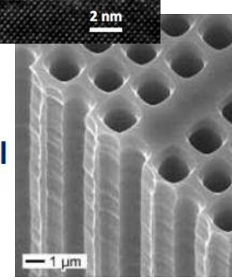
source: Nanomaterials in Chemistry, WILEY, 2001

6. Manufacturing nanomaterials (rough overview)

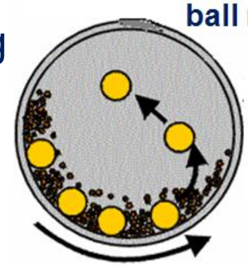
inorganic nanomaterials

- physically → vaporization &deposition (PVD)
  → sputtering; laser ablation
- chemically (precipitation, flame processes, microwave plasms, CVD, CCVD)
- molecular beam epitaxy (MBE), and MOCVD
- controlled electrochemical corrosion (nanoporous structures)
- deagglomeration by grinding (not applicable for large primary particles)
- sol-gel processes



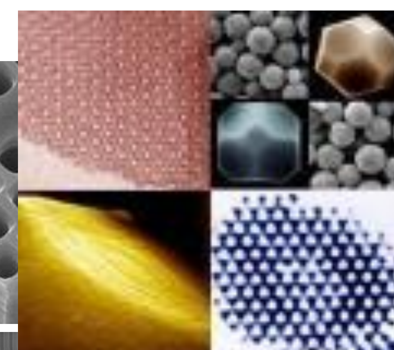


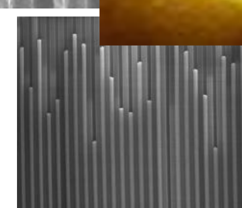
ball mill

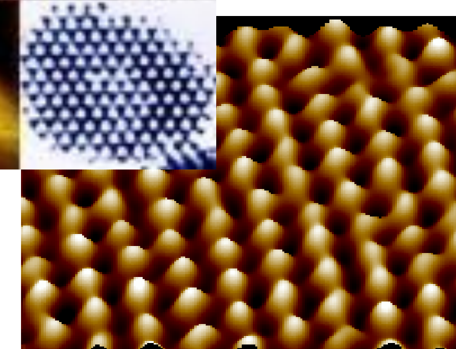


organic materials/(bio-)polymers

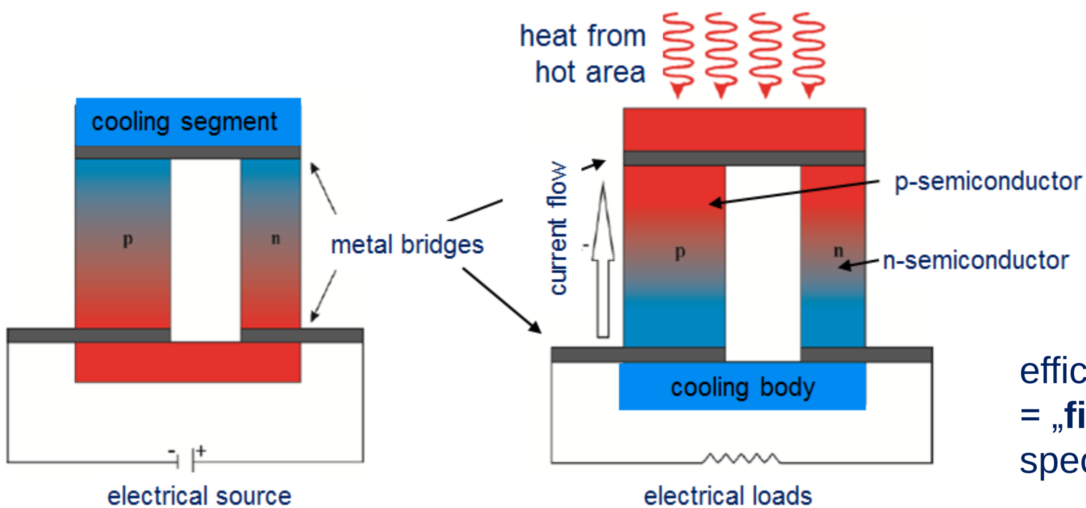
- solvent-antisolvent processes
- mini-emulsion polymerisation
- supramolecular chemistry
- self-assembling monolayers (LB technique)







7. Example: thermoelectric energy conversion



thermoelectric cooler (TEC; PELTIER element)

thermoelectric generator (TEG; SEEBECK effect)

source: S. Heimann, University Duisburg-Essen 2010

electric charges are transported by holes and electrons,
heat is conducted mainly by phonons (lattice vibration),
and electrons too

efficiency of the energy conversion = „**figure of merit**“ = zT (material specific index)

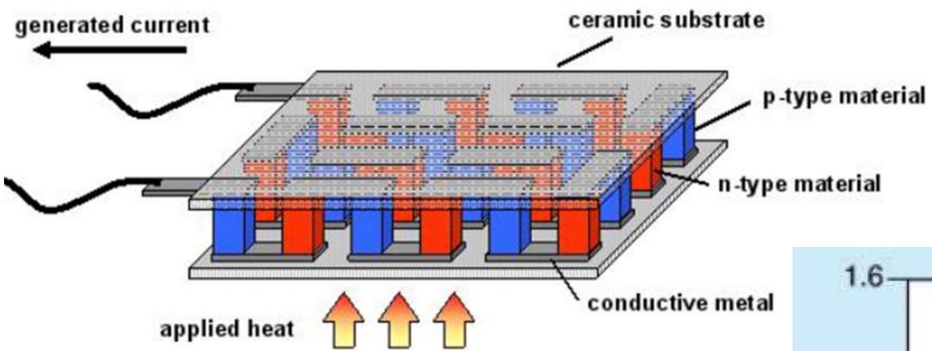
$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

α: SEEBECK coefficient,
σ: electrical conductivity,
T: temperature
κ: thermal conductivity

Bi_2Te_3 in TEC: for $\Delta T = 100$ °C, $0{,}8 \le zT \le 1{,}0$
$\eta = \le 7\%$, power density: $1 W/cm^2$

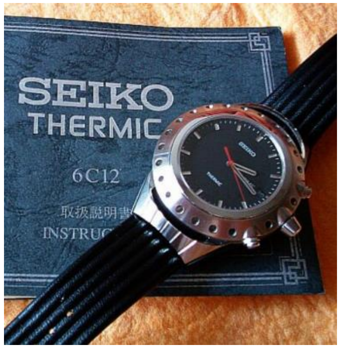
Skutterudite based (varieties of $CoSb_3$) TEG: different solutions for low and high temperatures; zT >1 (…..2)

technical solutions

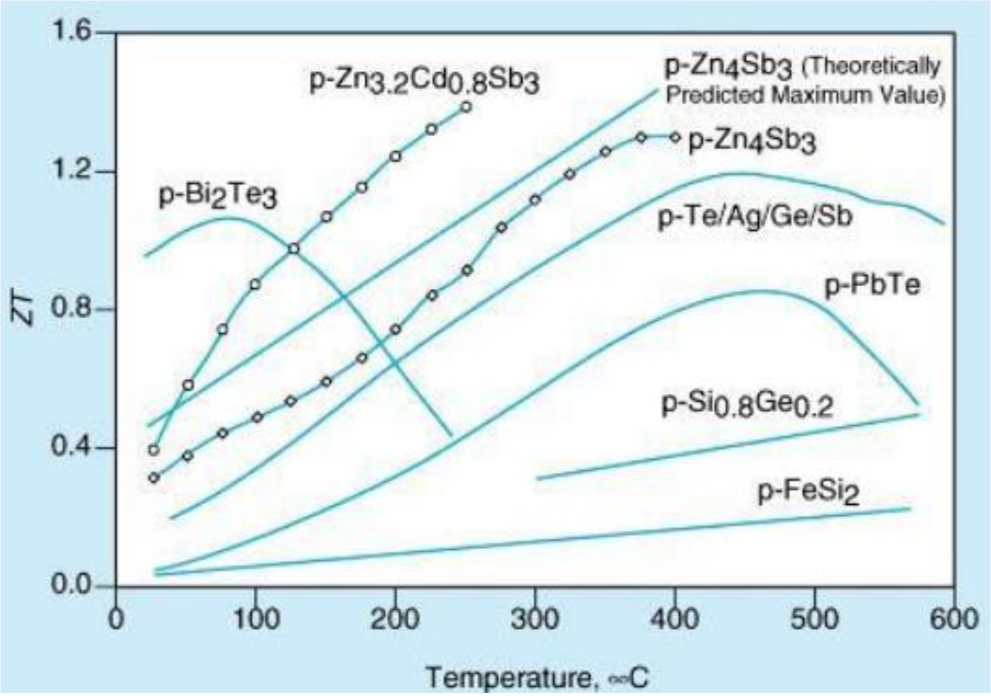


ternary or quaternary chalkonides
as semiconductors of n- and p-types
provide large *zT*-indices

noiseless refrigerator
opering with TEC



TEG driven
wrist watch



Nanoscaled thermoelectric materials

Nanoscaled thermoelectric materials and nano-structuring can enhance the „figure of merrit“ zT

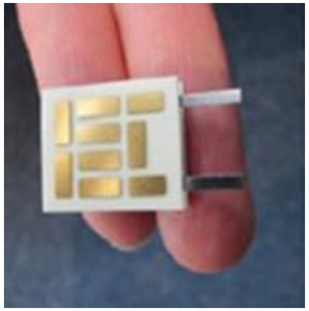
Simplest method:

semiconductor **nanopowder**

high pressure →

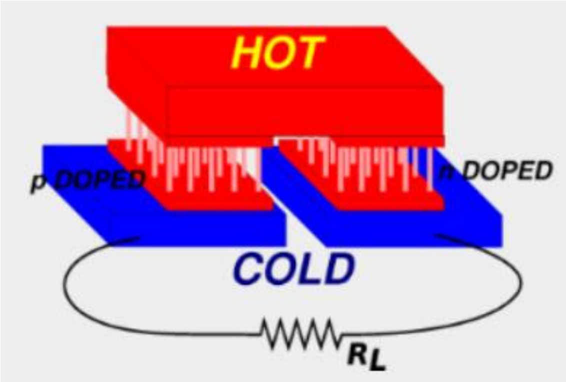
compact bloc of nanscaled semiconductor particles

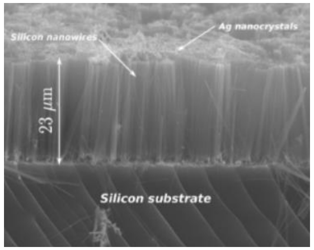
slicing → fabrication of thin layers

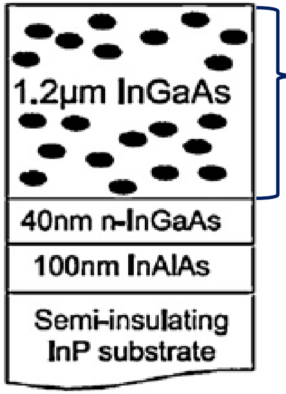


thin layer parts for TEC assemblies

matrix embeded **nanowires**:





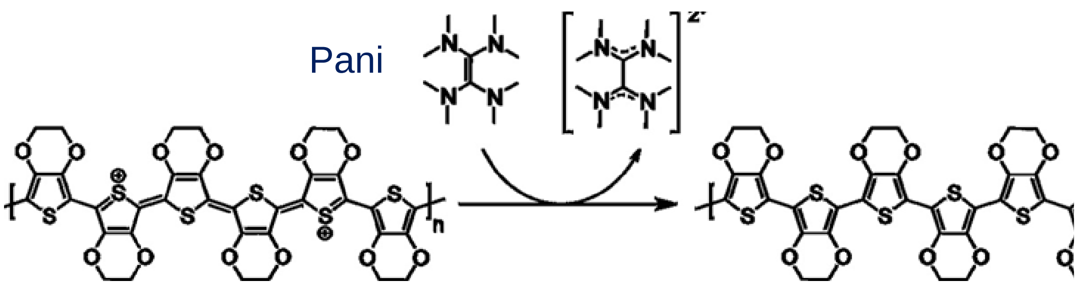


thin film power generators: ErAs:InGaAs/InGaAlAs superlattice; comprising 70 periods of 10 nm InGaAlAs and 20 nm InGaAs, fabricated through molecular beam epitaxy

Semiconducting, π-electrons containing polymers in thermoelectrics

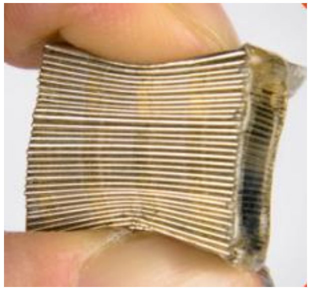
Derivates of polypyrrols (PPy), polyanilines (Pani) and polythiphened (PTh) are enabled by π-electrons to conduct electricity, and can act as semiconductors. The π-orbitals enable characteristic charge-transport and optical properties.

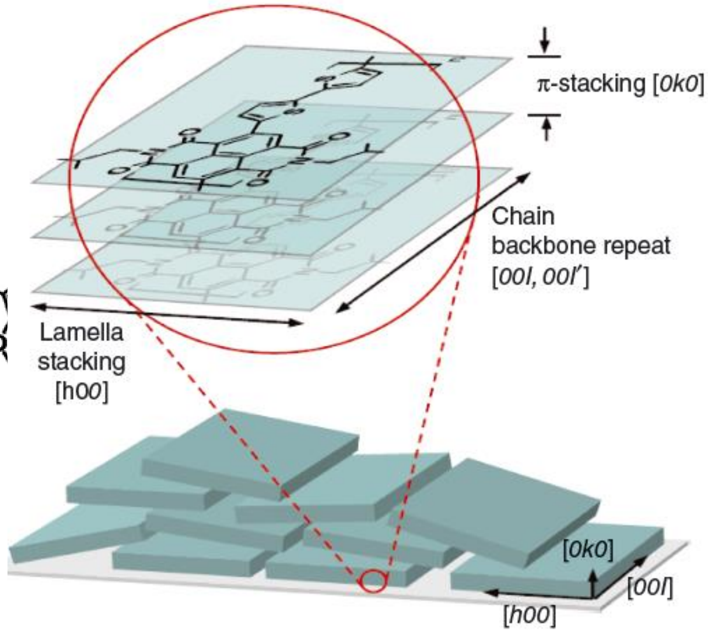
Pani



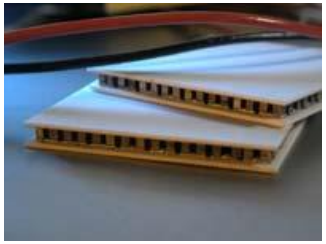
Poly(3,4-ethylene-dioxythiophene), PEDOT

folded ultra-thin layers to compact small TEC with 140 mV/K (otega/KIT, Karlsruhe)





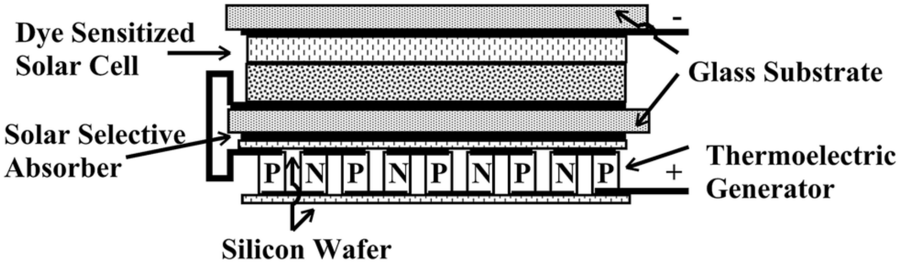
arrangement of the crystallites indicating slight disorder in the π-stacking and lamella stacking directions of the flat, platelet-like crystallites

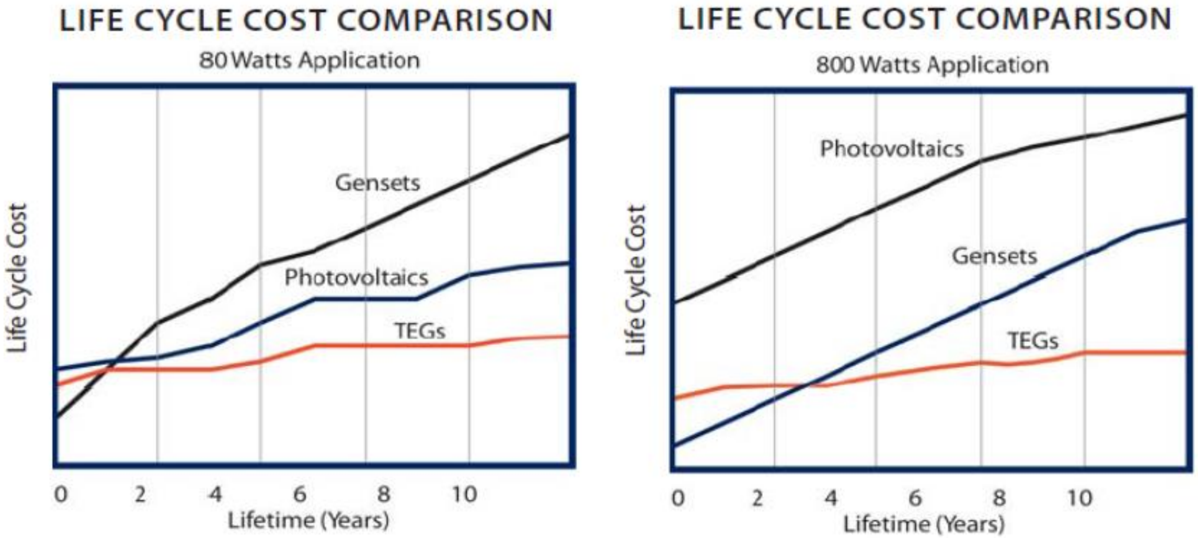


TEC-modul
(Peltier-modul)
ADV Engineering,
Moscow

BMW Series 5, Model Year 2010, 3.0 Liter
Gasoline Engine w/ Thermoelectric Generator

Photovoltaic device combined with TEG:





source: global TE, 2012

8. Example: supercapacitors

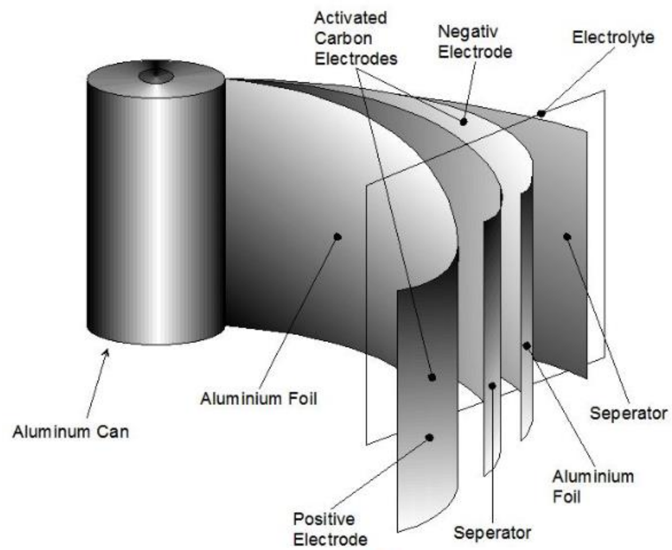
Standard capacitors: ≤ 100 F/g
Supercapacitors: > 300 F/g -->´1.000 F/g (?)

nanomaterials are involved such as

- SWCNT, MWCNT, graphene
- nanoporous NiF_2 layers
- high-orderly porous Al_2O_3 with TiN
- surfaces fixed polymer/organic semiconductors

in order to

- increase the specific capacity
- achieving large number of charge-discharge cycles
- decrease the manufacturing costs (mass production)

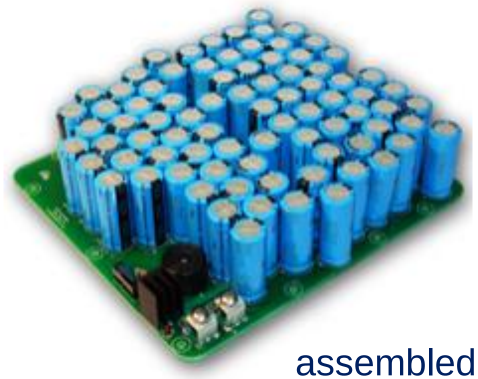


enlarging capacity & efficiency

physically (nano-) improved double layer capacitors

electrochemical double layer capacitors (EDLC)

pseudo–capacitors



assembled cylindic supercapacitors

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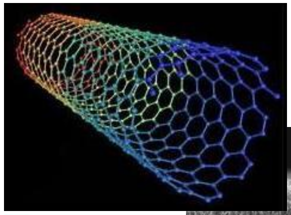
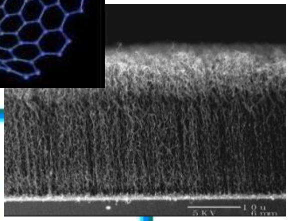
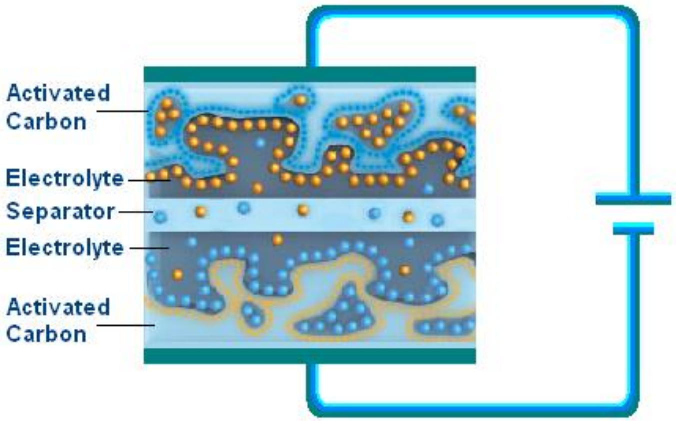
Examples of double layer electrolytic capacitors



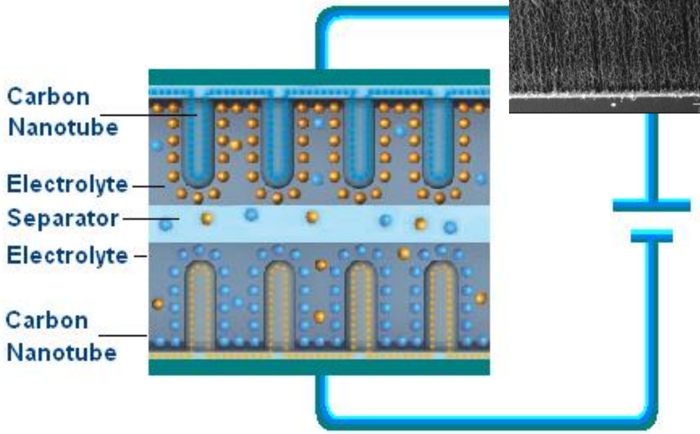


using activated carbon:



- two layers consisting of nanoporous electrodes
- separator is impregnated
  with an organic electrolyte
- thin separator can only withstand low voltages

using carbon nanotubes:

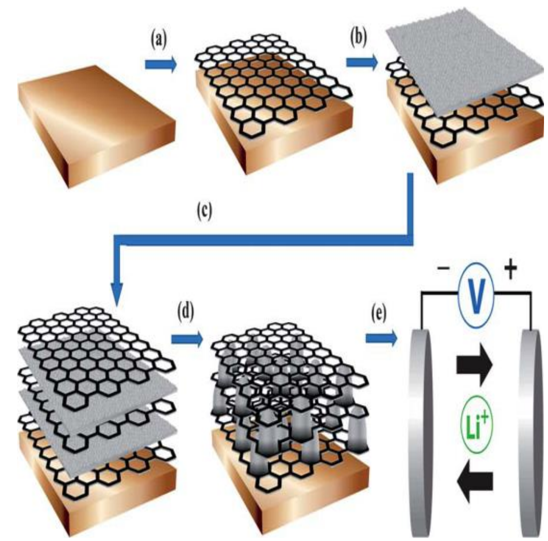


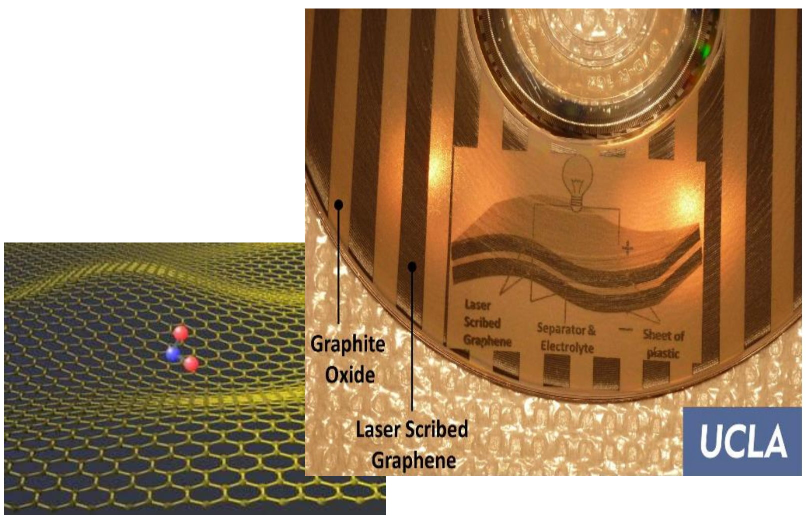
- replace of activated charcoal with carbon nanotubes
- aligned in a regular pattern that exposes greater surface area
- strong increase of the effective area of electrodes
- increase of the power density

Carbon nano-structures for enegergy storage

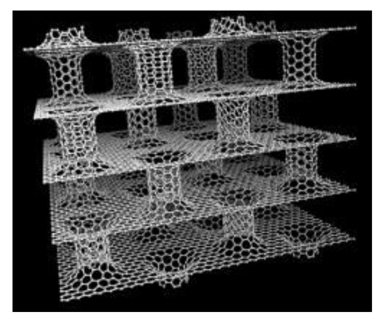
Graphene is being experimented in both, supercapacitor and battery construction

Graphene based supercapacitors provide the potential to replace small batteries.
Combination with CNT discloses additional potentials: multi-nanosupercapacitors, storage of hydrogen ….





graphene based ultra-thin supercapacitor
fixed on chips or tapes

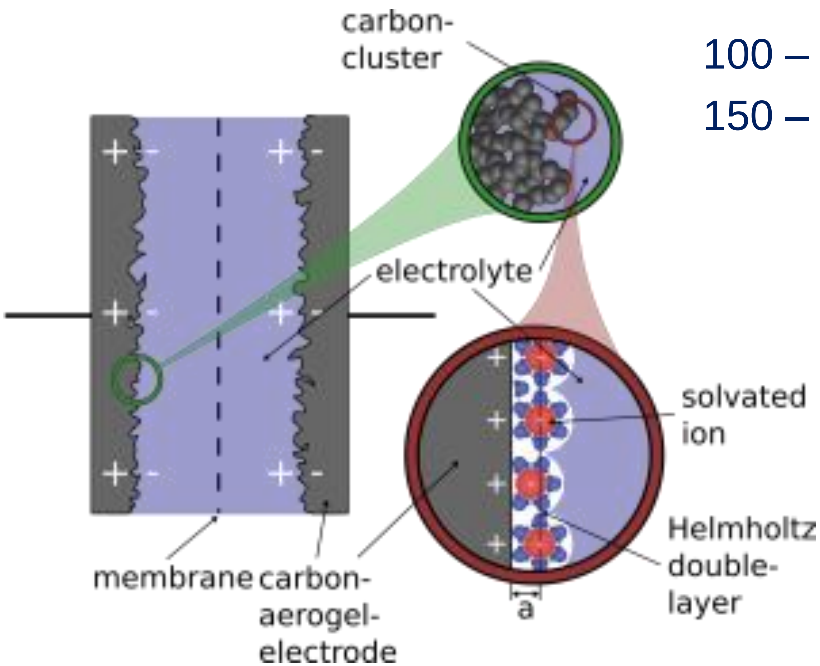


nanomodul constructed
from graphene and nanotube pillars

Sources:Steven Douglas, Uni of Maryland 2015 & Ille Gebeshuber, Uni of Vienna 2010

Electrochemical double layer capacitors (EDLC)

- store energy using ion adsorption (**no faradaic (redox) reaction**)
- high specific surface area (SSA) electrodes (carbon, MWCNT, SWCNT, nano-porous and modified Al_2O_3 etc.)



source: A. Lisowska-Oleksiak et al., Gdansk University of Technology 2012

100 – 120 F/g (nonaqueous electrolyte)

150 – 300 F/g (aqueous electrolyte)

C-aerogel membrane:
nanometer sized particles covalently bonded together,
high porosity (>50% under 100 nm)
large surface area (400 – 1.000 m²/g)

pseudo–capacitors

storing energy using **fast surface redox reactions**:

---> redox reaction occurs at the surface of the active material (metal oxides (RuO_2, Fe_3O_4, MnO_2), conducting polymers (polyaniline, polypyrrole, polythiophene etc.)

Materials of electrods:

Metal oxides:

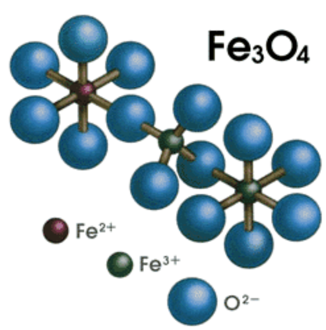
Capacity 1.300 F/g (RuO_2)

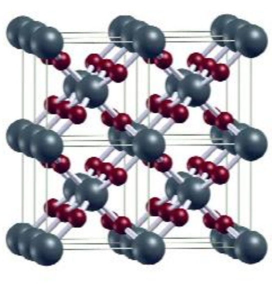
Nominal voltage 1.2 V

Conducting polymers:

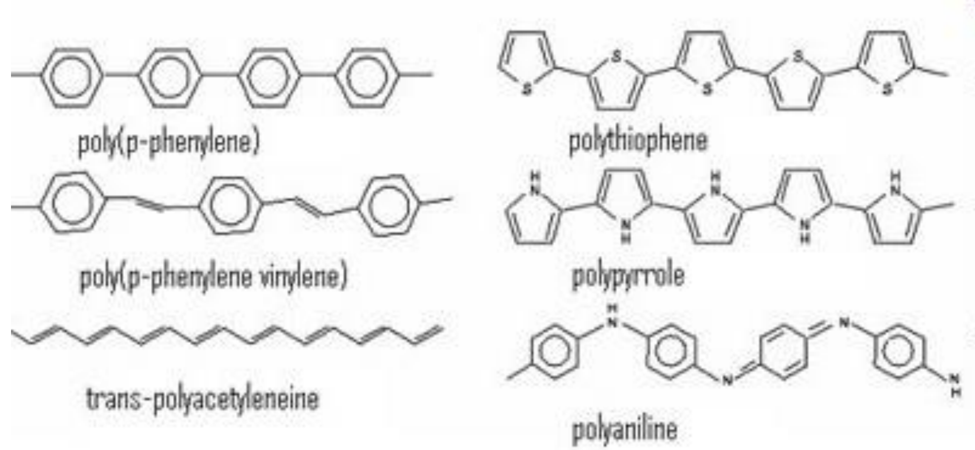
capacity 30 – 40 mAh/g

nominal voltage 1.0 V





RuO_2



hybrid systems consisted of organic and inorganic conducting materials, e.g. poly(3,4-ethylenedioxythiophene) modified with transition metal hexacyanoferrate

Micro-nanoporous PEDOT: 100 F/cm^3

supercapacitors going public …

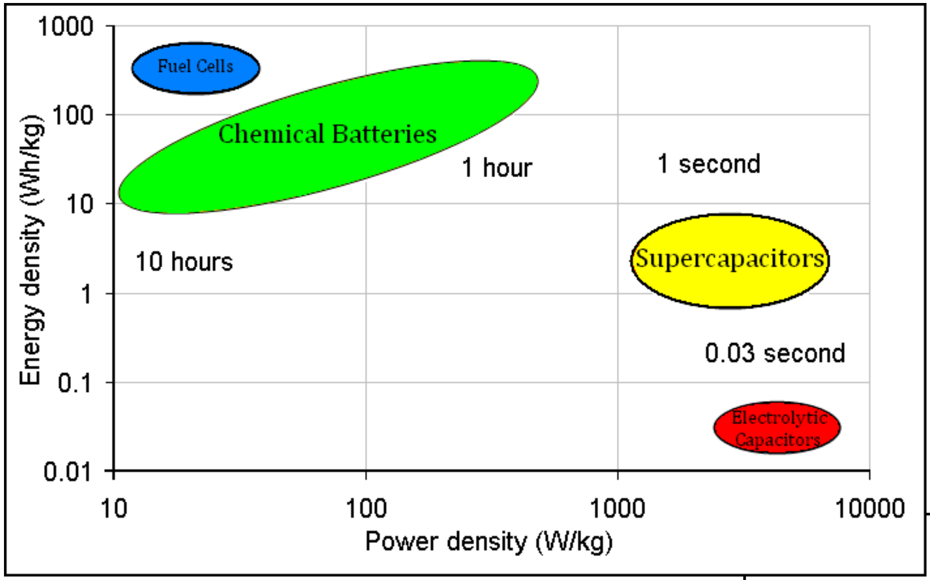
Prototype of Shanghai super-capacitor electric bus

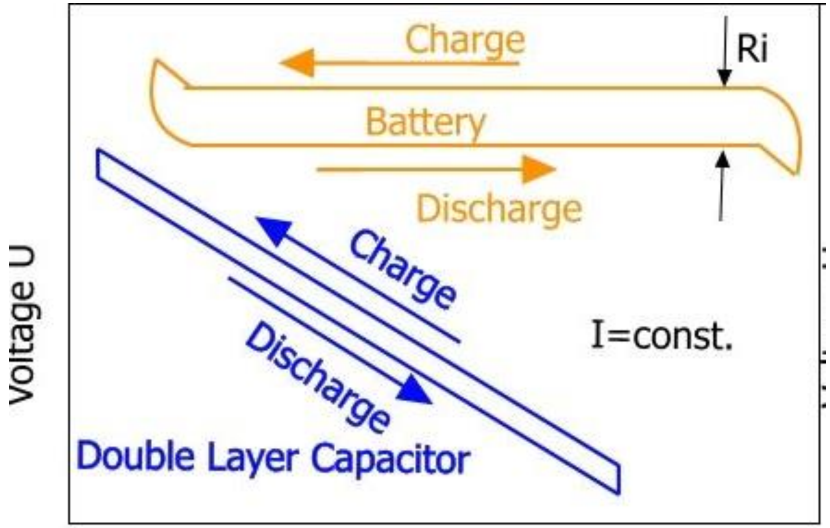
costs ~ 8000 €
(after 12 years one may save 160.000 €)
speed (max) 45 km/h
capacity 6 Wh/kg
distance (max) 5-9 km
charging time 5-10 min

charging station for wind power

source: www.citytransport.info/Electbus.htm

Comparison to batteries



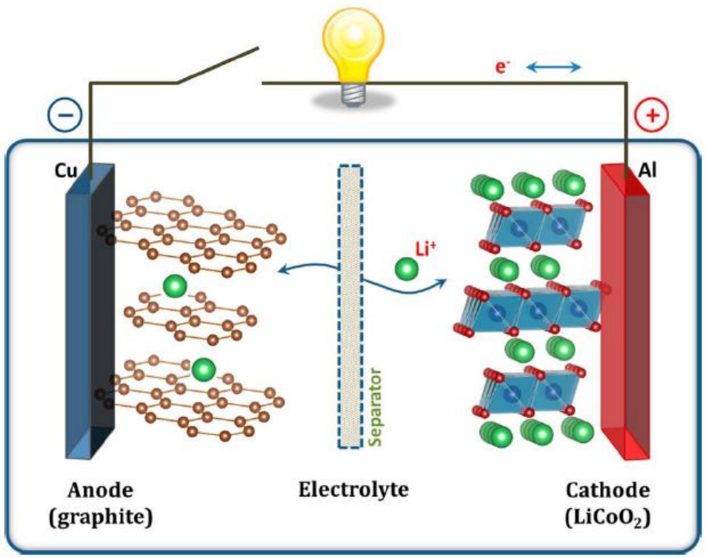


	supercapacitors	battery
charge time	70% charged in seconds	hours
discharge time	short	long
charge/discharge cycles	10.000 -1000.000	500 - 1.000
pollutants	none	metals

source: A. Lisowska-Oleksiak et al., Gdansk University of Technology 2012

9. Example: Batteries

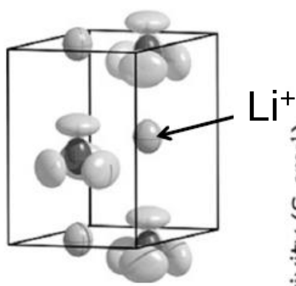
Li-ion battery:



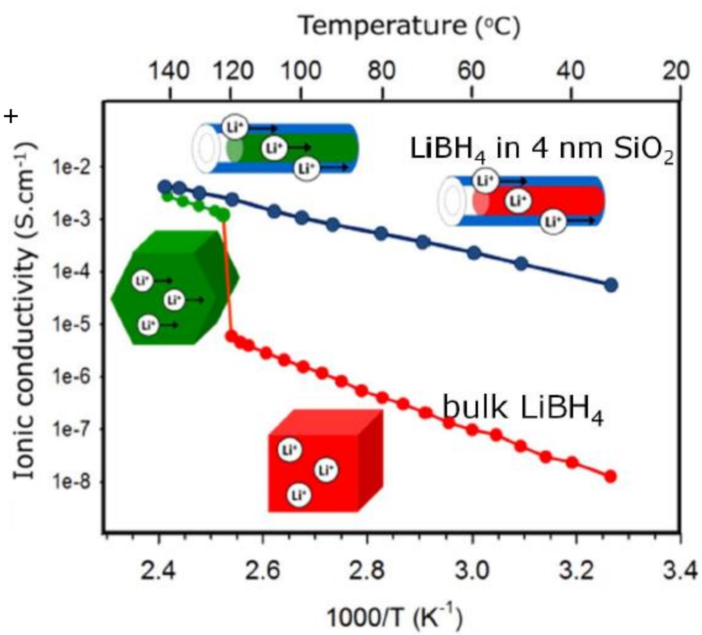
present problems:

- long charge time
- more or less memory effects
- insufficient density of stored energy
- rather short lifetime
- overheating, risk of sponaneous destruction

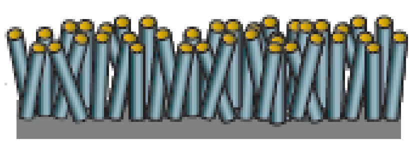
a) solid nanomaterial that do not conduct current, but that do conduct Li^+ ions:



$Li^+ [BH_4]^-$



b) Nanostructured electrodes



Si-Ge-nanowires (efficient 1D electron transport)

Conclusion and outlook

- nanomaterials and nanotechnology in energy conversion and storage provide a huge potential
  - to increase efficiency
  - to protect the environment, and
  - to save fossil and mineral resources
- a large number of promising solutions are already on the market, but manifold current R&D activities are promising progress
- cooperation of Russian and German researches and developers in the sophisticated area of „nano for energy“ would be useful and profitable for both partners

Financial supports for bilateral projects can be obtained by

- European grants such as ERA.rus-net, HORIZON 2020
- FASIE & BMBF for German-Russian projects
- grants from Skolkovo Foundation

in addition: exchanges of scientists, internships and bilateral R&D cooperations are recommended!