ENERGY SYSTEMS: THE IMPORTANCE OF ENERGY STORAGE

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NEED FOR ENERGY STORAGE

Novel energy landscape

From fossil fuels to renewable energy

e-mobility

Individual mobility with zero emissions

Power grid extension

Efficient transport and distribution of electricity

German ‚Energiewende'

Pictures: bmu.de/themen/klima-energie/energiewende

Outline

- The Challenge: Different Forms of Energy and How to Store Them
    - Thermal Energy
    - Electrical Energy

- The Devices: Selected Energy Storage Systems
    - Batteries
    - Redox Flow Batteries
    - Supercaps
    - Electrolyzers & Fuel Cells

- The Big Picture: Do We Need a New Energy Architecture?

THE CHALLENGE

DIFFERENT FORMS OF ENERGY AND HOW TO STORE THEM

History & Definitions

Aristotel:
energeia = activity

Leibniz & Newton:
First concept of kinetic energy and thermal energy

Young, Coriolis & Rankine:
Kinetic and potential energy in the modern sense

Mayer:
Conservation of energy

Joule & Kelvin:
Laws of thermodynamics

Key parameters for energy storage

Energy density	Amount of energy stored in a system of given mass or region of space ▪ Gravimetric: $J \cdot kg^{-1}$ ▪ Volumetric: $J \cdot m^{-3}$
Power density	Power of energy converters or storage devices related to their mass or volume ▪ Gravimetric: $J \cdot s^{-1} \cdot kg^{-1}$ ▪ Volumetric: $J \cdot s^{-1} \cdot m^{-3}$
Storage time	Typical time of energy storage characteristic for specific device design
Self-discharge	Internal reactions reduce the stored charge in a device without any load connected in the external circuit

Pictures: wikipedia.com

Storage Capability

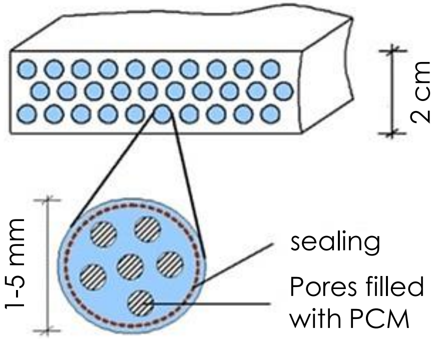
Thermal Energy

"Kinetic energy of a system's constituent particles, which may be atoms, molecules, electrons"

$E_{th} = c \cdot m \cdot T$

Energy stored as latent heat:
Phase change materials (PCMs) absorb/release heat when they change from solid to liquid (vice versa)

thermodynamic



New building material with micro-encapsulated PCMs

Electrical Energy

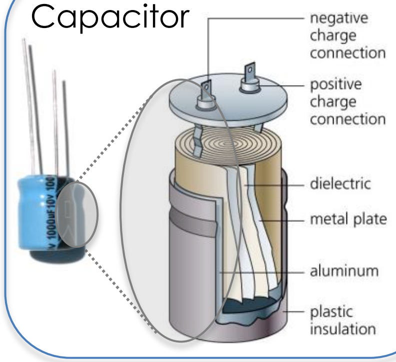
„Potential energy stored in electromagnetic fields and transported as electricity"

$$E_{el} = \int_{t_0}^{t_1} u(t) \cdot i(t) \cdot dt$$

Multiple ways of energy storage

electrical

Capacitor



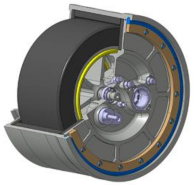
chemical

Battery,

Electrolysis combined with fuel cell

mechanical

Flywheel,



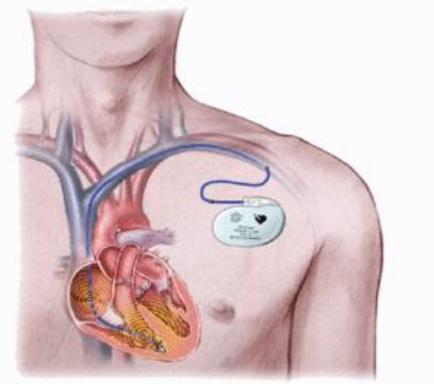
Pumped-storage plant

2nd law of thermodynamics: Heat cannot be converted into work without losses

Source: J. Manara, ZAE Bayern, 2007

Scale of Application

Capacitor: Implantable defibrillator



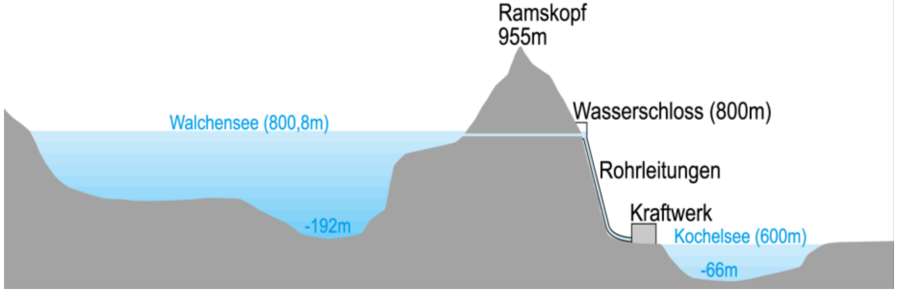
- Voltage: 800 V
- Capacitance: 100 µF

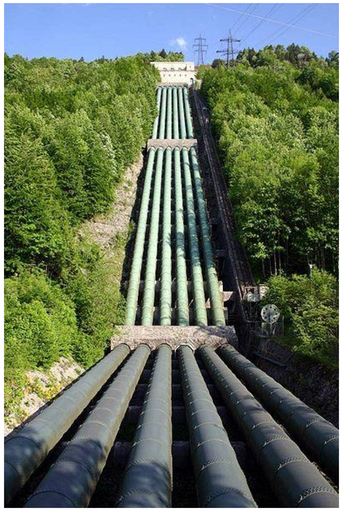
U = 800 V, C = 10^{-4} F

$E = 1/2 \cdot C \cdot U^2$

Theoretical energy content:
$E = 8.8 \cdot 10^{-6}$ kWh

Pumped-storage power plant: ‚Walchensee'





- Height difference: 200 m
- Max. lowering of water table: 6 m
- Equivalent in water volume: 10^{11} L

m = 10^{11} kg, g = 9,81 m/s^2, h = 200 m

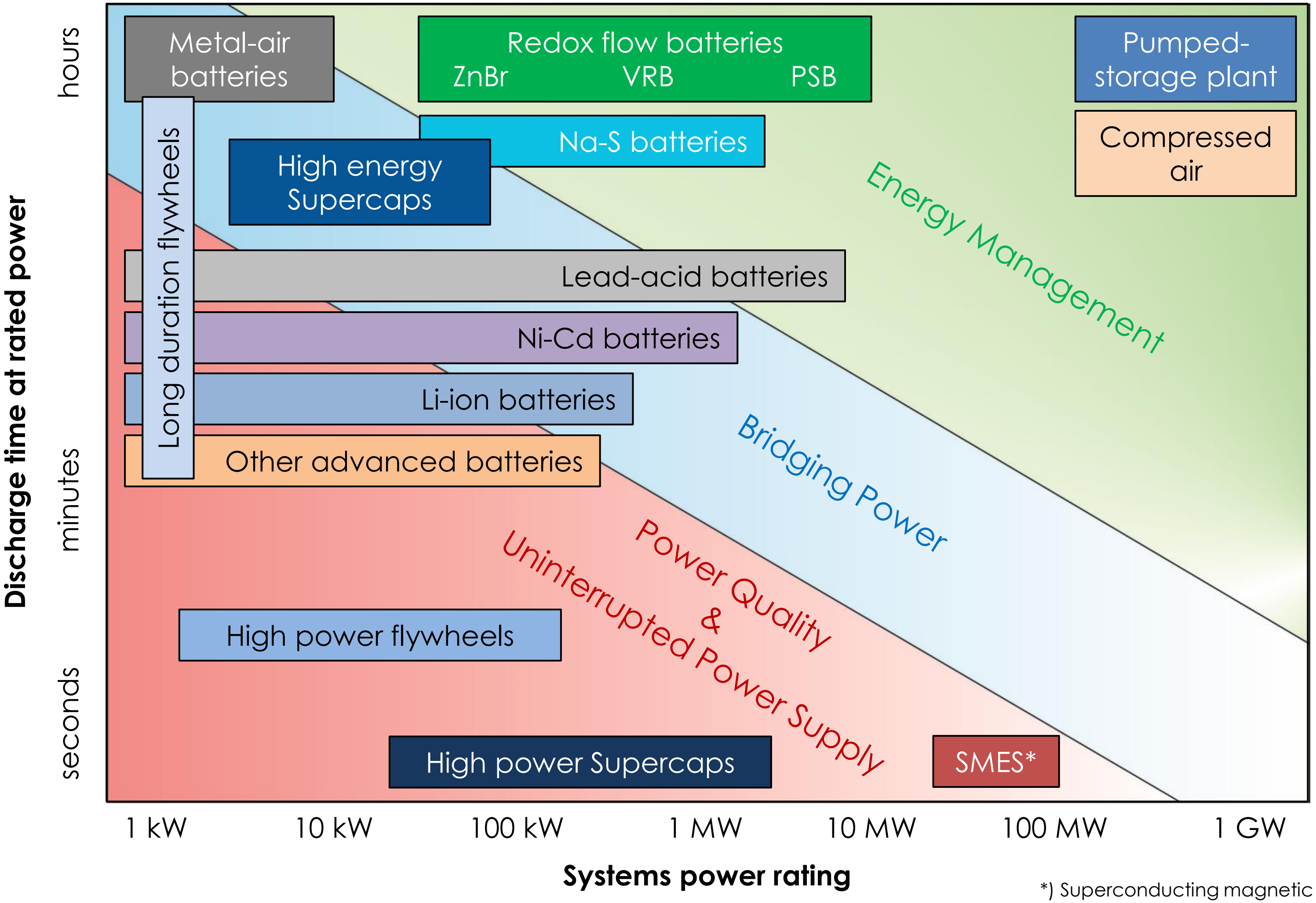
$E = m \cdot g \cdot h$

Theoretical energy content:
$E = 60 \cdot 10^{6}$ kWh

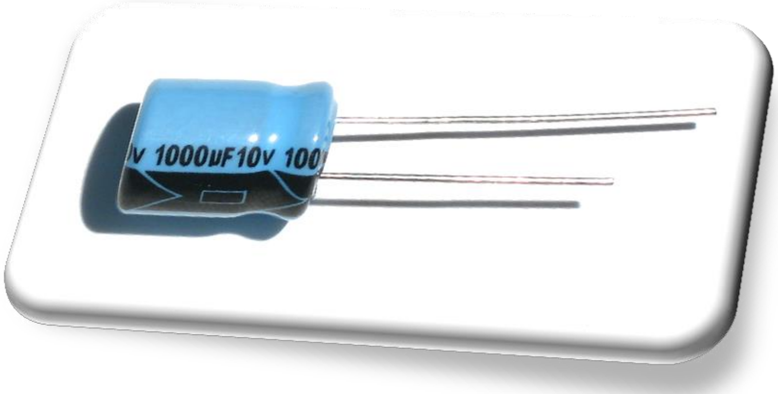
Energy and power density determine field of application for different technologies

Sources: H. Haase, Institut für Grundlagen der Elektrotechnik und Messtechnik, Leibniz Universität Hannover, 2007 | E.ON Wasserkraft, 2010

Choice of Technology



*) Superconducting magnetic energy storage

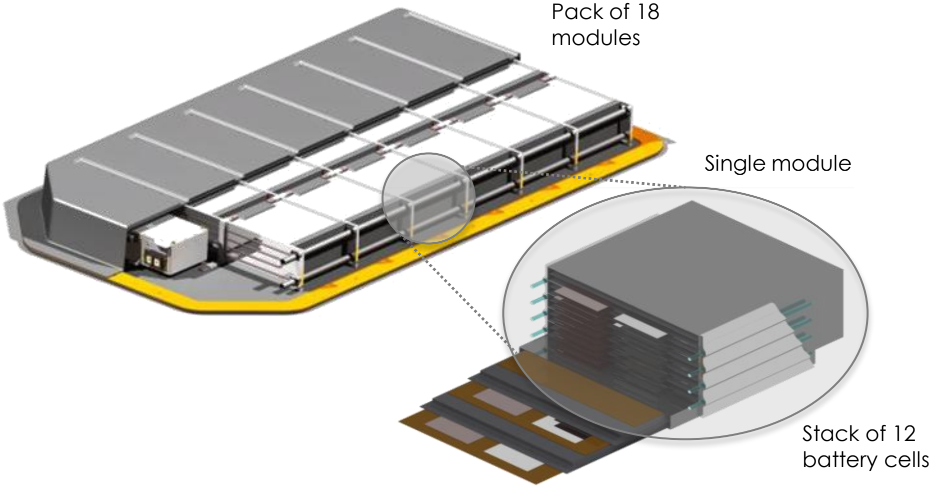


THE DEVICES

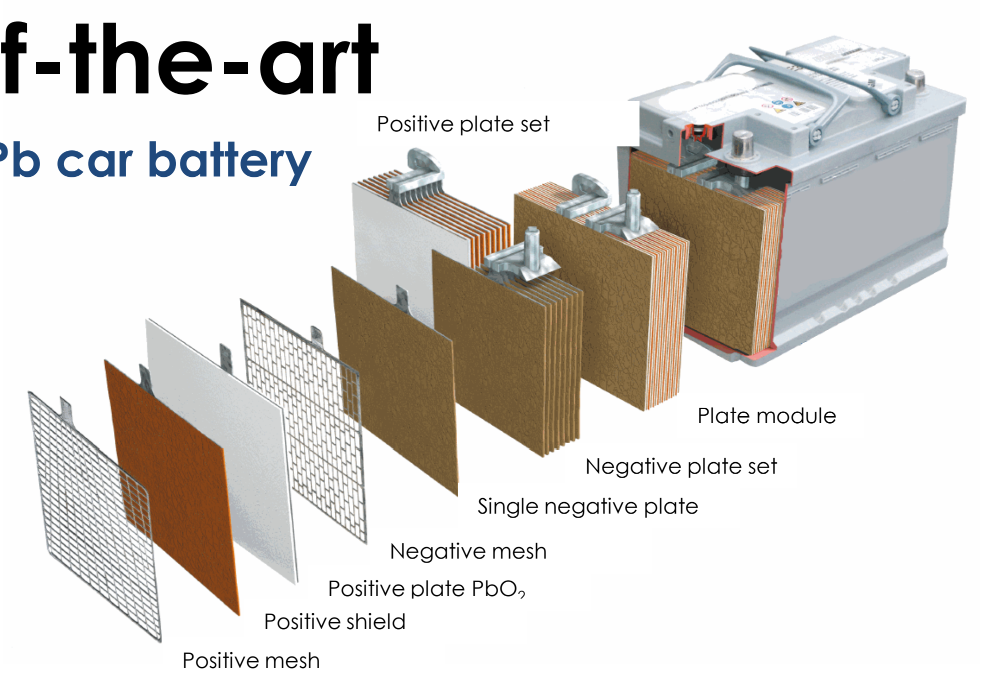
SELECTED ENERGY STORAGE SYSTEMS

Batteries – state-of-the-art

Li-ion battery pack



Pb car battery



Battery type	**Pb**	**Ni-Cd**	**Ni-MeH**	**Na-S/Na-NiCl$_2$**	**Li-ion**
Energy density vol. [Wh/L]	90	150	200	345/190	300-400
Energy density grav. [Wh/kg]	35	50	70	170/120	200-300
Power density vol. [W/L]	910	2000	3000	270	4200-5500
Power density grav. [W/kg]	430	700	1200	180	3000-3800
Self-discharge	+	+	+	-	++
Fast charging	--	++	+	-	+

Sources: Christian Linse, Christian Huber, Robert Kuhn, TUM CREATE, 2013, unpublished | Mario Wachtler, Margret Wohlfahrt-Mehrens, ZSW Ulm, 2011

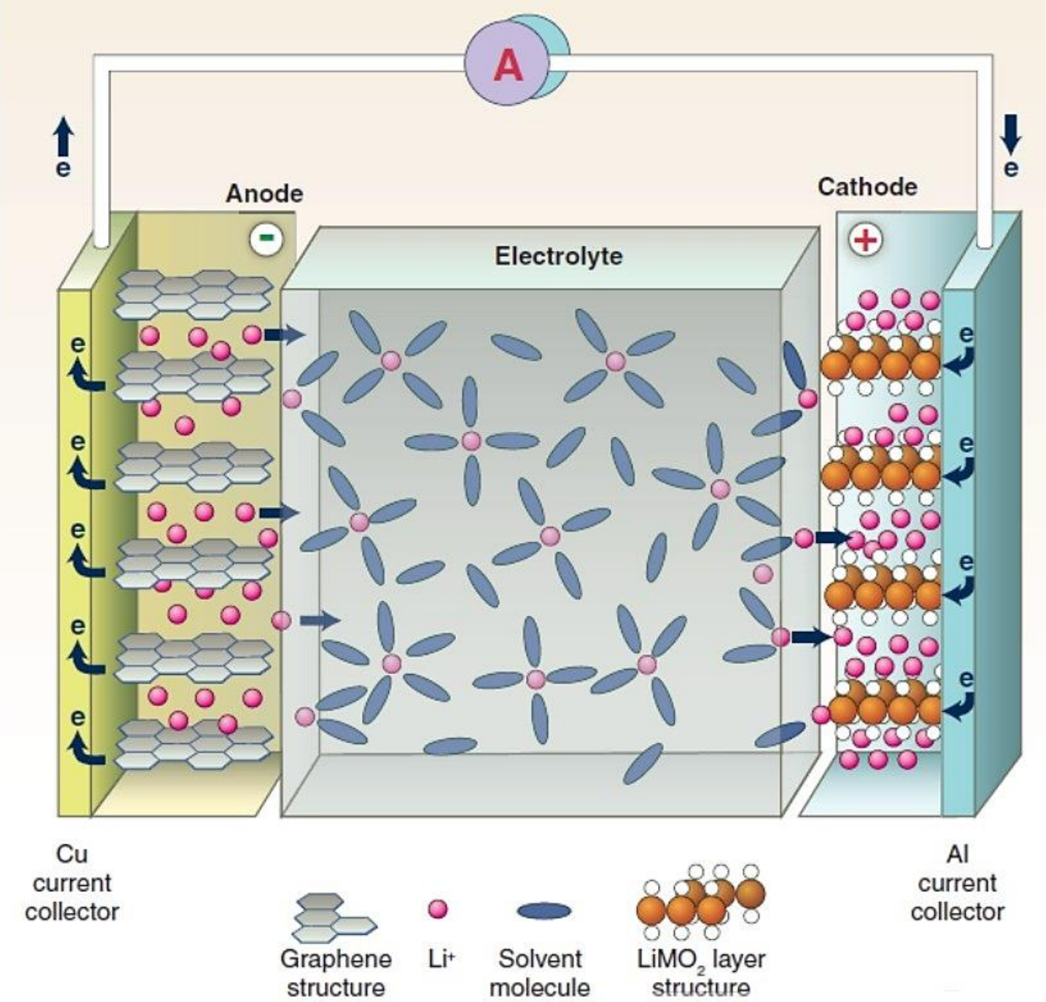
Li-ion Battery – Principle

Reaction mechanism

$$Li^+ + e^- + 2\,Li_{0.5}CoO_2 \leftrightarrow 2\,LiCoO_2 \qquad \text{(cathode)}$$

$$LiC_6 \leftrightarrow Li^+ + e^- + 6\,C \qquad \text{(anode)}$$

$$\overline{\quad LiC_6 + 2Li_{0.5}CoO_2 \leftrightarrow 2LiCoO_2 + 6C\ ;\ \Delta U_0 \approx 4.1\ V \quad}$$



Electrodes

Intercalation / deintercalation of Li^+ ions into host structures

Limit: Energy density

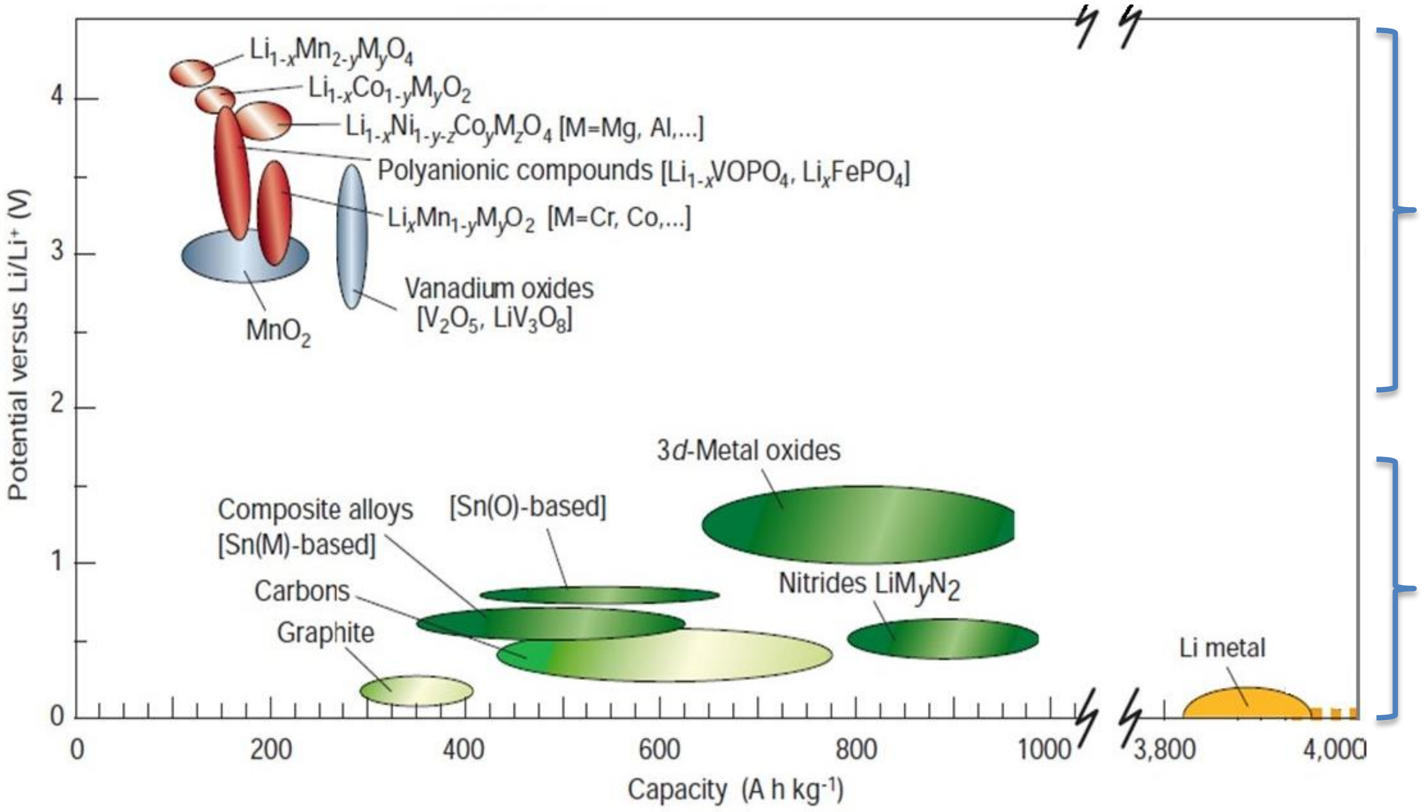
Example: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ / Graphite

Electrodes: 70 % of cell weight
Rest (current collectors, electrolyte): 30 %

- Electrodes : 430 Wh/kg
- Complete cells: 300 Wh/kg
- Total battery pack: **200 Wh/kg**

Sources: B. Dunn, et al., Science, 2011, 334, 928 | F. T. Wagner, B. Lakshmanan, M. F. Mathias, J. Phys. Chem. Lett., 2010, 1, 2204

Active Materials for Batteries



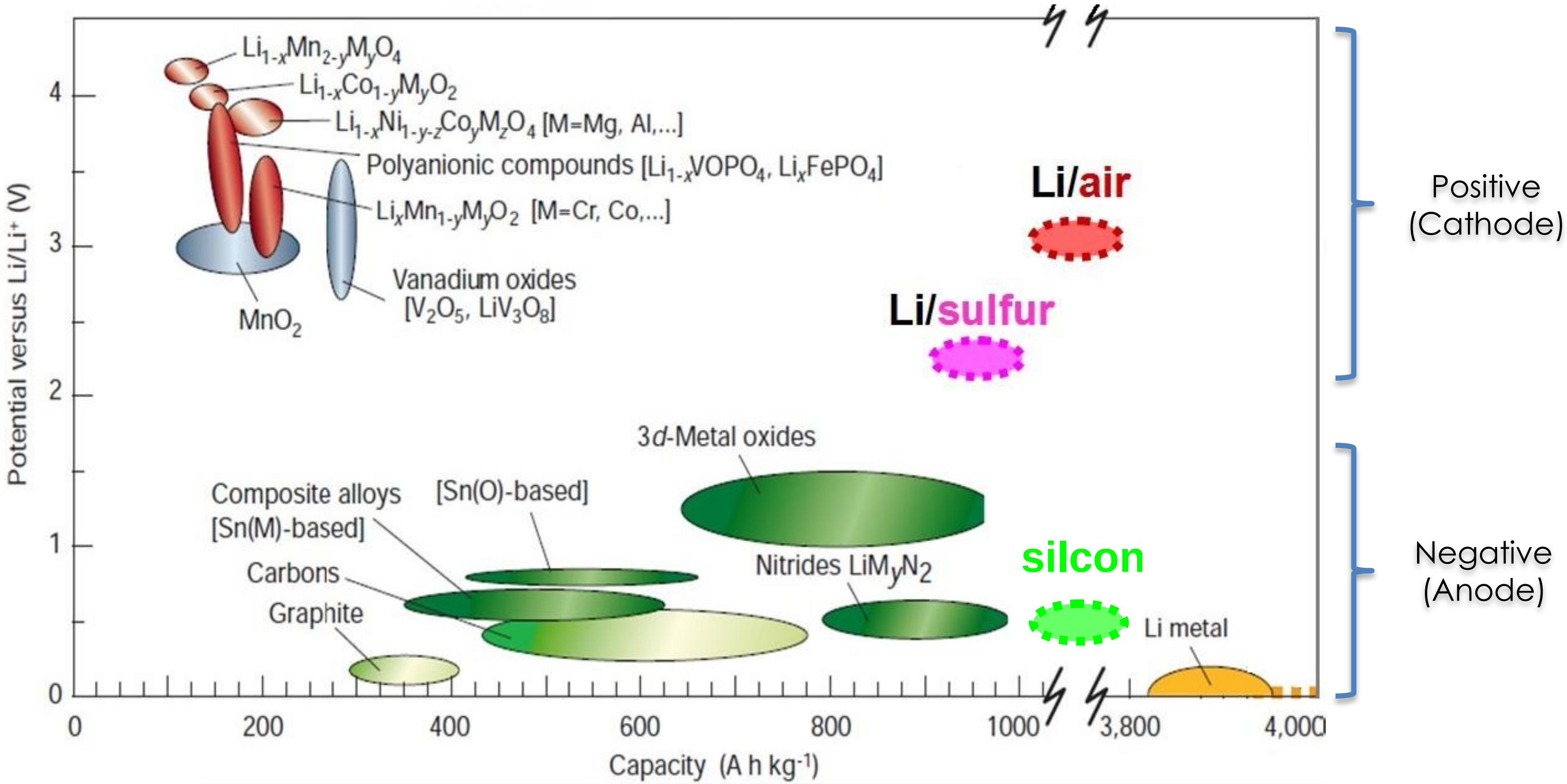
Positive
(Cathode)

Negative
(Anode)

Main disadvantages of Li-based battery systems:
- Scarceness of lithium
- Security concerns (thermal runaway, organic solvents)

Source: J.-M. Tarascon, M. Armand, Nature, 2001, 414, 359

Active Materials for Batteries



Compound formation / alloying rather than **intercalation** in host structure

Post Li-ion batteries: Li-air and Li-S batteries with Si or Li anodes

Source: J.-M. Tarascon, M. Armand, Nature, 2001, 414, 359

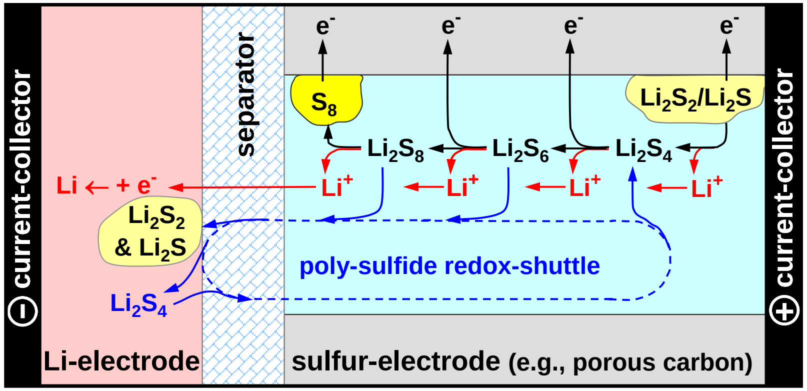
Future Concepts – Li-S Batteries

Concept

$S + 2\,Li^+ + 2\,e^- \leftrightarrow (Li_2S)_{solid}$ (cathode)

$2\,Li \leftrightarrow 2\,Li^+ + 2\,e^-$ (anode)

$2\,Li + S \leftrightarrow (Li_2S)_{solid}$; $\Delta U_0 \approx 2.0$ V



Challenges and R&D needs

- Polysulfide diffusion to anode ➡ Li^+-conducting diffusion barrier
- Poor C-rate & cathode “clogging” ➡ Cathode design
- Stable anode configuration ➡ Improved Li-metal anode design or alternative

Advantages

- High specific capacity: 630 $Ah/kg_{electrode}$
- High energy density: **950 $Wh/kg_{electrode}$**
- Low cost of sulfur
- Minimal degradation during charge cycling

**Gain vs. state-of-the-art batteries:
2-fold**

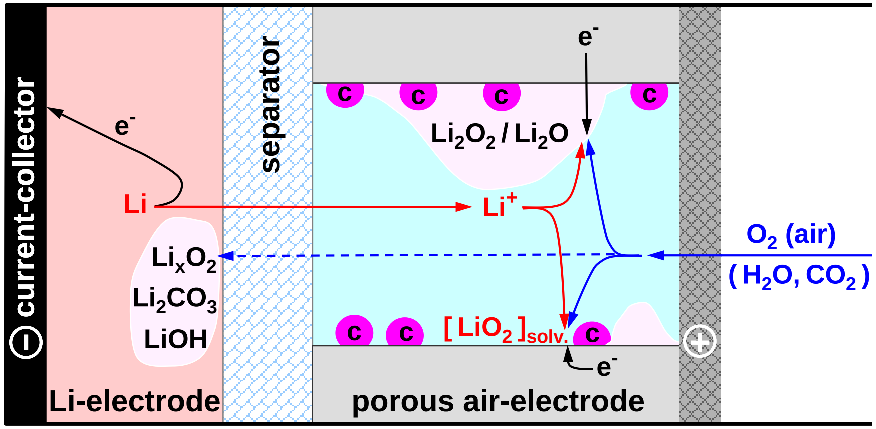
Source: Y.-C. Lu, H. A. Gasteiger, M. C. Parent, V. Chiloyan, Y. Shao-Horn, Electrochem. & Solid-State Lett., 2010, 13, A69

Future Concepts – Li-air Batteries

Concept

$$\begin{aligned} O_2 + 2\,Li^+ + 2\,e^- &\leftrightarrow (Li_2O_2)_{solid} && \text{(cathode)} \\ 2\,Li &\leftrightarrow 2\,Li^+ + 2\,e^- && \text{(anode)} \\ \hline 2\,Li + O_2 &\leftrightarrow (Li_2O_2)_{solid}\ ;\ \Delta U_0 \approx 2.96\ V \end{aligned}$$

$$\begin{aligned} O_2 + 4\,Li^+ + 4\,e^- &\leftrightarrow (Li_2O)_{solid} && \text{(cathode)} \\ 4\,Li &\leftrightarrow 4\,Li^+ + 4\,e^- && \text{(anode)} \\ \hline 4\,Li + O_2 &\leftrightarrow (Li_2O)_{solid}\ ;\ \Delta U_0 \approx 2.91\ V \end{aligned}$$



Challenges and R&D needs

- Battery has to be protected from environment (O_2 must be present at cathode/humidity can cause degradation)
- Blockage of porous carbon cathode with discharge products (“clogging”)
- Presence of significant charge overpotential indicating secondary reactions besides recharging

Advantages

- Specific capacity even higher than for Li-S: 800 $Ah/kg_{electrode}$
- Very high energy density: **1700 $Wh/kg_{electrode}$**
- Oxygen from air instead of storing an oxidizer internally

Gain vs. state-of-the-art batteries: 4-fold

Source: Y.-C. Lu, H. A. Gasteiger, M. C. Parent, V. Chiloyan, Y. Shao-Horn, Electrochem. & Solid-State Lett., 2010, 13, A69

Novel Concept – F-ion Batteries

Concept

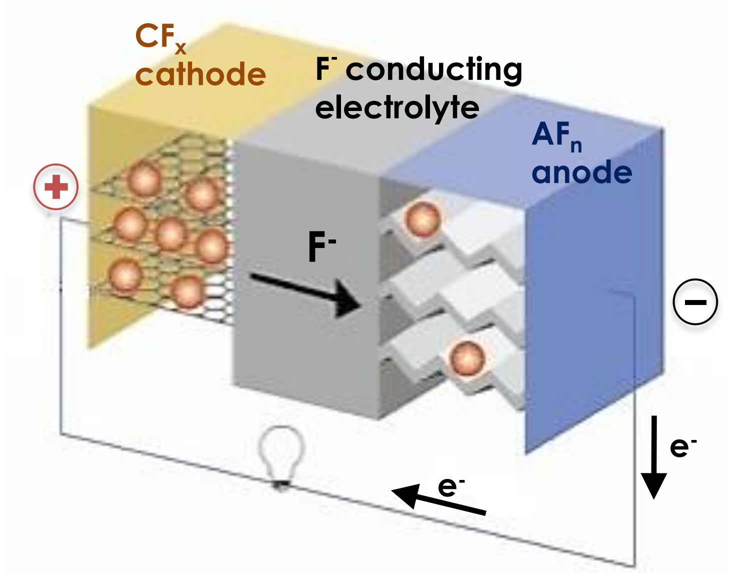
Reminder: Li-ion reaction

$$LiC_6 + 2Li_{0.5}CoO_2 \leftrightarrow 2LiCoO_2 + 6C\ ;\ \Delta U_0 \approx 4.1\ \mathrm{V}$$

F-ion reaction

$$\boxed{LaF_3 + 3CF_y \leftrightarrow LaF_{3(1-x)} + 3CF_{x+y}\ ;\ \Delta U_0 \approx 4.5\ \mathrm{V}}$$

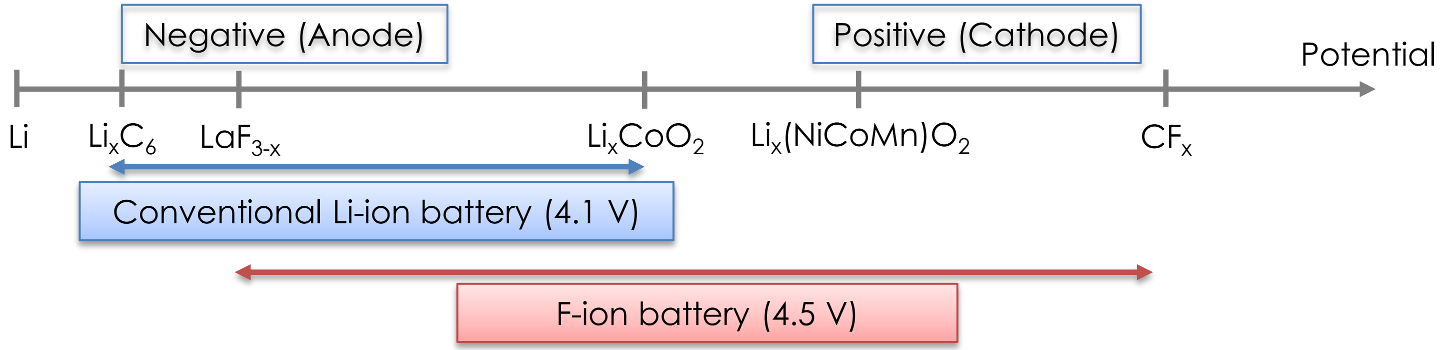
Discharge (charge vice versa)



Advantages

- High theoretical energy density: **1560 Wh/kg**
- No need for scarce elemental lithium
- **Safer** than Li-ion batteries (no oxygen present)

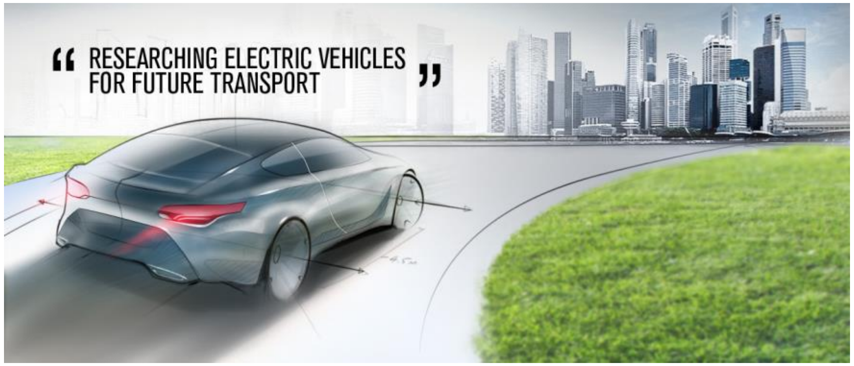
Choice of redox couple



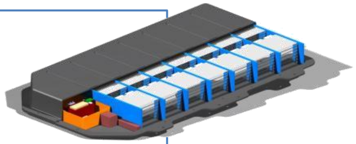
Source: R. Yazami, CNRS, Nanyang Technological University, 2012

Battery Applications

Battery stacks for e-mobility



High power battery pack



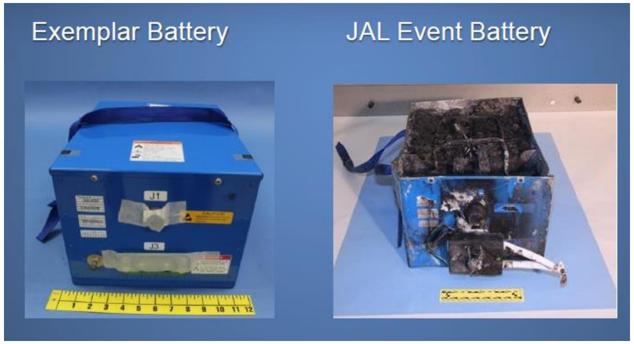
Number of cells:	216
Number of modules:	18
Weight:	max. 550 kg
Energy content:	48 kWh
Battery voltage:	300 … 450 V
Battery current:	max. 360 A

Overall design optimization

- Integration of cooling plates into battery structure
- Maximize mechanical safety
- Specific energy module / pack level

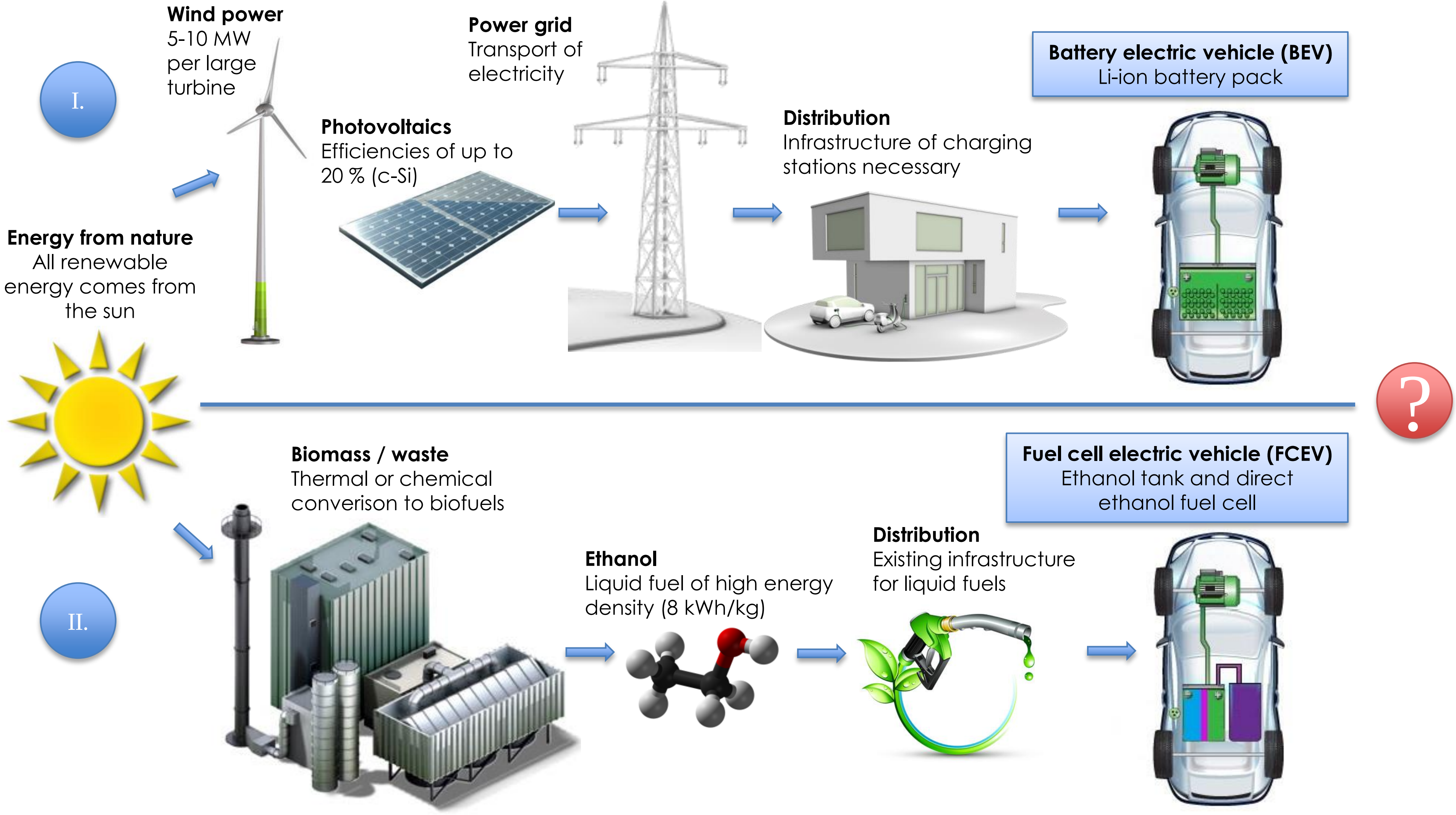
Batteries for aviation

- Ni-Cd batteries used as start-up and emergency power supply
- New Boeing 787 Dreamliner uses 2.2 kWh GS Yuasa $LiCoO_2$ batteries



Sources: Christian Linse, Christian Huber, Robert Kuhn, TUM CREATE, 2013, unpublished | J. Garche, unpublished

Fueling the e-car



Energy from nature
All renewable energy comes from the sun

I.

Wind power
5-10 MW per large turbine

Photovoltaics
Efficiencies of up to 20 % (c-Si)

Power grid
Transport of electricity

Distribution
Infrastructure of charging stations necessary

Battery electric vehicle (BEV)
Li-ion battery pack

?

II.

Biomass / waste
Thermal or chemical conversion to biofuels

Ethanol
Liquid fuel of high energy density (8 kWh/kg)

Distribution
Existing infrastructure for liquid fuels

Fuel cell electric vehicle (FCEV)
Ethanol tank and direct ethanol fuel cell

Redox Flow Battery – Principle

Reaction mechanism

$\underline{V^{5+} \rightarrow V^{4+}}$: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$

$U_0 \approx +1.00$ V vs. NHE

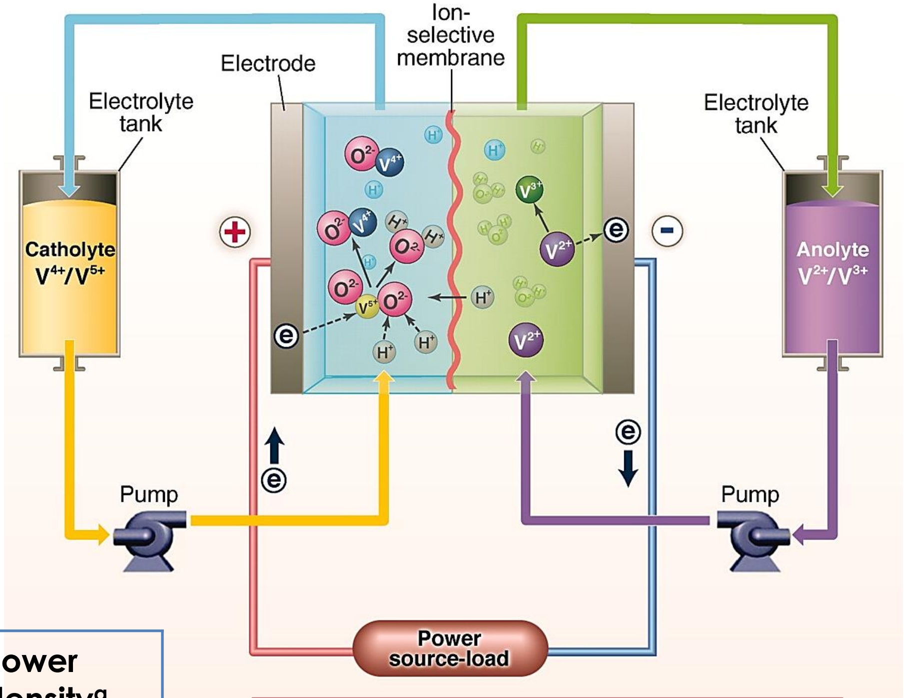
$\underline{V^{2+} \rightarrow V^{3+}}$: $V^{2+} \rightarrow V^{3+} + e^-$

$U_0 \approx -0.26$ V vs. NHE

Discharge operation (charge operation vice versa)

Advantages of Redox flow batteries

- Energy and power of battery scale independently
- Instantaneously refuelable
- High cycle-lifetime
- Non-hazardous materials



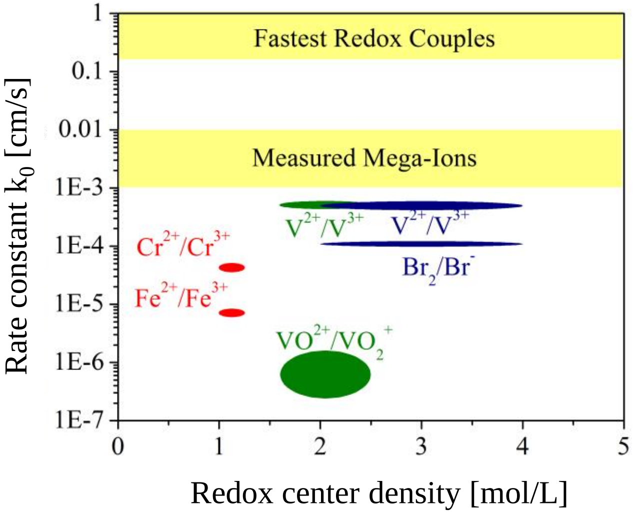
Redox couple	E_{cell} [V]	Overall efficiency [%]	Energy density [Wh/L]	Power density[a] [W/m²]
Iron-Chromium	1.2	95	13-15	200-300
All-Vanadium	1.6	83	25-35	600-700
Vanadium-Bromide	1.4	74	35-70	220-320
Mega-ions	**1.5**	**96[b]**	**250[c]**	**2000**

**Low energy and power density!
Compare to Li-ion battery:
300 Wh/L and 4200 W/L**

[a] Estimated as measured current density times cell voltage
[b] Coloumb efficiency of half-cell
[c] Estimated value based on solubility of 1 mol/L and 6 electrons per redox molecule

Sources: Jochen Friedl, Ulrich Stimming, TUM CREATE, 2013, unpublished | M. Skyllas-Kazacos, et. al., J. Electrochem. Soc., 2011, 158 (8), R55-R79

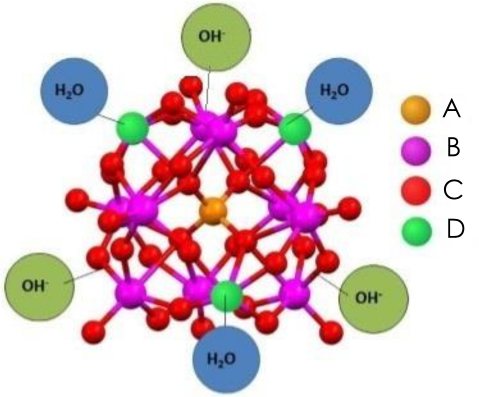
Novel approach: Mega-ions for RFBs



Concept

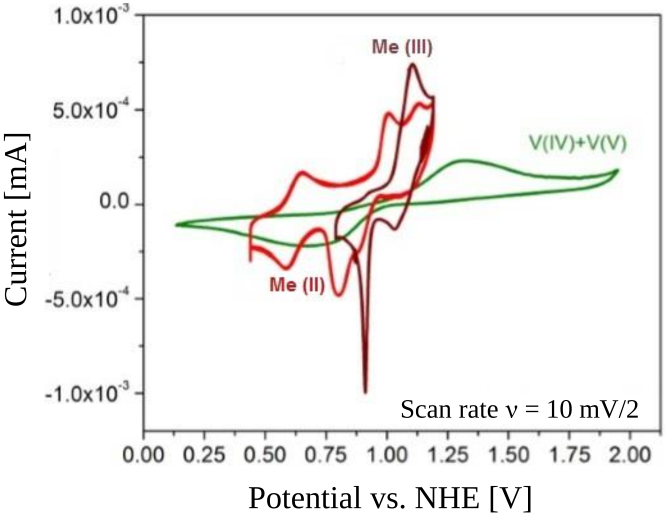
Mega-ions containing multiple transition metal redox centers

- Metal (Me) ions as redox centers
- Two e^- oxidation possible
- Use molecules containing 3 to 19 Me atoms, so 6 to 38 e^- per molecule



Diameter ≈ 12 Å

Cyclic voltammetry



Scan rate ν = 10 mV/2

CVs show that metal redox potential lies approx. at same value as for Vanadium

Metal redox centers suitable for use in RFBs

Temperature-dependent current

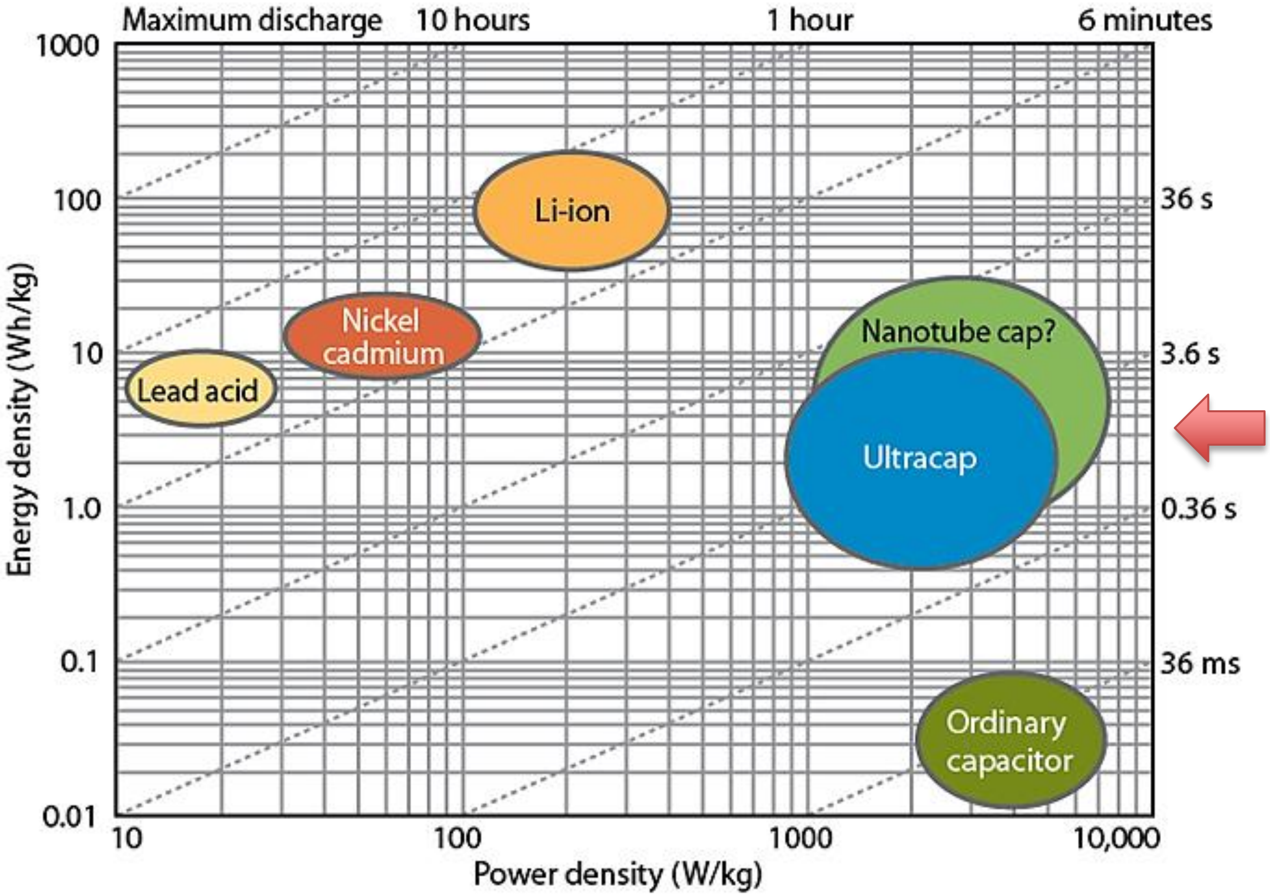
Increase in power density by enhancing reaction speed

Fast electron transfer kinetics: $k_0 \approx 10^{-2}$ cm/s

Source: Jochen Friedl, Ulrich Stimming, TUM CREATE, 2013, unpublished

Supercaps – state-of-the-art

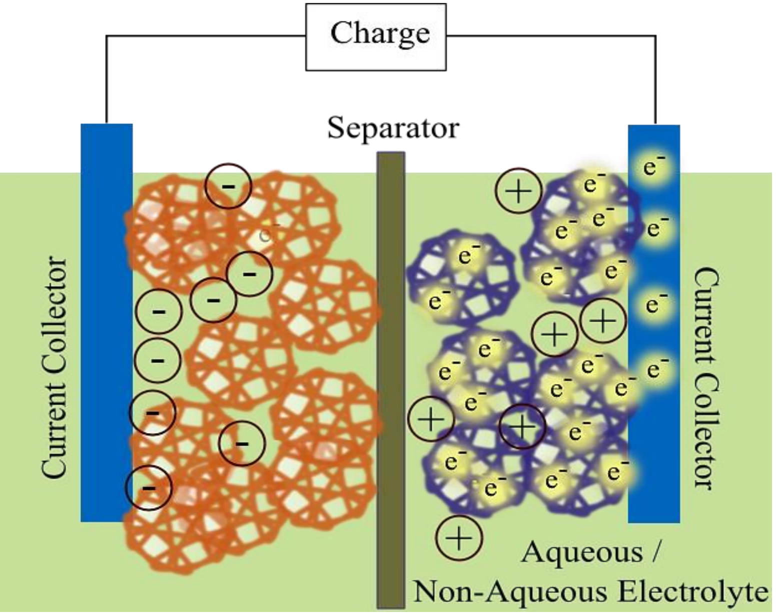
Ragone chart



High power density!
Low energy density!

Source: electronicdesign.com

Supercaps with Mega-ions



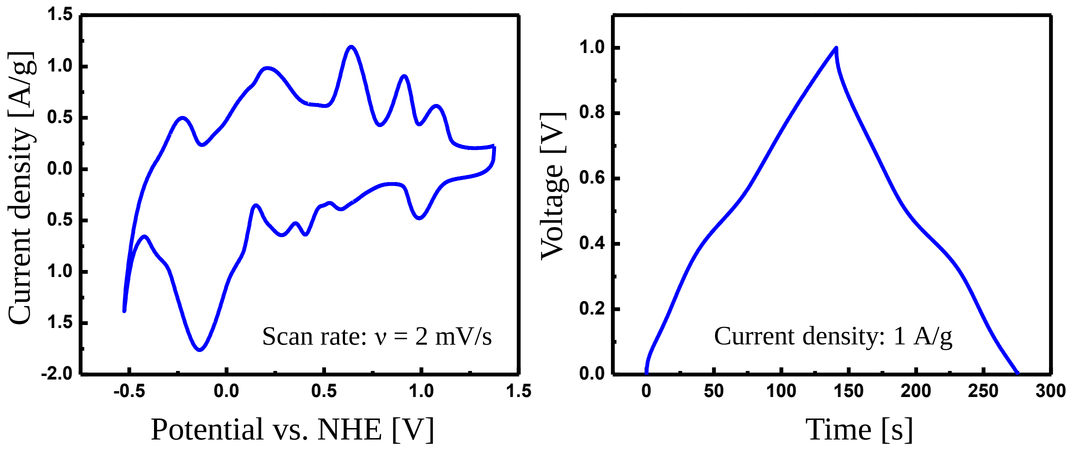
Concept

- Mega-ions incorporated in electrode structure
- Material: Transition metal provides multiple redox centers
- High number of electrons per unit volume

Energy stored in:

Electrochemical double-layer + Oxidation state of mega-ions

CV & galvanostatic charge-discharge



Mega-ions show fast and reversible multi-electron redox activity

Source: Jochen Friedl, Han-Yi Chen, Ulrich Stimming, TUM CREATE, 2013, unpublished

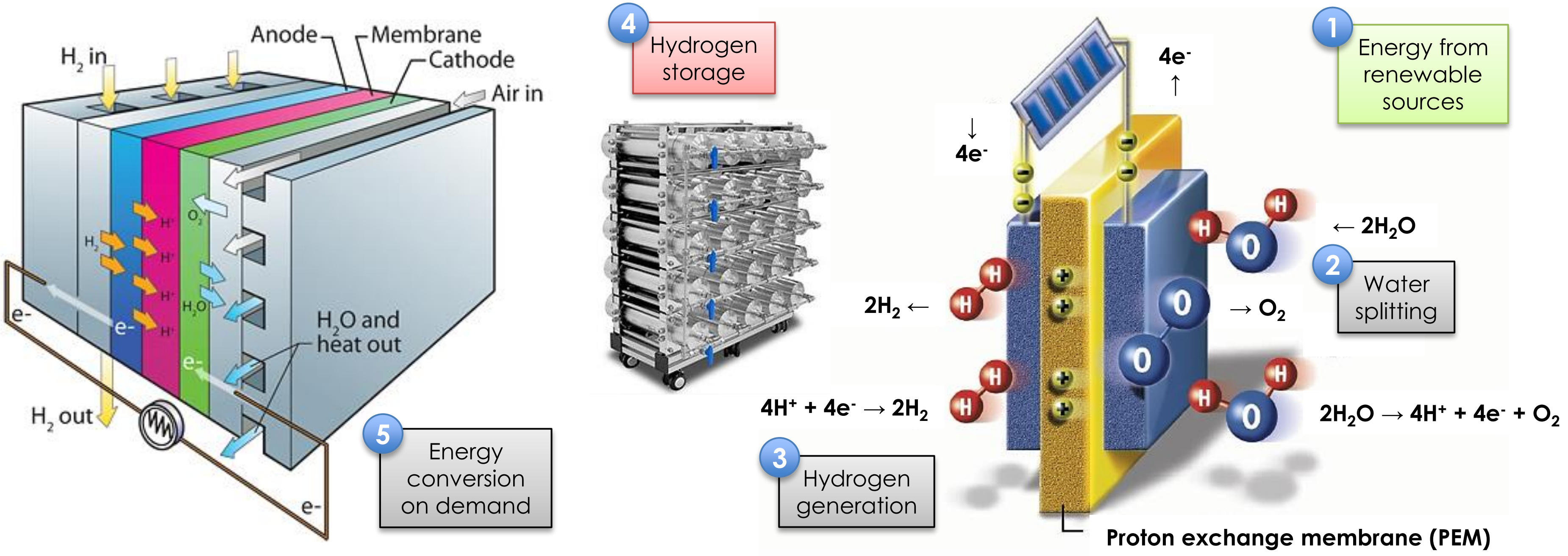
Performance

(Electrolyte: 1 M H_2SO_4)

Specific capacitance [F/g]	Energy density [Wh/kg]	Power density [kW/kg]
500	15*	15*

*Estimated value based on solubility of 1 mol/L and 6 electrons per redox molecule

Electrolysis & Fuel Cells



1 Energy from renewable sources

2 Water splitting

3 Hydrogen generation

4 Hydrogen storage

5 Energy conversion on demand

Proton exchange membrane (PEM)
fuel cell operating principle

Electrolyzer operating principle
inverse to PEM fuel cell

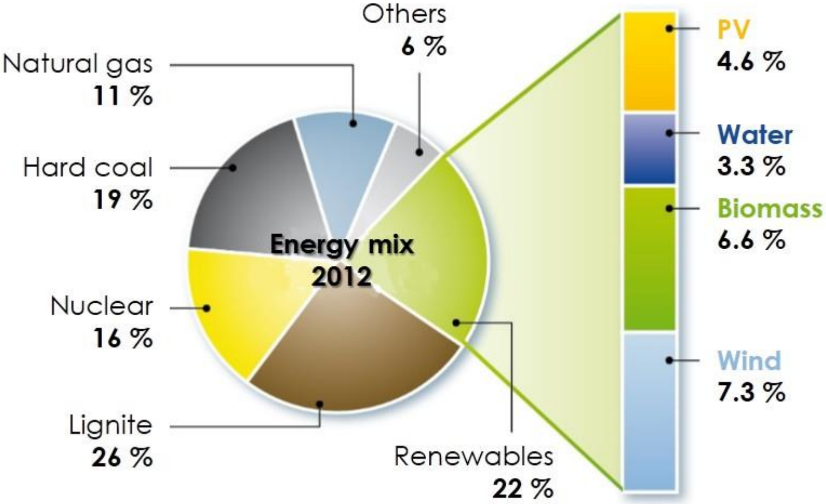
PEM fuel cell and electrolyzer as complementary techniques for energy conversion on demand

Sources: Los Alamos National Laboratory, U.S. Department of Energy, 2011 | puregasproducts.com | marqumtech.com

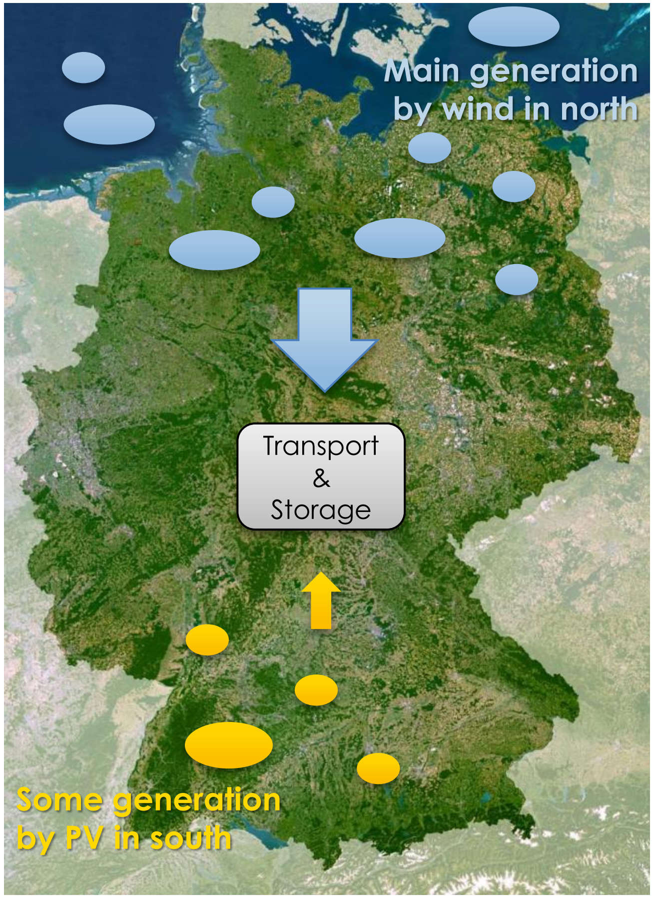
THE BIG PICTURE

DO WE NEED A NEW ENERGY ARCHITECTURE?

Top-Down Approach



2050:
100 %
Energy target 2050:
100% renewable electricity supply



Conventional approach: Centralization

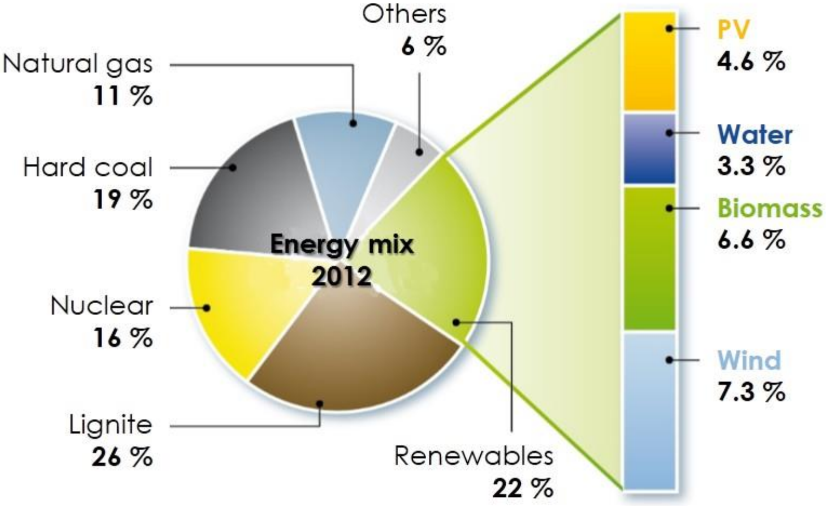
„Few large-scale producers vs. many consumers“

- Rapid development of renewable energy (100 % in 2050)
- Construction of large-scale wind parks (N) and PV sites (S)
- Grid extension for transport of electricity from N to S
- Storage capacity of grid to be increased

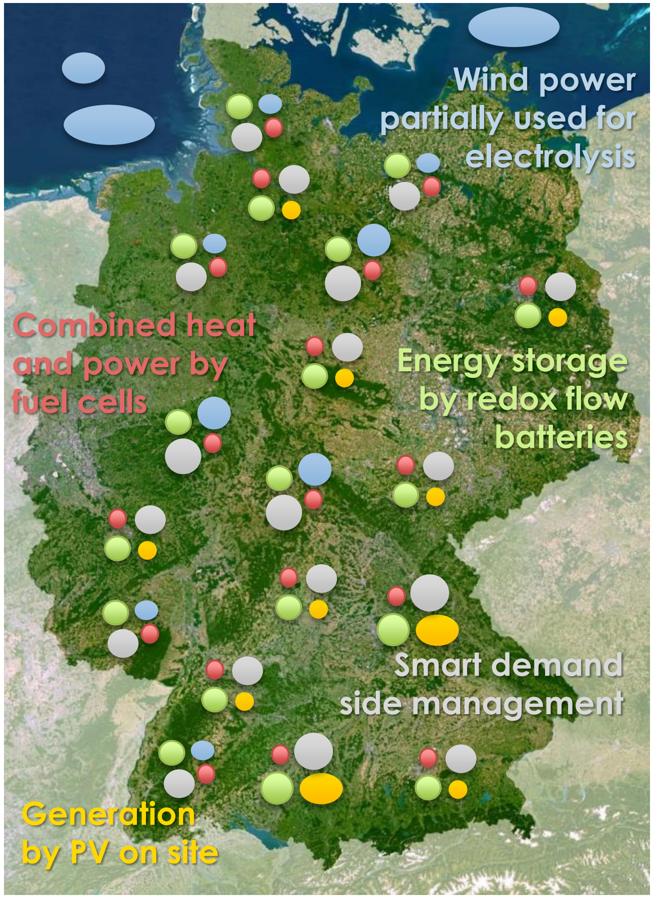
Effective energy management only by a limited number of **large-scale storage technologies** (pumped-storage plants, compressed air storage)

Source: bmu.de/themen/klima-energie

Bottom-Up Approach



2050:
100 %
Energy target 2050:
100% renewable electricity supply



Alternate approach: Decentralization

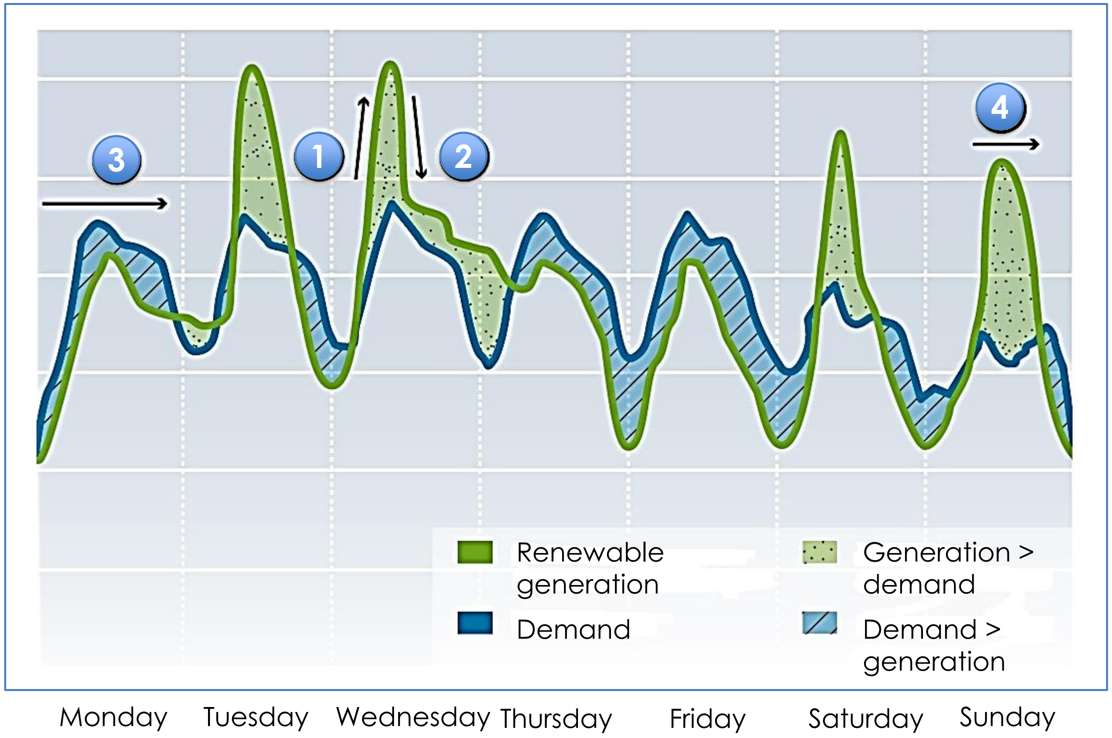
„Many small producers vs. many consumers“

- Self-sustaining communities / production sites / households / …
- Generation of electricity where it is needed
- Minimized need for energy storage and minimal supplement from the grid

Combination of multiple **small-scale technologies** to design generation, storage and consumption in a **smart** way!

Source: bmu.de/themen/klima-energie

Demand Side Management (DSM)

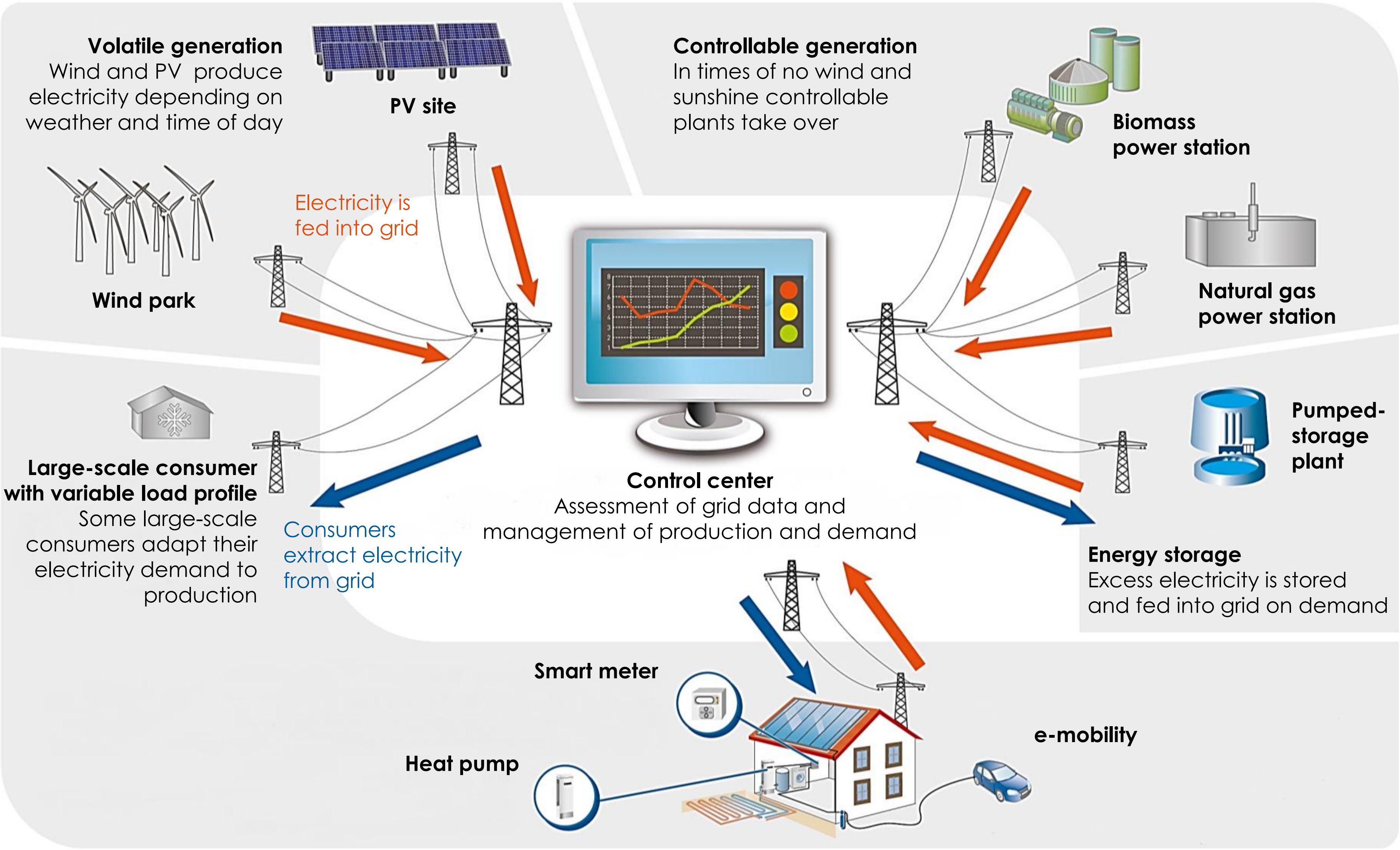


1. Generation from renewable sources is volatile, typical peak shape at noon from PV
2. Rapid decline in renewable generation due to weather conditions
3. Demand > generation: Controllable consumers (heat pumps, BEVs, cold storage houses) reduce load and electricity from energy storage devices is fed into grid
4. Generation > demand: Energy storage devices and controllable consumers take up excess electricity

→ DSM and energy storage compensate volatile renewable generation

Source: Agentur für Erneuerbare Energien, 2012

The Smart Grid



Volatile generation
Wind and PV produce electricity depending on weather and time of day

PV site

Wind park

Electricity is fed into grid

Controllable generation
In times of no wind and sunshine controllable plants take over

Biomass power station

Natural gas power station

Pumped-storage plant

Large-scale consumer with variable load profile
Some large-scale consumers adapt their electricity demand to production

Consumers extract electricity from grid

Control center
Assessment of grid data and management of production and demand

Energy storage
Excess electricity is stored and fed into grid on demand

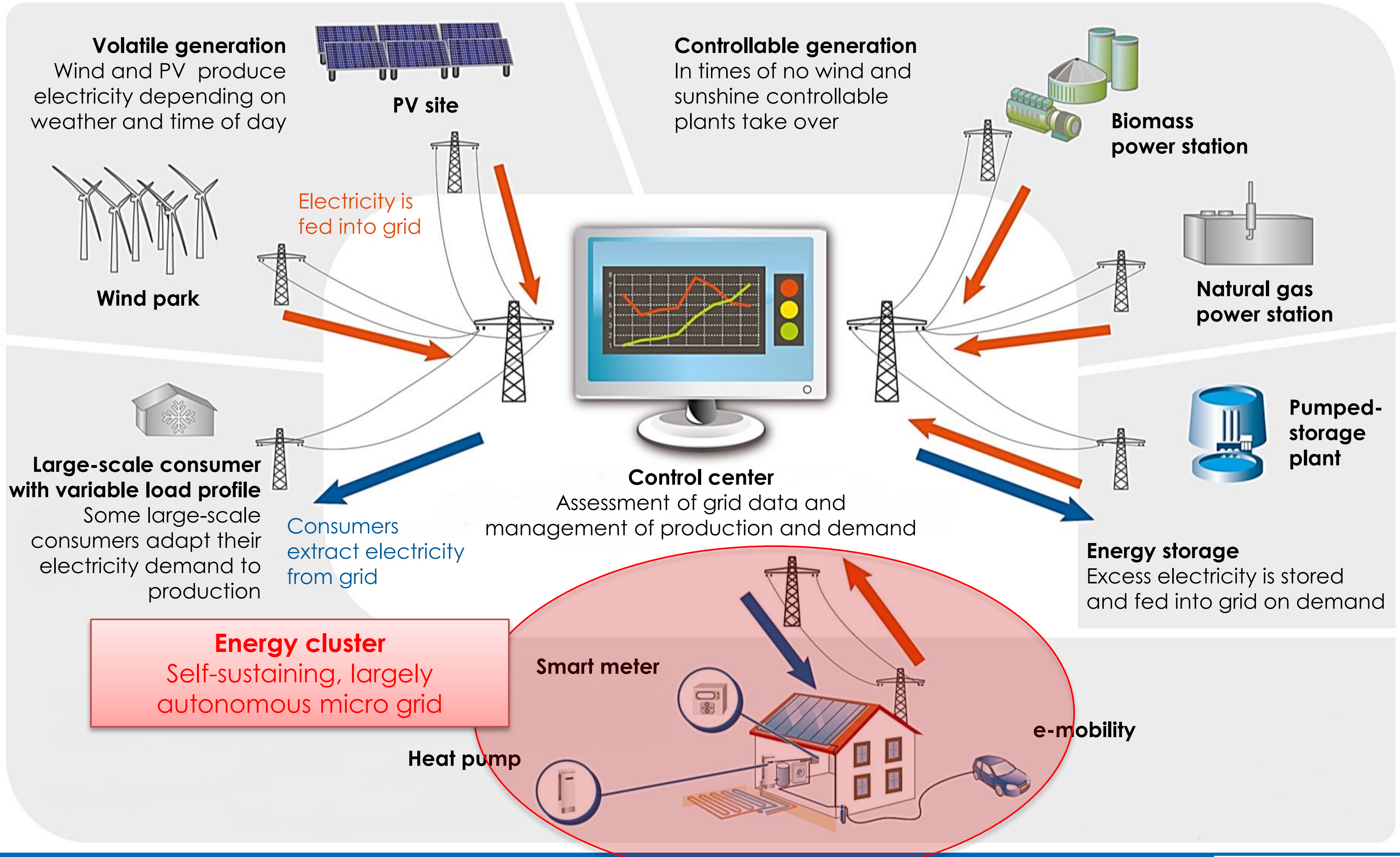
Smart meter

Heat pump

e-mobility

Pictures: Agentur für Erneuerbare Energien, 2012

The Smart Grid



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Energy cluster
Self-sustaining, largely autonomous micro grid

Smart meter

Heat pump

e-mobility

Pictures: Agentur für Erneuerbare Energien, 2012

Energy Clusters

Single-family home

Block

District

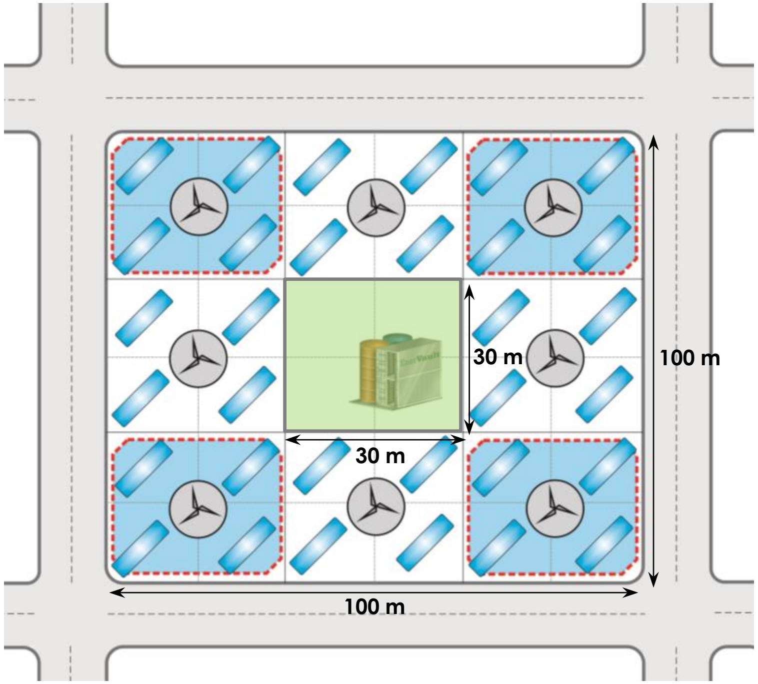
Scalable by choice of technology for energy conversion and storage

Quasi-autonomous energy clusters are defined by:

- Local conditions (irradiance in kWh/m^2 a, adequacy for wind power, access to long-distance heating, need for air conditioning)
- Size of respective area in m^2
- Utilization (private housing, shops, service industry, manufacturing industry)
- Total electricity consumption
- Flexibility (demand side management)

Pictures: EA EnergieArchitektur, 2010

Example: City Block



Consumption

Avg. elec. consumption of shop: 100 kWh/m^2 a[a]
⇨ 900 000 kWh/a

Avg. elec. consumption of 2-person household: 2 500 kWh/a[a]
⇨ 1 125 000 kWh/a

Total consumption: 2 025 000 kWh/a

Generation

9 000 m^2 PV: $\eta = 20$ %[b]
⇨ 1 350 000 kWh/a

1 000 m^2 organic PV: $\eta = 10$ %[b]
⇨ 75 000 kWh/a

8 wind turbines: 10 kW per turbine[c]
⇨ 160 000 kWh/a

Total generation: 1 585 000 kWh/a

Supplement from grid: **440 000 kWh/a**
(22 % of total consumption)

Storage

Goal: Store energy equal to an average 30 % of daily consumption
⇨ 1 660 kWh

Pumped-storage plant: 4 times volume of 10^6 L, height 20 m
⇨ 220 kWh

Redox flow battery: capacity 0.25 kWh/L, store 1 440 kWh
⇨ 5 760 L RFB tank needed

Size

5-story city block:

1st floor: shops and service industry (9 000 m^2)
2nd-5th floor: two-person flats (36 000 m^2, 80 m^2 / flat)
⇨ Corresponds to 450 flats

Legend

PV module
Organic PV 🟩
Wind turbine
Redox Flow Battery
Pumped-storage plant

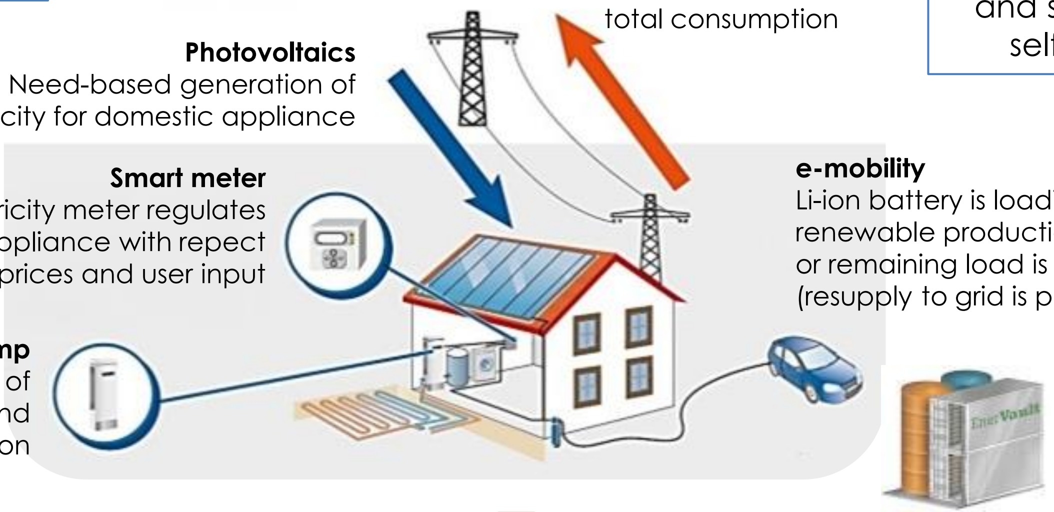
Sources: a)Strom.info | b)B. Laquai, hbw-solar, 2003 | c) EA EnergieArchitektur, 2010

Summary

Development of a **novel architecture** for the energy system!

Adapt structure to existing technologies

Combination of decentral generation and storage enables self-sustainability



Supplement from grid
Estimated reduction to 10-20% of total consumption

Photovoltaics
Need-based generation of electricity for domestic appliance

Smart meter
Digital electricity meter regulates demestic appliance with repect to prices and user input

Heat pump
Heat pump operates in times of small load (e.g. at night) and during high wind production

e-mobility
Li-ion battery is loading when renewable production is high or remaining load is small (resupply to grid is possible)

Redox Flow Battery
Small-scale storage technology provides electricity during load peaks

Diversification instead of focus on single technologies

Need for grid extension can be reduced

Computational Energy Science
Development of an efficient management structure, which sets the goals for hardware architecture

Pictures: Agentur für Erneuerbare Energien, 2012

Thank you for your attention!

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