MATERIALS FOR ELECTROCHEMICAL ENERGY STORAGE:

AN EVOLUTIONARY APPROACH

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Outline

1 Introduction

- Energy conversion and storage: system considerations

2 Material aspects of galvanic systems

- Solid and liquid electrolytes
- Electrode-electrolyte interface: SEI
- Materials for LIB and LAB

3 Evolutionary Development Approach

- New Li-anode material
- Zinc-air

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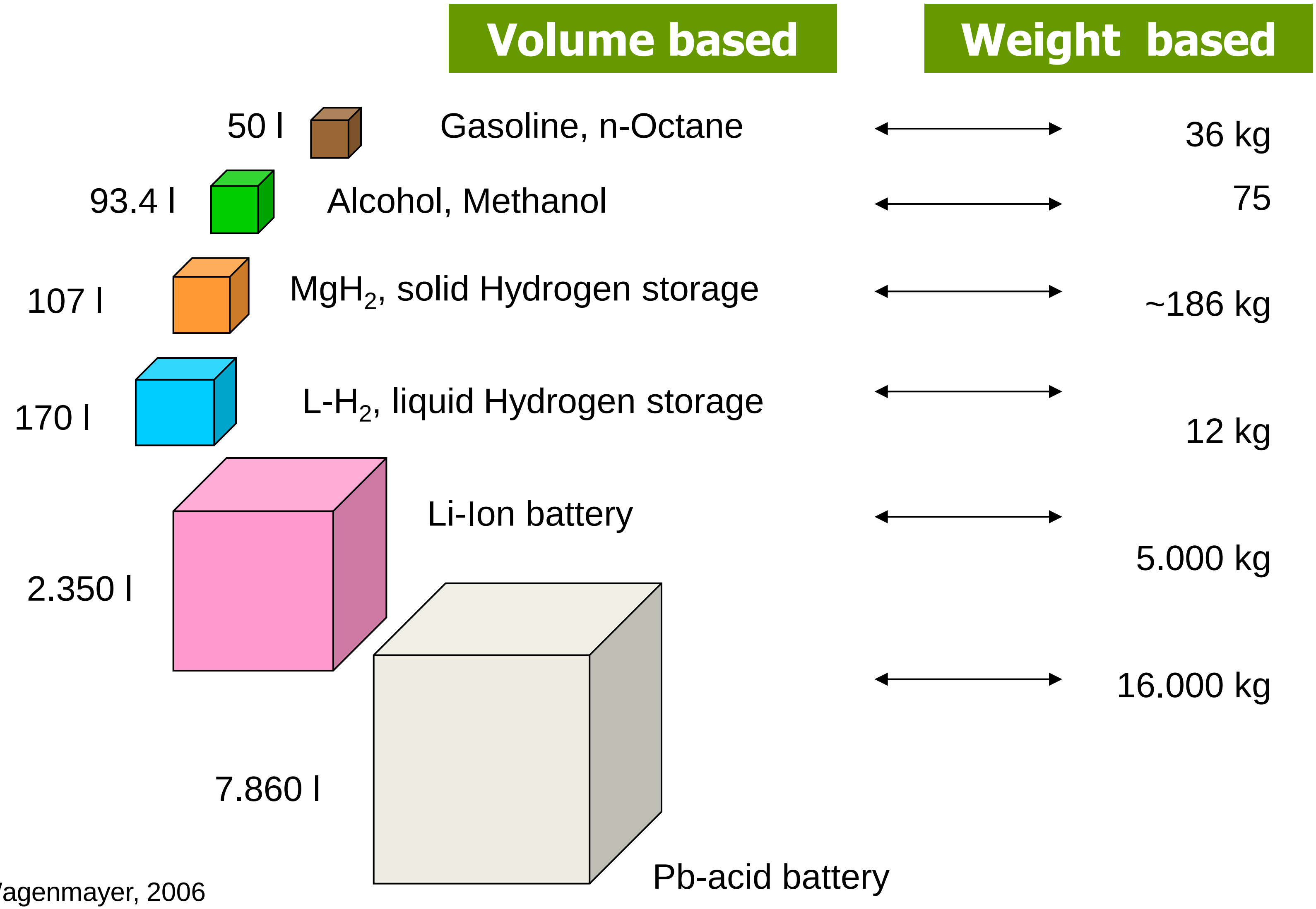
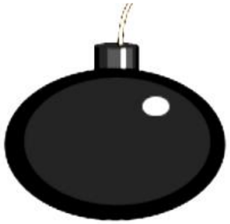
Specific energy content



After Wagenmayer, 2006

Volume specific energy content

- **Energy density of TNT**
  6.7 kJ/cm^3

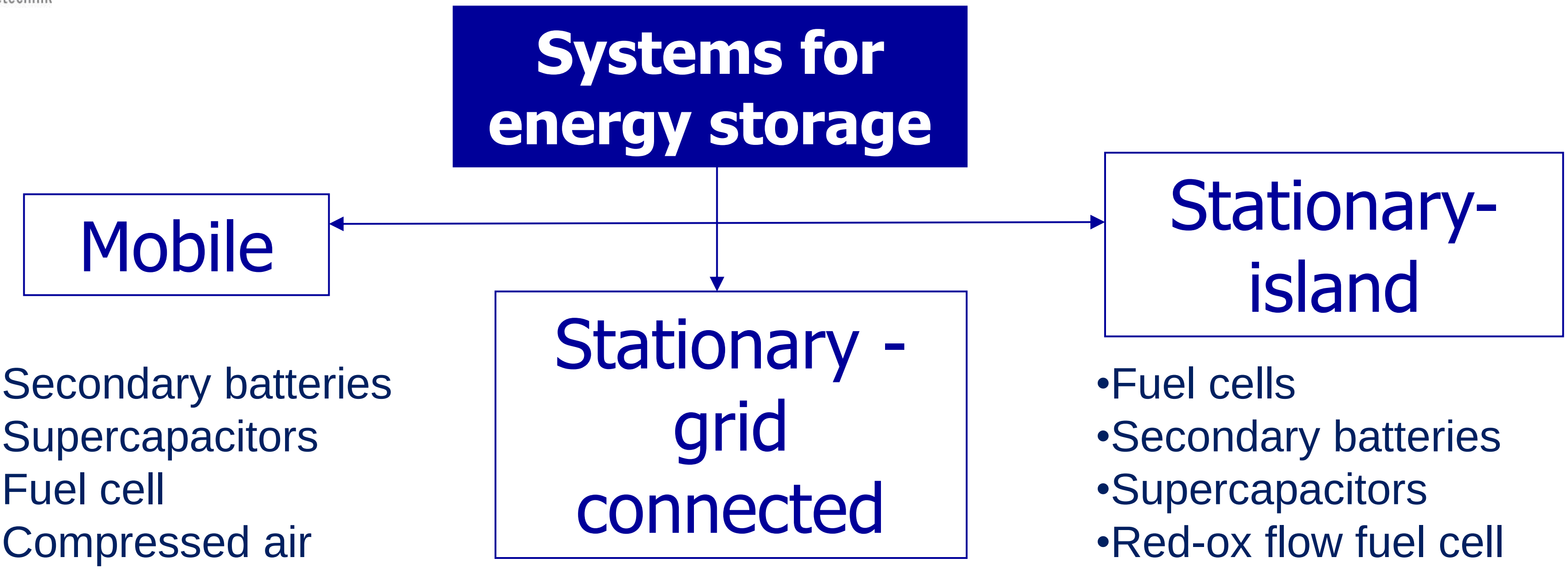


- **Energy density of advanced batteries**
  3.6 kJ/cm^3

- **Energy density of chocolate**
  22 kJ/cm^3

Source: Internet, 2012

System considerations



Mobile

- Secondary batteries
- Supercapacitors
- Fuel cell
- Compressed air
- Flywheel

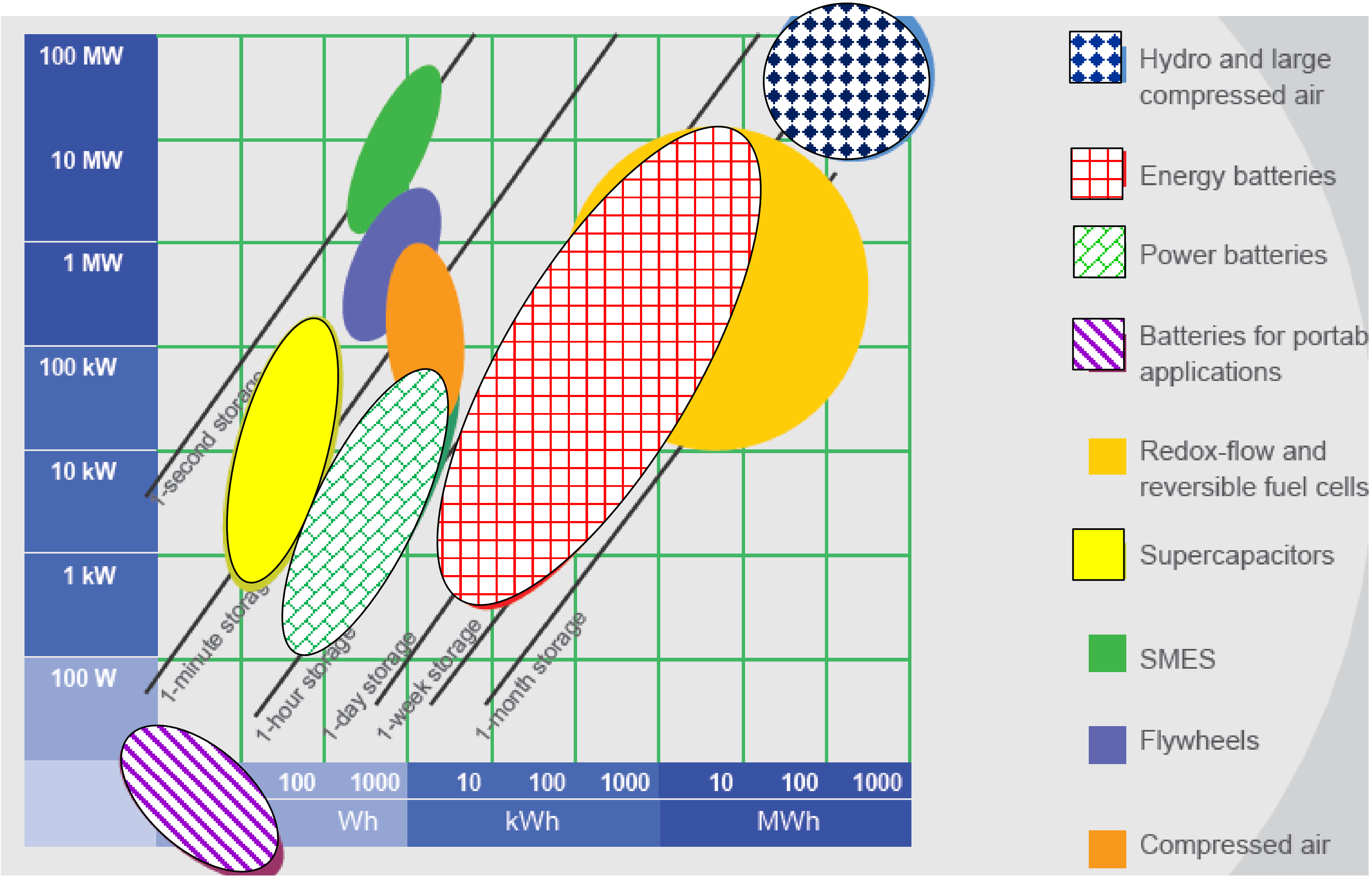
Stationary - grid connected

- Hydro
- Large compressed air
- Compressed hydrogen
- Secondary batteries
- Supercapacitors
- Red-ox flow fuel cell
- Compressed air
- Flywheel
- SMES

Stationary-island

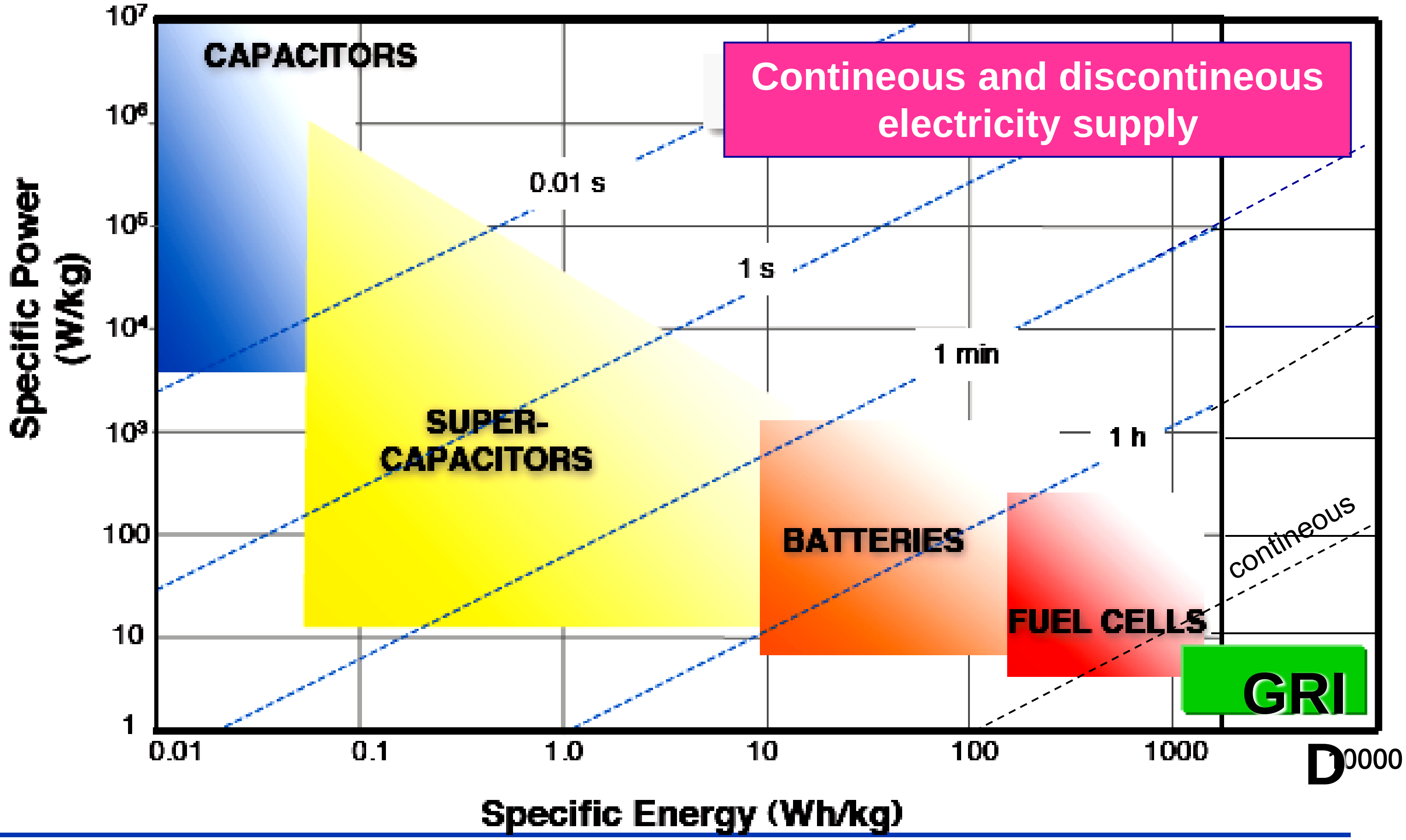
- Fuel cells
- Secondary batteries
- Supercapacitors
- Red-ox flow fuel cell
- Compressed air
- Flywheel

System considerations



Data after Rahner, Euro 2001

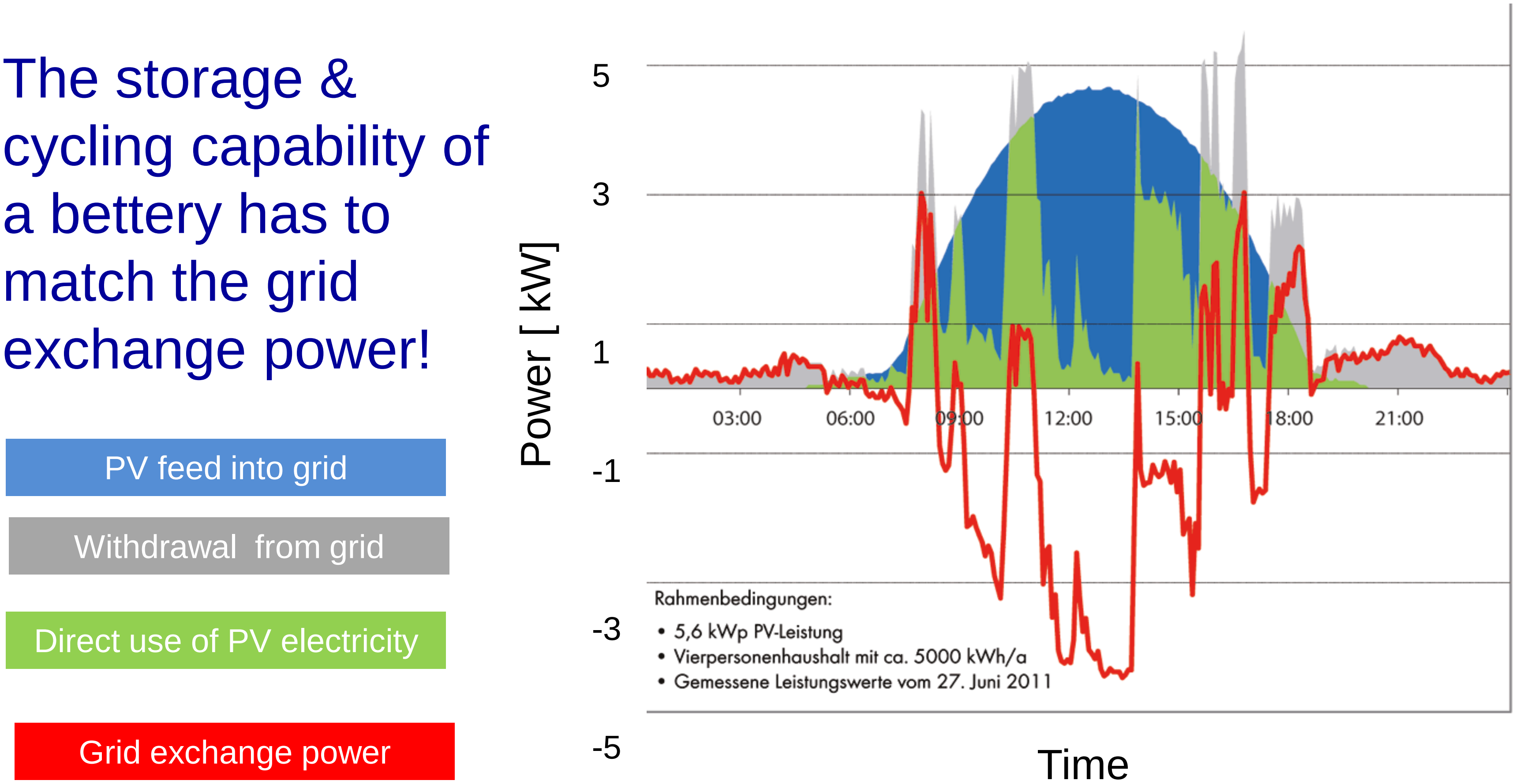
Choice of devices for electricity supply



Ragone plot after F. N. Büchi et al., PSI-Seminar, May 11th, 2005, Villingen, CH

System considerations: PV grid connected

The storage & cycling capability of a bettery has to match the grid exchange power!



Electricity balance of a 4 person household utilising a 5,6 kWp-grid connected PV installation

(Source: 19.6.2012, Intersolar-Bericht)

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Material aspects of galvanic systems

- Selection of anode and cathode materials

1 H 1.01																	2 He 4
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16	9 F 19	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.1	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.9	36 Kr 83.8
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.6	53 I 126.9	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226.03	89 Ac 227	104 Rf 261	105 Db 262	106 Sg 263	107 Bh 262	108 Hs 265	109 Mt 265									

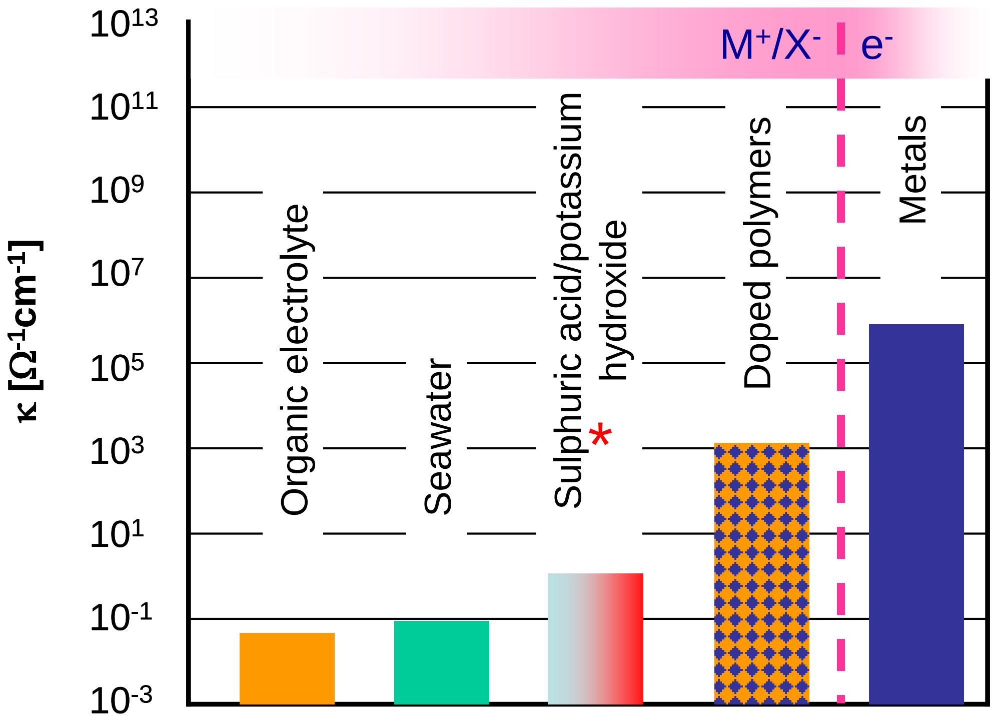
B-FC-PV-Lecture M. Willert-Porada,UBT- 2012

Material aspects: electrolytes

- The **electrolyte** serves as the path for completing the electrical circuit inside of the cell via the transport of **ions** from one electrode to the other, without electronic conduction in the electrolyte.

- The **electrolyte** may be a **liquid, gel** or a **solid**.

- The electrolyte influences the **chemical potential** of the anode and cathode.

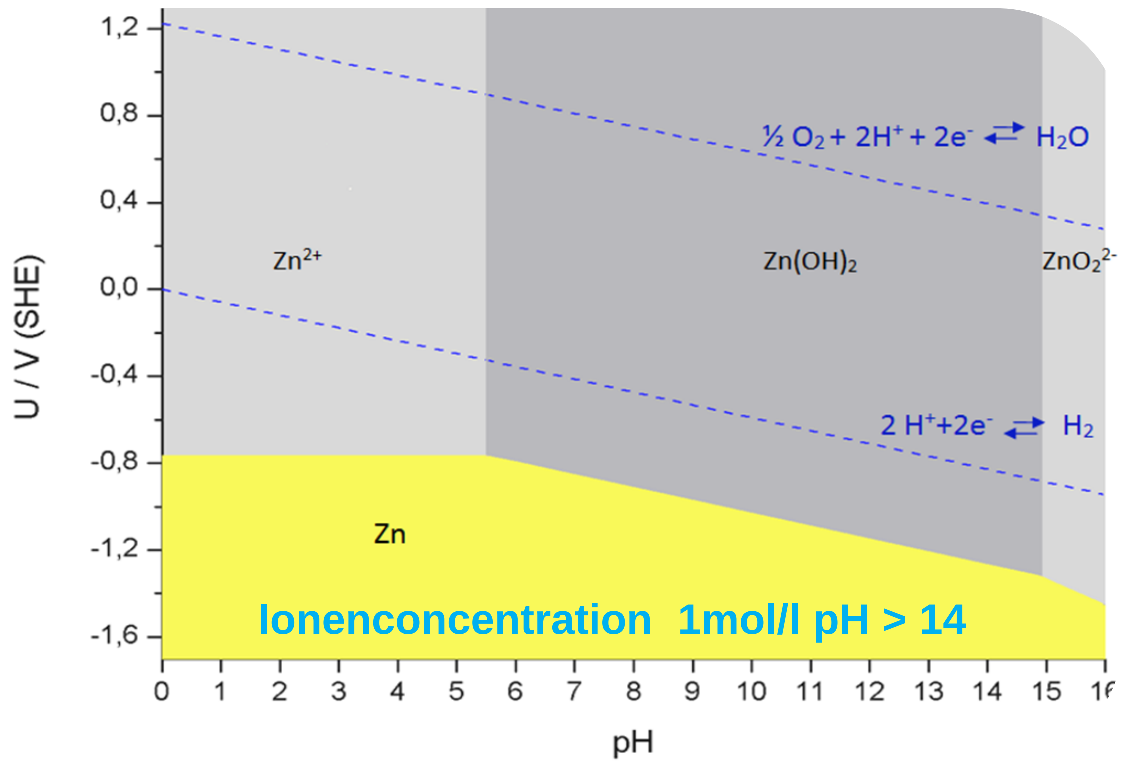


B-FC-PV-Lecture M. Willert-Porada,UBT- 2012

Example: aqeuous electrolytes

Zinc-air battery

H_2-over-potential 0,76 V



+0,40V

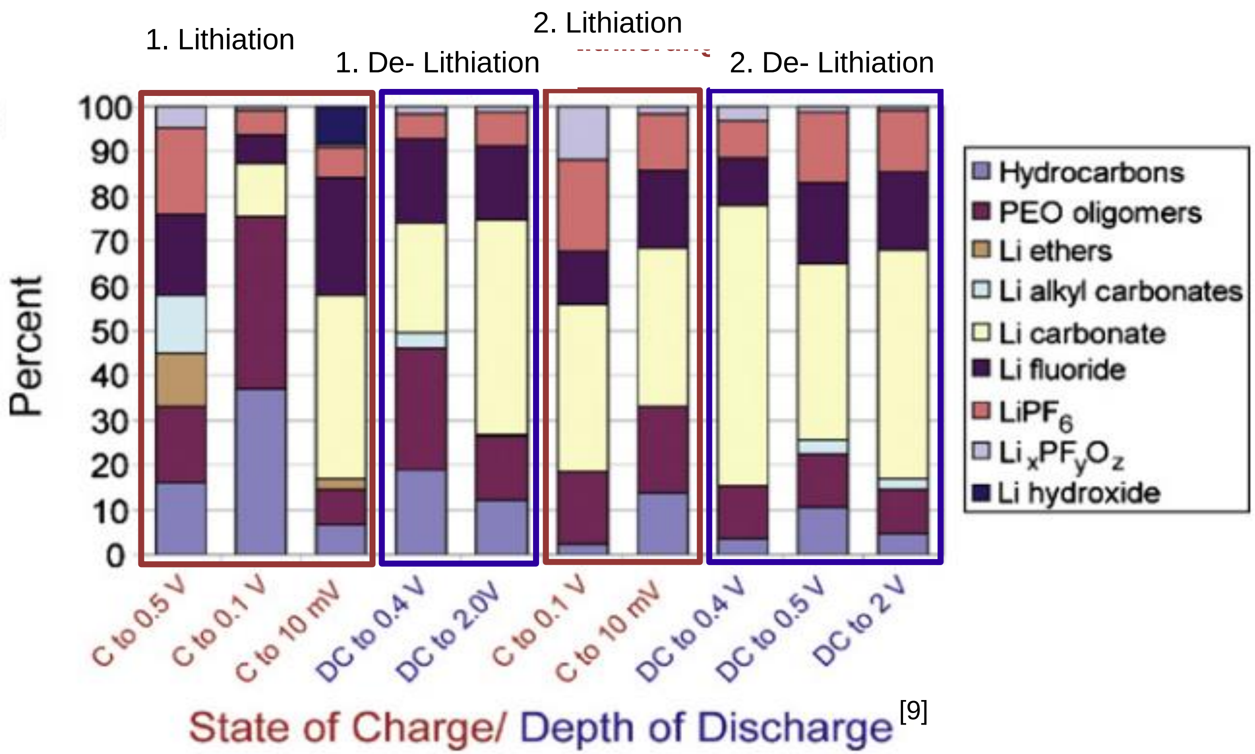
Theoretical cell voltage 1,65 V

-1,25V

M. Schmid, UBT, 2014, Calculation after Pourbaix M.; Atlas of electrochemical equilibria in aqueous solutions; National Assoc. of Corrosion Engineers, 1974, DoITPoMS, Universität Camebridge http://www.doitpoms.ac.uk/tlplib/pourbaix/index.php

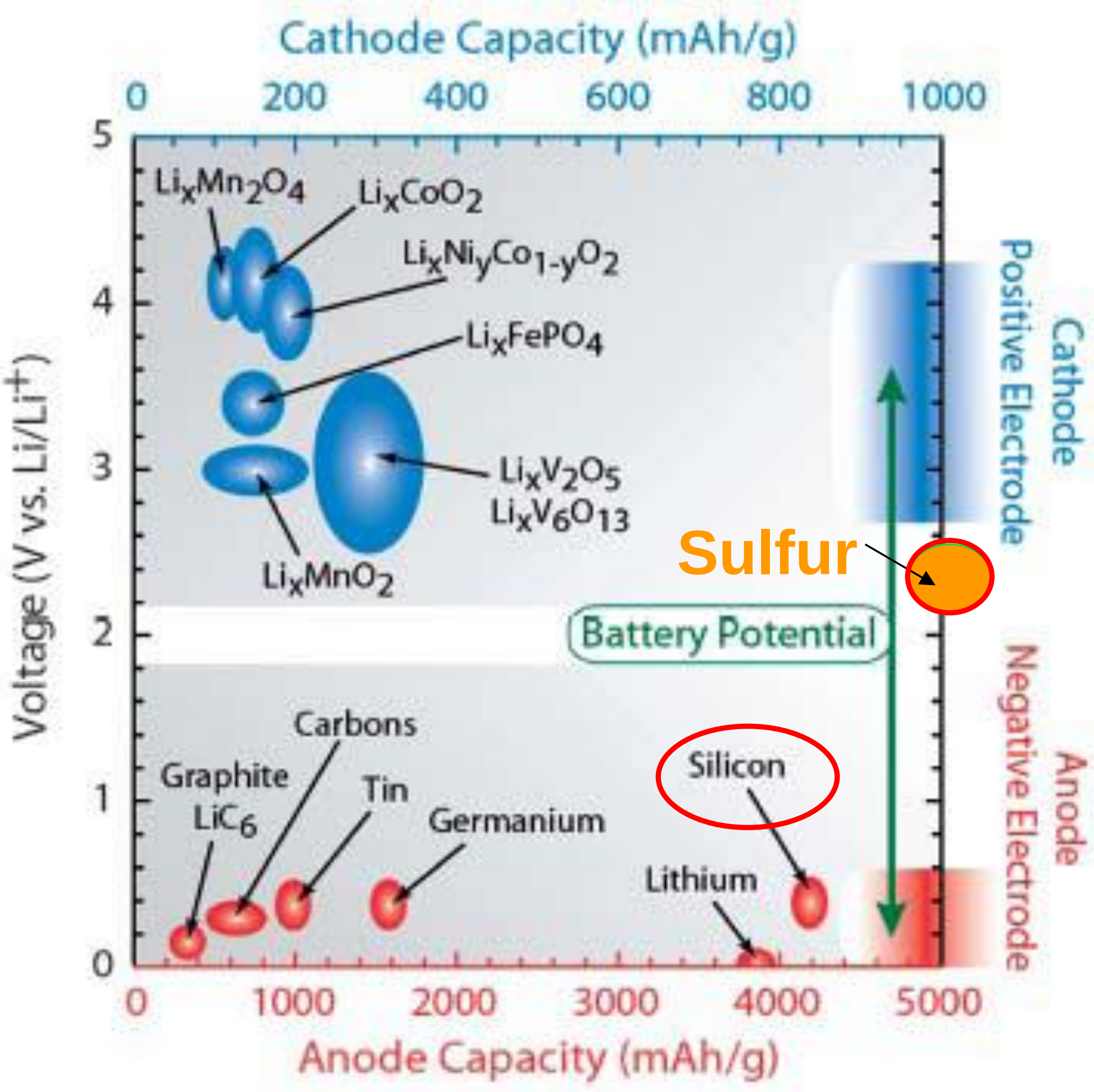
Solid Electrolyte Interface

- SEI formation occurs with an electronic conductor on the active material surface
- Chemical source of SEI is the electrolyte !



After : C. K. Chan et al., „Surface chemistry and morphology of the solid electrolyte interphase on silicon nanowire lithium-ion battery anodes“, *Journal of Power Sources*, Bd. 189, Nr. 2, S. 1132-1140, 2009

Materials for LIB



B-FC-PV-Lecture M. Willert-Porada,UBT- 2012, data from G. Ceder, MRS Bull., 2010

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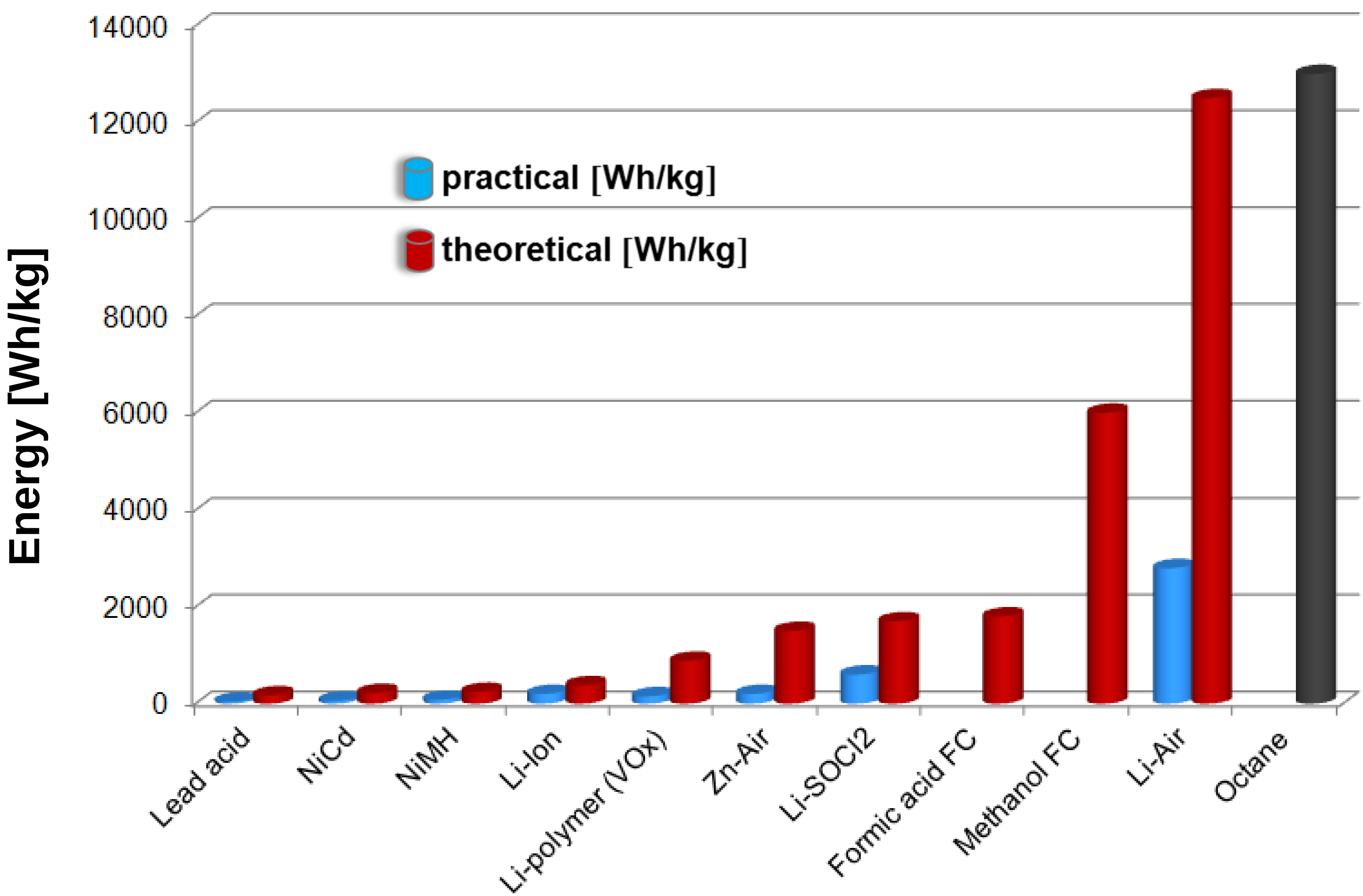
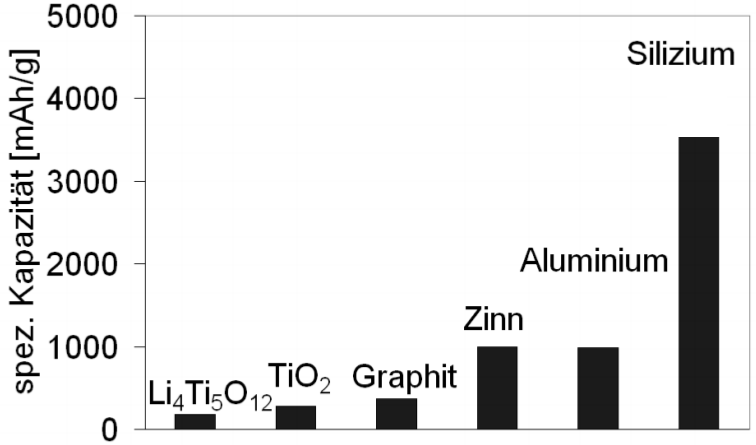
Batteries: comparison



E. Aleksandrova, Honda Germany, 2011

Silicon as LIB anode material



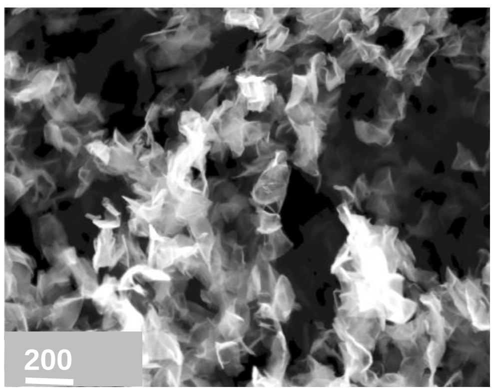
Specific capacity of different anode materials for Li-Ion batteries (LIB), data from [2]

	Graphite	Silicon
Theoretical specific capacity	**372 mAh/g[3] (LiC_6)**	**3579 mAh/g ($Li_{15}Si_4$)[4]**
Spec. density	**2,26 g/cm³**	**2,34 g/cm³**
Volume increase upon complete lithiation	**~ 9%[5]**	**Up to 280%[6]**
Electrical conductivity	**$3 \bullet 10^6$ S/m (parallel to C6-layer)**	**$2.5 \bullet 10^{-4}$ S/m**

[2] H. Wolf, *Neue kohlenstoffbasierte Materialien für Lithium-Ionenbatterie-Anoden*. Dissertation, Shaker Verlag, 2010.
[3] J. Graetz et al., „Highly Reversible Lithium Storage in Nanostructured Silicon“, *Electrochemical and Solid-State Letters*, Bd. 6, Nr. 9, S. A194-A197, 2003.
[4] M. N. Obrovac et al., „Structural Changes in Silicon Anodes during Lithium Insertion/Extraction“, *Electrochemical and Solid-State Letters*, Bd. 7, Nr. 5, S. A93-A96, 2004.
[5] Y. Liu et. al., „Silicon/Carbon Composites as Anode Materials for Li-Ion Batteries“, *Electrochemical and Solid-State Letters*, Bd. 7, Nr. 10, S. A369-A372, 2004.
[6] M. N. Obrovac et al., „Reversible Cycling of Crystalline Silicon Powder“, *Journal of The Electrochemical Society*, Bd. 154, Nr. 2, S. A103-A108, 2007.

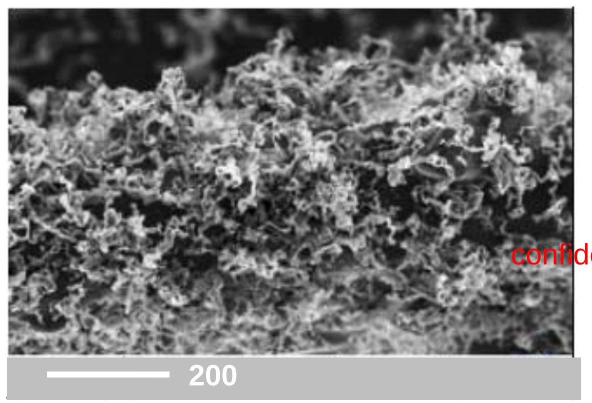
Synthesis by Microwave Plasma CVD

py-Carbon



H. Wolf, Z. Pajkic, E. Aleksandrova, M. Willert-Porada, AMPERE Conf., 2009, Karlsruhe, Germany

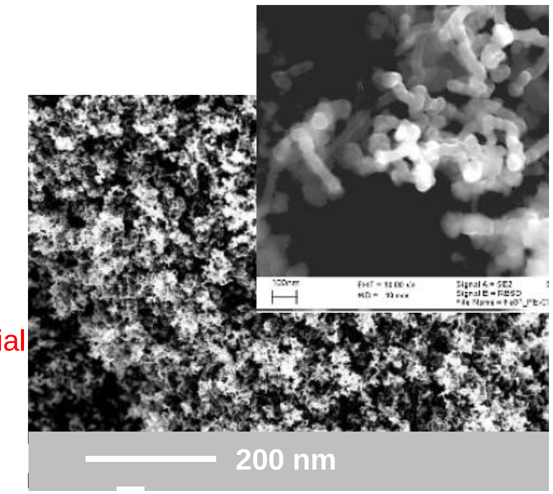
C-CNW, kat



confidential

K. Mees, M. Willert-Porada, N.N., unpubl. res., 2010

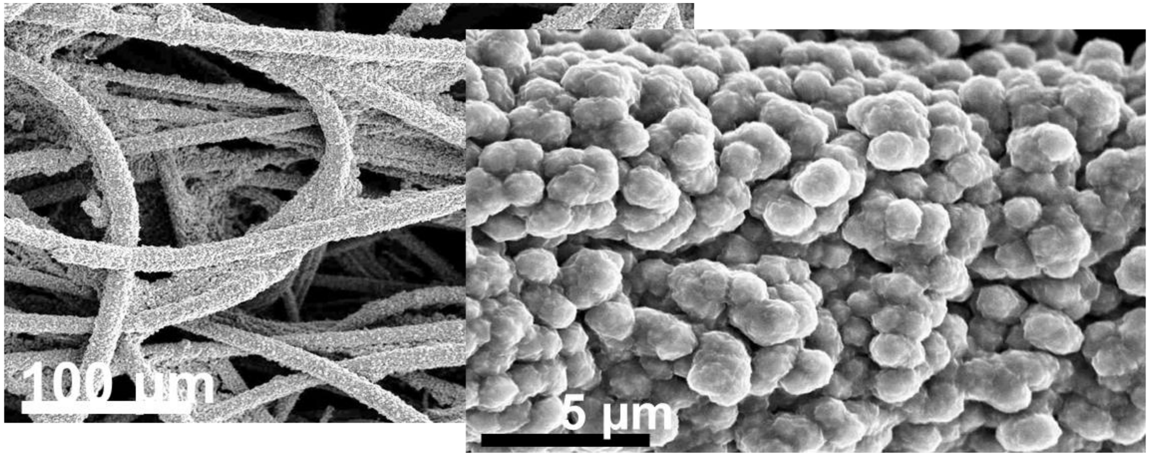
C-SiNW, kat



K. Mees, M. Willert-Porada, N.N., unpubl. res., 2010

PE-CVD synthesis of textile Carbon-n-Si-Anode

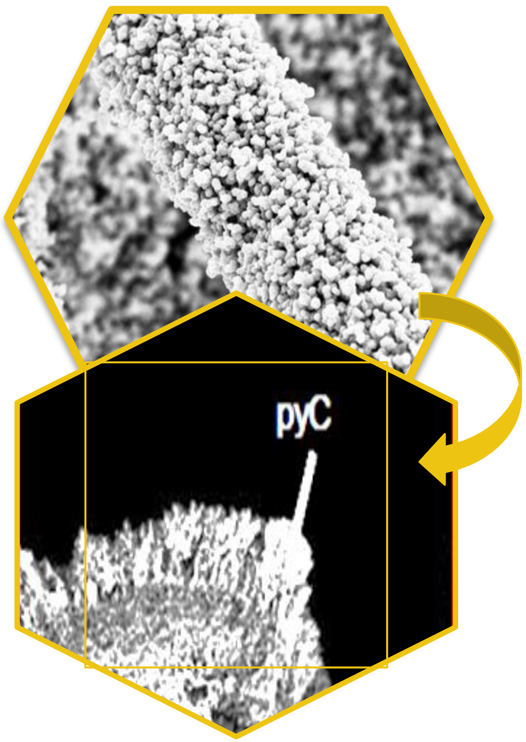
Feed rate control upon Microwave Plasma Enhanced CVD with $SiHCl_3$ as precursor

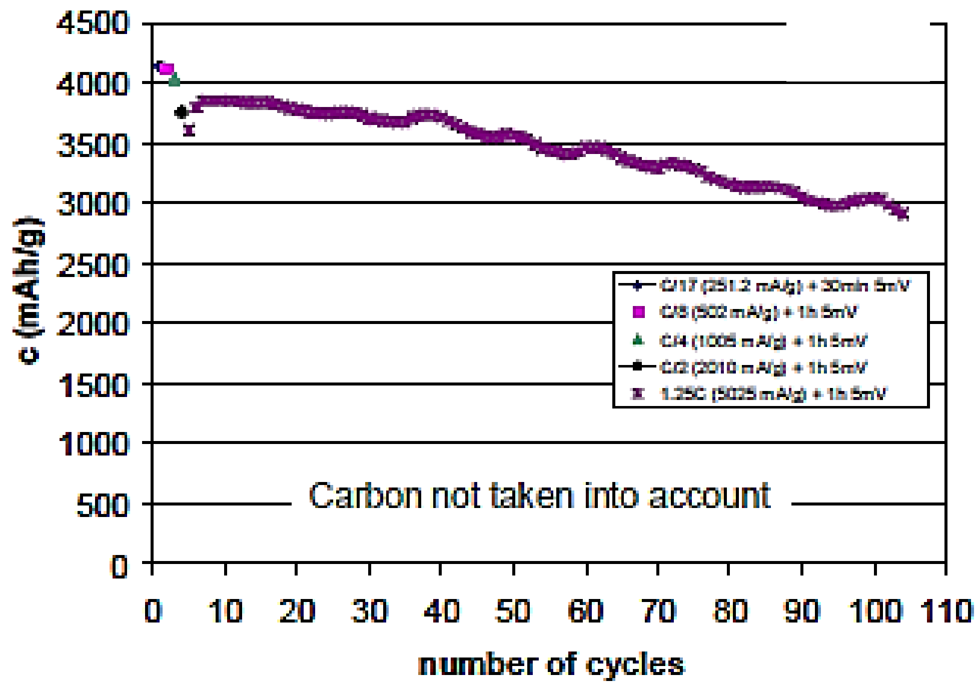


Power (W)	Time (s)	T (°C)	p(TCS) (mbar)	Si (wt.%)	primary particle size (nm)	
700	300	800	668	24,6	35	homogeneous
400	600	600	668	7,4	77,1	inhomogeneous
1000	210	950	437	33,8	68,3	homogeneous
1000	405	950	287	28,8	68,9	homogeneous

Willert-Porada, Mees, Pajkic, Wolf, Kontrolle des Partikelwachstums bei Abscheidung von nano-Si- aus TCS mittels Mikrowellenplasma-CVD, unpubl. Results, 2010

Si on C-fibre composite anode for LIB





M. Willert-Porada, K. Mees, internal report, 2010

Electrochemistry of SEI-modified Si electrodes

- ❑ Electrode (anode) is modified by ex-situ SEI-formation: artificial SEI
- ❑ Performance of PAA slurry based Si-electrodes without and with artificial SEI is compared

Results

- ➢ Artificial SEI is not preventing further reaction in half cell tests in high voltage region (0.5 – 1V) → dynamic character of SEI
- ➢ In presence of an artificial SEI lithiation of amorphous Si starts in the first cycle
- ➢ The De-Lithiation peak is shifted towards lower potentials in 2nd cycle

→ The irreversible capacity is decreased in presence of an artificial SEI

M. Willert-Porada, K. Mees, internal report, 2011

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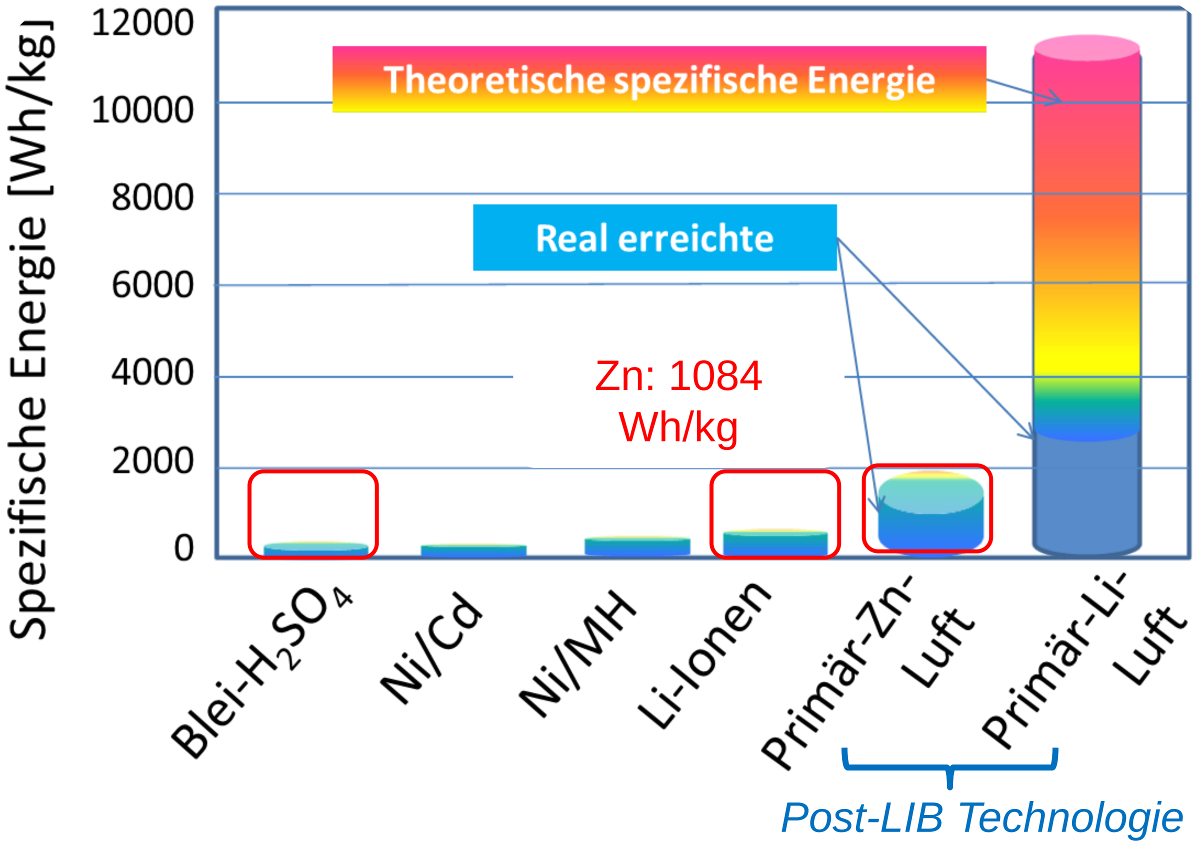
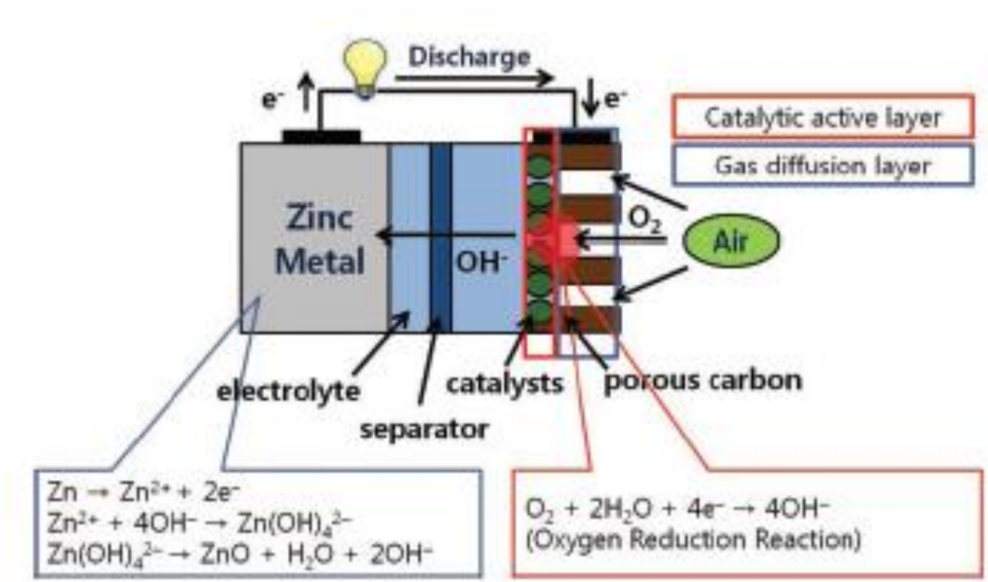
Metal-Air as compared with other batteries



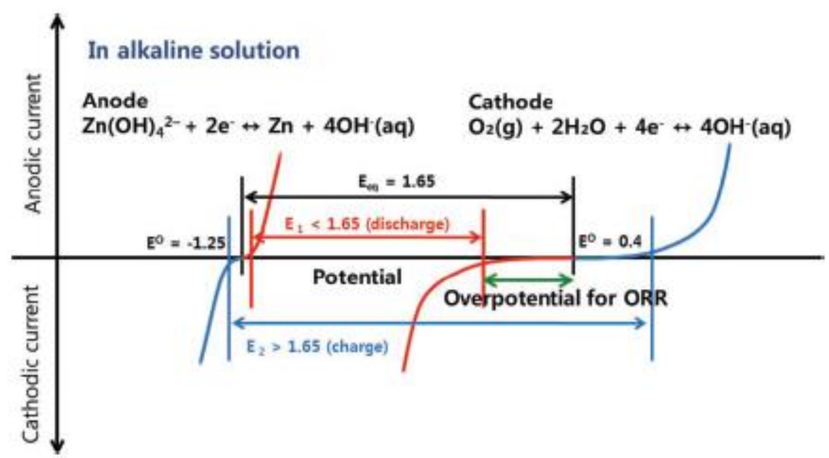
Data taken from :
J. Park, Principles and Applications of Lithium Secondary Batteries, Wiley-VCH, Weinheim (2012)
J. Cho et.al., Metal–Air Batteries with High Energy Density: Li–Air versus Zn–Air, Adv. Energy Materials, N° 1, 34-50 (2011)

Metal-Air Primary Batteries

Zinc-Air



Reactions in an alkaline electrolyte



Anode: $Zn \rightarrow Zn^{2+} + 2e^-$

$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-}$

$(E^\circ = -1.25\ V\ vs.\ NHE)$

$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^-$

$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2\uparrow$ [114]

(also possible)

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$(E^\circ = 0.4\ V\ vs.\ NHE)$

Overall reaction: $2Zn + O_2 \rightarrow 2ZnO\ (E^\circ = +1.65\ V)$

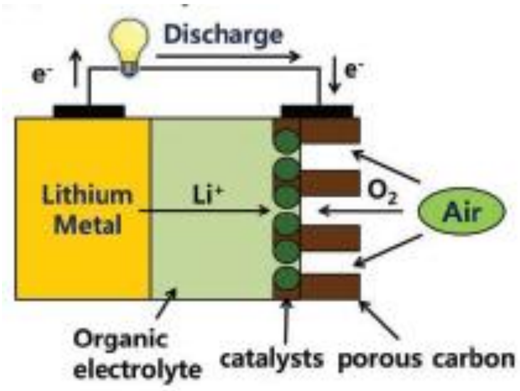
Problems:

- Full utilization of Zinc
- Reaction of alkaline electrolyte with CO_2
- Drying of cell
- Control of overpotential

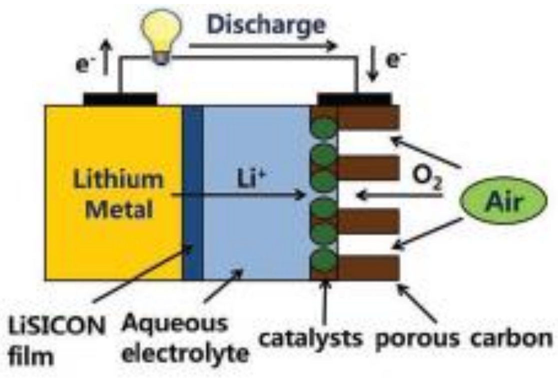
DOI: 10.1002/aenm.201000010

Metal-Air Primary Batteries

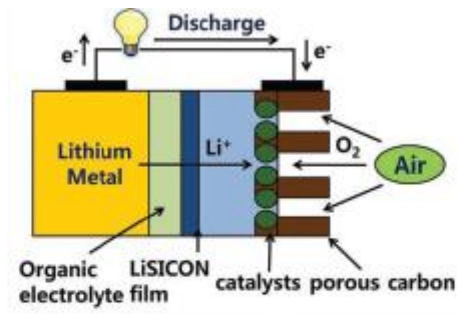
Lithium-Air



Concept for Lithium-Air battery with organic electrolyte



Concept for Lithium-Air battery with aqueous electrolyte

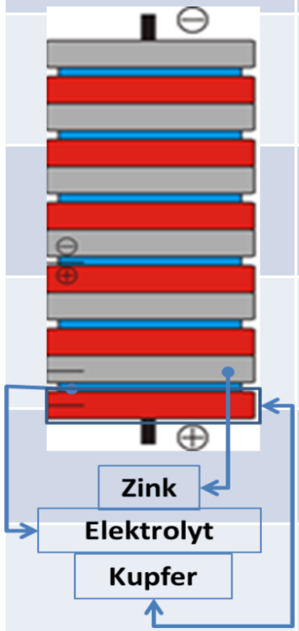


Concept for Lithium-Air battery with hybrid electrolyte

DOI: 10.1002/aenm.201000010

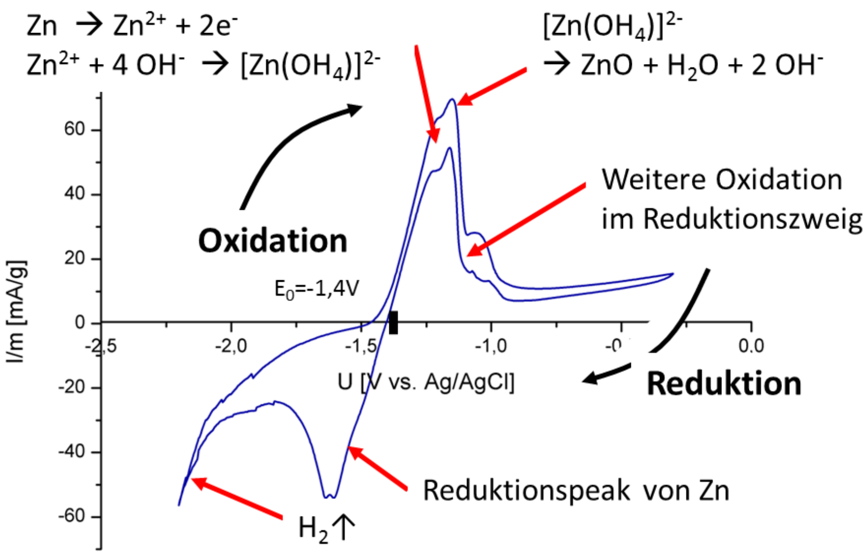
Evolutionary approach: Zinc batteries

Until 1800	1800 - 1860	Around 1900	1940-now
1800 Volta pile	1836 Daniell element $Zn\text{-}CuSO_4$	1872 Daniell-element $Zn\text{-}HgSO_4$	1941 Zn-AgO, sec.
	1838 $Zn\text{-}HNO_3\text{-}Pt$	1882 Alkaline $Zn\text{-}MnO_2$	**1950** **Zn-air sec., mechanical**
	1842 Zn, Bi-chromate, C	1883 Zn-CuO, sec.	Ab 1950 Alkali ne$Zn\text{-}MnO_2$, commercial
	1843 $Zn\text{-}PbO_2$	1884, Zn-HgO Commercial since 1947	**1960** **Zn-air primary, button cell**
	1868 Leclanche , $Zn\text{-}MnO_2$	1884-85 $Zn\text{-}Cl_2$, $Zn\text{-}Br_2$	**1971** **Zn-air FC, hydraulic**
	1869 **Zn-primary commercial since 1932**	1899 Zn-NiOOH, sec..	since 1970 Sec., alkaline $Zn\text{-}MnO_2$



Daten: X.G Zhang, Encyclopedia of electrochemical power sources, Secondary Batteries – Zinc system, Overview, Elsevier, 2009, p. 454-468

EC fundamentals of Zinc-air battery



SoA Batterie-Zink, CV: Scanrate: 10 mV/s / Zyklenzahl: 5 / Elektrolyt: 1 M KOH/ Pt-Gegenelektrode; Messung Dipl.-Ing. M. Schmid, Juli 2013, ZiBa-Projekt, Uni Bayreuth.

Anode

$$Zn \rightarrow Zn^{2+} + 2\,e^-$$

$$Zn^{2+} + 4\,OH^- \rightarrow Zn(OH)_4^{\,2-}$$

$$Zn(OH)_4^{\,2-} \rightarrow ZnO + H_2O + 2\,OH^-$$

NR Anode (HER)

$$H^+ + e^- \rightarrow \frac{1}{2} H_2$$

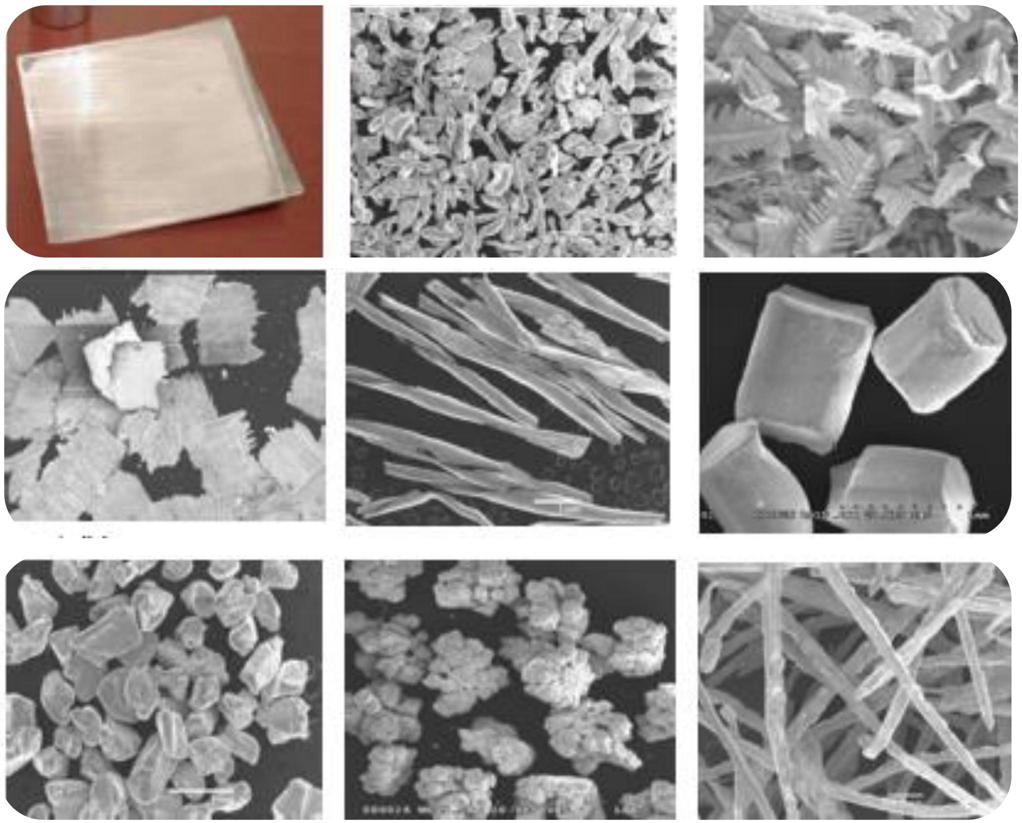
Kathode (ORR)

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$$

- **Avoid HER**
- **Avoid Zinc passivation**
- **Enhance ORR**

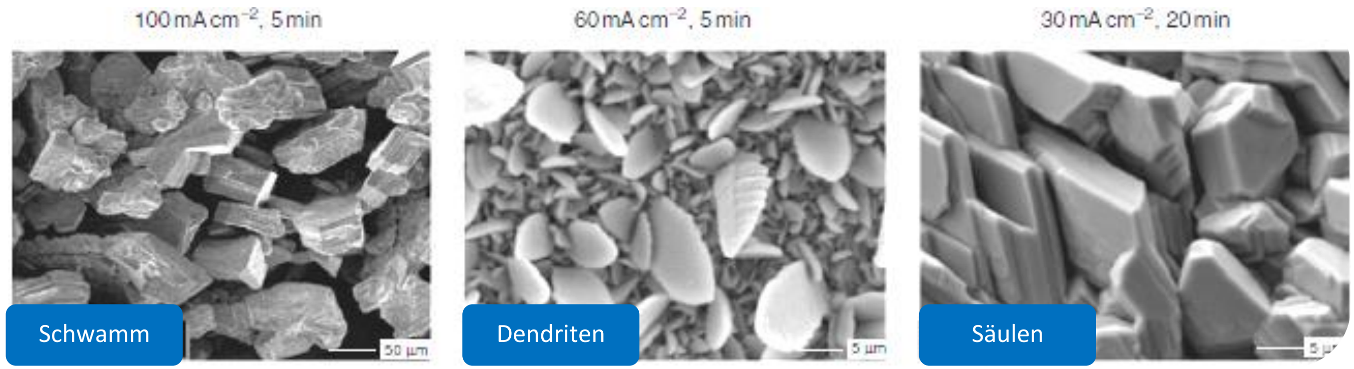
M. Schmid, Willert-Porada, IZiBa-project results, 2013

Zinc before discharging

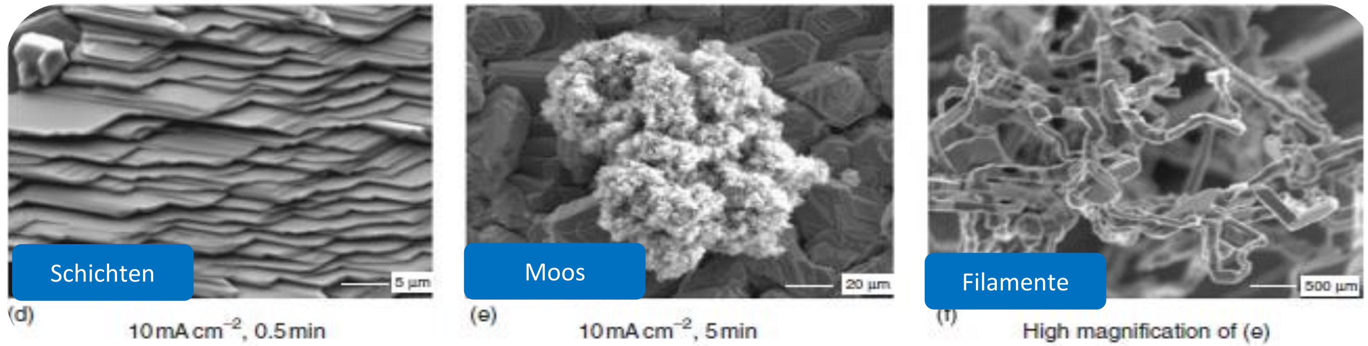


Picture source: X.G Zhang, Encyclopedia of electrochemical power sources, Secondary Batteries – Zinc system, Overview, Elsevier, 2009, p. 454-468

Zinc after reduction of zincate (Charging)

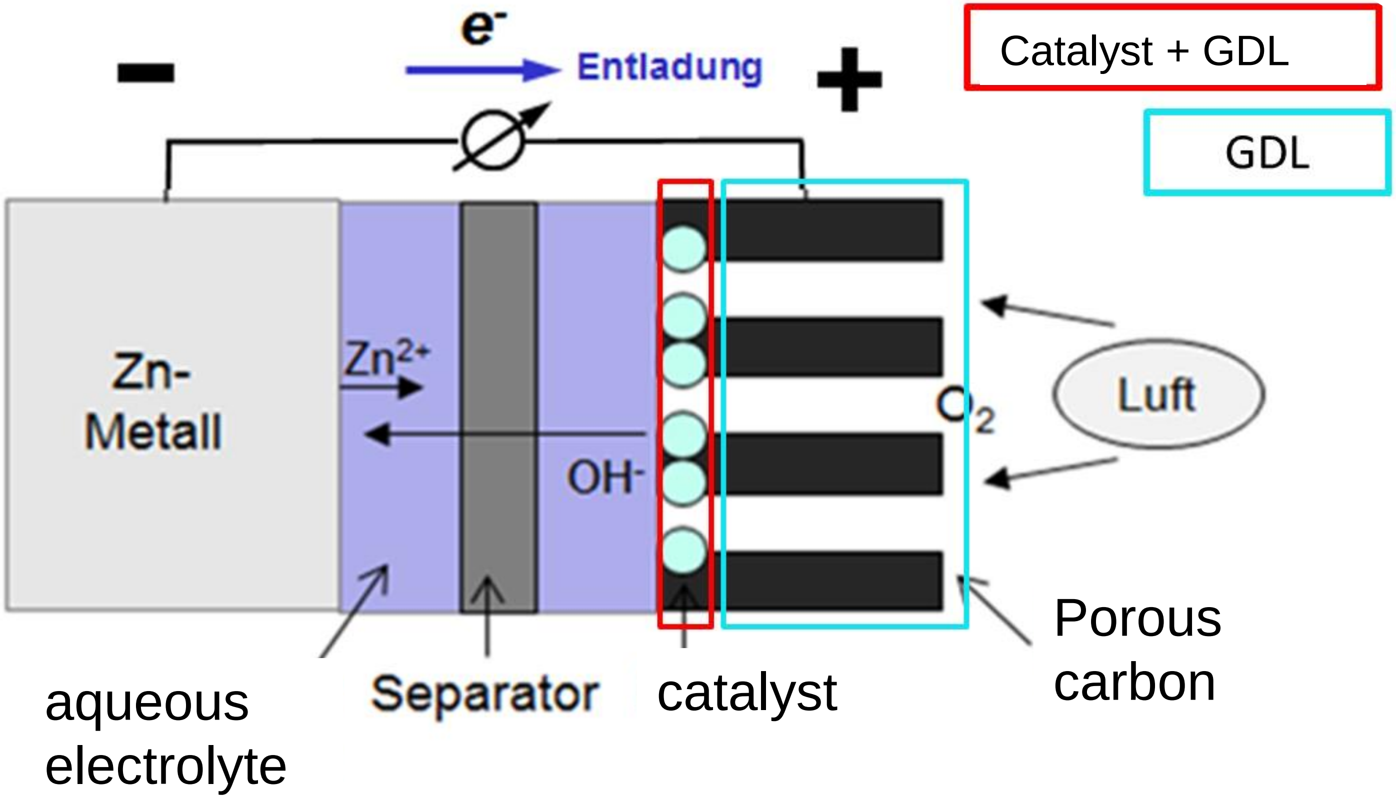


$Zn_{solid} \leftrightarrow$ Zincate-solution/solid deposit $\leftrightarrow ZnO_{solid}$



Picture source: X.G Zhang, Encyclopedia of electrochemical power sources, Secondary Batteries – Zinc system, Overview, Elsevier, 2009, p. 454-468

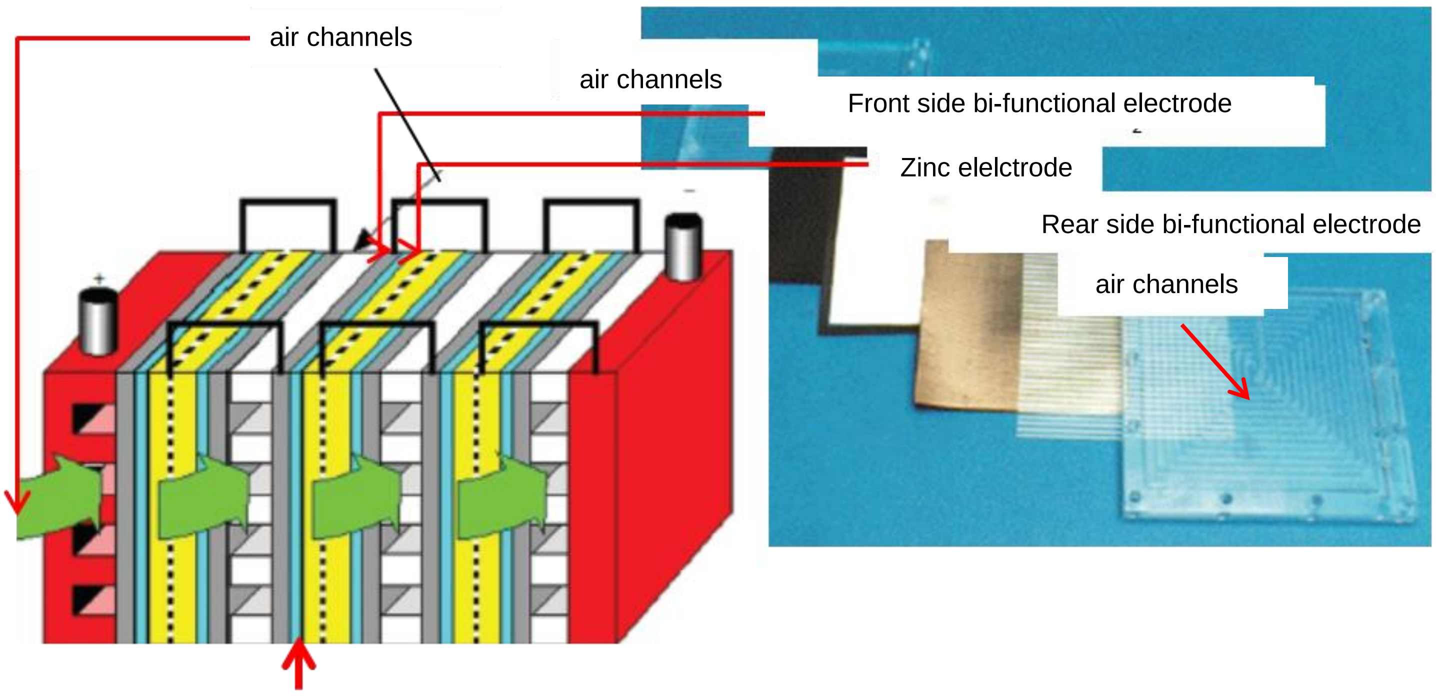
Zinc-air electrical charging cell architecture



Scheme after: J. Cho et.al., Metal–Air Batteries with High Energy Density: Li–Air versus Zn–Air, Adv. Energy Materials, N° 1, 34-50 (2011)

Zinc-air re-chargeable cell

200 cm² Zn-air cell, $P_{max,105mA/cm^2}$: 63 mW/cm²

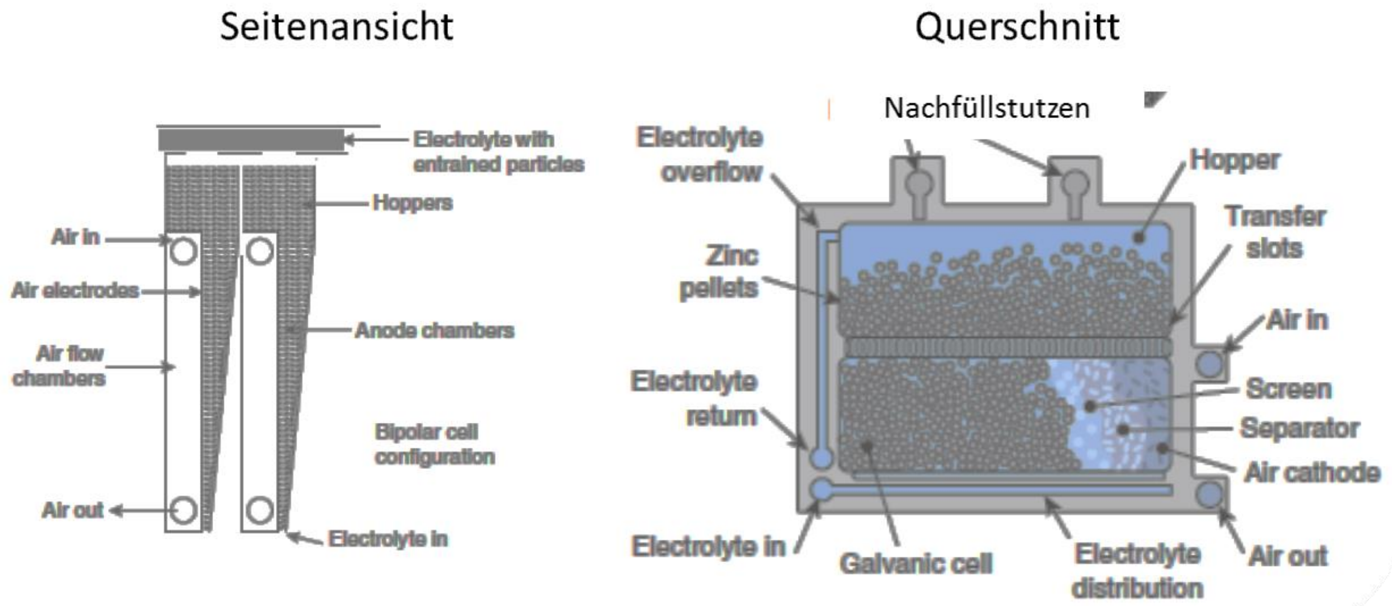


Electrolyte soaked separator

Data from EEPS, O. Haas, J van Wesemael, Zinc-Air: Electrical recharge, Elsevier, 2009

Zinc air, hydraulic charging

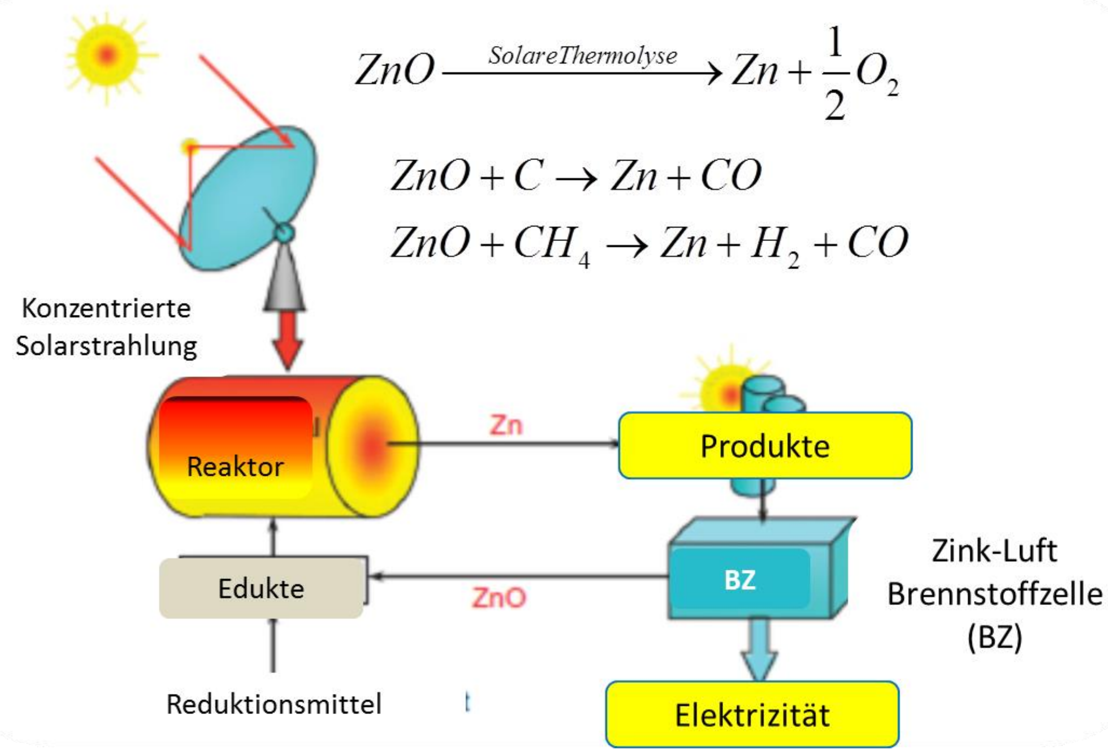
LLNL-Zink-BZ (1995)



- LLNL, η ~35%
- (η%): Sony (26), LBL (50-60), CGE (40), MPI (40)

Daten aus EEPS, Zinc – Air: Hydraulic Recharge , S Smedley, XG Zhang, Elsevier 2009.

Zinc air „mechanical“ charging



Direct-Reduction of ZnO

Daten aus EEPS, Elsevier 2009: Zinc Electrodes: Solar Thermal Production, C Wieckert, M Epstein, G Olalde, S Sante´ n, A Steinfeld.

Zinc air primary battery SoA

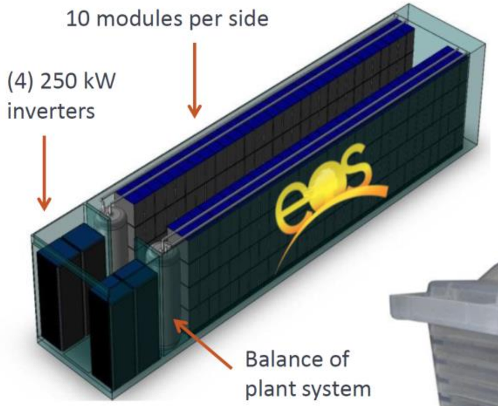
- Yearly production: 1,2 Mrd Batteries (08-2013)
- Leaders: VMB VartaMicrobattery (DE), Rayovac (USA), ZeniPower (China)

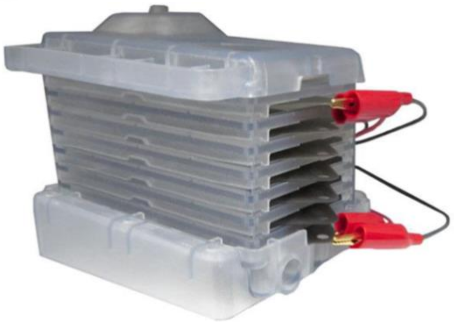
http://company.varta.com/de/content/presse/download/zink_air_plakat_d.pdf

Zinc air: USA

Technology Attributes	
Low-Cost	$1,000/kW or $160/kWh
Long Life	10,000 cycles (30 years)
Ample Storage	1 MW for 6 hours = 6MWh in a 40' ISO shipping container
Efficient	75% round-trip efficiency
100% Safe	Non-toxic, non-combustible, no risk of catastrophic failure

Eos Aurora 1000 | 6000





- Since 2009 media reports, current status unknown

Internetseite der Fa. Eos

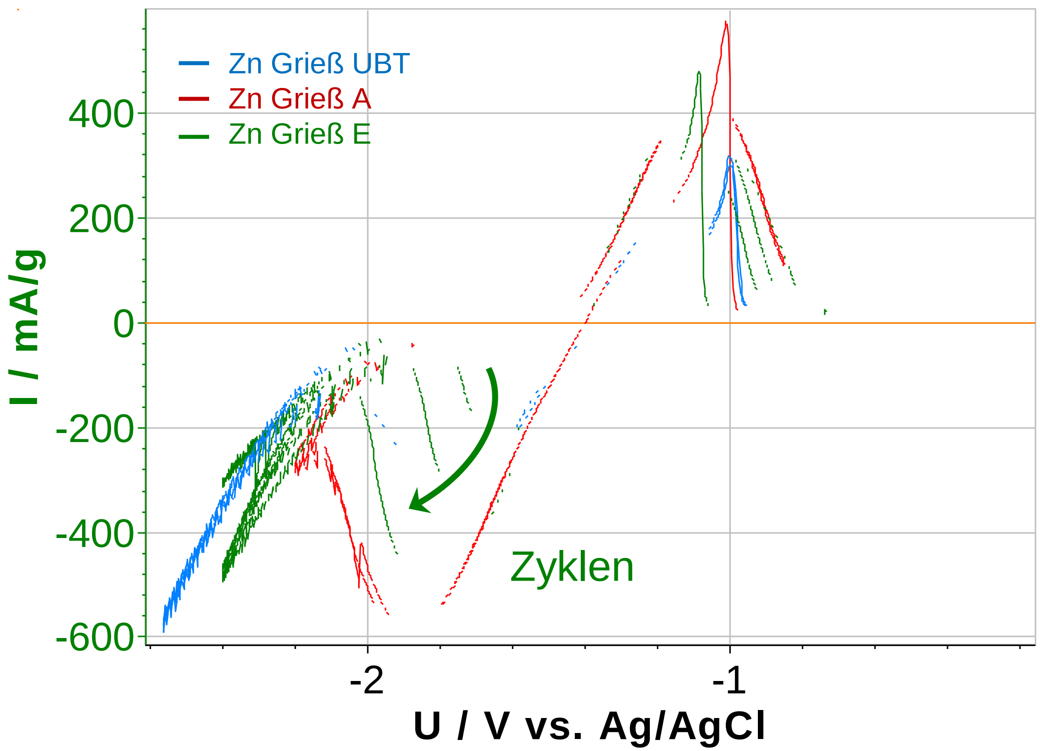
Zentrum für Energietechnik

Zinc-air rechargeable battery: ZiBa Project

- Novel approach: nanocomposite materials , new additives to reduce HER

Field of expertise	Consortium member
Material development Zinc	Eckart GmbH
Material development anode & electrolyte	**University Bayreuth, Chair of Materials Processing**
Material development cathode	Fraunhofer Institut für Silikatforschung, ISC
Zinc air cells	Varta Microbattery GmbH

Comparison of different encapsulation materials



Powder, 1M KOH, Scanrate: 10mV/s, 1-4. Zyklus

M. Schmid, UBT, unpubl. Results, 2014

- Granules (σ ~110 S/cm):
High current, low passivation but high gassing (HER)
starke H_2-Entwicklung

- Granules, encapsulated, varaint E **(σ ~3-4 S/cm)**:
Stably cycling after some cycles, partial loss of capsule material

- Granules, encapsulated, variant UBT **(σ ~140 S/cm)**:
stabile discharge and charge but low current, low gassing (HER)

High optimisation potential

Zentrum für Energietechnik

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