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Druckbare und flexible Polymerbatterien und OLED und ihre vielfältigen Einsatzmöglichkeiten

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Need for energy storage systems I

Need for energy storage systems II

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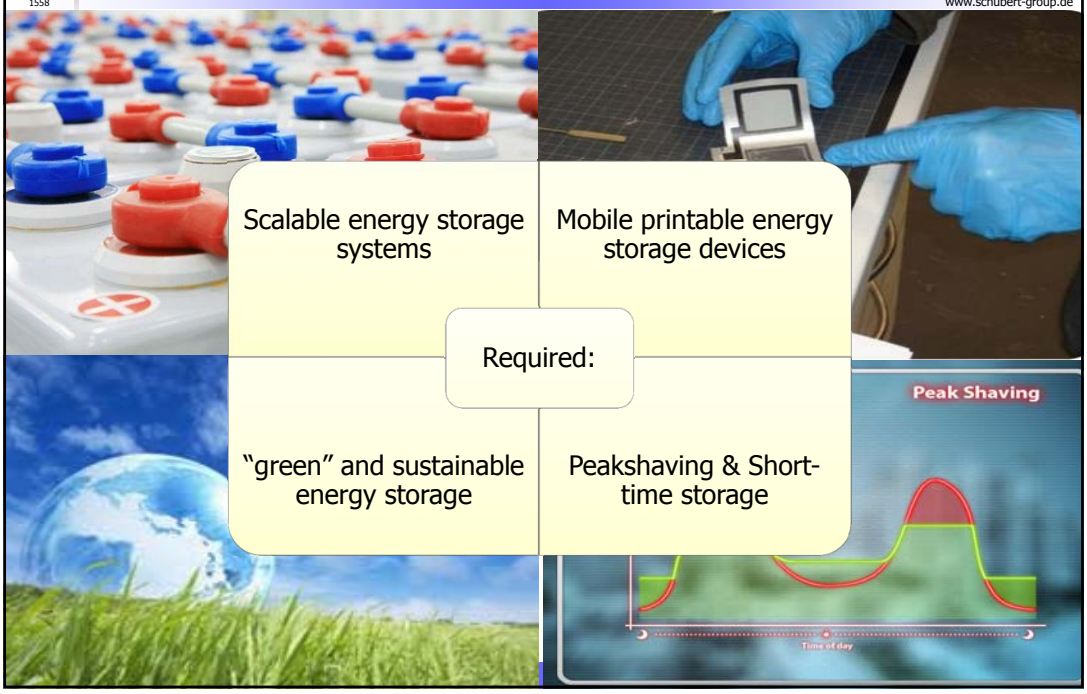

Energy storage in everyday life

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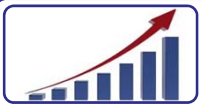
10 battery systems; 300 designs

1.5 Bill. batteries per year in Germany (= 33,000 t)
Sales volume: 50% lead acid (invented 150 years ago) Revenue generated: 50% Li-ion 40%, alkaline 15%, NiMeH 5%, carbon/zinc 5%, automotive lead acid 5%

Global consumer batteries market:
$47 Bill. in 2009 ($74 Bill. 2015; 82% rechargeable batteries)

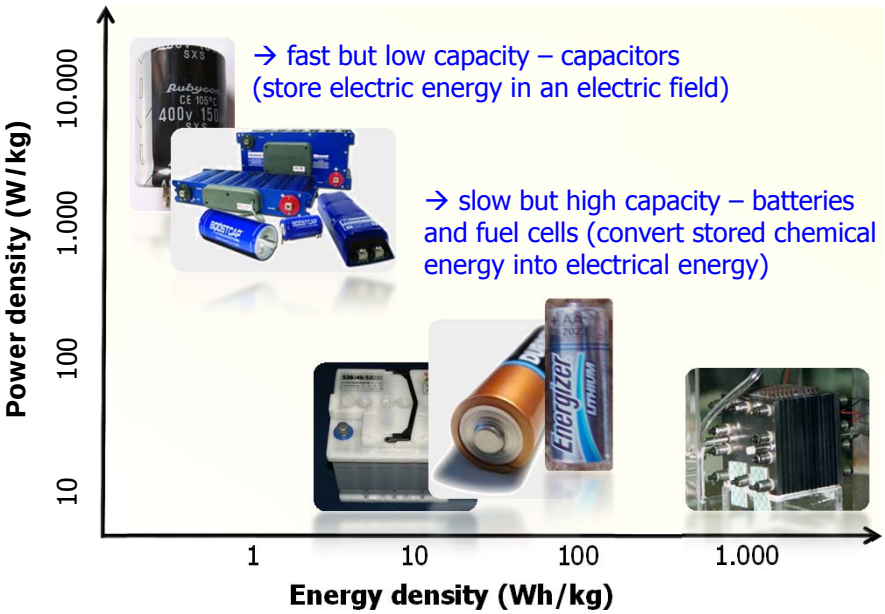
Political target: 1 Mio. E-cars in Germany (2020)



Only 3% average annual increase in energy density of rechargeable batteries over the past 60 years (Li-ion capacity: 95-190 Wh/kg (ca. 130 g $LiCoO_2$/kWh))

www.umweltprofis.at; www.duden.de; www.autozeitung.de

Electrical energy storage



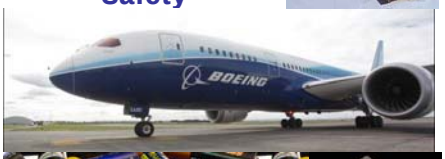
→ New systems are required: Faster & more capacity, less (rare) metals …

Images: http://en.wikipedia.org

Future challenges

Safety

High capacity



Sustain-
ability

Scalability

www.batterie2020.de

Polymers

Why use synthetic polymers?

Why think about synthetic polymers for battery applications?

Advantages:

- **Cheap** (polyethylene: 220 €/ton, nylon: 2140 €/ton, steel 600 €/ton)
- Good quality
- **Easy to process**, fast to process, *i.e.* to convert into certain forms, such as bottles or fibers (lower temperatures than needed for metals)
- Light (energy-saving in cars or planes)
- Sufficient petrochemical resources
  (at present, more than 90% are used for energy production)
- Possibility to switch to natural resources (poly(lactic acid), soy beans, cellulose)
- **Easy formulation compounding**
  → a broad spectrum of different properties is available
- **Recycling possibilities** (thermal recycling, reuse)
- **Tunable properties** (choice of monomer, constitution, molar mass, …)

Current material basis

Rare earths
(Ni-MeH)

Cobalt
(Li-ion)

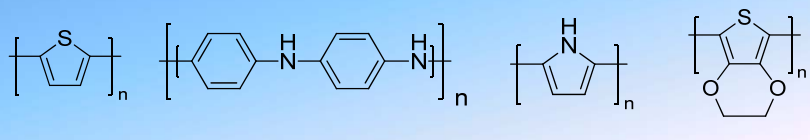
Lithium
(Li-ion)

Basis of our future energy storage???

Historical perspective

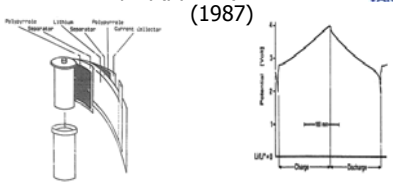
conductive polymers

poly(thiophene) poly(aniline) poly(pyrrole) PEDOT



Commercial button cells flopped

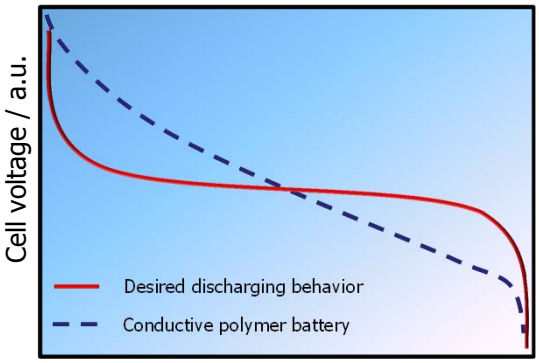
BASF The Chemical Company VARTA/BASF poly(pyrrole)/lithium (1987)



Bridgestone-Seiko poly(aniline)/lithium (1987-1992) SEIKO

J. S. Miller, *Adv. Mater.* **1993**, *5*, 671-676; D. Naegele, R. Bittihn, *Solid State Ionics* **1988**, *28-30*, 983-989.

Why twice? What has changed?



- conducting polymers
- sloping redox potential (varying cell voltage as their redox potential gradually changes upon charging/discharging) and doping/undoping)
- useless for numerous applications

vs.

- polymers with distinct redox potential attributed to localized redox sites
- stable cell voltage

T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397–6409.

Organic radical batteries (ORB)

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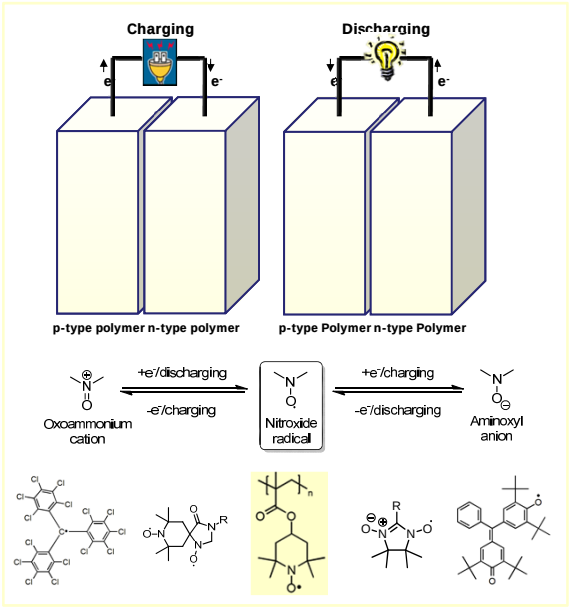
Environmentally benign
- no heavy metals
- simple disposal with household garbage
- energetic recycling

Simple processing
- inkjet printing
- screen printing
- thin paper-like and flexible design

High power density
- rapid charging
- high charging and discharging rate performance

Excellent cycle life
- simple redox chemistry
- >1000 charging/discharging cycles



K. Nakahara, *Chem. Phys. Lett.* **2002**, *359*, 351-354; H. Nishide *et al.*, *Electrochim. Acta* **2004**, *50*, 827-831.

Polymers for batteries

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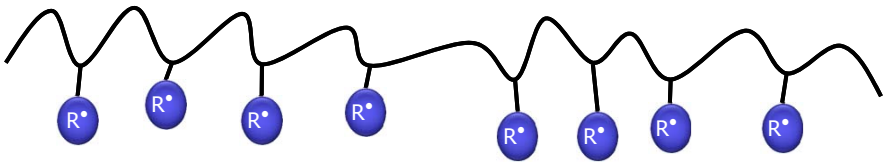
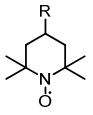
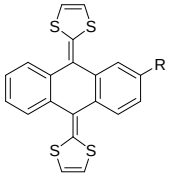
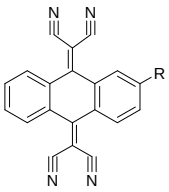
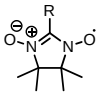
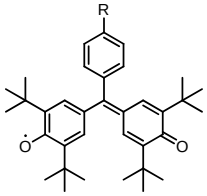
Polymers carrying stable radicals as redox-active pendant groups



p-type polymer (cathode) bipolar n-type polymer (anode)

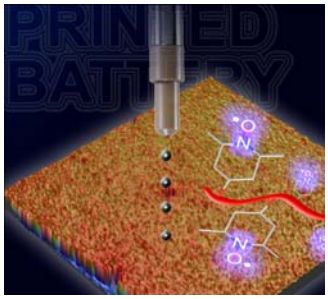
E vs. Ag/AgCl

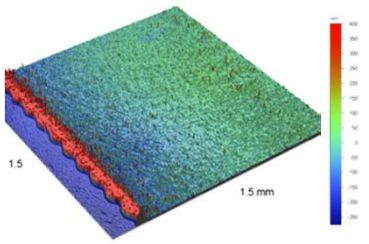
Highest achieved cap.

0.73 V	ca. 0.3 V		-0.61/0.72 V	0.06 V
				
111 Ah/kg	132 Ah/kg	160 Ah/kg	44 Ah/kg	42 Ah/kg

Tuning the voltage

Inkjet printing



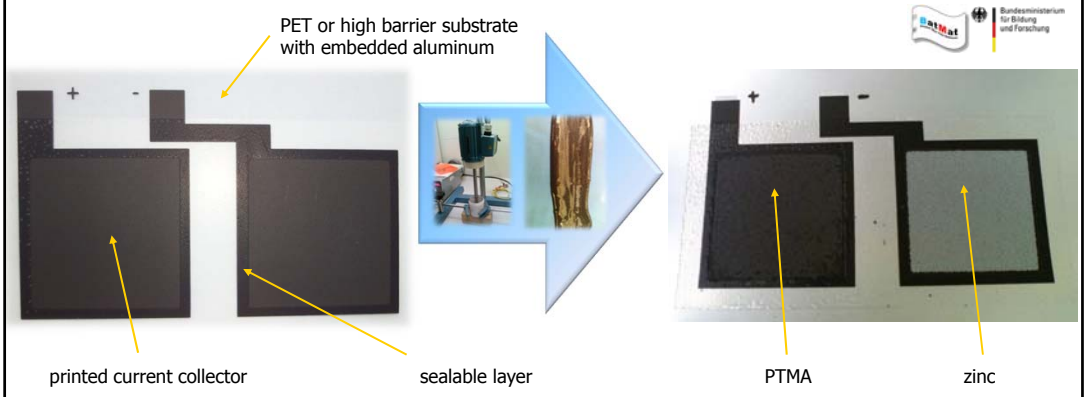


Printing of thin electrodes

Challenge:
stability *vs.* printability

T. Janoschka, A. Teichler, B. Häupler, T. Jähnert, M. D. Hager, S. Schubert; *Adv. Energy Mater.* **2013**, *3*, 1025-1028.

Battery fabrication

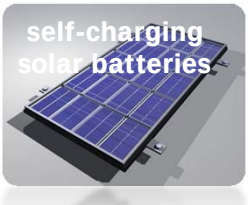


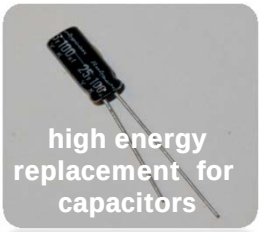
- PTMA (free radical polymerization), binder, and graphite for **screen printing**

Screen printing of a „foil battery“

Cooperation with the "Hochschule der Medien Stuttgart", Prof. Gunter Hübner.

New targets

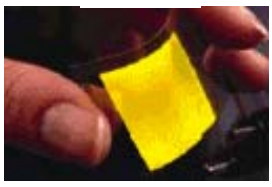


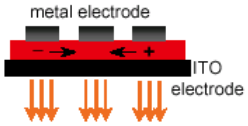


Images from: www.matbase.com/img/web_newsmodule/News_Ciba_OnVu_food_packaging_high_temperature_indicator.jpg; www.sharecg.com/images/medium/5981.jpg; ultimachine.com/sites/default/files/imagecache/product_full/Capacitor.jpg; giantcrystals.strahlen.org/america/cobalt3.jpg

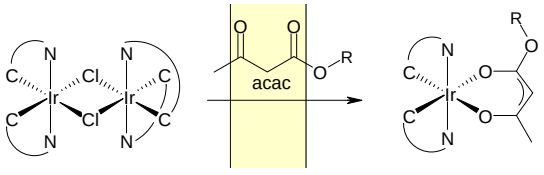
PLEDs

OLED





Synthesis



Inkjet printing

Application - device

Inkjet printing 1

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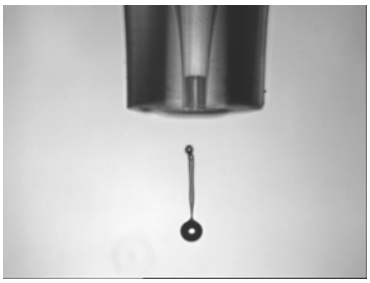
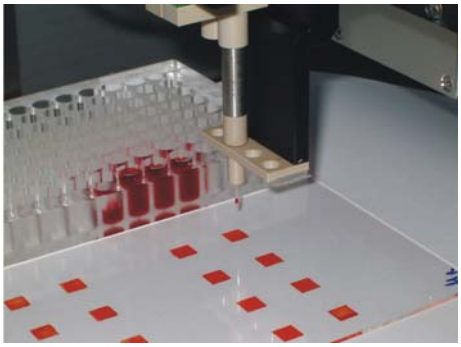
Microdrop-Autodrop Platform

Micropipette
AD-K-501





Adv. Mater. 2004, *16,* 203; *J. Mater. Chem.* 2004, *14,* 2627; *Soft Matter* 2008.

Inkjet printing 2

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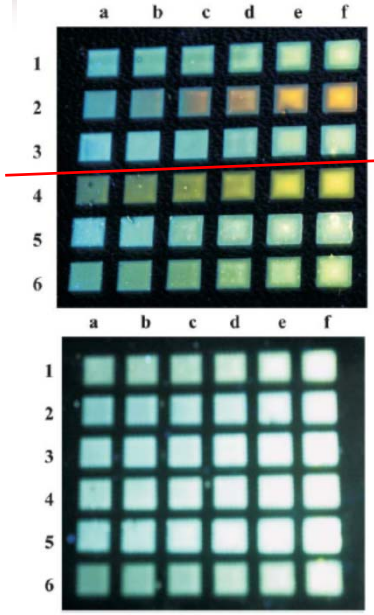
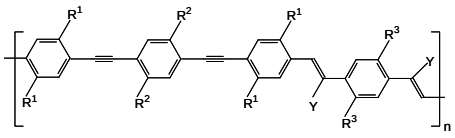


after annealing (70 °C, 2 h)

Increasing thickness from ~50 nm to ~150 nm

printed polymer films for potential application in OLEDs

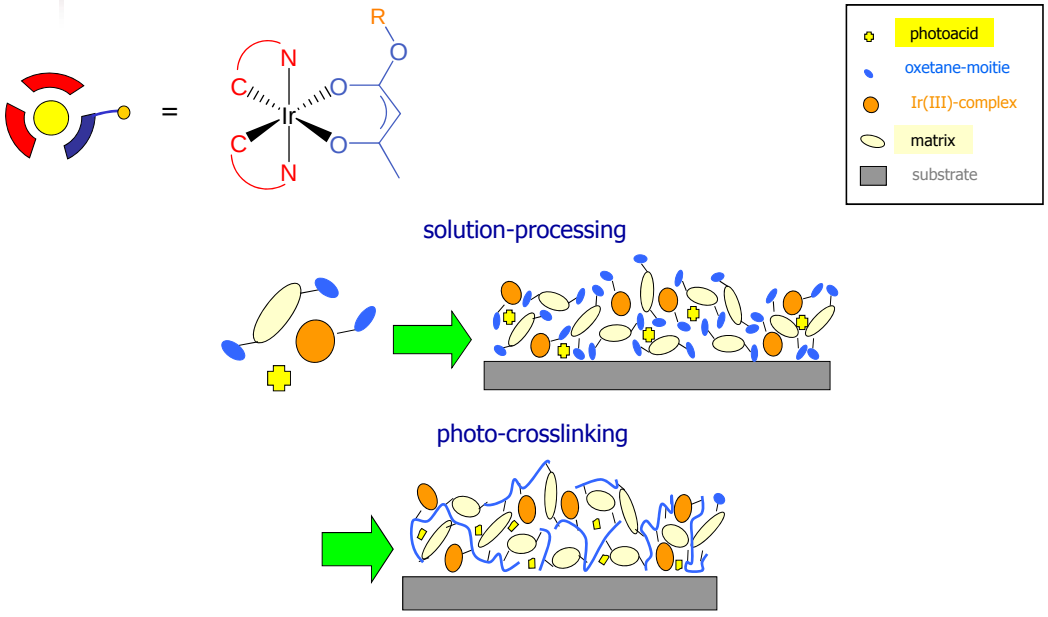
Solvent : 90% toluene - 10% dichlorobenzene,
Printed area: 6 x 6 mm Velocity: 15 mm/s,
Voltage: 74 V, Pulse width: 45 μs



1: R^1 = H, R^2 = octyloxy, R^3 = octadecyloxy, (Mn = 50,000)
2: R^1 = H, R^2 = octadecyloxy, R^3 = octyloxy, (Mn = 38,400)
3: R^1 = H, R^2 = octadecyloxy, R^3 =heptyloxy, (Mn = 41,000)
4: R^1 = H, R^2 = octadecyloxy, R^3 =decyloxy, (Mn = 43,200)
5: R^1 = H, R^2 = octadecyloxy, R^3 =dodecyloxy, (Mn = 10,200)
6: R^1 = H, R^2 = R^3 = dodecyloxy, (Mn = 25,600)

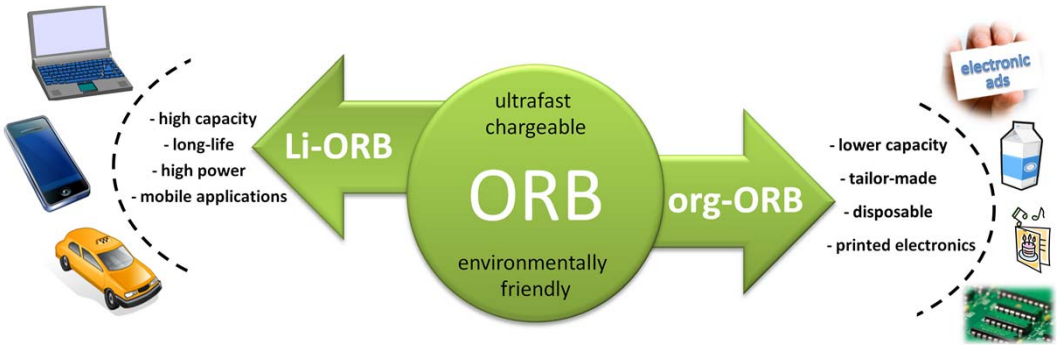
J. Mater. Chem. 2006, *16,* 4294; *Adv. Funct. Mater.* 2007, *17,* 277.

Iridium complex based OLED I



Cooperation with K. Meerholz, Universität Köln: *Adv. Mater.* 2008, *20*, 129.

Conclusion



- Organic radical batteries offer a great potential
- New processing possibilities for batteries
- New properties (sustainability, fast charging,…)

Adv. Mater.. **2012**, *24*, 6397-6409.

Team & partners

Infos
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Tobias Janoschka, Bernhard Häupler, Thomas Jähnert, Dr. Andreas Wild, Anke Teichler, Prof. Dr. Ulrich S. Schubert, Michael Wendler (Stuttgart), Prof. Dr. Gunter Hübner

Carl-Zeiss-Stiftung, Ernst-Abbe-Stiftung, Thüringer Ministerium für Bildung, Wissenschaft und Kultur, …