Stefano Passerini

TOWARDS SUSTAINABLE BATTERIES:
SAFER AND ENVIRONMENTALLY-FRIENDLY MATERIALS AND PROCESSES

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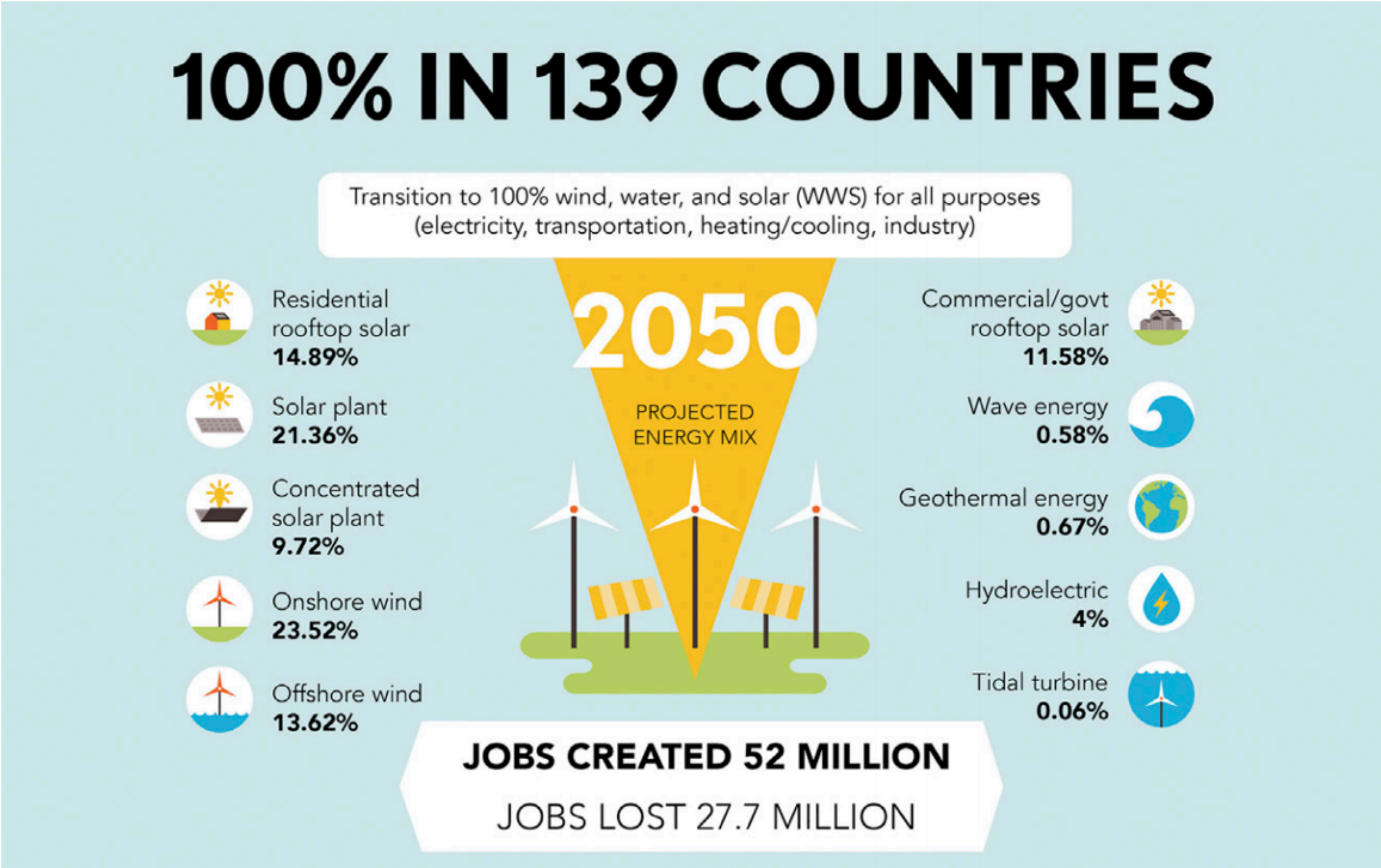
A complete transition to renewables by 2050 is theoretically possible!

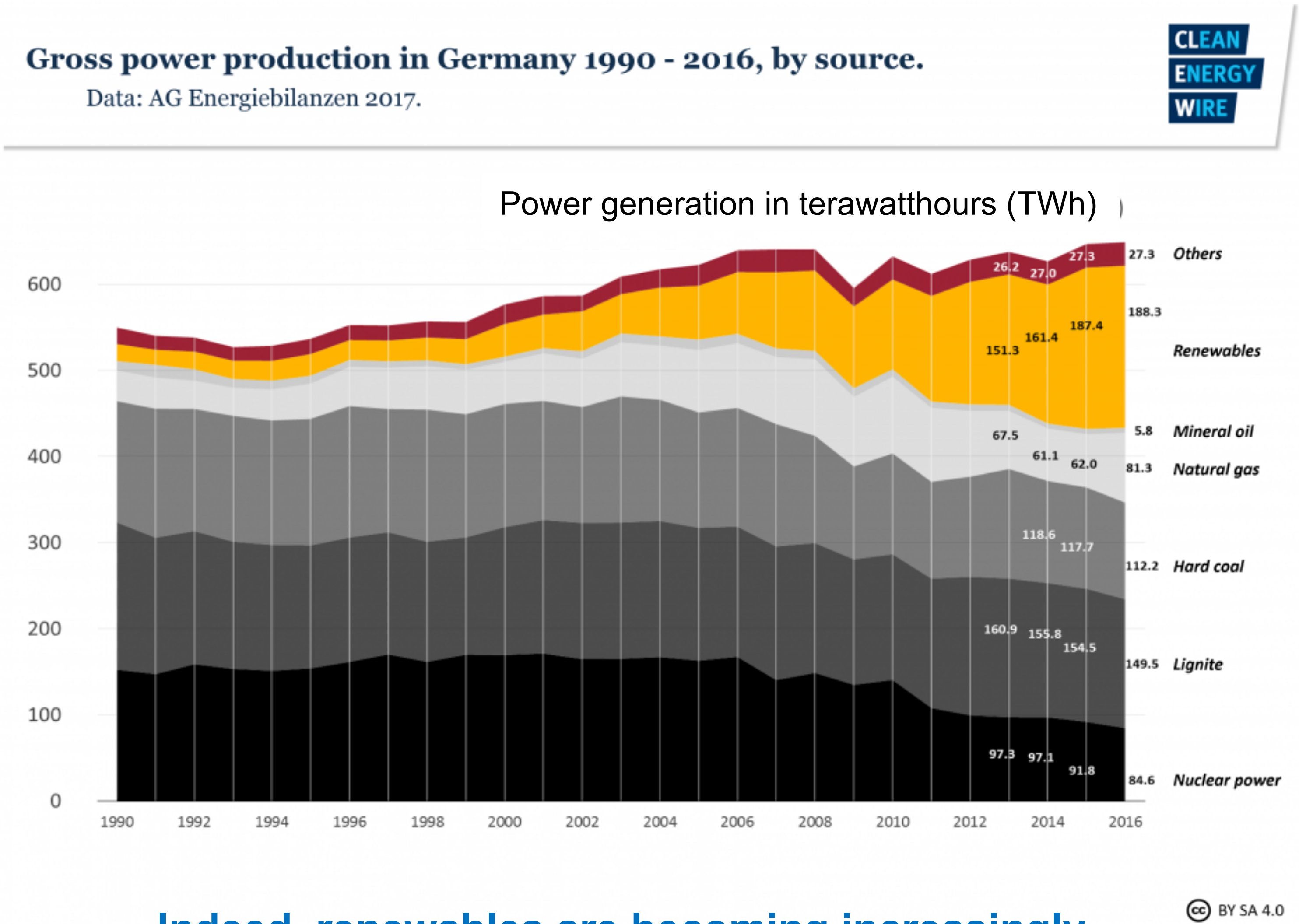


Goal of the German Federal Government:

by 2050: 80% of the total energy supply by renewables

Source: http://kateisolarinc.com.ph/100-renewable-energy-2050-possible/. Jacobson & Delucchi, Energy Policy 2011 (39) 1154-1169; Delucchi & Jacobson 2011 (39) 1170-1190.

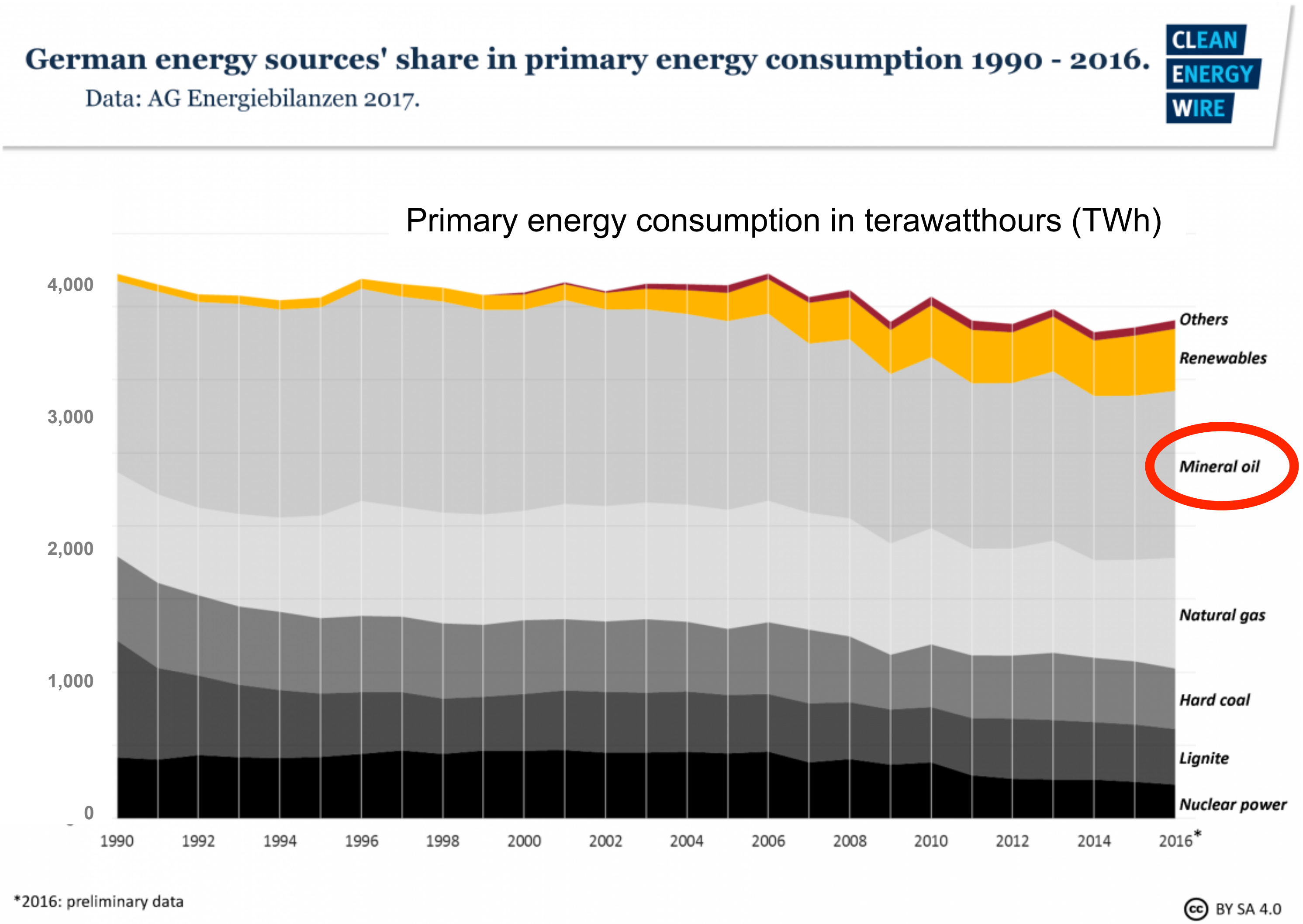
Roadmap towards sustainable energy: Power production



Indeed, renewables are becoming increasingly important for the electric power production in Germany

Source: https://www.cleanenergywire.org/factsheets/germanys-energy-consumption-and-power-mix-charts.

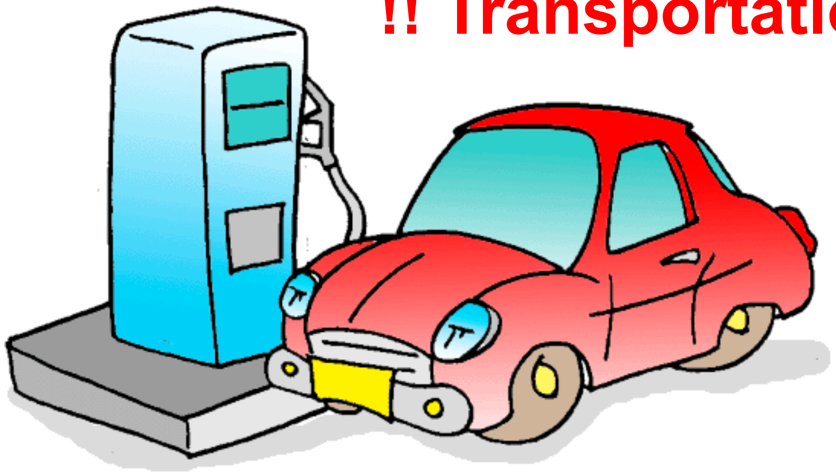
Roadmap towards sustainable energy: Energy consumption



However, the overall energy consumption in Germany remains highly dependent on fossil fuels

Source: https://www.cleanenergywire.org/factsheets/germanys-energy-consumption-and-power-mix-charts.

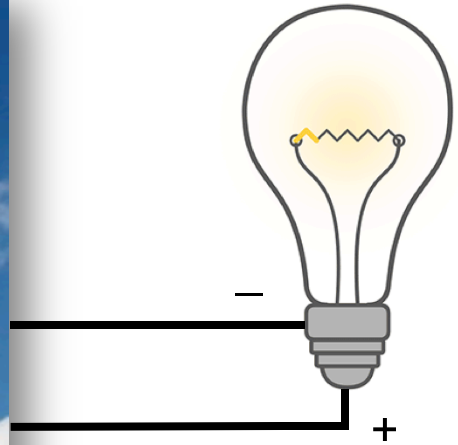
!! Transportation !!



Petrol

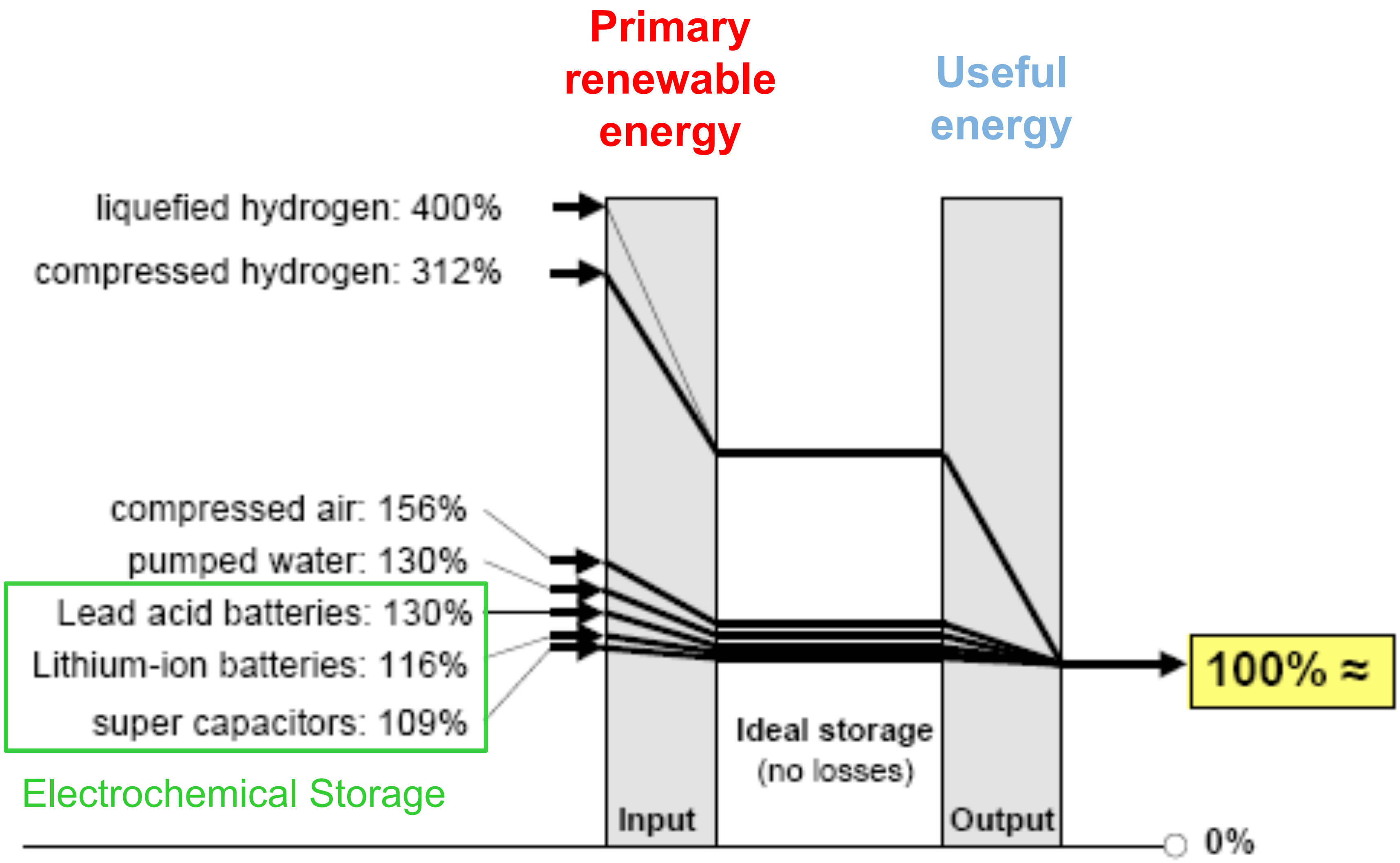
Source: http://emblazeindia.com/aircraft-engine-fuel/; Yang et al., Chem. Rev. 2011 (111) 3577-3613; https://www.clipartfreebee.com/clip-art-gallery-with-gratis-images/cars-clipart-images-download-and-print-for-free/petrol-station-clip-art-image-free-cars-clip-art-images-free-198.html

Harmless, free, renewable and easily accessible, sun and wind are in principle inexhaustible energy suppliers…but…



They are intermittently available!

Energy Storage Efficiency



Source: Ulf Bossel - 070917 Reykjavik

Alessandro Volta

1839 Fuel cell

1859 Pb battery

1899 Ni-Cd

1973 Li metal

1975 Ni-MH

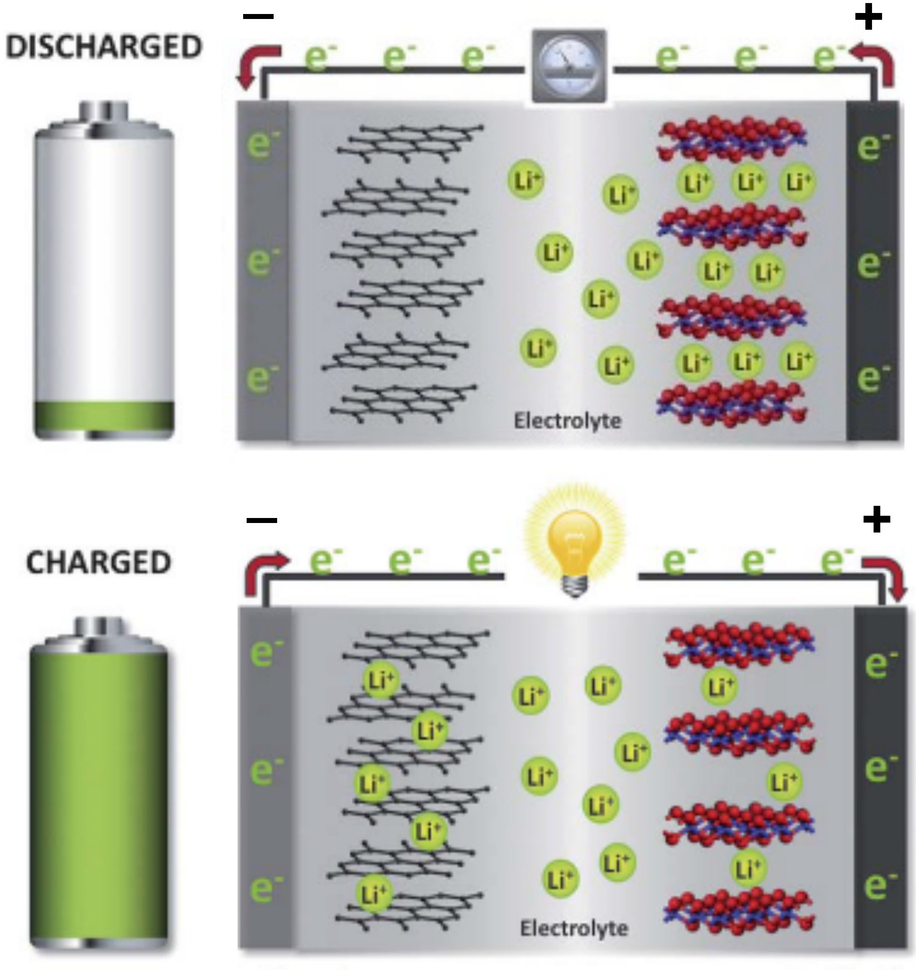
1991 Li-ion

1799

Cu/Zn pile

Sony

Lithium-ion battery – The "rocking chair" mechanism



$$yC + LiMO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC_y + Li_{(1-x)}MO_2$$

Average Cell Voltage ~ 3.6 V

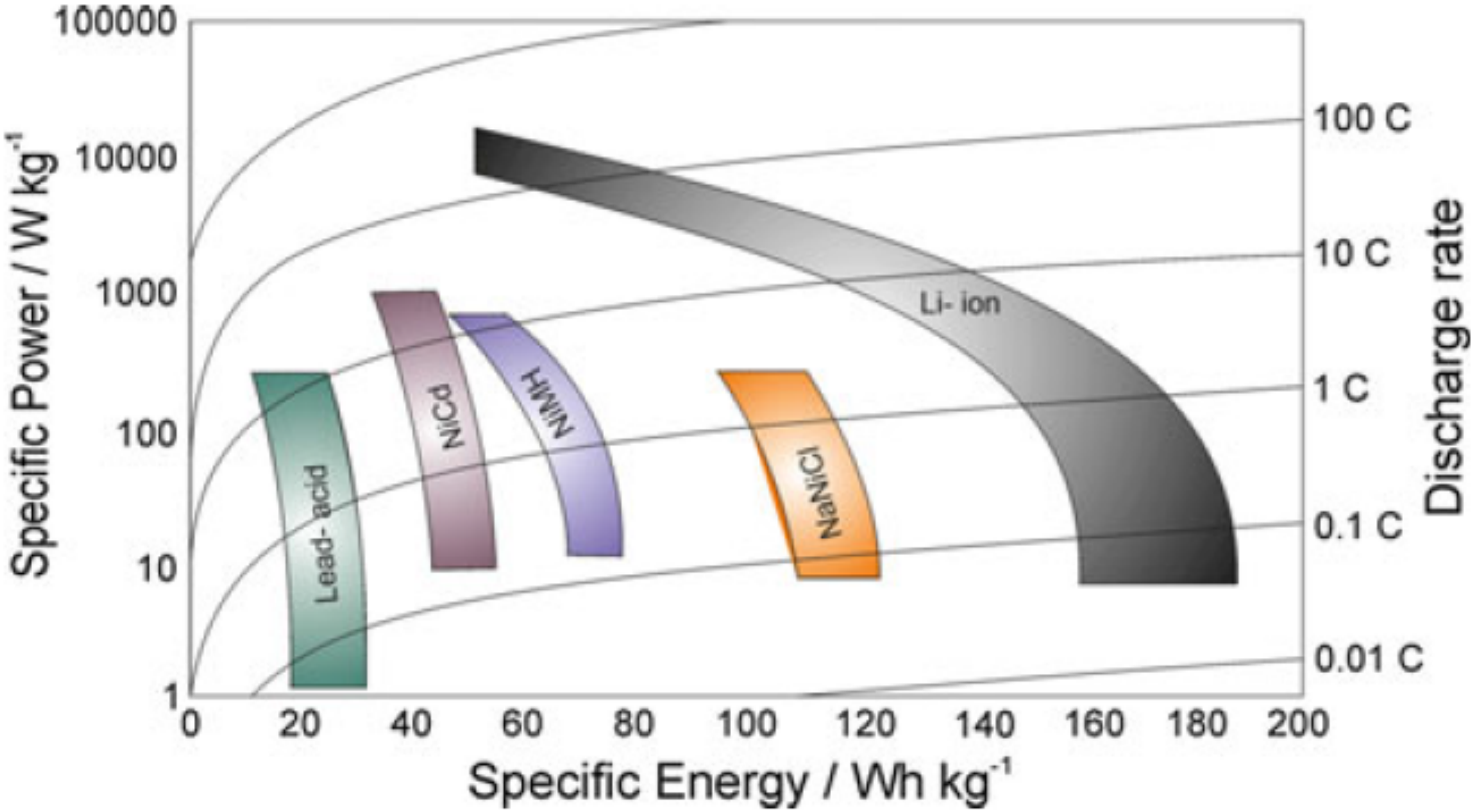
Energy (Wh) = Voltage (V) x Capacity (Ah)

System	Nominal Voltage / V	Energy*	
		Gravimetric / Wh kg^{-1}	Volumetric / Wh L^{-1}
Pb-Acid	2.1	40	90
Ni-Cd	1.2	60	130
Ni-MH	1.2	80	215
Li-ion	**3.6**	**135**	**320**

*Practical values on battery pack level

These values have more than doubled in the past 20 years, „just" by optimizing cell design...

M.M. Thackeray et al., Energy Environ. Sci., 2012, 5, 7854



Lithium-ion batteries outperform all other commercial battery technologies!

Wagner et al., J. Appl. Electrochem. 2013, 43, 481-496.

Roadmap towards electromobility

Journal of Power Sources 382 (2018) 176–178

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/jpowsour

Perspectives of automotive battery R&D in China, Germany, Japan, and the USA

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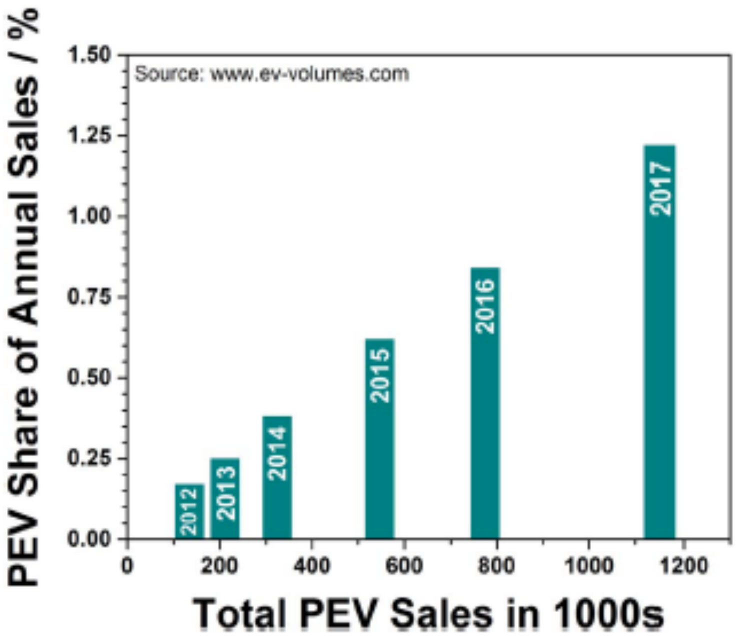
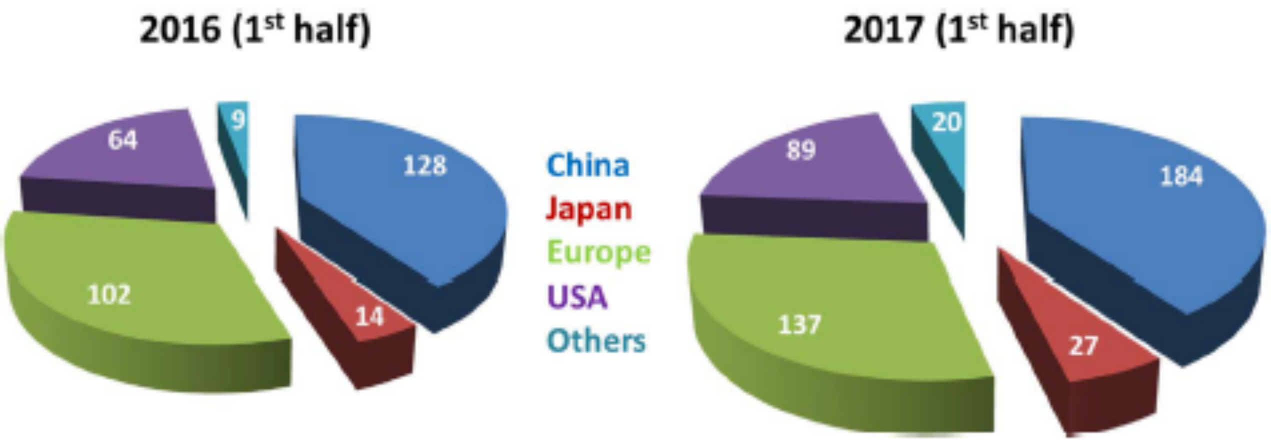
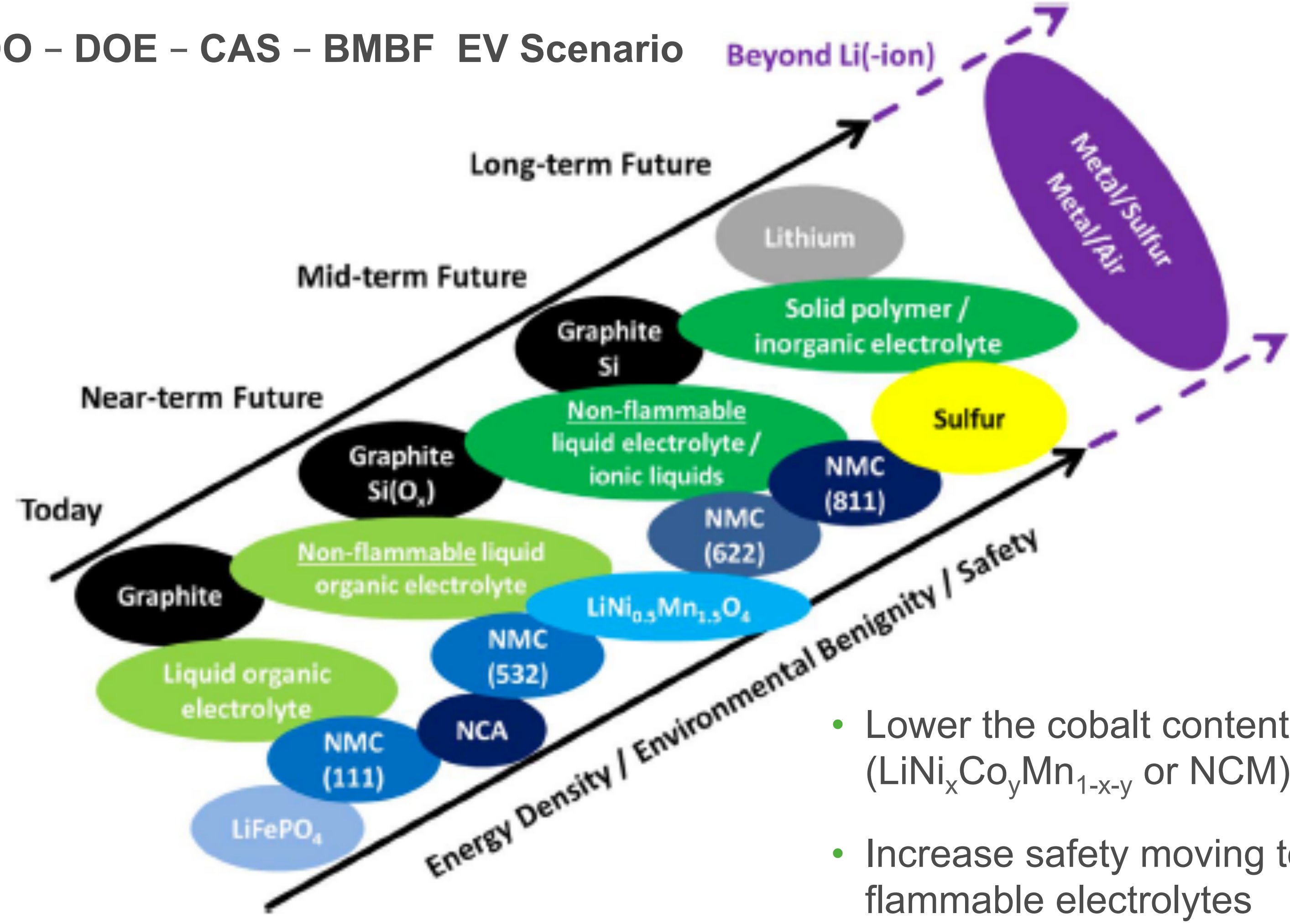
[d] Office of Energy Efficiency & Renewable Energy, US Department of Energy (DOE), 1000 Independence Avenue, SW, Washington, DC 20585, USA
[e] Institute of Physics, Chinese Academy of Sciences (CAS), P.O. Box 603, Beijing 100190, China
[f] Key Technologies for Growth, Federal Ministry of Education and Research (BMBF), Heinemannstrasse 2, 53175 Bonn, Germany
[g] Chemical Sciences and Engineering Division, Argonne National Laboratory (ANL), 9700 South, Argonne, Illinois 60439, USA





Battery roadmap towards electromobility

NEDO – DOE – CAS – BMBF EV Scenario

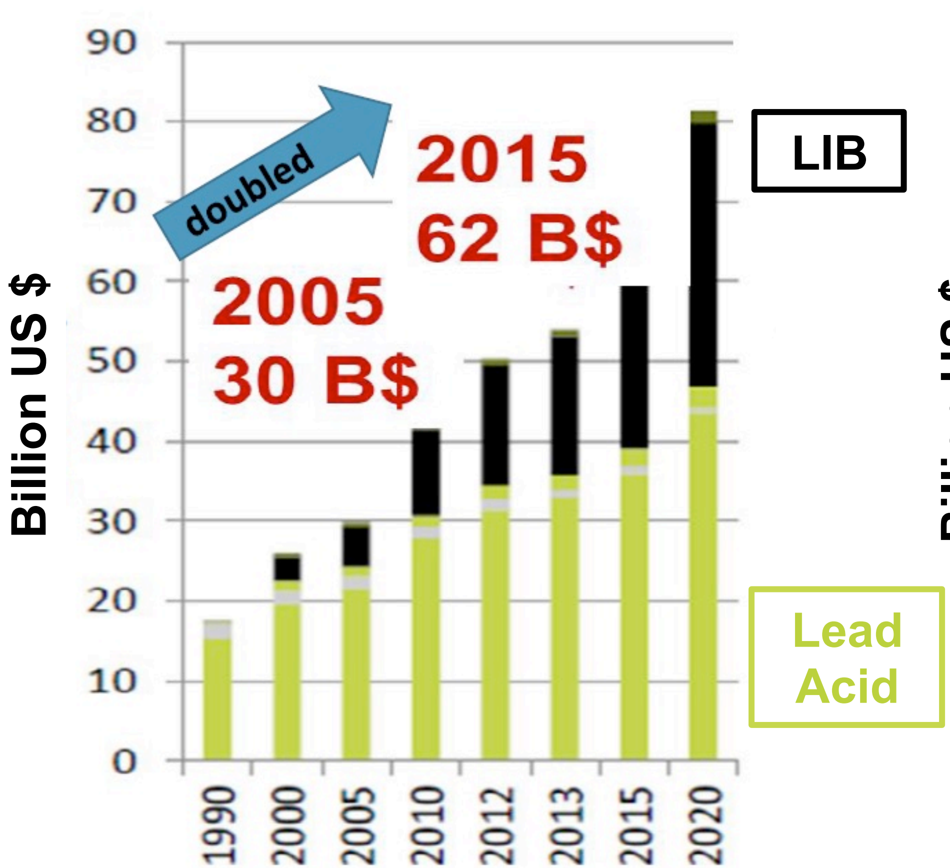


- Lower the cobalt content in the cathode ($LiNi_xCo_yMn_{1-x-y}$ or NCM)
- Increase safety moving toward non flammable electrolytes
- Increase the volumetric energy of the anode via alloy and Li metal

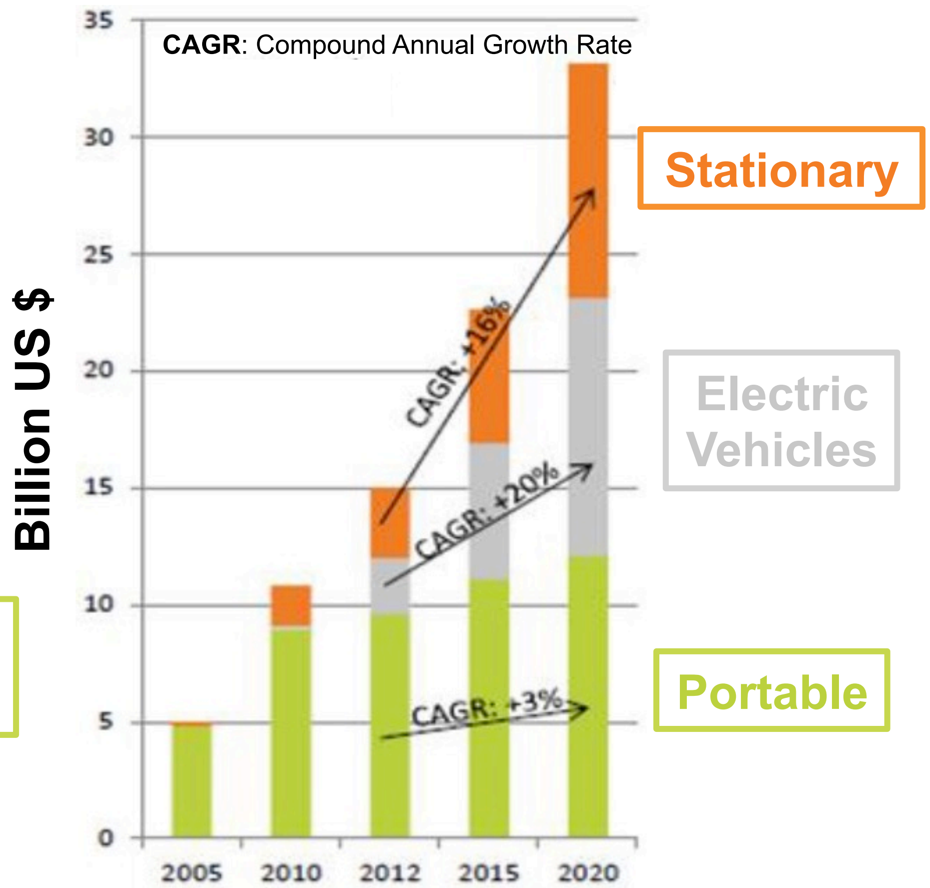
D. Bresser et al. J. Power Sources, 382 (2018) 176

Worldwide battery market 2005-2020

Market share by battery chemistry



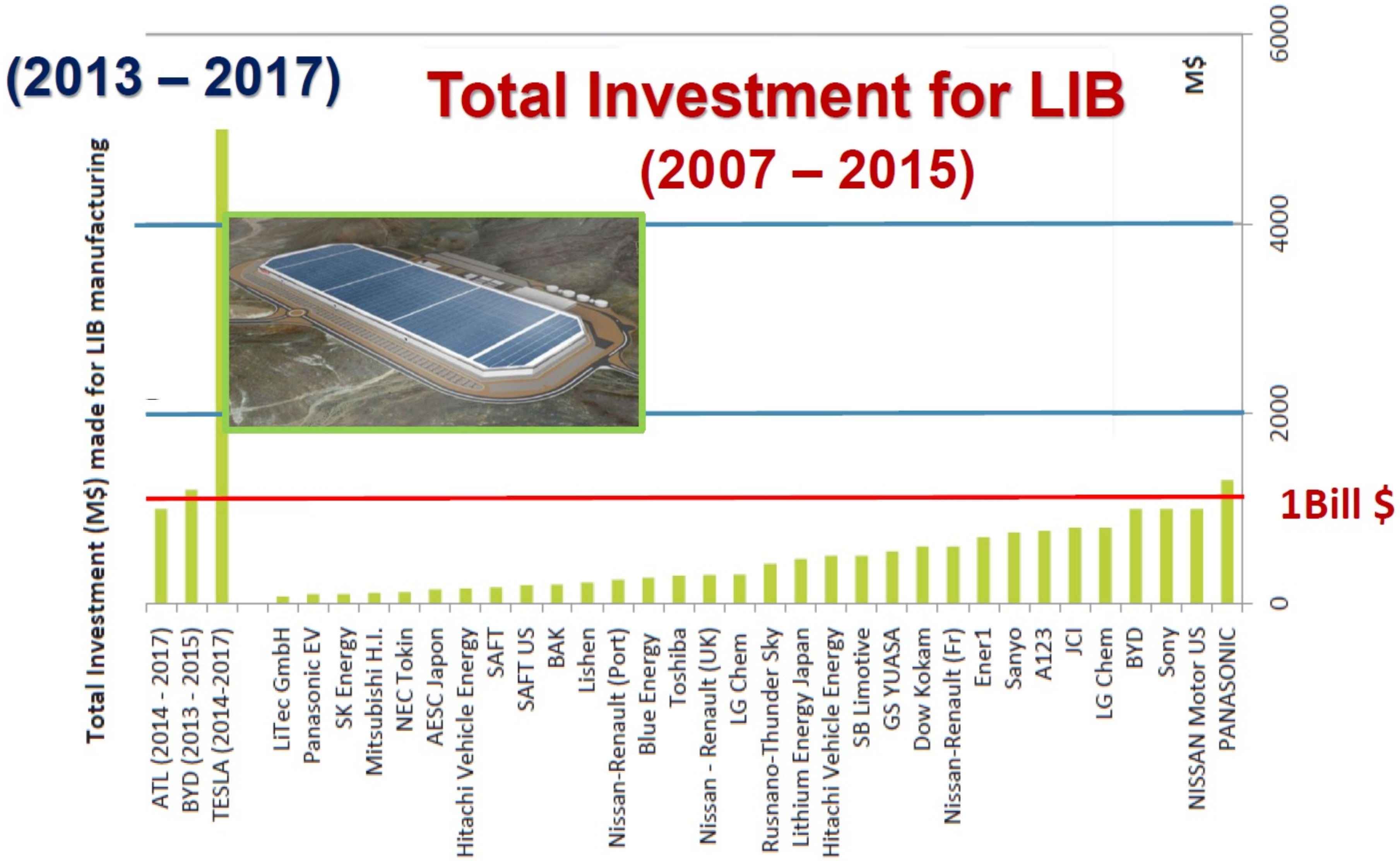
LIB market growth by application



The stationary and EV markets are showing the fastest growing rate

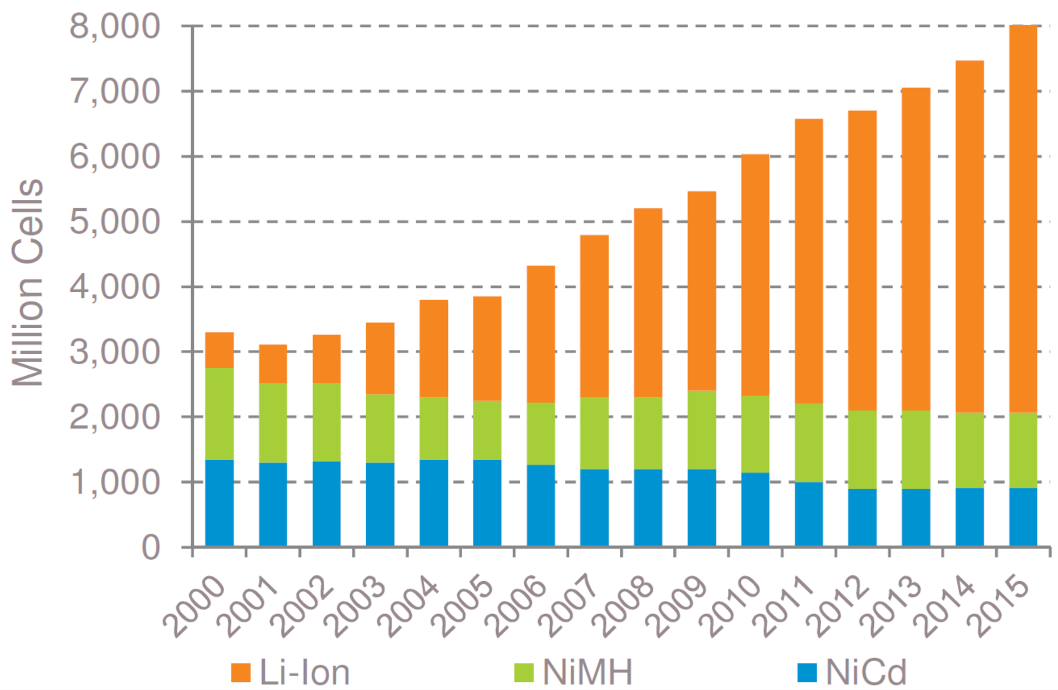
Curtesy of Prof. Jürgen Garche

Growing Investments in this field



Curtesy of Prof. Jürgen Garche

Environmentally-Friendly Materials and Processes



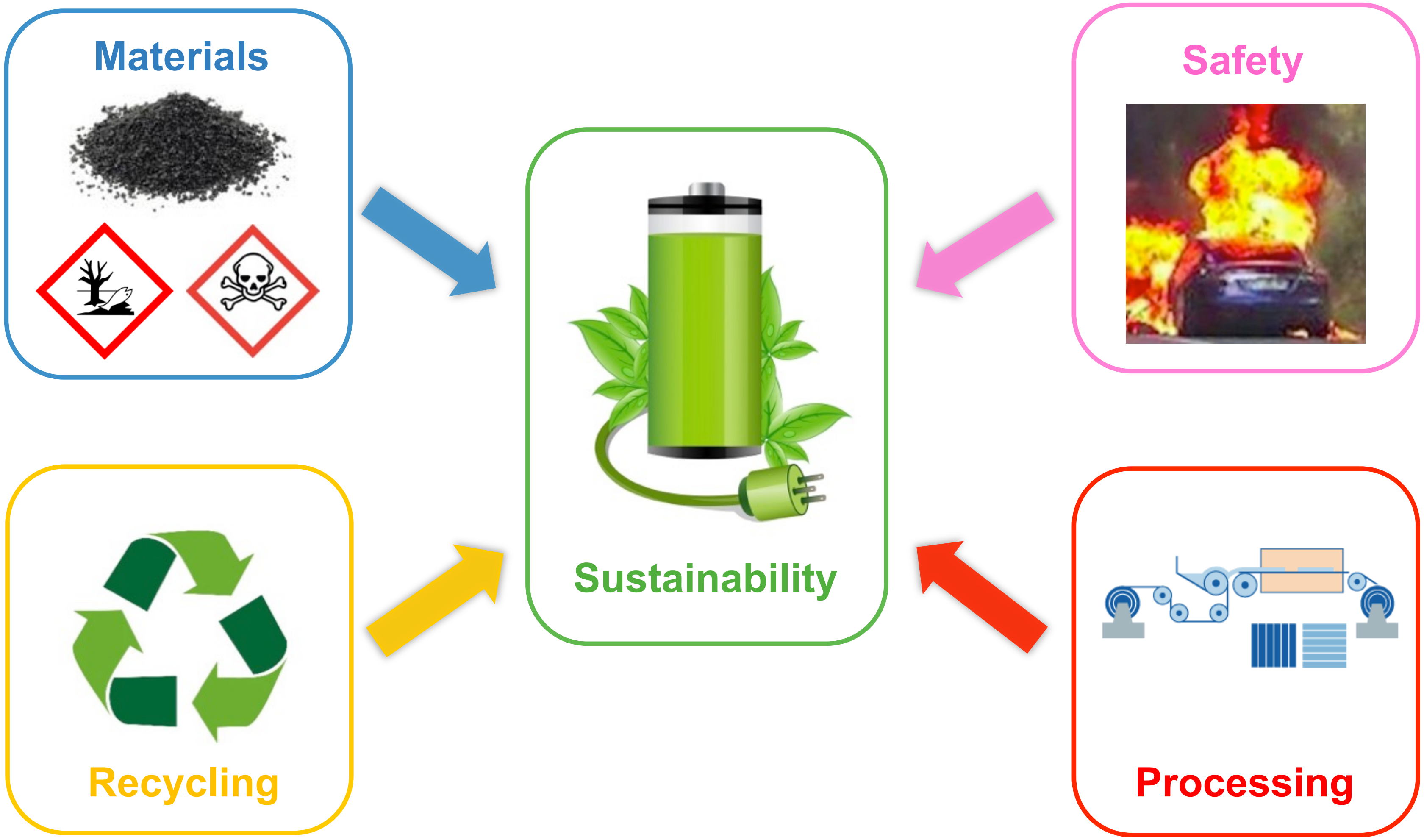
Lithium-ion battery (LIB) production is continuously increasing at the expense of other battery chemistries

Need to address the production-related environmental impact of LIBs!

* Source: Christophe Pillot, Avicenne Report 2015.

Environmental impact needs to be considered

Several factors affect the sustainability of a battery…

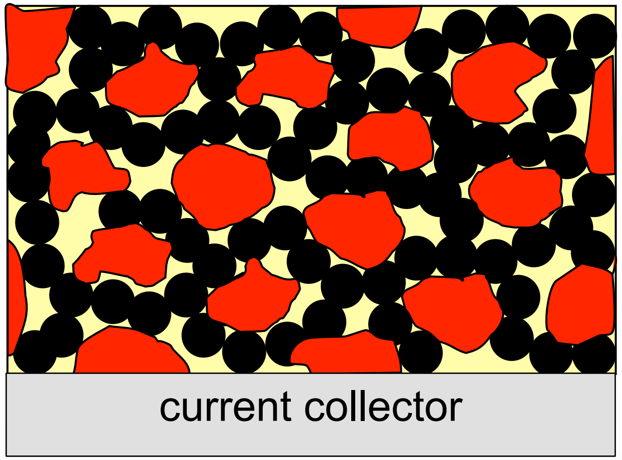


N. Ogihara et. al, J. Electrochem. Soc., **2012**, *159*, A1034, G. Liu et. al, J. Electrochem. Soc., **2012**, *159*, A214
D. Bresser et. al, *"Advances in batteries for large- and medium-scale energy storage"*, Woodhead Publishing, **2014**

Processing: The underrated role of the binder

The binder is an INACTIVE MATERIAL, with the only function of keeping together the composite electrode components (active material, conductive additive, etc)

composite electrode



- Active material
- binder
- conductive additive

Role and requirements:

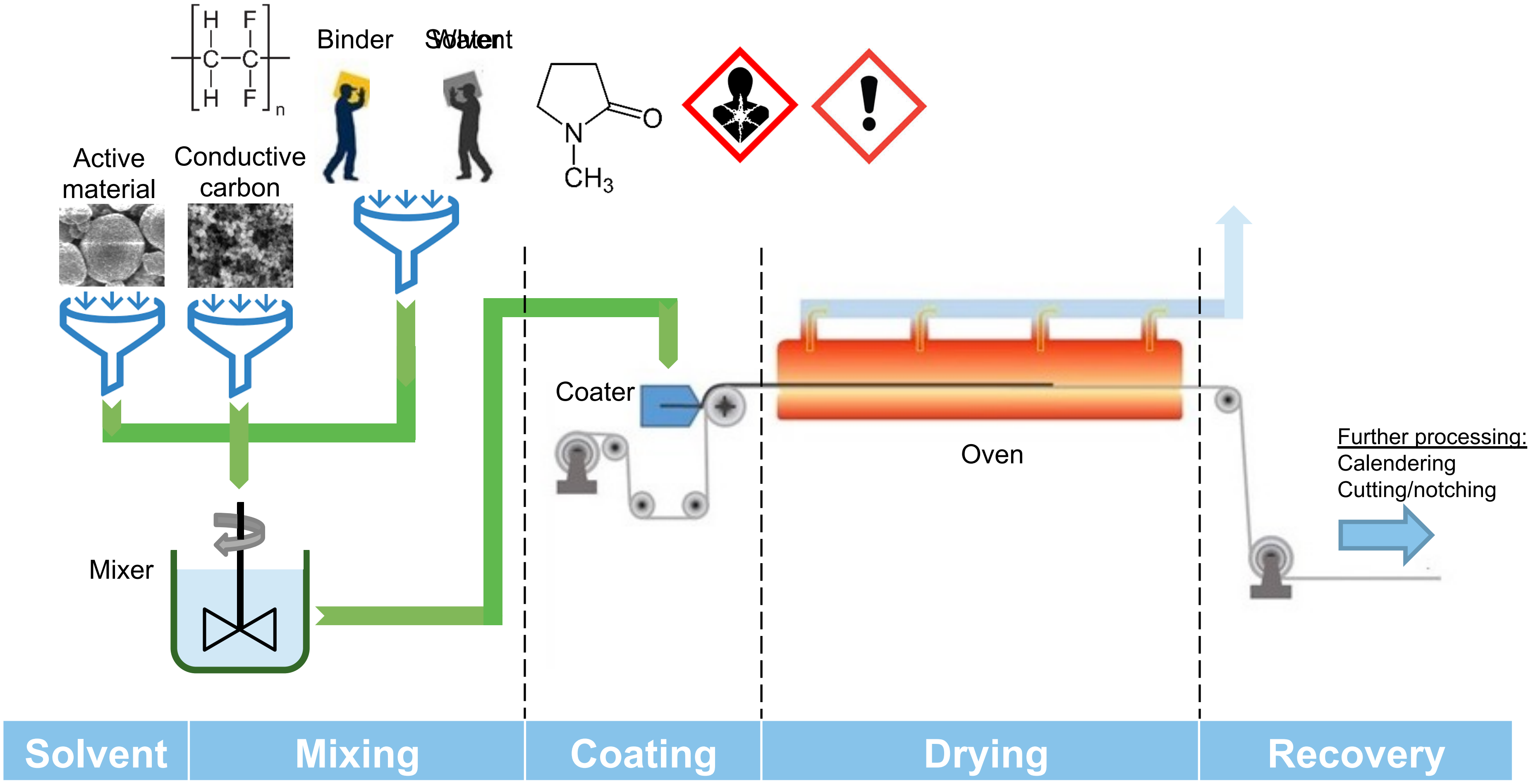
- Provides good adhesion to the current collector
- Does not affect electronic conductivity and porosity of the electrode
- (Electro)chemical stability at the working voltage

However:

- The binder has a huge impact on the environmental impact (and cost)

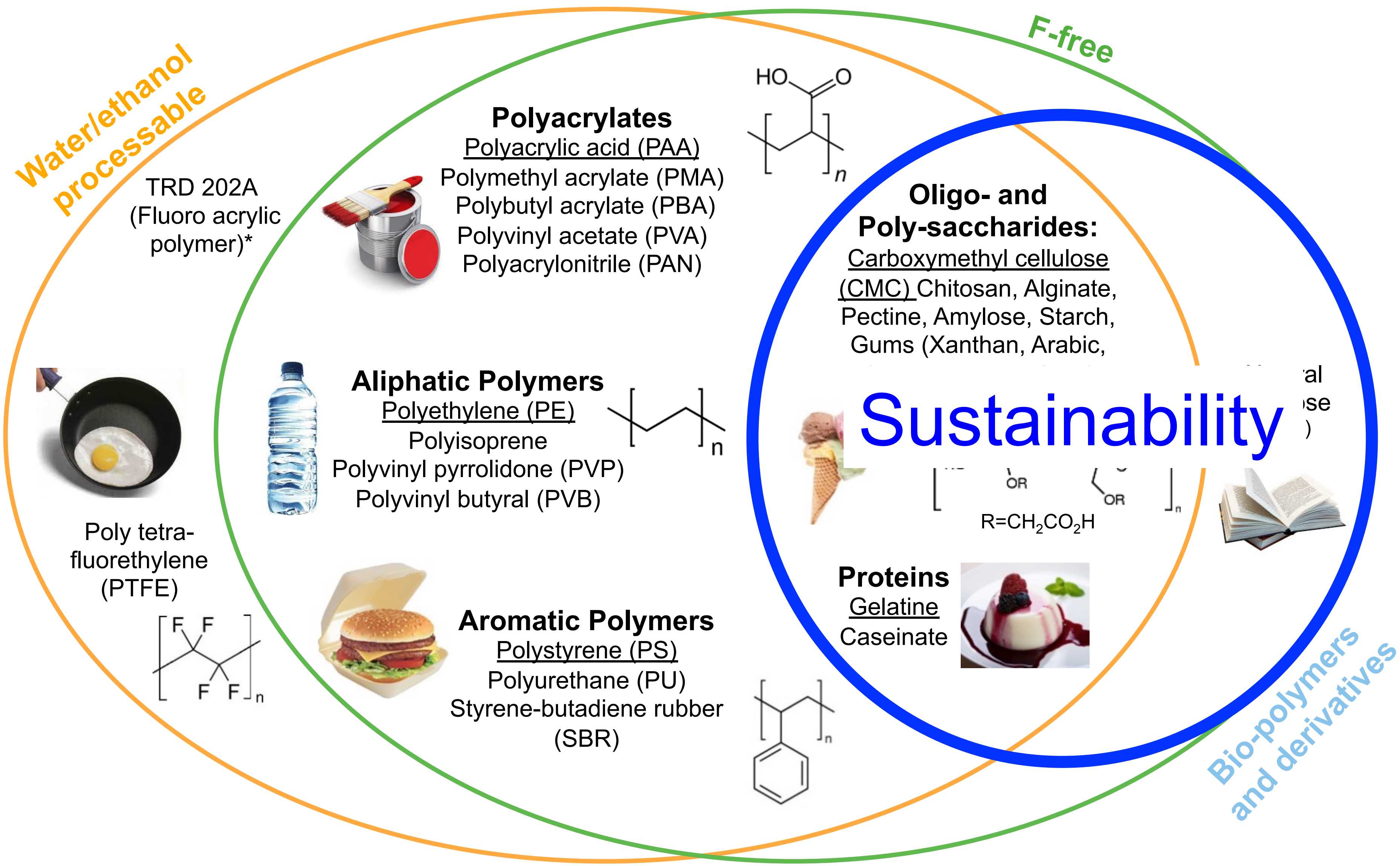
Determines the **solvent** required for processing and recycling!

Effect of solvent in processing



A. Moretti, D. Bresser, D. Buchholz, A. Varzi, S. Passerini, Energy and Envvironmental Science (2018) invited review

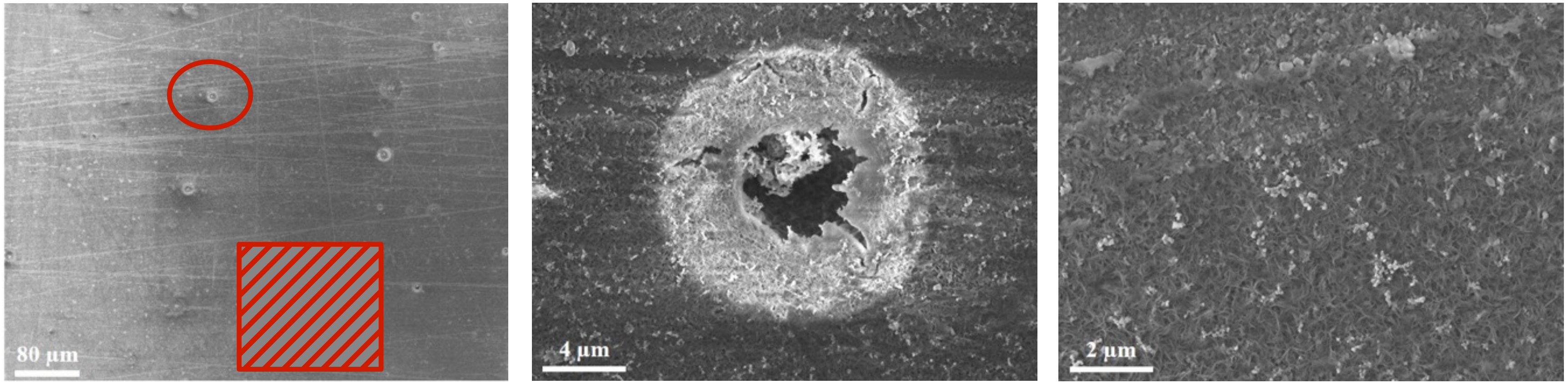
Alternative Binders



A. Varzi, A. Moretti, D. Bresser, D. Buchholz, S. Passerini, manuscript in preparation

Environmentally-Friendly Processes

Water-sensitivity of cathode materials (e.g., $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC))



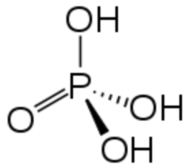
G. V. Zhuang et. al, *J. Power Sources* **2004**, *134*, 293, C. C. Li et. al, *J. Mater. Sci.* **2007**, *42*, 5773, N. Loeffler et. al, *J. Power Sources* **2014**, *248*, 915

Development of environmentally friendly electrode coating processes

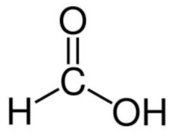
- Keep slurry's pH within aluminum passivation regime

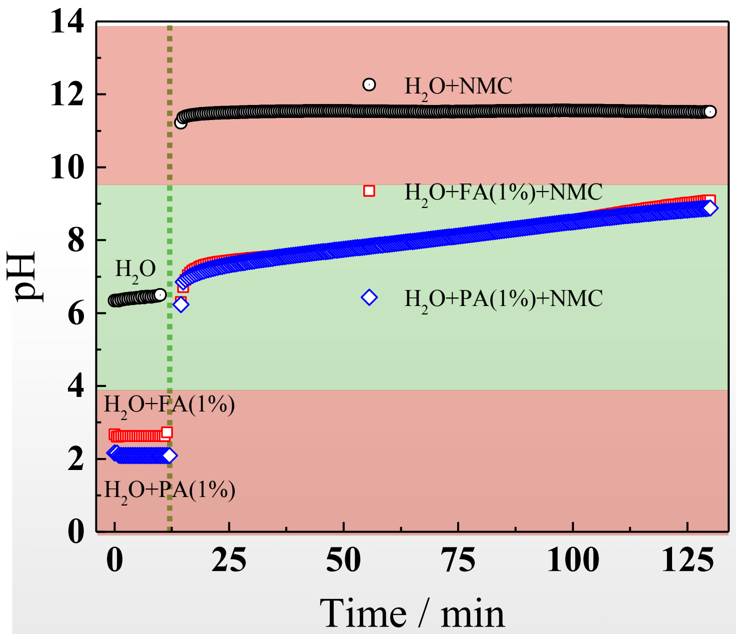
- Acids chosen in this work:

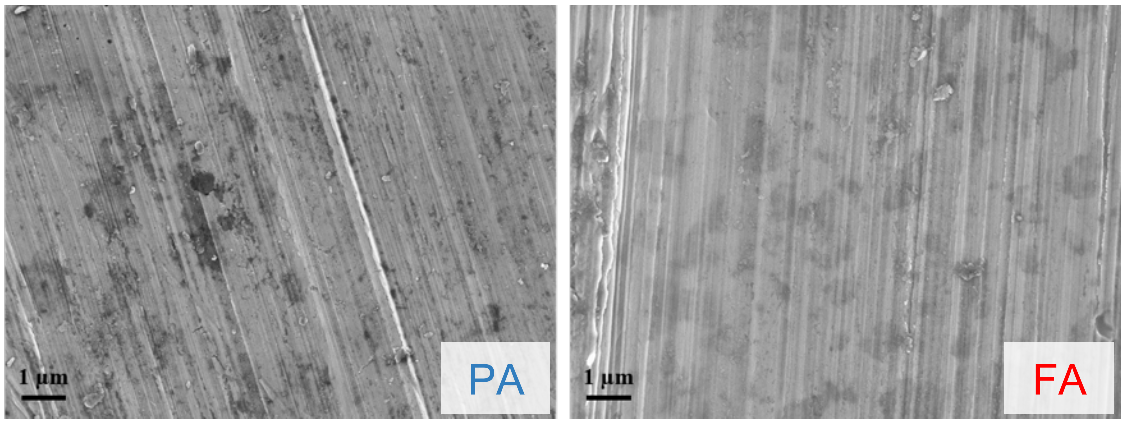
phosphoric acid (PA)



formic acid (FA)



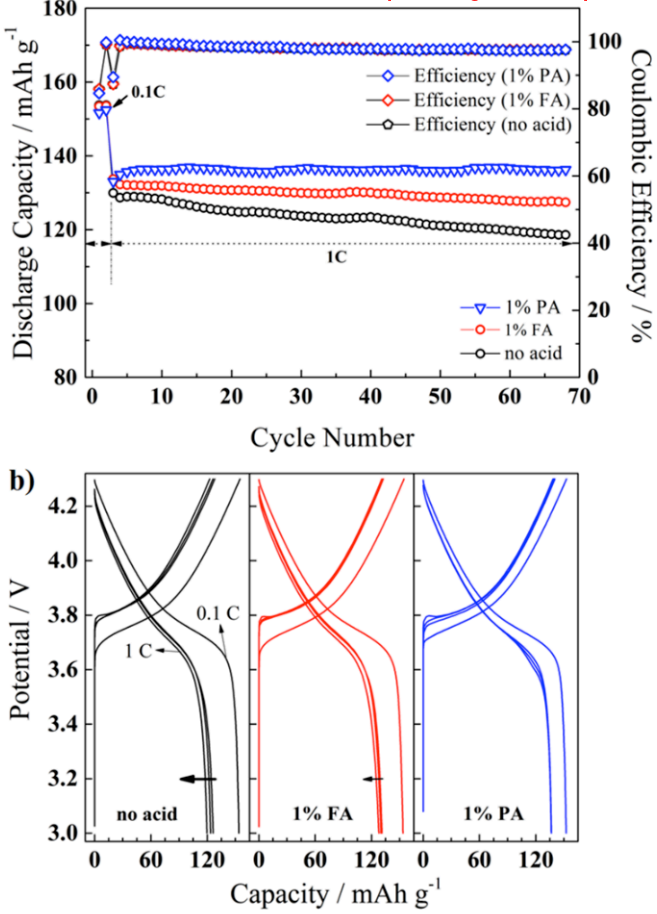




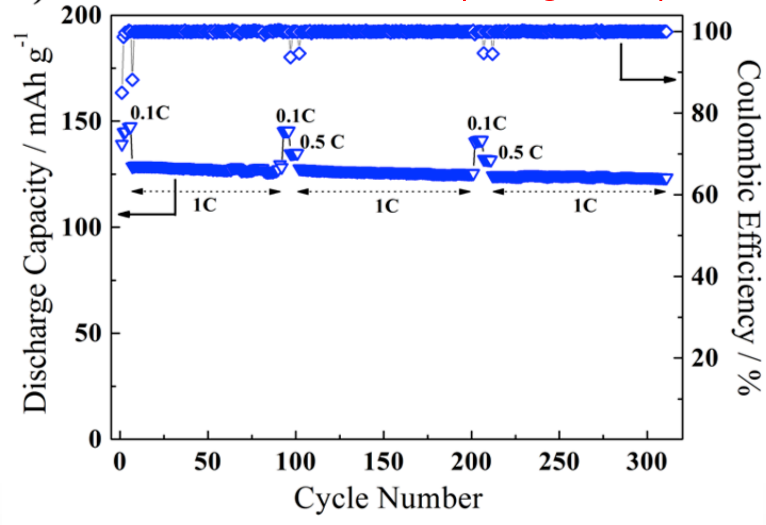
N. Loeffler et. al, *ChemSusChem* **2016**, *9*, DOI: 10.1002/cssc.201600353.

Addition of phosphoric acid during the electrode slurry preparation

Li / LP30 / NMC (8 mg cm^{-2})



C / LP30 / NMC (8 mg cm^{-2})



In-situ formed Me-phosphate coating:

- Long term cycling stability of NMC in half and full Li-ion cells
- Excellent capacity performance

N. Loeffler et al ChemSusChem 2016 (9) 1112-1117.

Aqueous Processing of High-Voltage (LNMO) Electrodes

Binder cross-linking → Stability

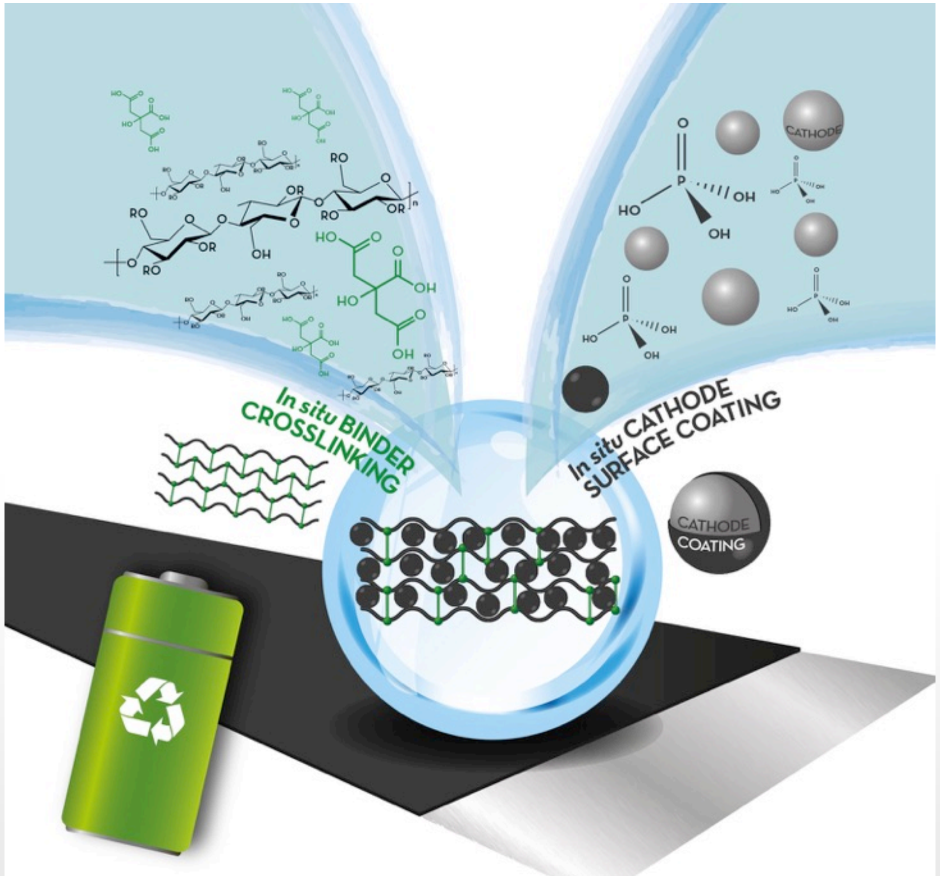
Performance ← Phosphate coating

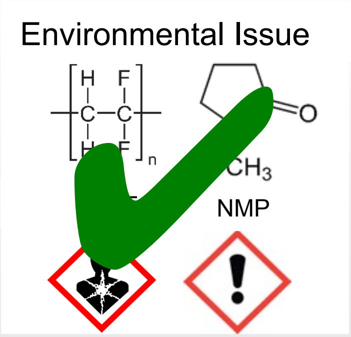
CMC

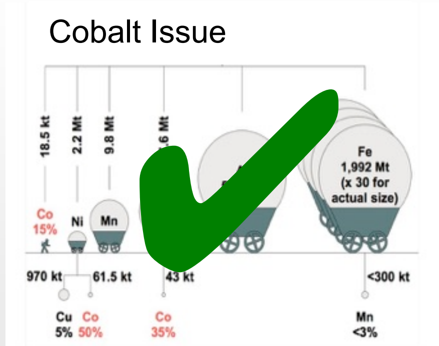
Citric acid

$LiNi_{0.5}Mn_{0.5}O_2$

H_3PO_4

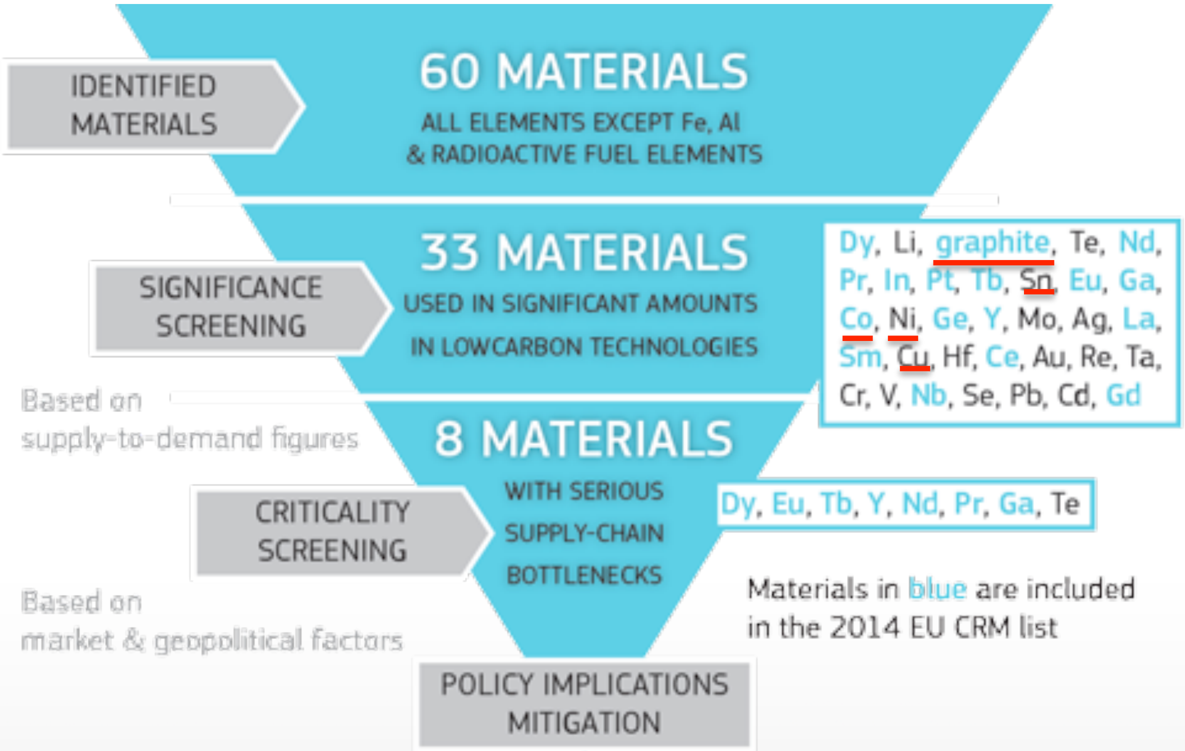






M. Kuenzel et al, ChemSusChem (2018) DOI: 10.1002/cssc.201702021.
EP-17-401-101.5 (**2017**), M. Kuenzel, **D. Bresser**, S. Passerini – Electrode material for lithium-ion batteries and method for preparing same.

Critical Raw Materials List (EU, 2014)



- Lithium
- Graphite
- Cobalt
- Nickel
- Copper

- **Sodium**
- **Hard C**
- **Manganese**
- **Iron**
- **Aluminium**

LIBs → SIBs

Criticality not only based on **abundance** but also **economic importance**, **easy replacement**

https://setis.ec.europa.eu/setis-magazine/materials-energy/critical-materials-energy-technologies-evangelos-tzimas-joint

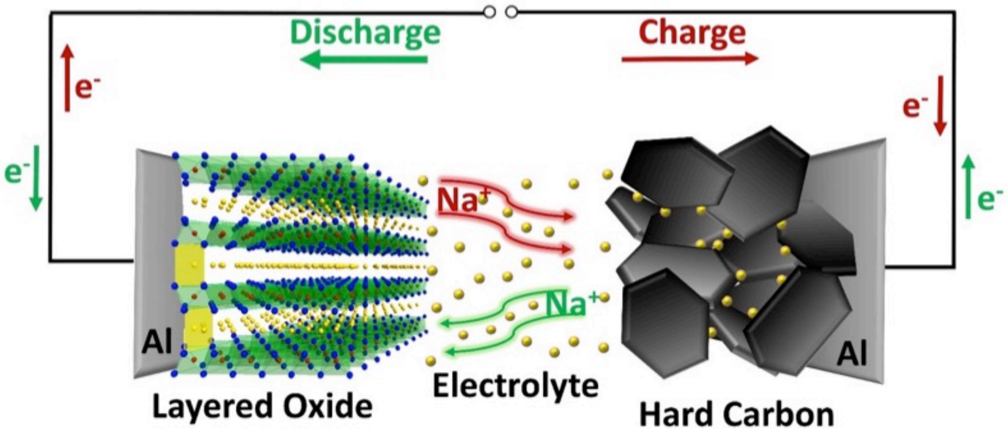
Na-ion batteries are a "drop-in" technology

Setup & working principle like LIBs

SIBs & LIBs: complementary

Large-scale energy storage systems

Electric vehicles



Characteristic	Lithium	Sodium
Crustal abundance (ppm)	20	23,600
Distribution (reserves)	70 % South America	Everywhere
Anode current collector	Cu	Al
Ionic radius (Å)	0.69	0.98
Molar mass (g mol^{-1})	6.94	22.99

SIB-philosophy:

- Low-cost & environmentally friendliness, - reduced dependence on critical materials

Keller, M.; Vaalma, C.; Buchholz, D.; Passerini, S. ChemElectroChem 2016, doi: DOI: 10.1002/celc.201600152.

Environmental Impact

Life cycle assessment for the production of a Na-Ion Battery

18650 cell, 128 Wh/kg

Layered $Na_{1.1}[Ni_{0.3}Mn_{0.5}Mg_{0.05}Ti_{0.05}]O_2$ – Hard Carbon (derived from sugar)

Three impact categories:

GWP = global warming potential
FDP = fossil depletion potential
MEP = marine eutrophication potential

Cathode production

Anode production

GWP: Emission of greenhouse gases like CO_2, CH_4, N_2O (measured in kg of CO_2 equivalents)

Lifetime is important

FDP: Depletion of fossil energy sources (measured in kg of oil equivalents)

MEP: Deposition of macronutrients in water (measured in kg of N- equivalents)

Peters, J.; Buchholz, D.; Passerini, S.; Weil, M. Energy Environ. Science, 2016, 9, 1744-1751.

Relative environmental impact per kWh over energy stored over lifetime

Lifetime based on existing LCA studies for better comparability

	GWP (in kg CO_2 eq.)		MEP (in kg N eq.)		FDP (in kg oil eq.)	
LFP-Graphite (3k)	48%		23%		38%	
LFP-LTO (14k)	13%		5%		13%	
LMO-Graphite (1k)	73%		44%		83%	
NCA-Graphite (2.2k)	38%		20%		39%	
Na-Ion (2k | 5k)	50%	20%	50%	20%	50%	20%

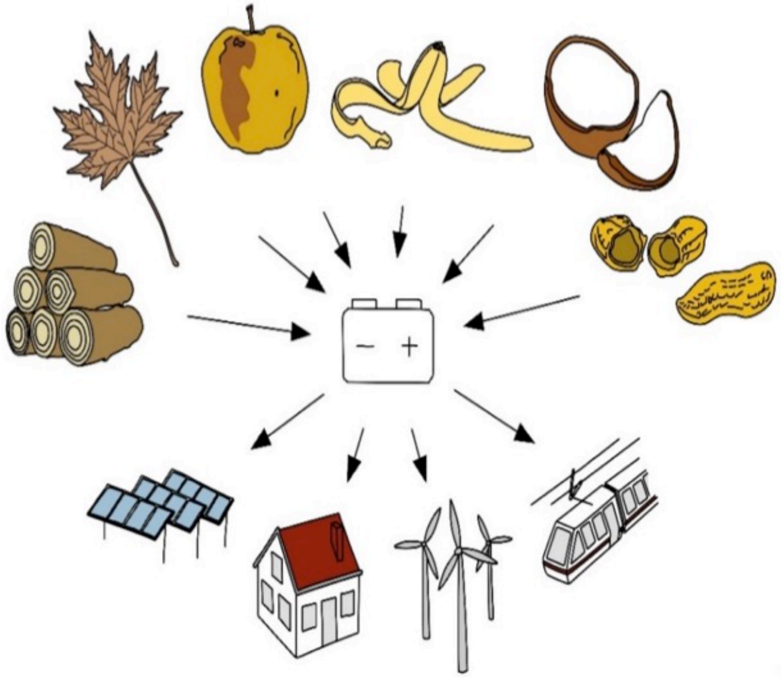
high

low

Battery lifetime fundamental for environmental impact (also for cost (€/kWh))
Use of bio-waste is a promising way to lower the environmental impact

Peters, J.; Buchholz, D.; Passerini, S.; Weil, M. Energy Environ. Science, 2016, 9, 1744-1751.

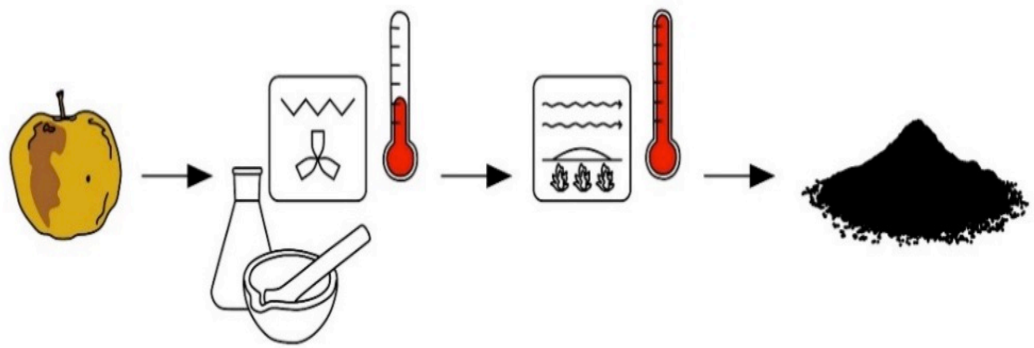
Why Bio-waste-Derived Hard Carbons?



Biowaste often can not be used:

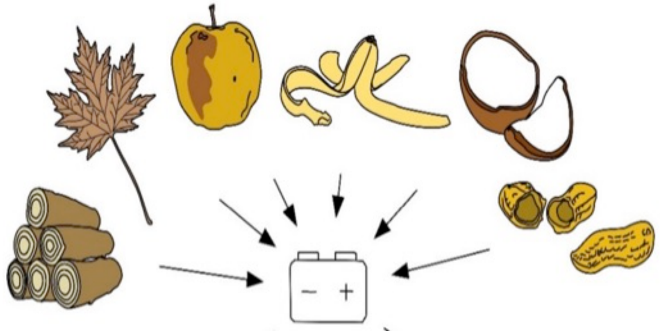
- Fermentation & low nutritional value (poor cattle food)
- High water content
- Often problematic/ inefficient biogas/ bioethanol generation

Biowaste is an abundant and cheap raw material

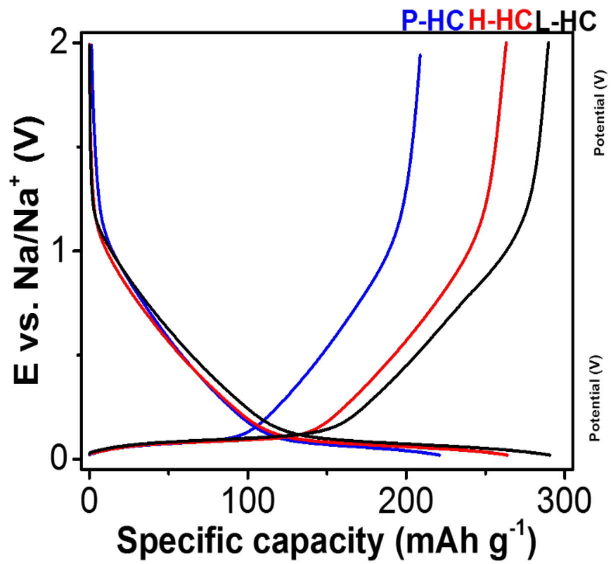


Peters, J.; Buchholz, D.; Passerini, S.; Weil, M. Energy Environ. Science, 2016, 9, 1744-1751.
Vaalma, C.; „Functional Materials with Apple Biowaste“, GIT Laboratory Journal;

Performance of Hard Carbons from different Bio-waste



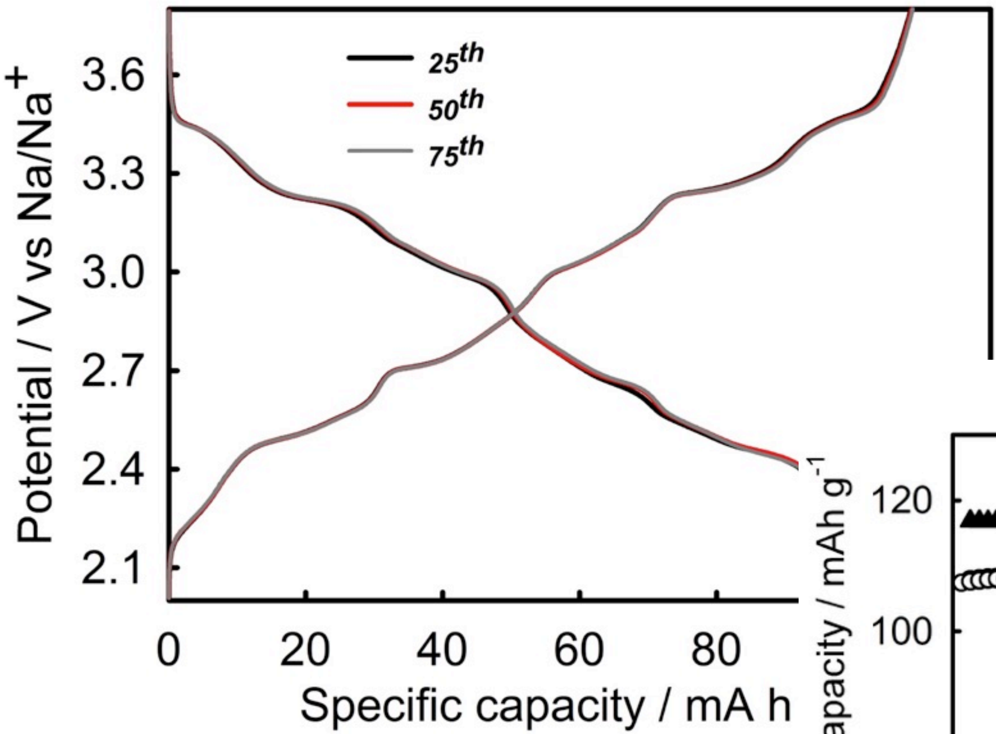
Target:
1.) Evaluation of the impact of biomass
2.) Design of powerful hard carbons (HC)



Classification of bio-waste from the main binder component

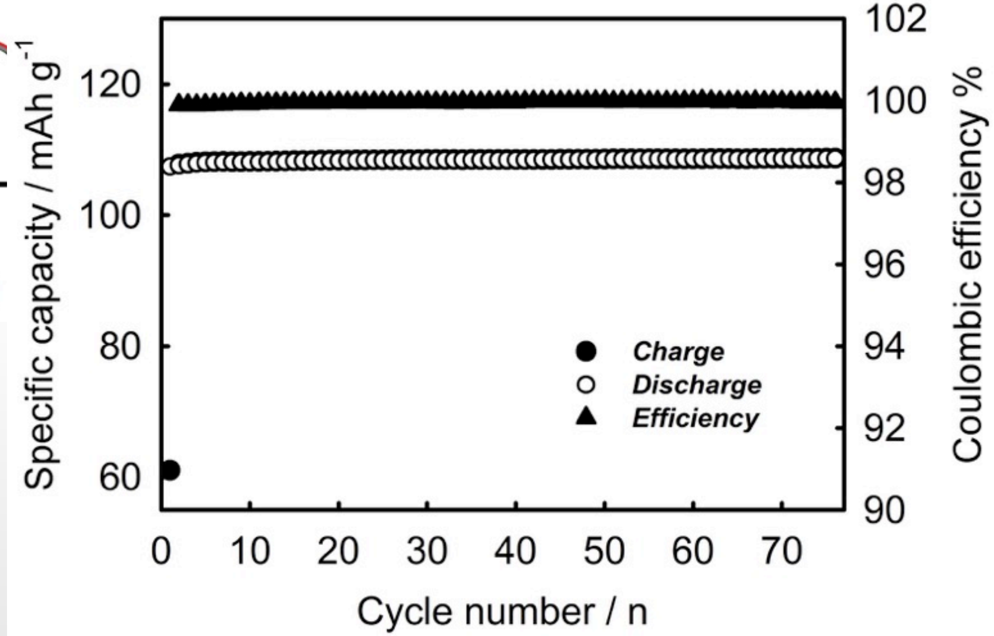
Hard carbon	Carbon source	Main binder component	Amount of main binder / %	Amount of cellulose (main component) / %
P-HC	**Apple**	Pectin	11.7 %	43.6%
H-HC	**Corn Cob**	Hemicellulose	35 %	45 %
L-HC	**Peanut Shell**	Lignin	27-40 %	34-45 %

Wu, L.; Vaalma, C.; Buchholz, D.; Giffin, G.; Passerini, S. ChemElectroChem (2015) doi: 10.1002/celc.201500437.
X. Dou, I. Hasa, M. Hekmatfar, T. Diemant, R. J. Behm, D. Buchholz, S. Passerini, ChemSusChem, 2017, doi: 10.1002/cssc.201700628.



HC (Corn Cobs)/ Na_xMnO_2

both electrodes are made with CMC as aqueous binder



Excellent cyclability
Acceptable capacity

Dall'Asta, V; Buchholz, D; Chagas, L; Dou, X; Ferrara, C; Quartarone, E; Tealdi, C; Passerini, S, ACS AM&I 2017, DOI: 10.1021/acsami.7b09464

Cars require SAFETY: general issue

NFPA Data

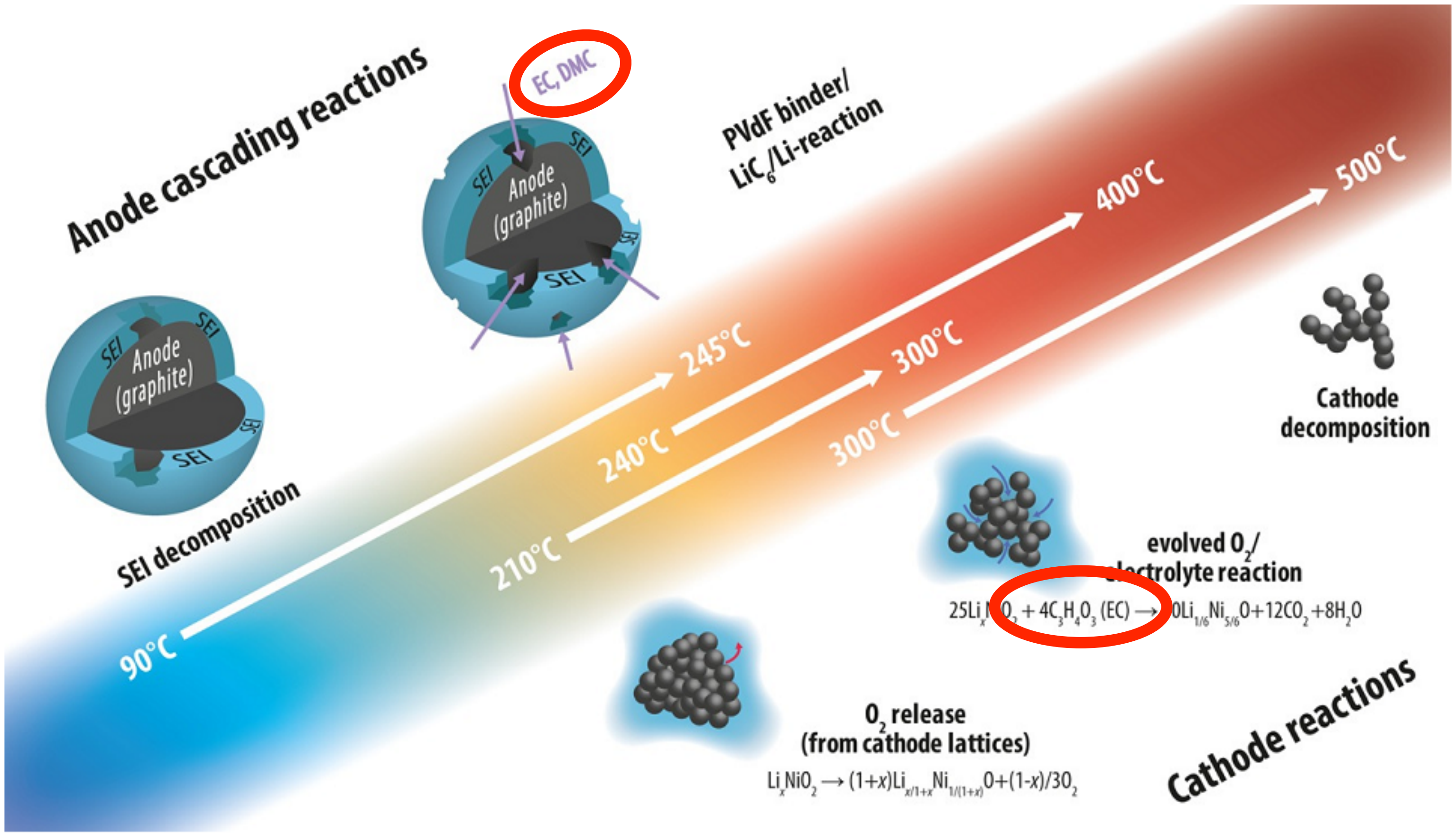
VEHICLES

In 2003-2007, U.S. fire departments responded to an average of 287,000 vehicle fires per year. These fires caused an estimated 480 civilian deaths, 1,525 civilian injuries and $1.3 billion in direct property damage annually.

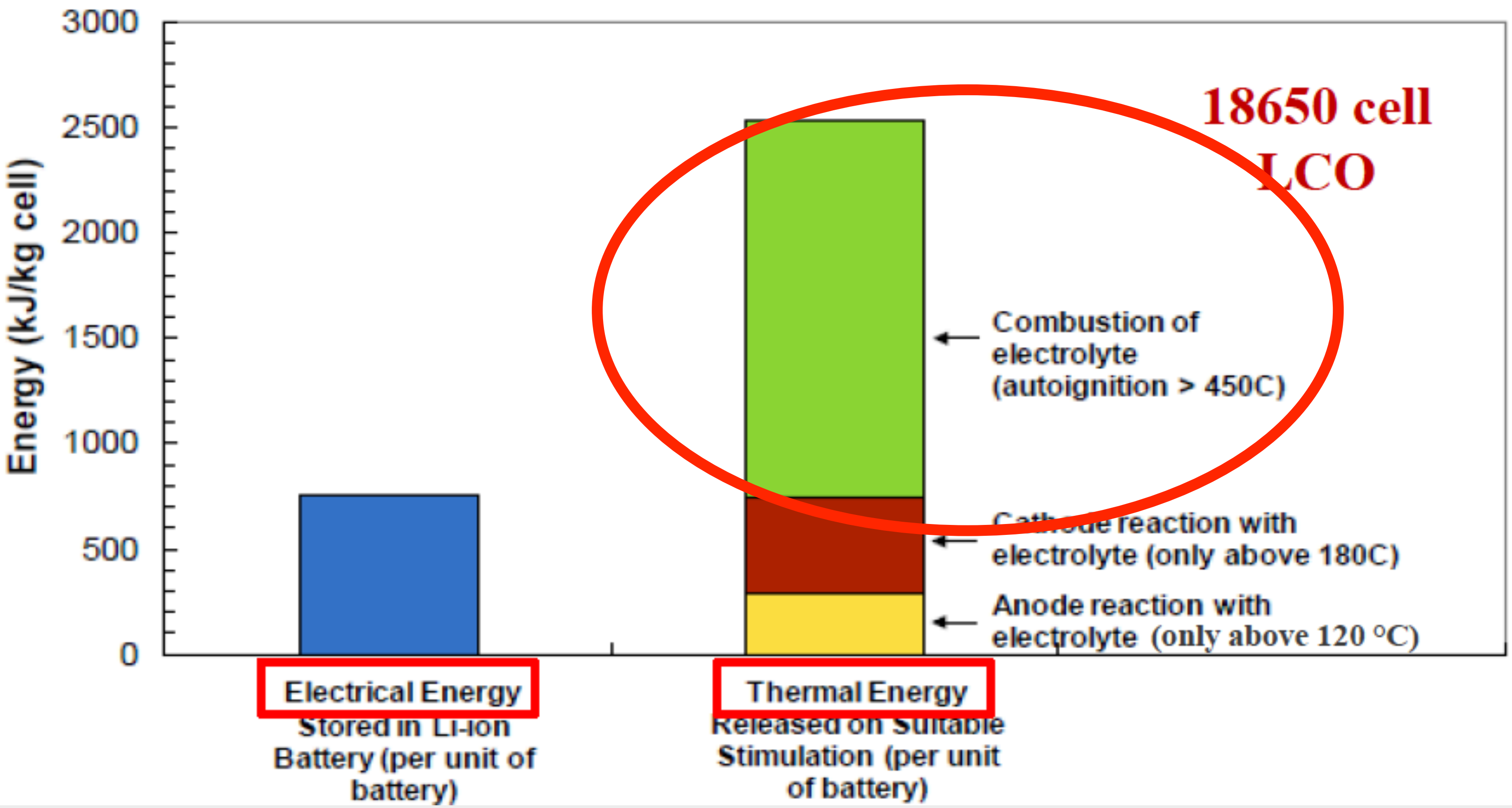
Every 2…3 minutes there is a ICE-car fire – USA

ca. 70 ICE-car fires per day in Germany

Safety Issue: LIB thermal runaway



J. Kalhoff, G.G. Eshetu, D. Bresser, S. Passerini *ChemSusChem* **8,** 2154–2175 (2015).
G. B. Appetecchi, M. Montanino, S. Passerini, in *Ionic Liquids: Science and Applications*, ACS Symposium Series., vol. 1117, p. 67–128, American Chemical Society (2012) http://dx.doi.org/10.1021/bk-2012-1117.ch004.

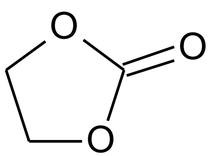

18650 cell
LCO
Energy (kJ/kg cell)
3000
2500
2000
1500
1000
500
0
Combustion of electrolyte (autoignition > 450C)
electrolyte (only above 180C)
Anode reaction with electrolyte (only above 120 °C)
Electrical Energy
Battery (per unit of battery)
Thermal Energy
Stimulation (per unit of battery)

Conventional Electrolytes

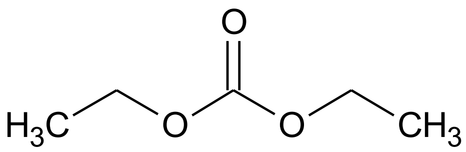
- ✓ High ionic conductivity
- BUT: High safety risk (high flammability and leakage issues)

Organic Solvents

Ethylene Carbonate (EC)

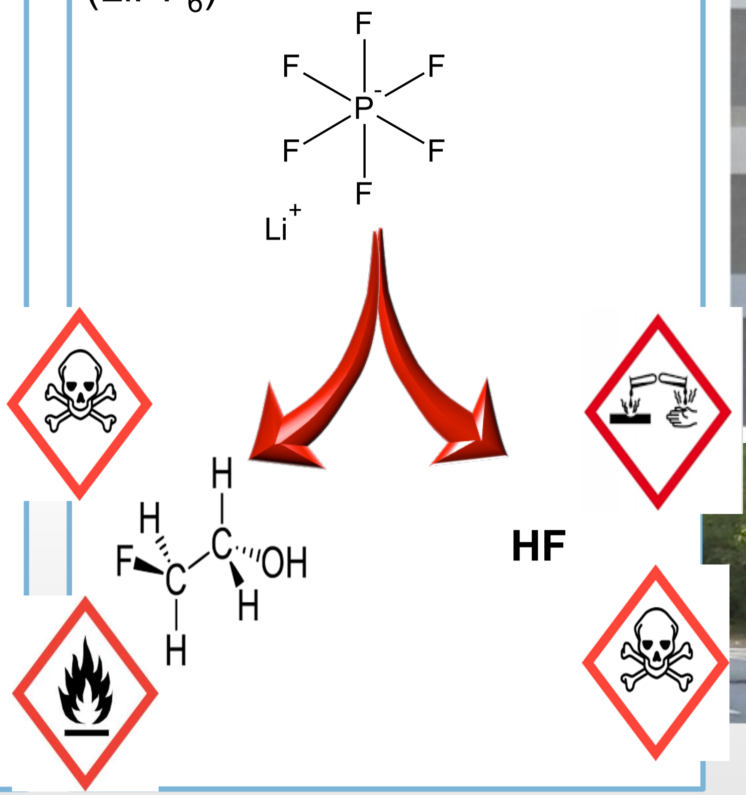


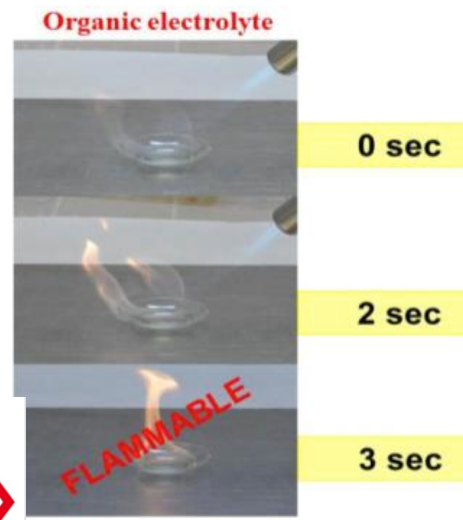
Dimethyl Carbonate (DMC)



Lithium Salts

Lithium hexafluorophosphate ($LiPF_6$)

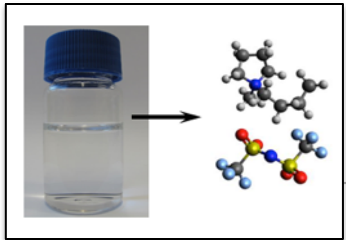




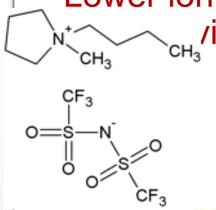
G. B. Appetecchi, M. Montanino, and S. Passerini, in *Ionic Liquids: Science and Applications*, ACS Symposium Series., vol. 1117, p. 67–128, American Chemical Society (2012)
https://arstechnica.com/cars/2016/08/tesla-model-s-france-battery-fire/

Alternative Electrolytes

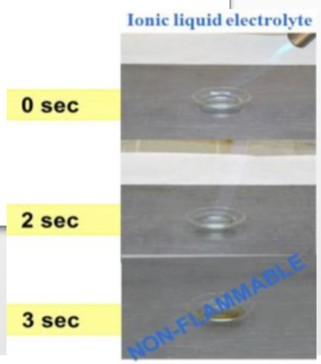
Ionic Liquids



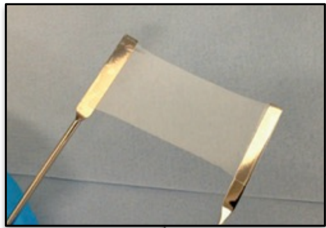
- Liquid at RT (‘molten salts’)
- Needs addition of Li-salt
- Low vapour pressure and low flammability
- Environmentally friendly
- Lower ionic conductivity



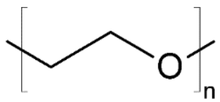
$Pyr_{14}TFSI$



Polymer Electrolytes



- Polymer, e.g. PEO
- Salt is coordinated
- Gelled with IL or conventional electrolytes
- Solid (safe)
- Easy to process
- Low cost
- Lower ionic conductivity
- Operation temperature above 60°C



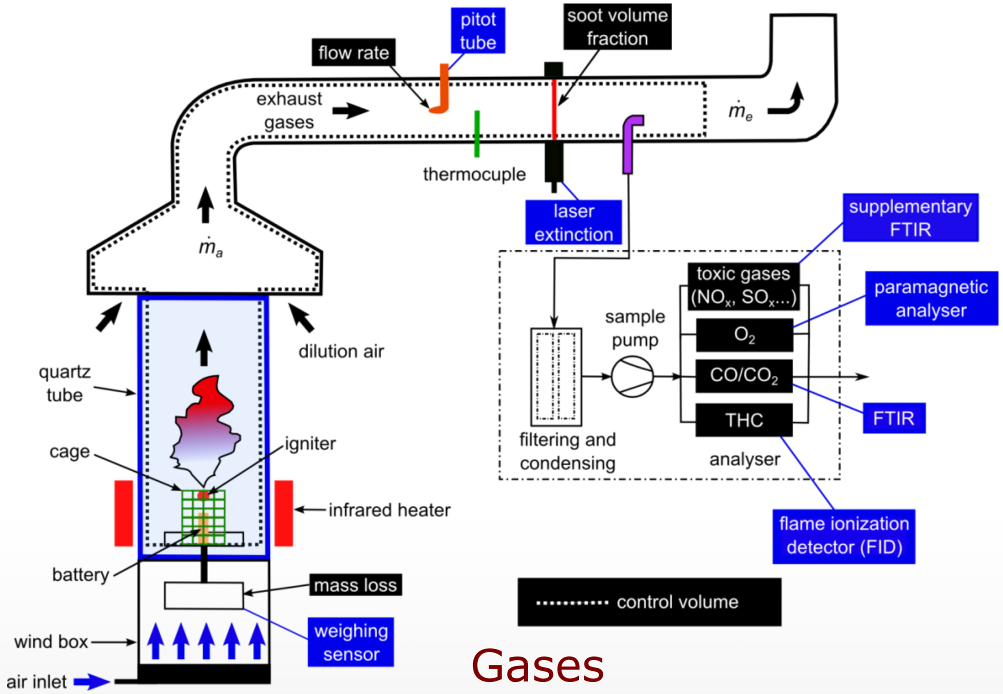
Inorganic Electrolytes

- Huge variety of chemistries
- $Li_7La_3Zr_2O_{12}$ (LLZO)
- Solid (safe)
- High ionic conductivity
- Single lithium ion conductors
- Higher cost
- Moisture/air sensitivity
- Processing difficulties (not commercialized)

Osada, I., de Vries, H., Scrosati, B. & Passerini, S. *Angew. Chem. Int. Ed.* **55,** 500–513 (2016).
G. B. Appetecchi, M. Montanino, and S. Passerini, in *Ionic Liquids: Science and Applications*, ACS Symposium Series., vol. 1117, p. 67–128, American Chemical Society (2012).

HIU Helmholtz Institute Ulm Electrochemical Energy Storage

Tewarson Apparatus



Gases detection

Thermal threats (Energetic parameters)

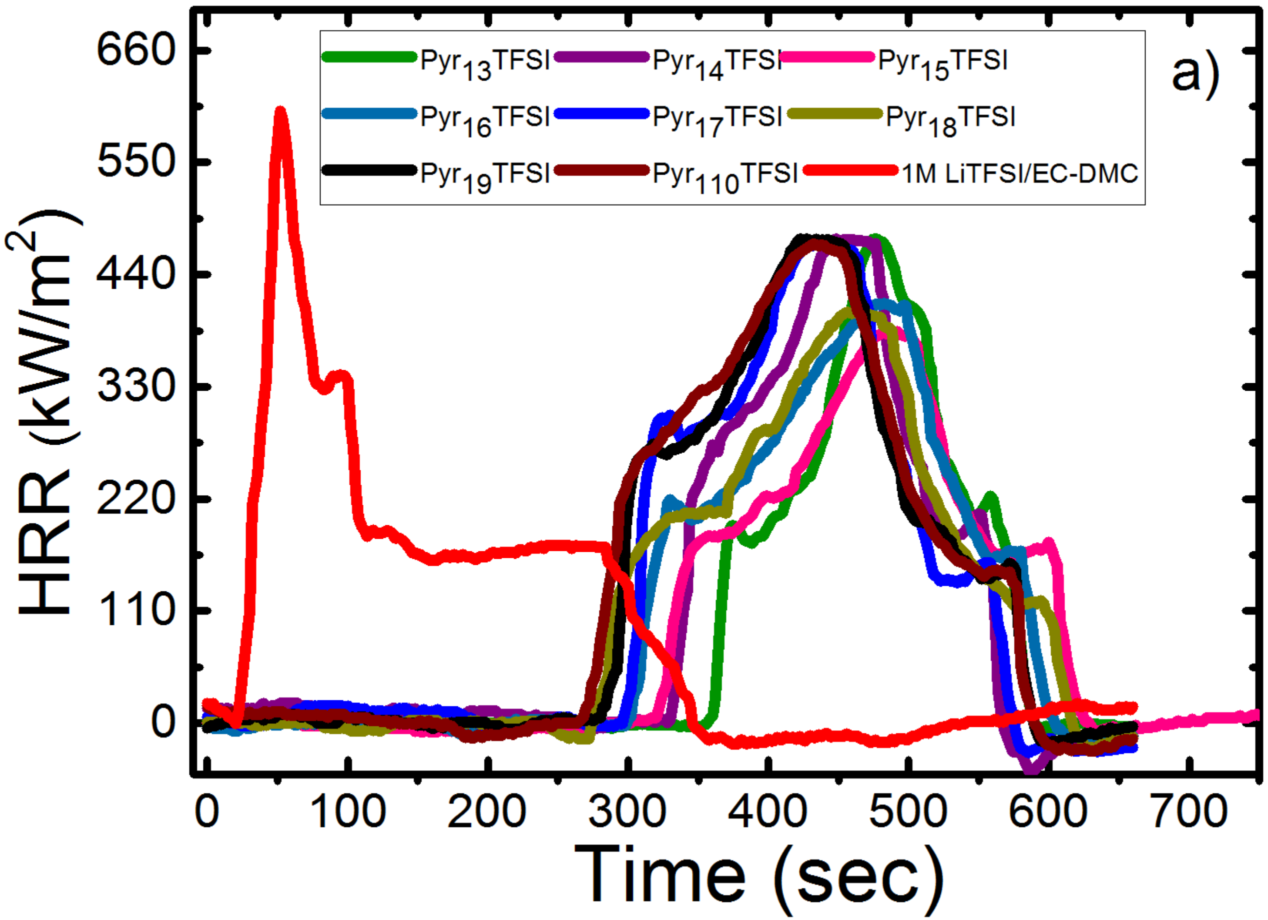
Chemical threats (Toxicity of gases)

Dr. Guy Marlair

INERIS maîtriser le risque pour un développement durable

Eshetu et al, ChemSusChem, 2017, DOI: 10.1002/cssc.201701006

Combustion behavior of electrolytes



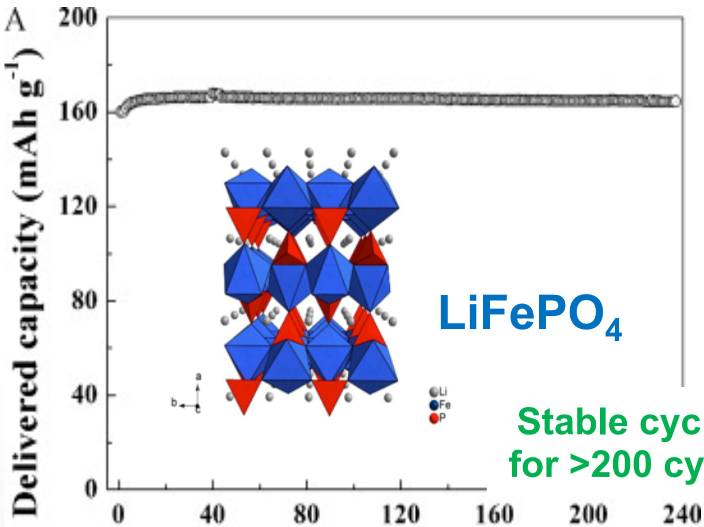
Ionic liquids and ionic liquid-based electrolytes have much longer ignition times than conventional electrolytes

Eshetu et al, ChemSusChem, 2017, DOI: 10.1002/cssc.201701006

Ionic liquid-based electrolytes for enhanced safety

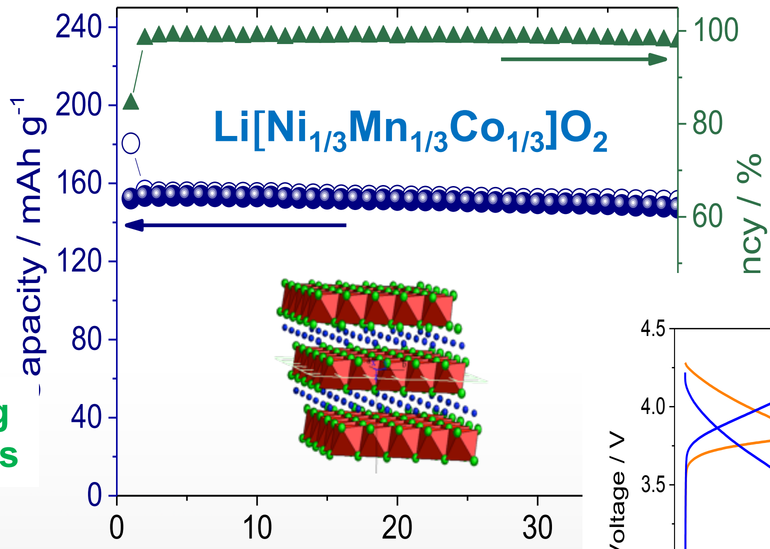
⟶ ILs as suitable electrolytes for *state-of-the-art* cathodes

$PYR_{14}FSI$-LiTFSI

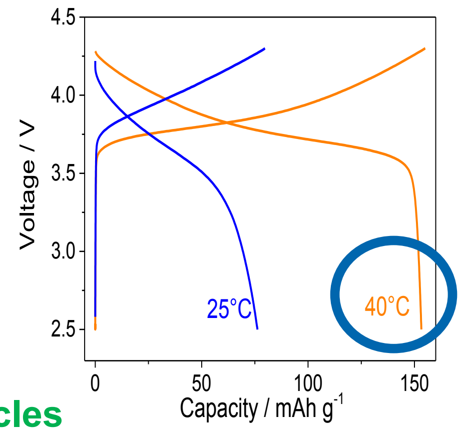


17 mA g^{-1}; 20 °C

$PYR_{14}TFSI$-LiTFSI



25 mA g^{-1}



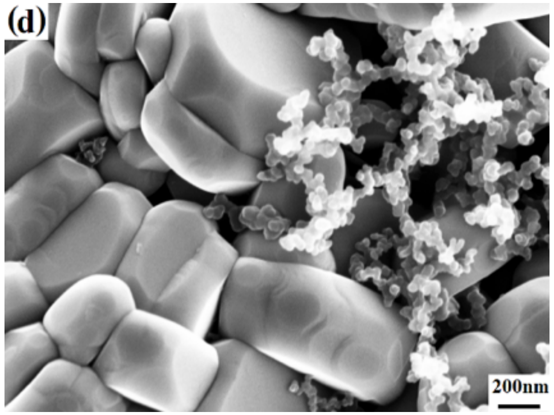
Importance of temperature, i.e., viscosity

Stable cycling for >40 cycles

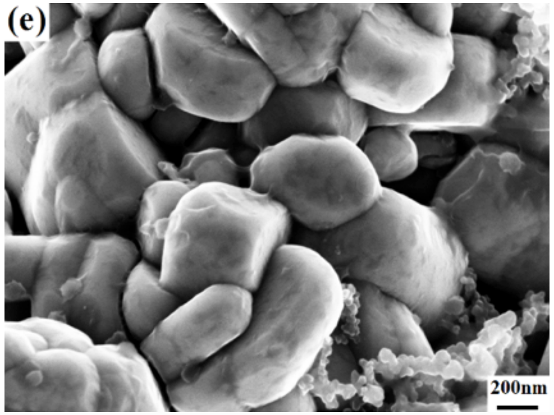
Kim et al., J. Power Sources 2011 (196) 2187-2194;
Molenda & Molenda, doi: 10.5772/21635.

ex situ SEM Analysis of NMC Electrodes

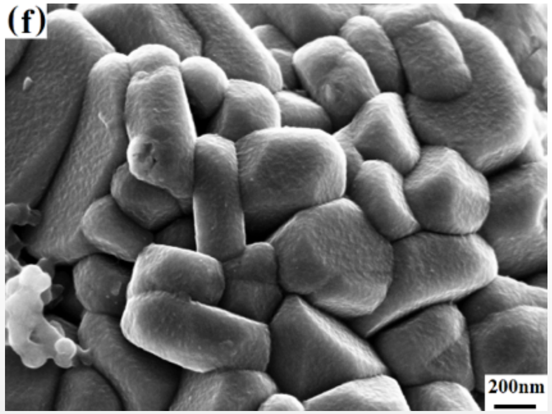
pristine



30 cycles in
organic electrolyte



30 cycles in
IL electrolyte

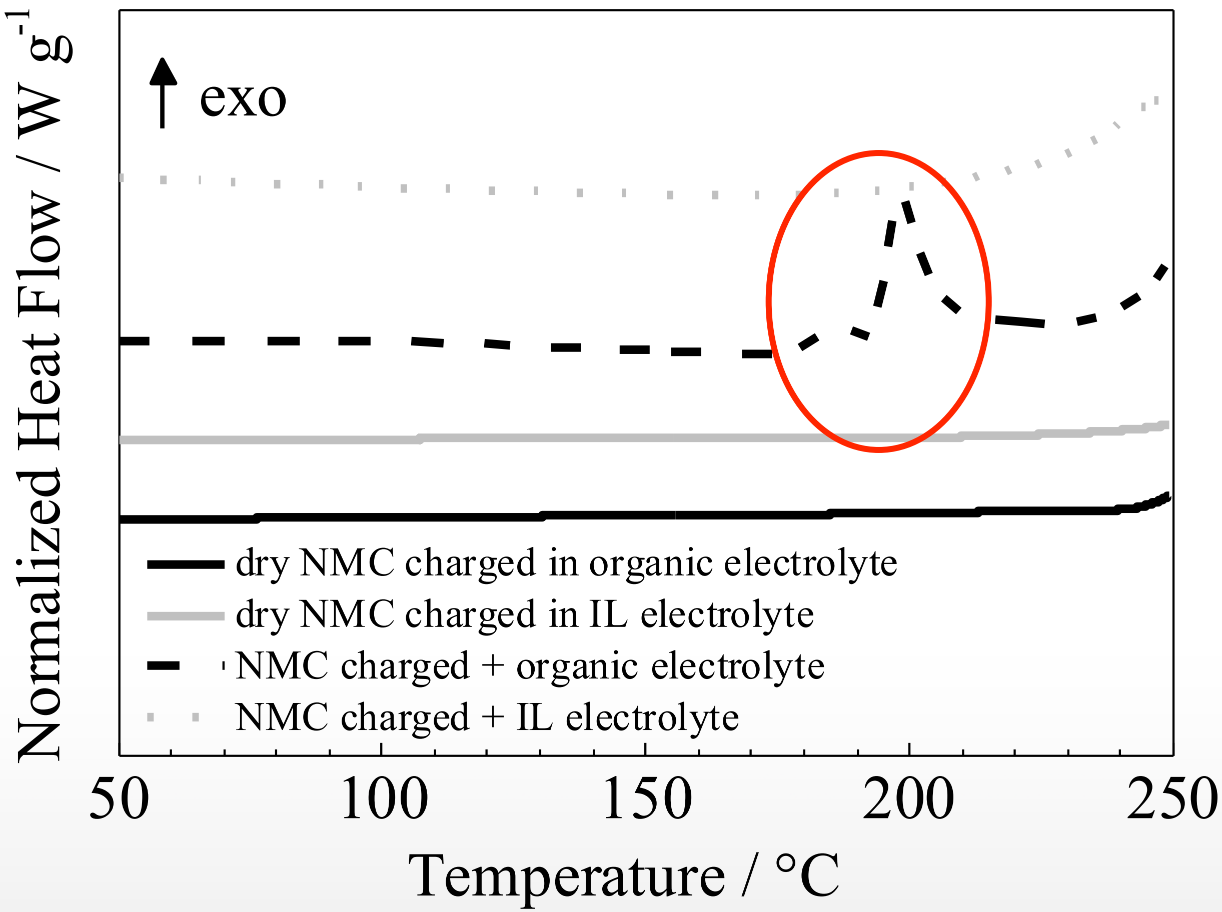


Partial surface coverage in conventional organic electrolyte (LP30)

Uniform surface film in **IL-based electrolyte** ($Pyr_{14}TFSI$ - 0.2 m LiTFSI)

Mueller, F. *et al.* ChemSusChem **2016**, DOI: 10.1002/cssc.201600296.

Ex situ DSC Analysis of NMC electrodes



Delithiated NMC
In organic electrolyte

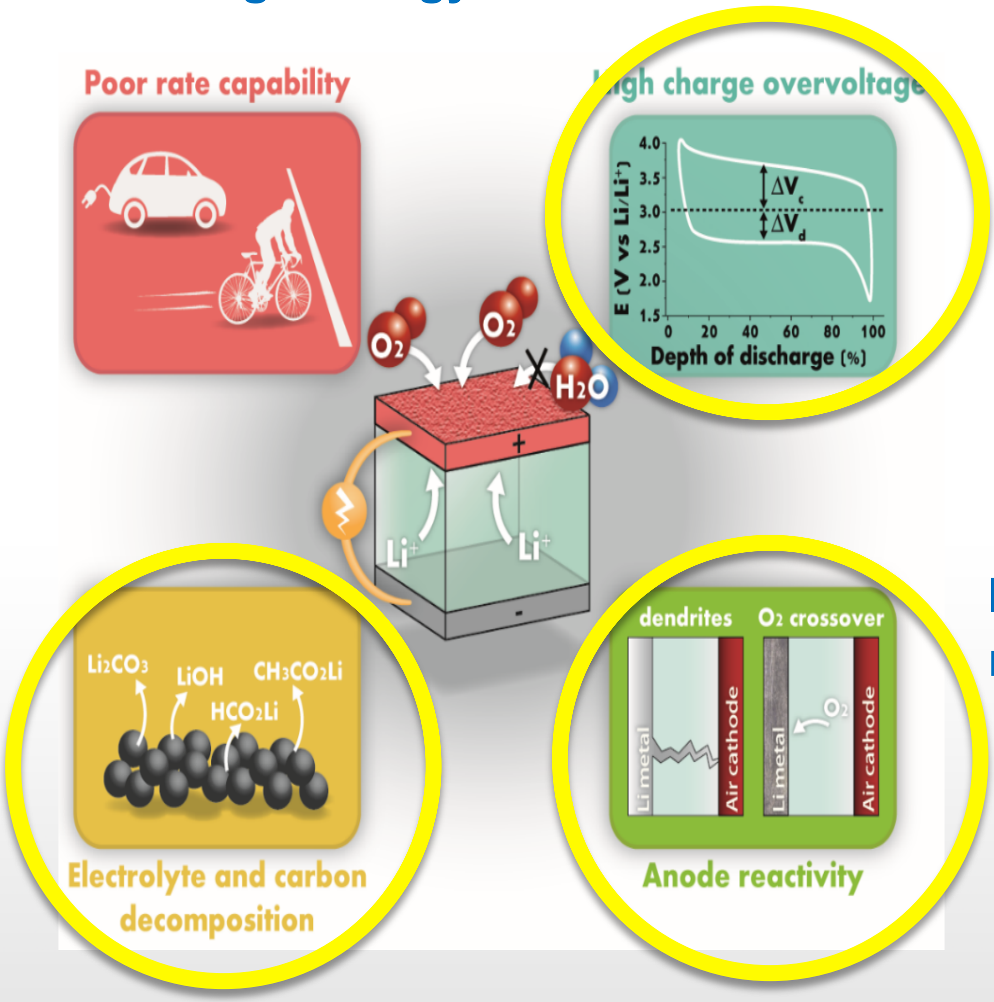
Exothermic reaction of delithiated NMC with electrolyte is absent in IL-based electrolyte

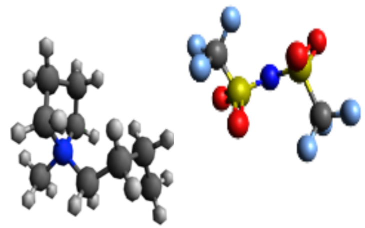
Mueller, F. *et al.* ChemSusChem **2016**, DOI: 10.1002/cssc.201600296.

Grande et al., Adv. Mater. 2015 (27) 784-800.

High energy cathodes

⟶ Oxygen-based high-energy cathodes and the main challenges





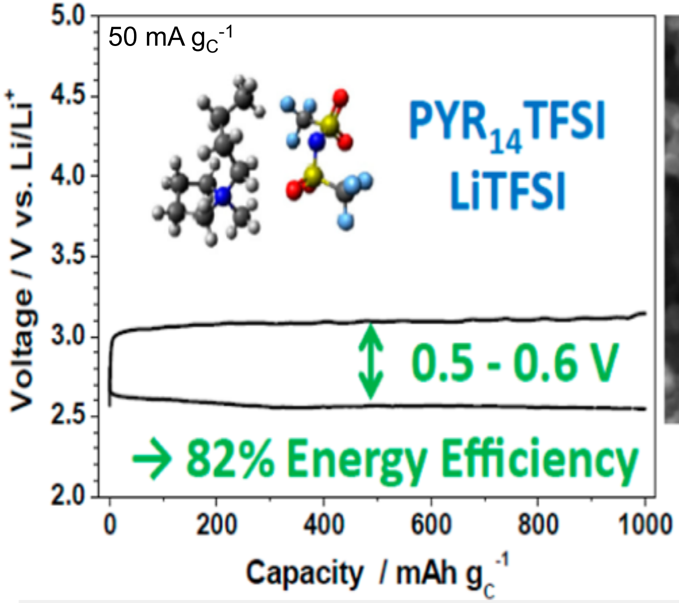
⤋

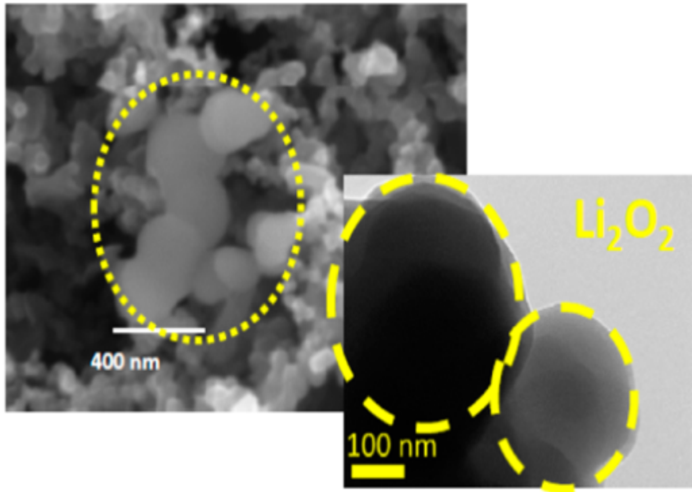
ILs may solve three main issues of Li/O_2 batteries

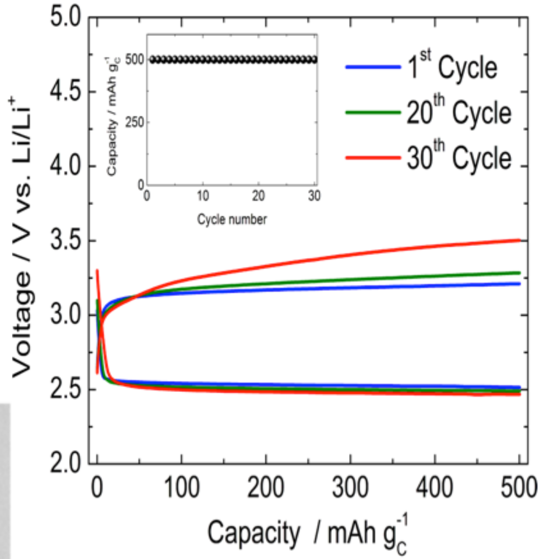
Elia et al., Nano Letters 2014 (14) 6572-6577.

High energy cathodes

→ O_2 / $PYR_{14}TFSI$-LiTFSI / Li





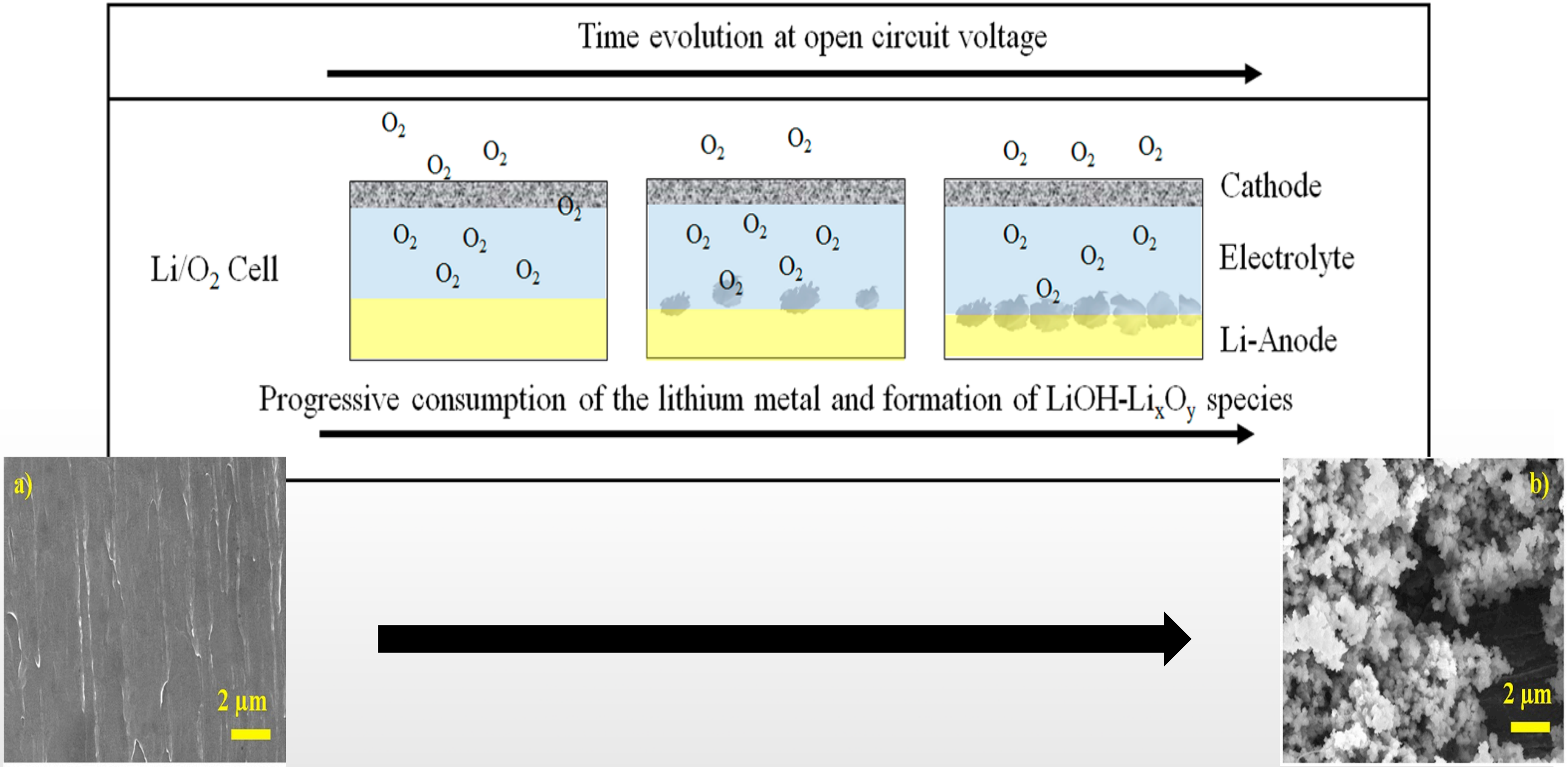


→ **stable cycling & low dis-/charge hysteresis, …**

but …

High energy cathodes

… the O_2 crossover remains an issue …



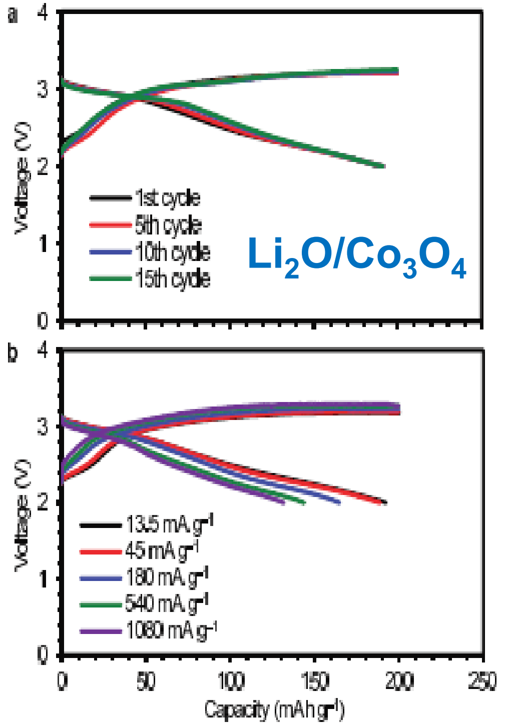
⟶ Potential alternative: Avoiding the presence of gaseous oxygen …

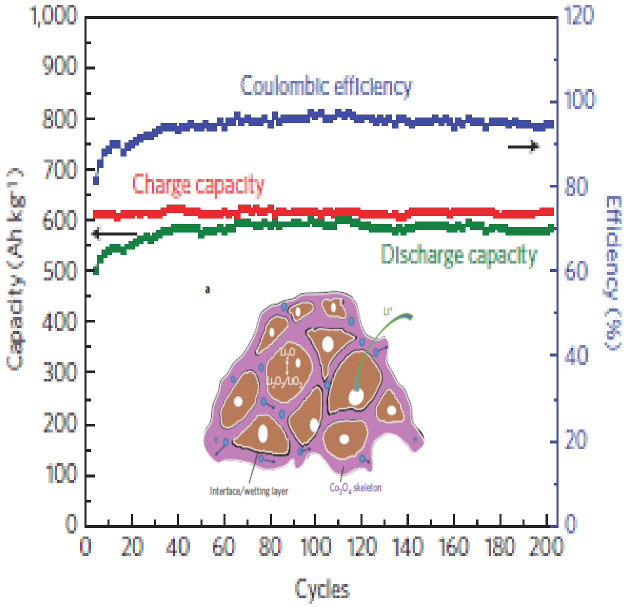
$Li_2O_2 + 2Li^+ + 2e^- \rightarrow 2Li_2O$

2.87 V; 897 mAh g-1

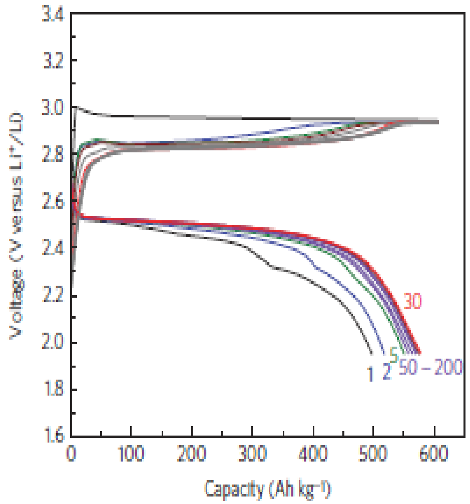
$LiO_2 + Li^+ + e^- \rightarrow Li_2O_2 + 2Li^+ + 2e^- \rightarrow Li_2O$

2.5-2.6 V; 2064 mAh g-1





⟶ 587 mAh g^{-1} @2.55 V



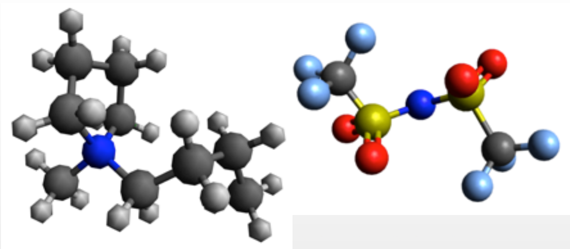
Mizuno and co-workers, Scientific Reports 2014, doi: 10.1038/srep05684
Zhu et al., Nature Energy 2016, doi: 10.1038(NENERGY.2016.111.

Recycling (Safety)

Water-based binders facilitate recycling of electrode materials

However, poor recyclability of the electrolyte is still a concern, mostly due to the poor stability of the active salt ($LiPF_6$ or $NaPF_6$) and solvent volatility

Solution: Switch to non-volatile solvents (IL) and chemical and thermally stable salts (imides, i.e., LiTFSI, LiFSI and LiFTFSI)

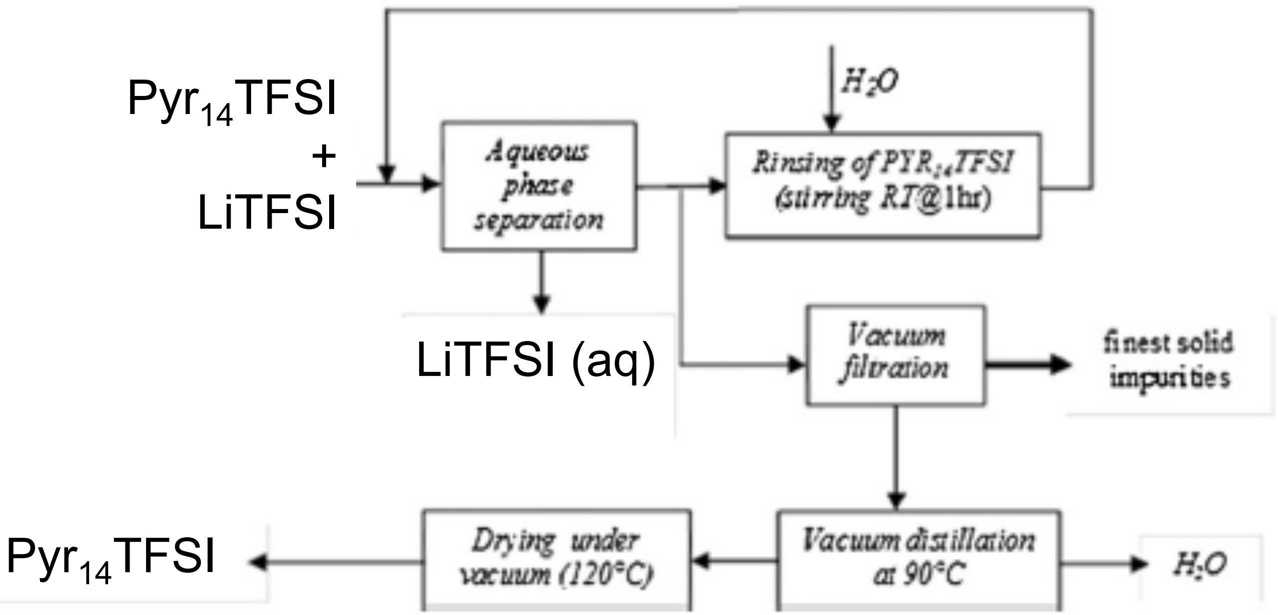


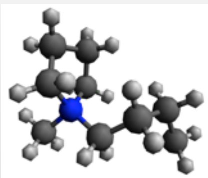
Ionic Liquid-based Electrolytes

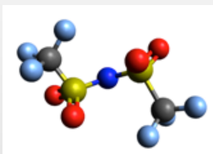
Good electrochemical stability
Non-volatile
Easy to recycle
(Environmentally-friendly)
…

Recycling of Ionic Liquid-based electrolytes

Ionic Liquids and Li-imide salts are easily recyclable through water-based processing







Appetecchi et al. Electrochim Acta 96 (2013) 124

HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

Sustainable Approaches for Batteries

Aqueous processing of Li-ion and Na-ion battery cathodes

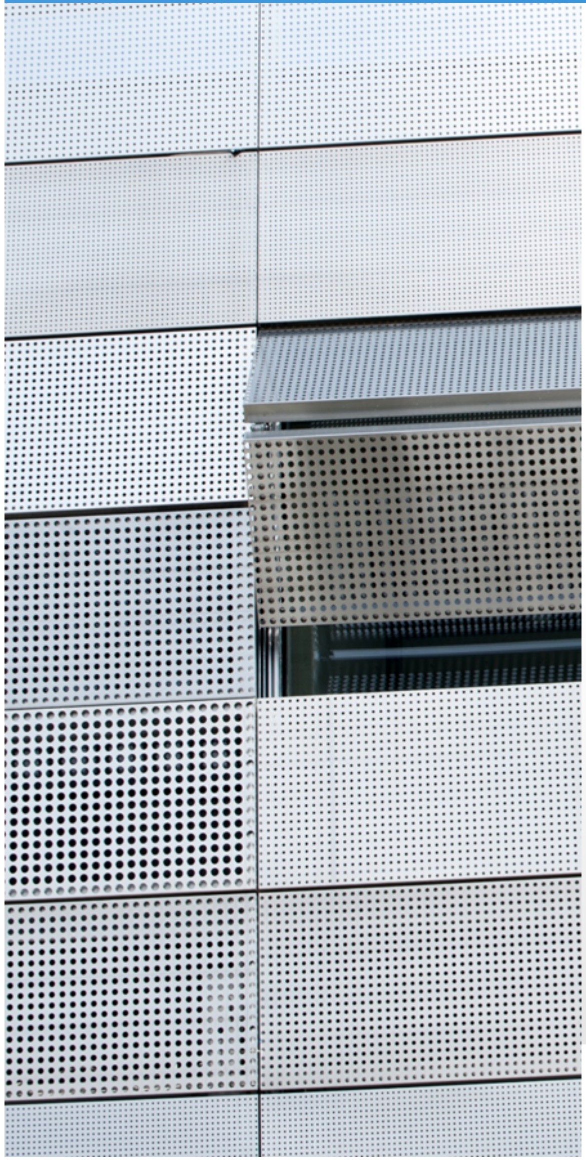
- Reduce pollution and cost
- Enhance stability of active materials upon cycling

Na-ion batteries

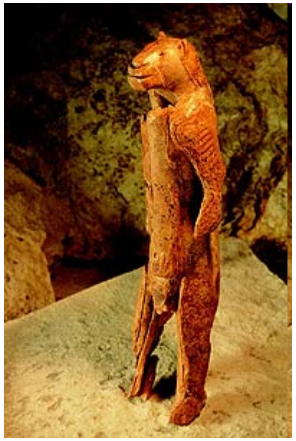
- SIBs are a complementary battery technology to LIBs
- Extremely promising anode materials from renewable sources
- Most promising candidates not identified; still rather unexplored field

High concentration LiX-IL electrolytes

- High Li^+ conductivity
- Li metal cells (including $Li\text{-}O_2$) with IL-based electrolyte show high capacity retention and coulombic efficiency

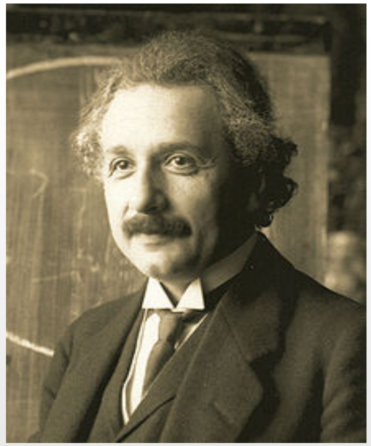


30.000 BC



161.4 m

1879 – 1955



www.hiu-batteries.de

Helmholtz Institute Ulm

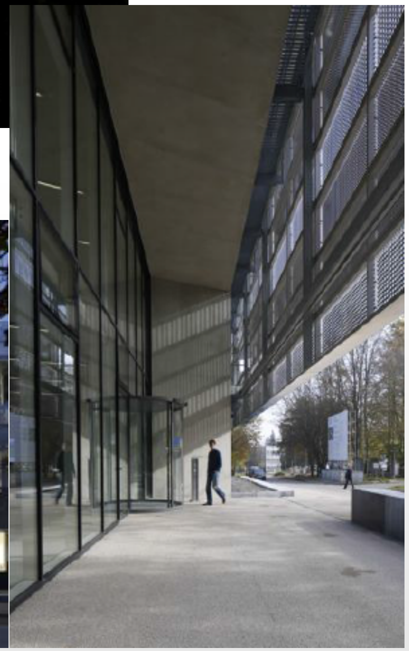
HIU
Helmholtz Institute Ulm
Electrochemical Energy Storage

KIT Karlsruher Institut für Technologie

Universität Ulm

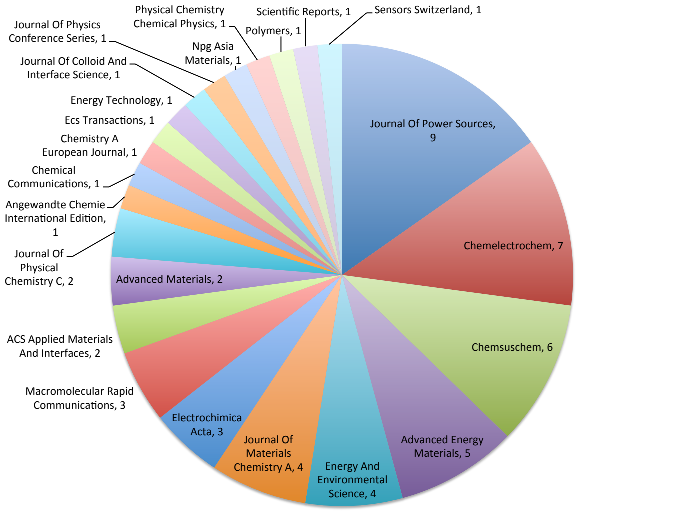
ZSW Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg

DLR Deutsches Zentrum für Luft- und Raumfahrt



Location:	Campus Ulm University
Labs & offices:	2.500 m^2
Staff:	about 110 employees inclunding 21 PIs
Inauguration:	31. October 2014

Research Group – Electrochemistry for Batteries



Peer-reviewed manuscripts 2016: 60

Battery Cyclers

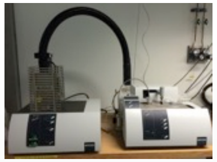
Potentiostats

+ access to SEM, TEM, XPS

XRD

DSC

& TGA



Glove Boxes

Dry Room

Group: 39 staff members

4 Group Leaders

5 Post-Docs

16 PhD students

9 Master & Bachelor students

➔ From about 10 countries (Germany, Iran, China, Italy, Brazil, Korea…)