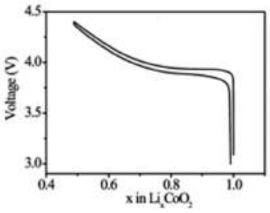
Structures of positive electrode materials

Lamelar structure
$LiCoO_2$



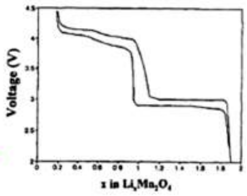
high cycling stability (>1200 cycles) and cycle life (2-3 years)

@ 130°C $Li_{0.5}CoO_2 \rightarrow 0.5LiCoO_2 + 1/6\ Co_3O_4 + 1/6O_2$

@ 190°C $Li_{0.5}CoO_2 + 0.1C_3H_4O_3\ (EC) \rightarrow 0.5LiCoO_2 + 0.5CoO + 0.3CO_2 + 0.2H_2O$

cell phones, laptops and digital cameras

Spinel structure 3D
$LiMn_2O_4$

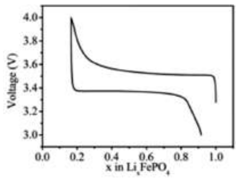


high rate capability fast charging and high-current discharging

capacity lower than that for lamelar oxides

power tools, medical instruments, hybrid and electric vehicles

Olivine structure 3D
$LiFePO_4$



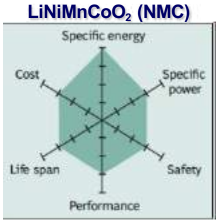
high safety and stability due to P-O covalent bond

poor electrical conductivity

transportations - hybrid and electric vehicles, bikes

Other positive electrode materials

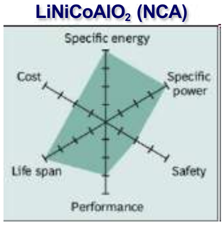
$LiNiMnCoO_2$ (NMC)



- High specific energy or high specific power,
- Low self-heating rate.

Applications: Power tools and power trains for vehicles.

$LiNiCoAlO_2$ (NCA)



- High specific energy and power densities,
- Long life span.

Applications: Automotive industry.

NMC – combination of nickel and manganese
Ni - high specific energy but low stability
Mn - formation a spinel structure → **low internal resistance but low specific energy**

Combining the metals brings out the best in each

Commercial positive electrodes

«Sony Energy» - 2009 commercialization
new long life LiB battery using olivine-type lithium iron phosphate as the cathode material

- Rapid charging: 99% charge completed in 30 minutes
- Power density: 1800W/kg (20A continuous discharge)
- Energy density: 95Wh/kg
- Long-life: more than 80% capacity retention after 2,000 charge-discharge cycles




ParisTech
INSTITUT DES SCIENCES ET TECHNOLOGIES
PARIS INSTITUTE OF TECHNOLOGY

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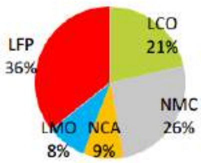
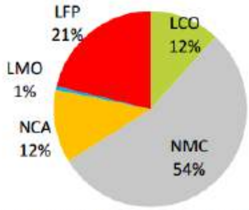
Commercial cathode materials

Cathode active materials in 2016
> 210 000 Tons



Cathode active materials in 2025
540 000 Tons



Assumption: Tesla keep NCA chemistry and have a relative success (+250 000 EV sold per year in 2025 – TESLA forecast 500 000)

Source Avicenne 2017

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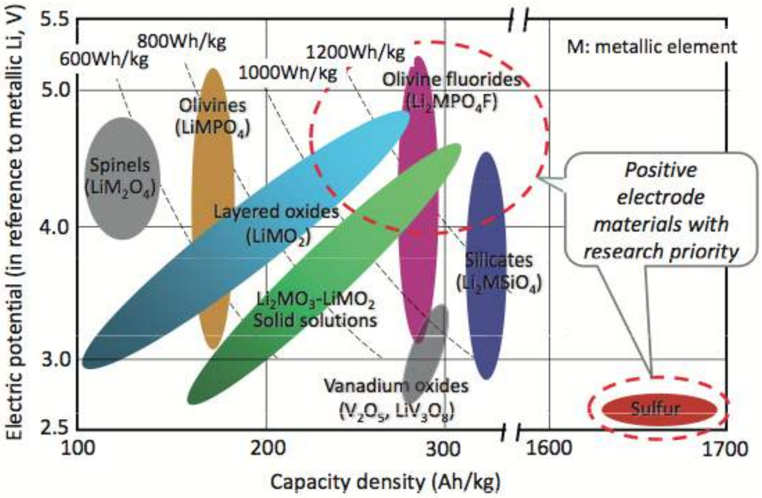
Research priority on positive electrode materials



Look and say what are the positive electrode materials with research priorities?
Why do you think that it is interesting to develop them?

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First batteries for EV – XIX, XX

1884, UK

First electric carriage
Thomas Parker

1899, Belgique

« La Jamais Contente » 100% electric, Pb-battery driven by Camille Jenatzy, 100 km/h, 1,5 tons (50% battery)

1907-1915, USA

Roadster with Edison Ni-Fe in series « New Edison Storage Batteries »

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Hybrid Electric Vehicles - HEV

1997, Toyota Prius
Battery Ni-MH, 170 km/h
1,3 tons (40 kg battery)

2012, Toyota Prius Plug-In Hybrid
Battery LiB 8,8 kWh
Autonomy 50 km (up to 135 km/h)

1997 – 2000….

Many companies starts productions of HEV: Honda EV Plus, G.M. EV1, Ford Ranger pickup EV, Nissan Altra EV, Chevy S-10 EV et Toyota RAV4 EV.

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Electric Vehicles

Plug-in vehicle with rechargeable battery only:

- Driving range limited by battery size – industry norm for range ~ 100 miles
  - – Tesla is exception, offering longer range
- Nominal recharge time of ~8 hours (fully depleted battery)

Nissan Leaf
Battery Electric Vehicle

- Battery : 24-30 kWh 360 V lithium-ion
- 200-250 km advertised range
- Charging: 20 hours at 120V, 12A 8 hours at 240V, 15A 30 min at 400V

2009, Pininfarina, Bolloré

- Batteries lithium metal polymer, 130 km/h,
- Power 50 kW, autonomy 250 km
- Acceleration 0 to 60 km/h in 6"3 s

Tesla Model S (2015)

- Battery Li-ion 450 kg,
- Power 215 kW, 60-85 kWh,
- Autonomy 370-480 km
- Acceleration 0 to 100 km/h in 3 s, 212 km/h max

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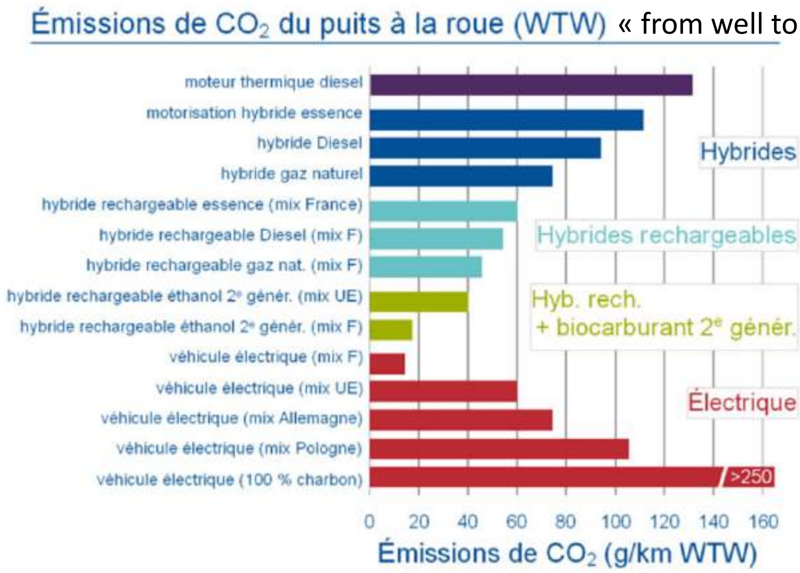
Carbon balance of electric vehicle



« from well to wheel » – WTW

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Other electric mobility

Hover board
LiB~**150 Wh**

Electric scooter
LiB ($LiFePO_4$) 12V, 12Ah, **144 Wh**
400W, 150 x 95 x 98, 1.9 kg

City electric bike, Emotion RS26
LiB 24V, 10Ah, **240 Wh**
Max speed with assistance : 25 km/h
Autonomy: 40 km

Yamaha EC-03
LiB 3 kWh, 4 kW
40-100 km at 30 km/h on flat road

Bluebus Bolloré
3 battery LMP® (LITHIUM METAL POLYMER) – all solid battery
« 3 batteries »: **90 kWh**, autonomy of 120 km, max 50 km/h, charge time 8 h

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Electric aviation

E-Fan, small electric plane (100% electric made in France)

https://mrmondialisation.org/le-fan-lavion-100-electrique-made-in-france/

Alice developed by Israeli firm Eviation

E-Fan X hybrid-electric flight demonstrator developed by Airbus, Siemens and Rolls-Royce

Shift to electric could significantly reduce operating costs, while eliminating greenhouse gas emissions

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LCA –life cycle assessment

LCA: Life-cycle assessment (LCA, also known as life-cycle analysis, ecobalance, and cradle-to-grave analysis)
Aim: LCA Study identifies opportunities for reducing impacts (from BATTERY SUPPLIERS, BATTERY MANUFACTURES and BATTERY RECYCLERS) of current and emerging LiB systems for different applications

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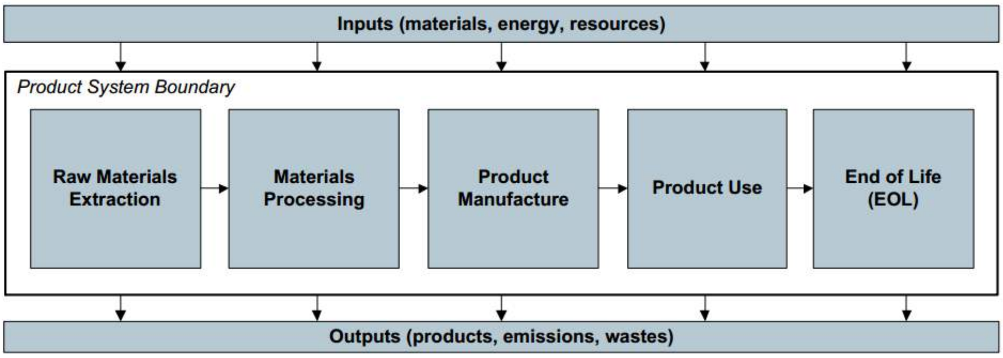
Life-Cycle Stages of the Product System



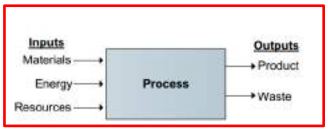
Activities related to the acquisition of natural resources, including mining non-renewable material, harvesting biomass, and transporting raw materials to processing facilities.

Processing natural resources by reaction, separation, purification, and alteration steps in preparation for the manufacturing stage; and transporting processed materials to product manufacturing facilities.

Manufacture of components of battery cells and battery packs.

Use of batteries in vehicles (PHEVs and EVs).

Recovery of the batteries at the end of their useful life.



Life-cycle inventory (LCI) for each process

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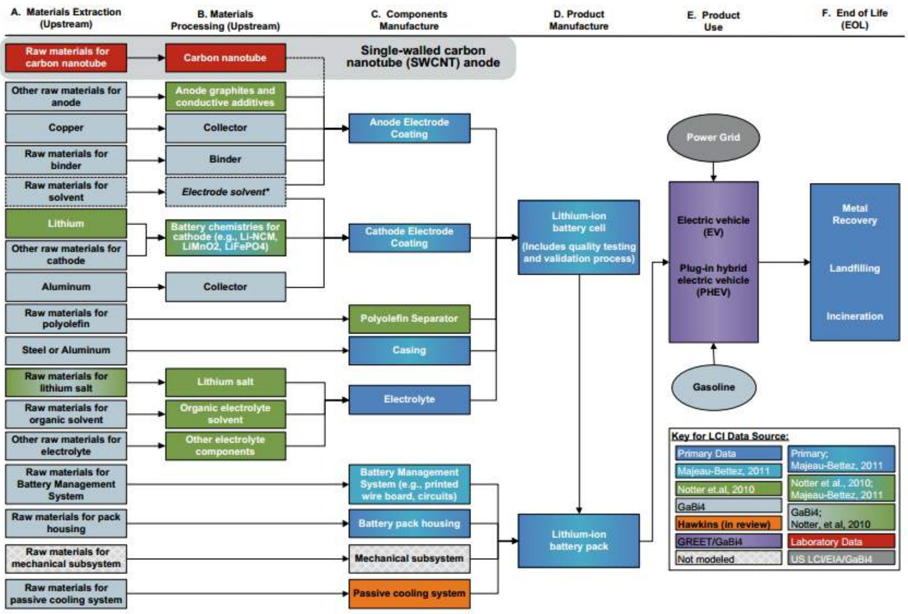
Generic Process Flow Diagram for LiB for Vehicles

CATHODE:
3 battery chemistries:
LiMnO2
Li-NCM
LiFePO4

ANODE:
Single-wall carbon nanotube (SWCNT) anode technology for next -generation LiB



Sources: DfE/ORD Li-ion Batteries and Nanotechnology for Electric Vehicles Partnership; NEC/TOKIN (http://www.nec-tokin.com, 2010; Olapiriyakul, 2008; Ganter, 2009.

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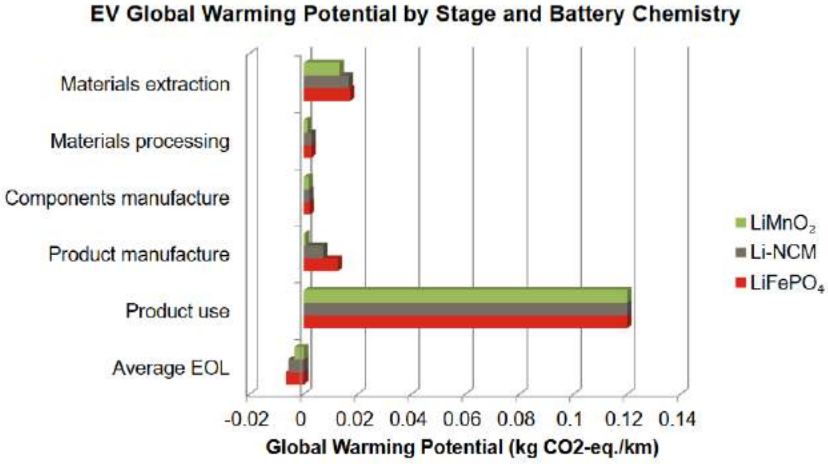
LCA impact

Impact Categories:
- Abiotic resource depletion
- Global warming potential
- Acidification potential
- Eutrophication potential
- Ozone depletion potential
- Photochemical oxidation potential
- Ecological toxicity potential
- Human toxicity potential
- Occupation cancer hazard
- Occupational non-cancer hazard



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Key opportunities for improvement

- Increase the battery life-span
- Reduce energy use for electrode production (cathode)
- Use a solvent - less or water based process
- Reduce the percentage of metals by mass
- Reduce cobalt and nickel use (& exposure upstream)
- Use recovered material
- More efficient production
- Other battery technologies

Reduce human health & environmental impacts of Li - ion batteries for EVs

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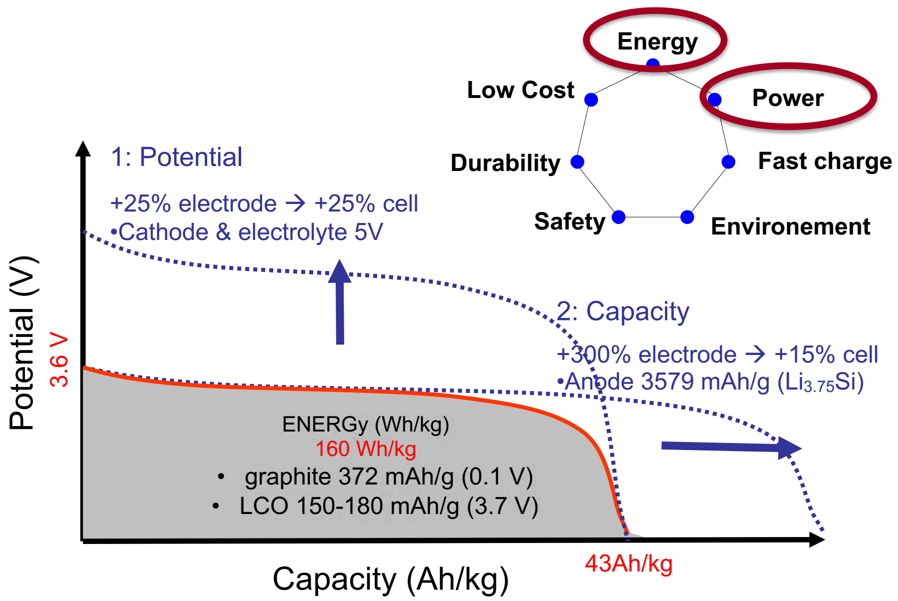
State of the art and perspectives



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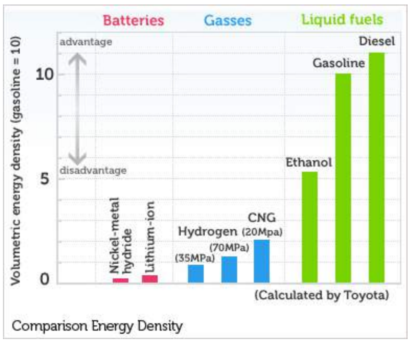
Limitations of LiB

- **Energy density**
- Safety issues
- Cost
- Resource of Li and Co, Ni, Mn



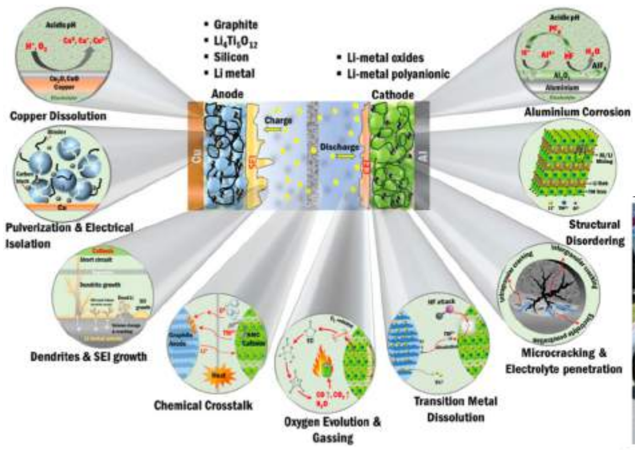
Comparison Energy Density

Types	Cell reactions	Theoretical energy density (Wh/Kg)	Practical energy density (Wh/Kg)
Lead–Acid	Pd +PdO_2+2HSO_4^- +2H+→2$PdSO_4$+2 H_2O	170	30–50
Ni–Cd	2NiO(OH)+Cd+2H_2O→2$Ni(OH)_2$+$Cd(OH)_2$	245	45–80
Ni–MH	x$Ni(OH)_2$+M→xNiOOH+MHx	280	60–120
Li-ion	$LiCoO_2$+C→LixC+Li1−xCoO_2	400	110–160
Li–S	xLi++S8+e→Li_2Sx	2600	~400
	Li_2Sx+ Li++e→Li_2S_2 or Li_2S		
Zn–air	2Zn +O_2→2ZnO	1084	~400
Li–air	2Li+O_2→Li_2O_2	11,680	~2000

Actions:
- enhancement of about 2-3 times in energy density is needed
- replacement of the present electrode materials with alternative compounds with higher values of specific capacity

Limitations of LiB

- **Energy density**
- **Safety issues**
- Cost
- Resource of Li and Co, Ni, Mn



Actions:
- replacement of the oxygen releasing cathode materials (ex. $LiCoO_2$) with more compounds like $LiFePO_4$
- replacement of the flammable liquid organic electrolytes by more stable ex. polymer, solid electrolytes, ionic liquids

Limitations of LiB

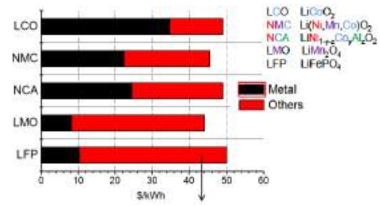
- Energy density
- Safety issues
- Cost
- Resource of Li and Co, Ni, Mn

Forecast of Li-ion battery pack cost and production 2010-2030

Li amount and price is no significant

Only 2.5%wt. of Li

Metal cost processed in positive electrode ($/kWh) (before cell and pack process yield)



Actions:
- replacement of expensive components of LiB, like cathodes containing (Co, Ni…) by low cost, abundant alternative compounds like Fe, S
- replacement of current collectors based on Cu by stainless steel

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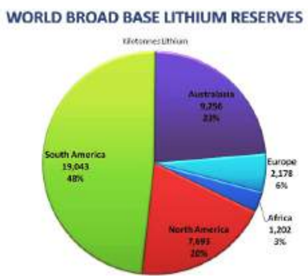
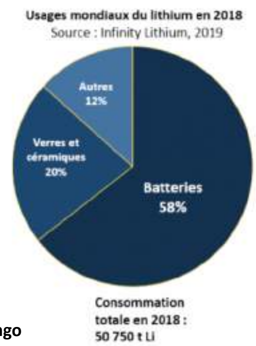
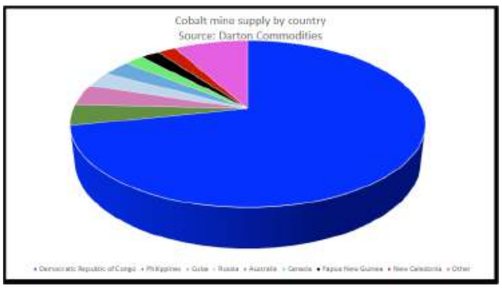
Limitations of LiB

- Energy density
- Safety issues
- Cost
- Resource of Li and Co, Ni, Mn



Minerals of Li:
- spodumene ($LiAl(SiO_3)_2$)
- petalite/castorite ($LiAlSi_4O_{10}$)
- salt water





Cobalt main producer: Democratic Republic of Congo (problems with human rights abuses)

https://smallcaps.com.au/cobalt-supply-chain-transparency-human-rights-violations-drc/

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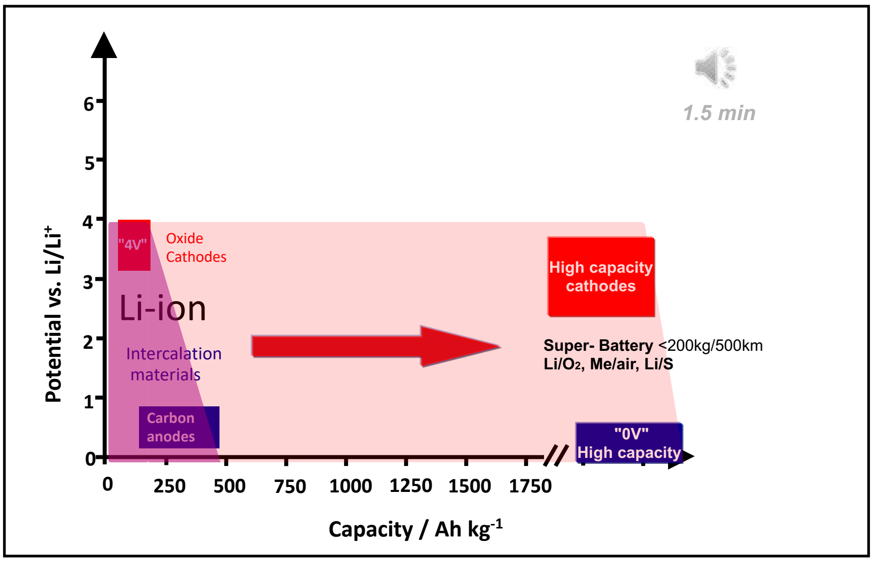
High energy density batteries



Courtesy of Dr. Stefano Passerini, Munster University

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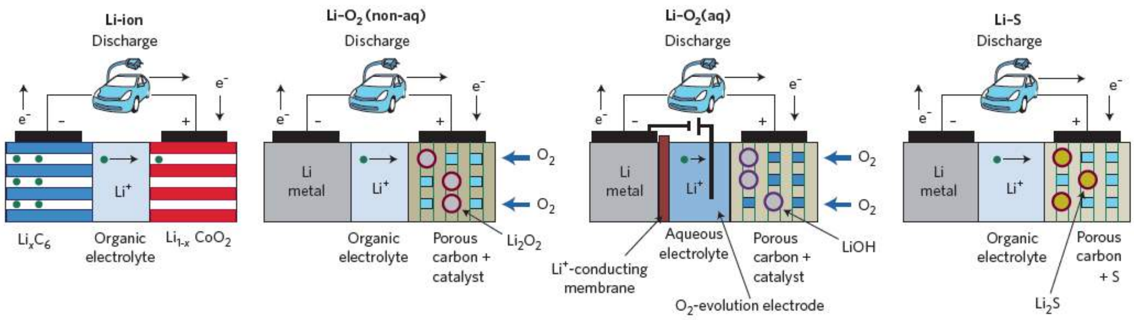
LiB, Li-O_2 and Li-S



$\frac{1}{2}\ C_6Li + Li_{0.5}CoO_2 \leftrightarrow 3C + LiCoO_2$

$2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$

$2Li^+ + 2e^- + \frac{1}{2}\ O_2 + H_2O \leftrightarrow 2LiOH$

$2Li^+ + 2e^- + S \leftrightarrow Li_2S$

@ discharge:
Li-metal oxidation → Li^+
O_2 from air dissolution & reduction → O_2^{2-}

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Li–O2 and Li–S batteries with high energy storage, Peter G. Bruce et al, Nature Materials, Vol 11, 2012

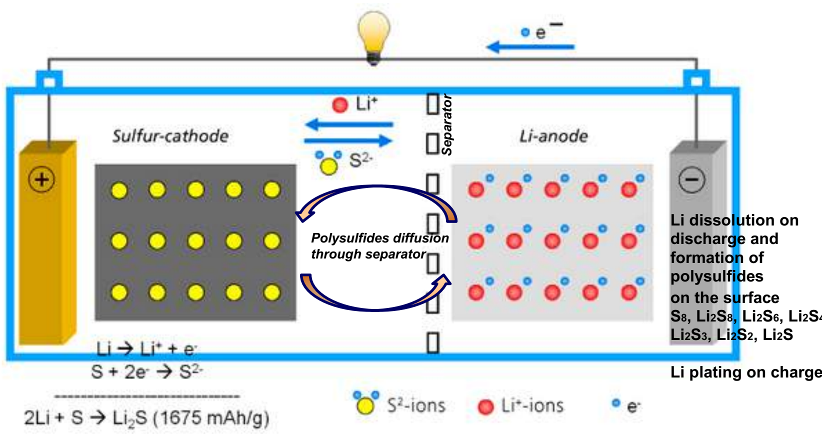
Comparision of LiB, Li-O_2 and Li-S

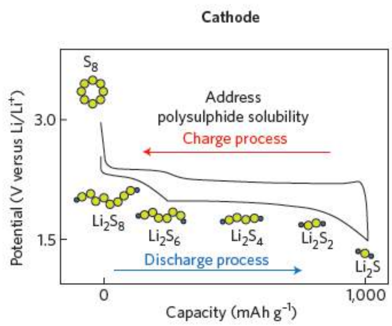
Battery	Cell voltage (V)	Theoretical specific energy (Wh kg^{-1})	Theoretical energy density (Wh l^{-1})
Today's Li-ion $\frac{1}{2}C_6Li + Li_{0.5}CoO_2 \leftrightarrow 3C + LiCoO_2$	3.8	387	1,015
Zn-air $Zn + \frac{1}{2}O_2 \leftrightarrow ZnO$	1,086	1,086	6,091[*] (ZnO)
Li-S $2Li + S \leftrightarrow Li_2S$	2,567	2,567	2,199[†] ($Li + Li_2S$)
Li-O_2 (non-aqueous) $2Li + O_2 \leftrightarrow Li_2O_2$	3,505	3,505	3,436[‡] ($Li + Li_2O_2$)
Li-O_2 (aqueous) $2Li + \frac{1}{2}O_2 + H_2O \leftrightarrow 2LiOH$[§]	3,582	3,582	2,234[‖] ($Li + H_2O + LiOH$)

[*]Based on volume of ZnO at the end of discharge; [†]based on the sum of the volumes of Li at the beginning and Li_2S at the end of discharge; [‡]based on the sum of the volumes of Li at the beginning and Li_2O_2 at the end of discharge; [§]assuming the product is anhydrous LiOH and alkaline conditions; and [‖]based on the sum of the volumes of $Li + H_2O$ consumed and the LiOH at the end of discharge.

Li–O2 and Li–S batteries with high energy storage, Peter G. Bruce et al, Nature Materials, Vol 11, 2012

Li-S batteries





Advantages:

- **High energy density (~1675 mAh/g for S, 2200 Wh/l and 2600 Wh/kg)**

Li–O2 and Li–S batteries with high energy storage, Peter G. Bruce et al, Nature Materials, Vol 11, 2012

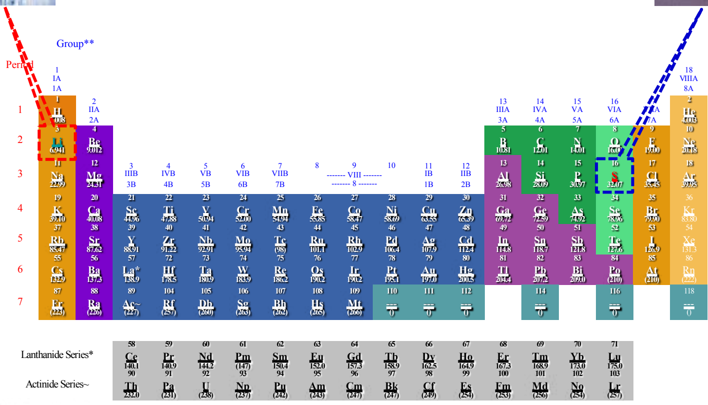
Why Li and S for electrode active material?

Lithium

- Atomic weight: 6.94 g/mol
- Lightest alkali metal (0.54 g/cm^3)
- Theoretical capacity: 3.86 Ah/g
- E = -3.045V$_{SHE}$

Sulfur

- Atomic weight: 32.06 g/mol
- Light yellow solid (2.07 g/cm^3)
- Theoretical capacity: 1.675 Ah/g
- Non-toxic, "green" material
- Abundant and cheap



Courtesy of Prof. K.Kim, Gyeongsang National University, Korea

http://periodic.lanl.gov

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Issues of Li-S battery

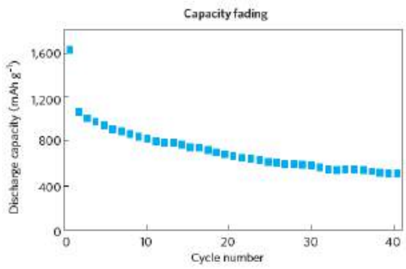
The Li/S concept is not new. However, so far limited progress due to a series of practical issues

Major Issues:

☹ solubility of the polysulphides Li$_x$S$_y$ in the electrolyte (loss of active mass → low utilization of the sulphur cathode and severe capacity decay upon cycling)

☹ low electronic conductivity of S , Li$_2$S and intermediate Li-S products (low rate capability, isolated active material)

☹ Reactivity of the lithium metal anode (dendrite deposition, cell short circuit, safety)



Challenge: find and an electrolyte to combat the irreversible loss of sulphur associated with the formation of soluble Li$_2$S$_6$, Li$_2$S$_4$ and insoluble Li$_2$S$_2$ or Li$_2$S
(cyclic or linear ethers, ionic liquids or polymers PEO-based electrolytes)

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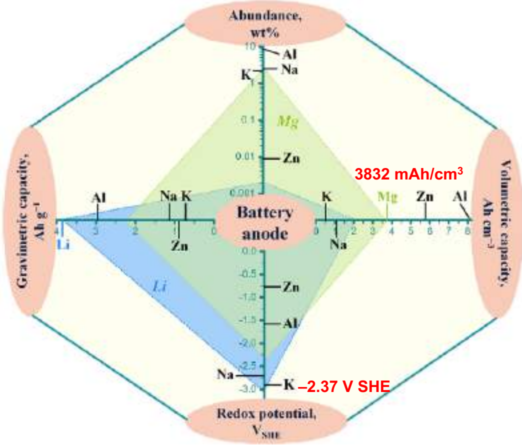
Me-air batteries

Important parameters of metal-air batteries [1]

Batteries	Year of invention	Theoretical working voltage (V)	Theoretical specific capacity (Ah/kg)	Theoretical energy density (Wh/kg)
Mg-air	1966	3.09	920	2843
Zn-air	1878	1.65	658	1085
Li-air	1996	2.96	1170	3463
Al-air	1962	2.71	1030	2791
Na-air	2012	2.33	687	1600
K-air	2013	2.48	377	935
Lithium-ion		**2.33**	**687**	**150-250**

- Low materials cost and great chemical stability
- Mg is also environmentally friendly, non-toxic

Key features of metallic anodes [2]



[1] N.S. Hazri, A.M. Zainoodin, International Journal of Energy Research, 45 (2021) 15739-15759.
[2] M. Deng, D. Snihirova, Energy Storage Materials, 43 (2021) 238-247.

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Zn-air battery working principle

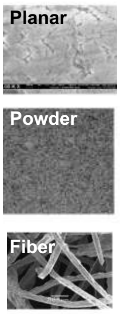
Anode (porous): $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$ $(E_0 = -1.2\ V)$

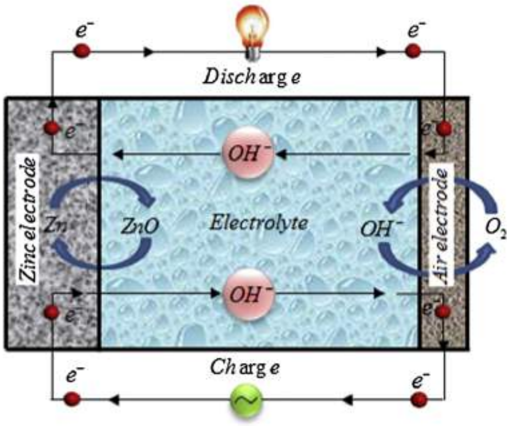
Migration to anode at discharge

Cathode: $1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$ $(E_0 = 0.44\ V,\ pH = 11)$

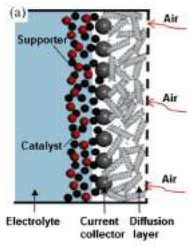
Overall: $2\ Zn + O_2 \rightarrow 2\ ZnO$ $(E_0 = 1.64\ V)$

Anode:
Metal mechanically reacheargable





Cathode:
supporter+calalyst
$(La,Sr)MO_3$, MnO_2,
NiFe-based, Co_3O_4



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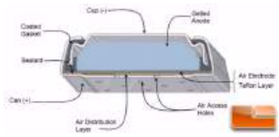
Application of Zn-air batteries

- hearing aids,
- patient monitors,
- road traffic signaling…

Energizer PP355 Zinc Air Prismatic 1.4V battery; size: 32.2 x 14.7 x 5.0 mm



Limiting the amount of air access to a zinc air battery can increase the battery life
- from 1 to 3 months with no air management
- from 1 to 2 years using air management

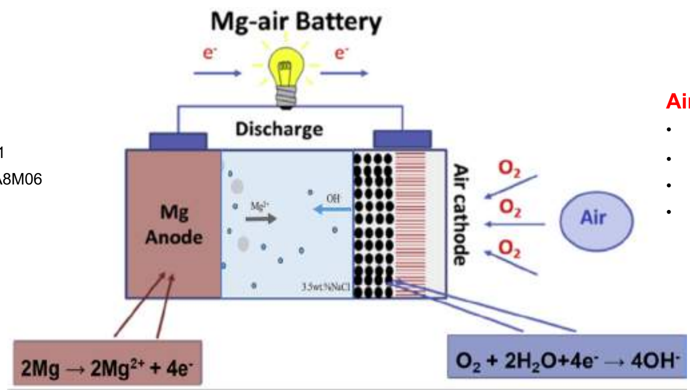
- transport

APET (Taiwan) Zinc-Air Battery
zinc filled pouch cells are assembled to a 30kWh (for extra 300 km)

Leo Motors –Zinc-Air Range Extender (Korea)
140-mile driving range

Mg-air batteries working mechanism

Mg anode:
- Mg *alloys*:
  - Mg/Al/Zn: AZ31, AZ61, AZ91
  - Mg/Al/Mn: AM50, AM60, MA8M06
  - Mg/Li alloys
- Pure Mg :
  - Commercial Mg
  - Nano/mesoscale Mg



Air cathode:
- Catalyst layer: Pt/C or MO_2/C;
- Gas diffusion layer
- Current collector layer
- Waterproof layer

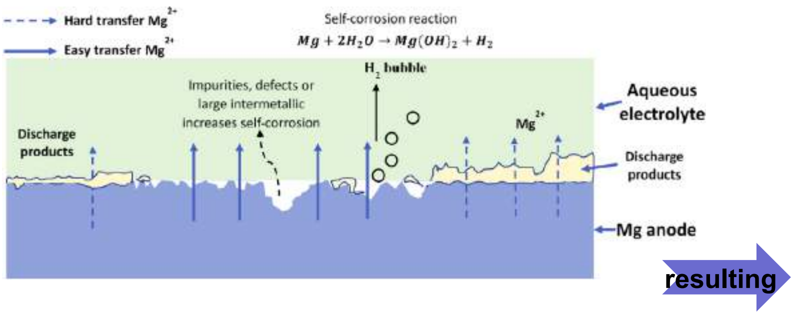
Electrolytes:

NaCl, $KHCO_3$, NH_4NO_3, $NaNO_3$, HNO_3, *Na_2SO_4*, $Mg(NO_3)_2 \cdot 6H_2O$ + $NaNO_2$, $MgCl_2$, and $MgBr_2$, ionic liquid

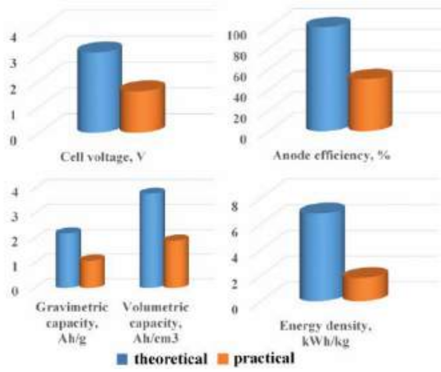
L. Zhang, Q. Shao, J. Zhang, Materials Reports: Energy, 1 (2021) 100002.

Drawbacks of Mg-air batteries

Mg anode degradation [1]



Theoretical vs practical battery properties [2]



- Self-discharge (self-corrosion and chunk effect), hydrogen evolution
- Sluggish kinetics of the oxygen reduction reaction
- Other cathodic reactions, e.g. $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$

[1] F. Tong, S. Wei, X. Chen, W. Gao, Journal of Magnesium and Alloys, 9 (2021) 1861-1883.
[2] M. Deng, 2020, Novel Mg-Ca-based alloys as anode materials for primary aqueous Mg-air battery, Christian-Albrechts-University in Kiel.

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Application of Mg-air batteries

Portable application

Light emitting diode, portable mini light, supporting mobile phone charging (5 V USB port)

Commercial Mg-air batteries

Lightweight, infinite shelf life at dry package and easy to handle

Emergency back-up power

Mg metal can be replaced by new Mg plate when the Mg anode is exhausted

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Li-air battery architecture

APROTIC:

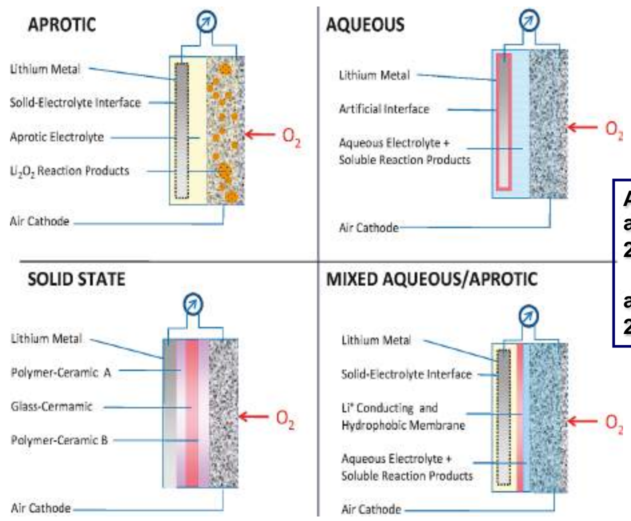
**$2Li + O_2 \rightarrow Li_2O_2$
@ 3.10 V**

and possibly

**$2Li + (1/2)O_2 \rightarrow Li_2O$
@ 2.72 V**

Max theoretical capacity
3862 mAh/g

Max theoretical specific
energy 5219 Wh/kg



AQUEOUS:
acidic media:
$2Li + (1/2)O_2 + H^+ \rightarrow 2Li^+ + H_2O$

alkaline media
$2Li + (1/2)O_2 + H_2O \rightarrow 2LiOH$

G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, and W. Wilcke, Lithium-Air Battery: Promise and challenges, J. Phys. Chem. Lett, (2010), 1, 2193–2203.

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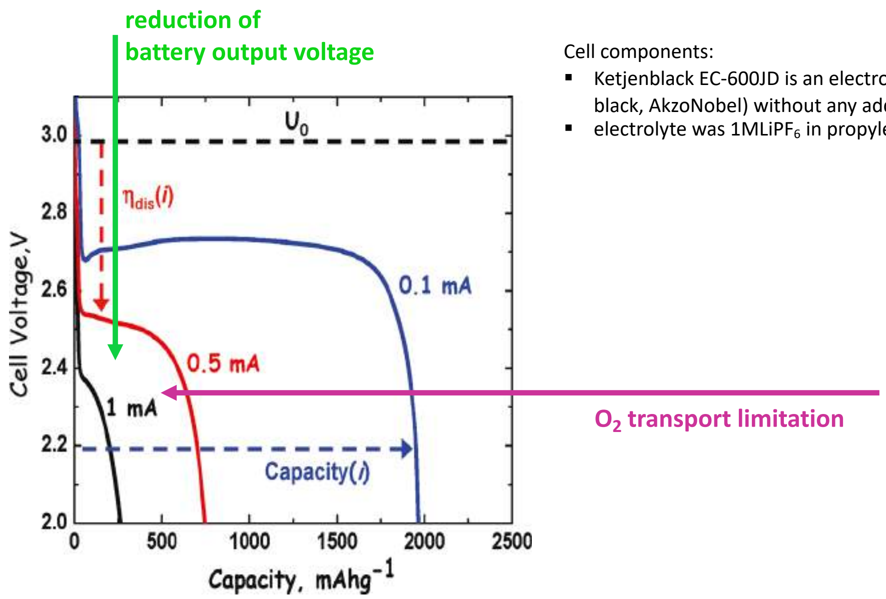
Discharge curves for an aprotic Li-air cell



Cell components:

- Ketjenblack EC-600JD is an electroconductive carbon black, AkzoNobel) without any added catalyst particles,
- electrolyte was 1MLiPF$_6$ in propylene carbonate.

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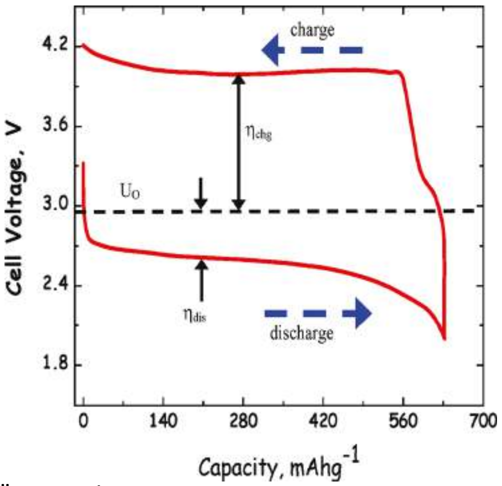
Discharge-charge cycle for Li-air aprotic cell



Cell components:

- Li metal foil
- porous cathode (high surface area Super P conductive carbon black - TIMCAL Graphite & Carbon) + carbon particles mixed with R-MnO2 nanorods as a catalyst,
- electrolyte 1 M $LiN(SO_2CF_3)_2$ [LiTFSI] in propylene carbonate

Irreversible charge/discharge (different products or kinetics during both steps)

Reduction of O2 @ discharge:

$$O_2 + e^- \rightarrow O_2^-$$

$$O_2^- + Li^+ \rightarrow LiO_2$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2$$

Other reduction processes:

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

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

Oxidation process:

$$Li_2O_2 \rightarrow 2Li^+ + 2e^- + O_2$$

Reduction processes ≠ Oxidation processes
thus occuring @ different potentials

$\eta_{chg} >> \eta_{dis} \Rightarrow$ energy efficiency 65 %
Problem with electrolyte and carbon oxidation, thus developement of electrochemical stability of electrolyte and cathode

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General problems in Me-Air betteries

Corrosion - Parasitic corrosion reaction (self-discharge) degrades the coulombic efficiency of the anode and must be controlled to minimize this loss of capacity.

$$M + nH_2O \rightarrow M(OH)_n + n/2H_2$$

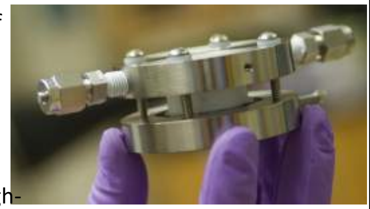
Polarization - voltage decrease with current increase – problems with diffusion and other limitations in the oxygen or air cathode ($\Rightarrow$ low- to moderate-power applications than to high-power ones)

Electrolyte Carbonation – absorption of carbon dioxide ($\Rightarrow$ crystallization of carbonate in the porous air electrode $\Rightarrow$ impeding air access and mechanical damage and a decreasing electrode performance).

Water Transpiration - water loss $\Rightarrow$ increase of the concentration of the electrolyte $\Rightarrow$ drying out and premature failure; Gain of water $\Rightarrow$ dilution of the electrolyte.

Efficiency - significant irreversibility during charge and discharge $\Rightarrow$ loss of overall energy efficiency

Charging - oxidation of catalysts and electrode supports, so application of oxidation-resistant substrates and catalysts or a third electrode for charging



An experimental lithium-air battery developed at MIT has inlet and outlet on the sides to provide a flow of air, providing oxygen for the battery's operation

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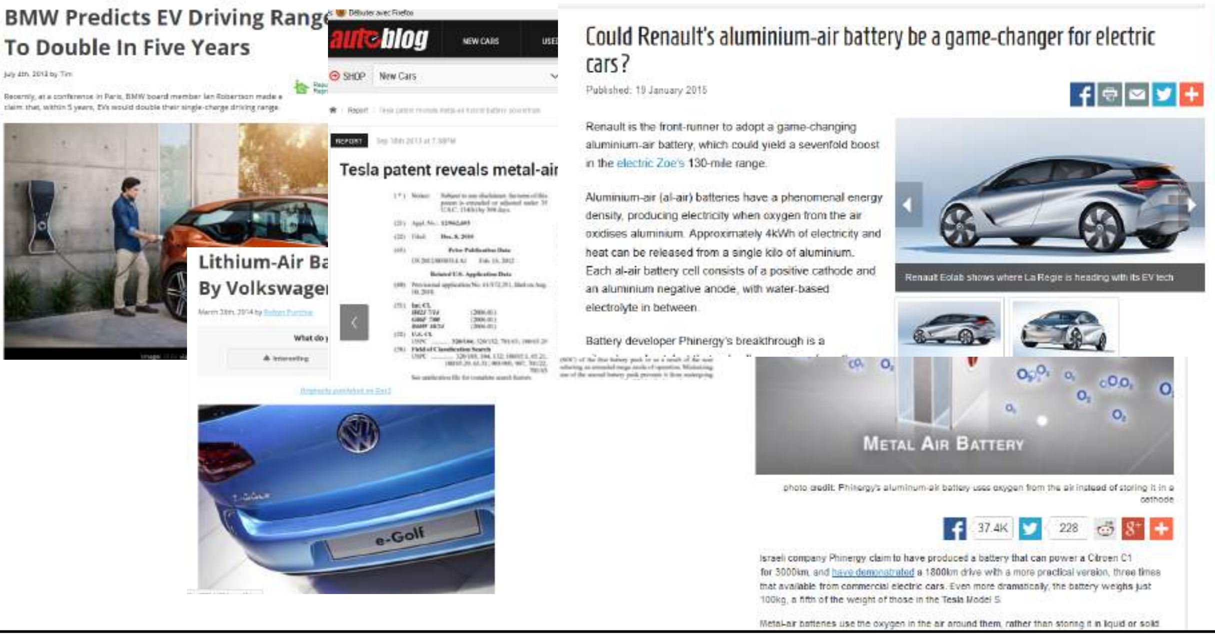
Press info on Li (Me)-air batteries



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Thank you for your attention!

jolanta.swiatowska@chimieparistech.psl.eu

cnrs ensc chimie paris ParisTech

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