Electrochemistry
For Renewable Energy

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p. 218 Gmach Starej Chemii

Electrochemistry For Renewable Energy

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Lorenzo Stievano, Iratxe de Meatza, Jan Bitenc, Carmen Cavallo, Sergio Brutti and Maria Assunta Navarra, Emerging calcium batteries, Journal of Power Sources, 2021, 482, 228875;
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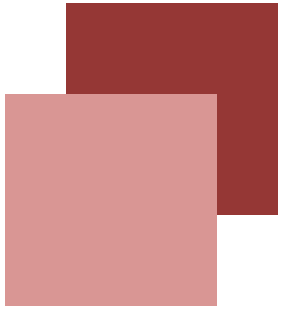
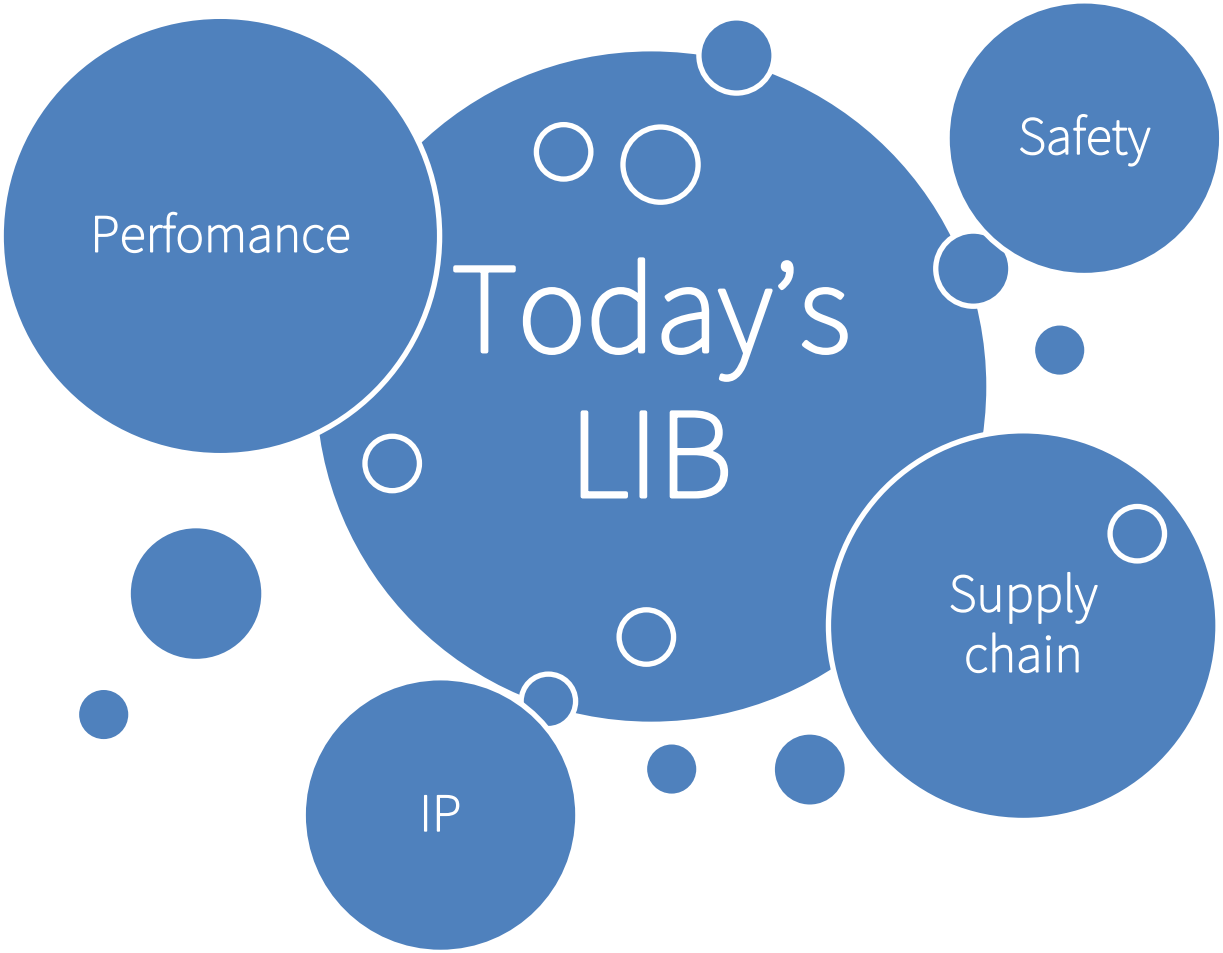
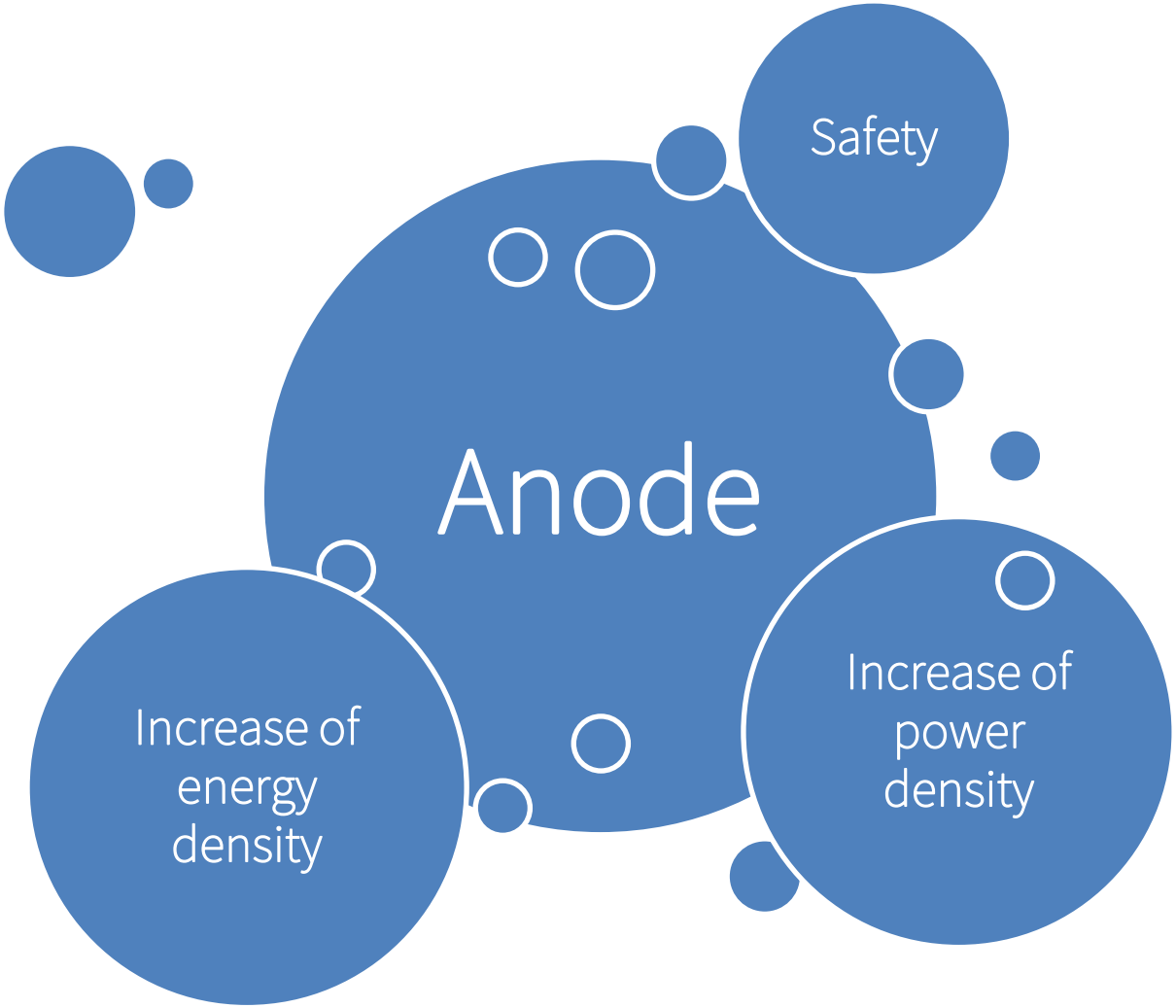
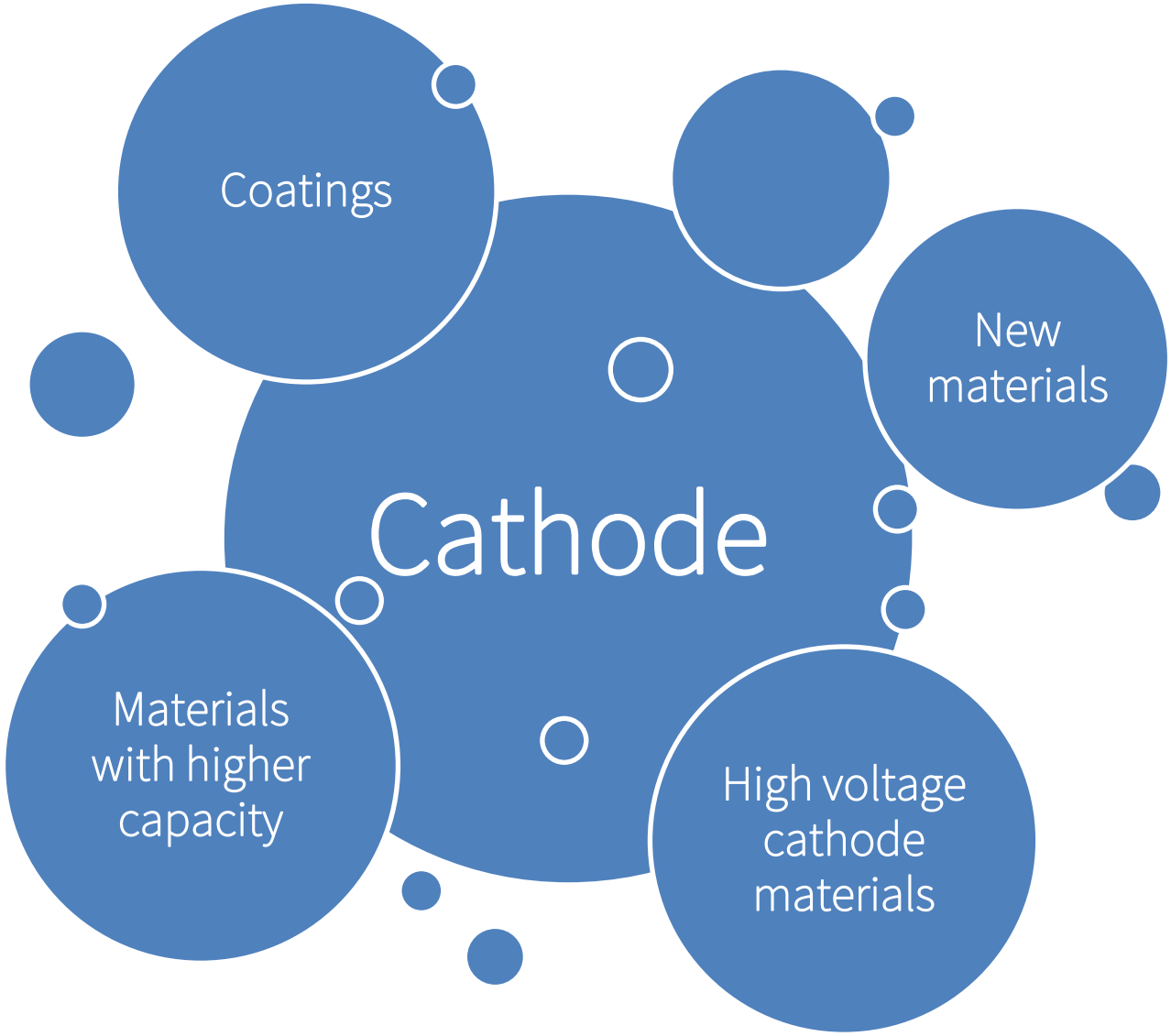


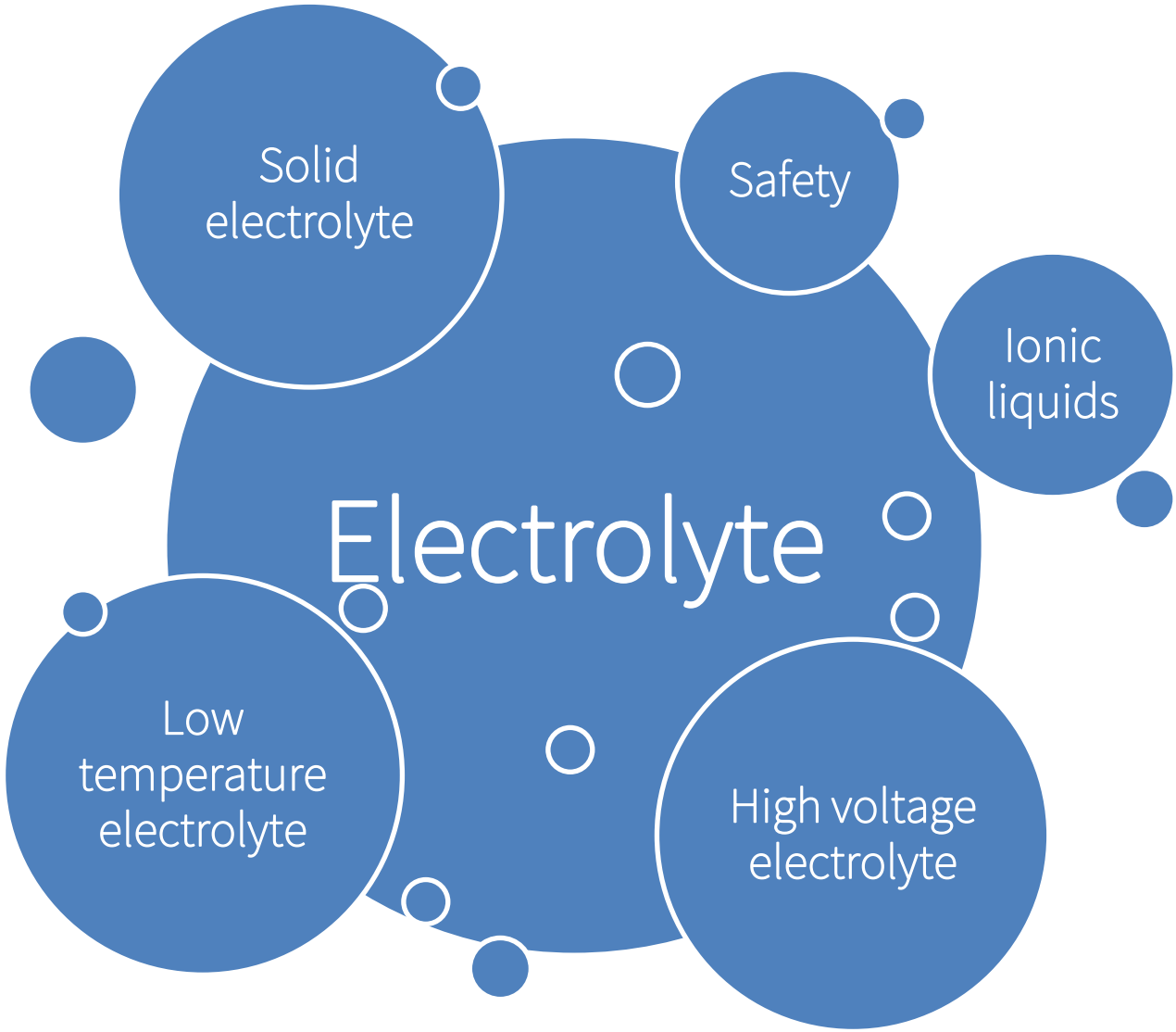
Beyond LIB

Development of LIB


Perfomance
Today's LIB
Safety
Supply chain
IP

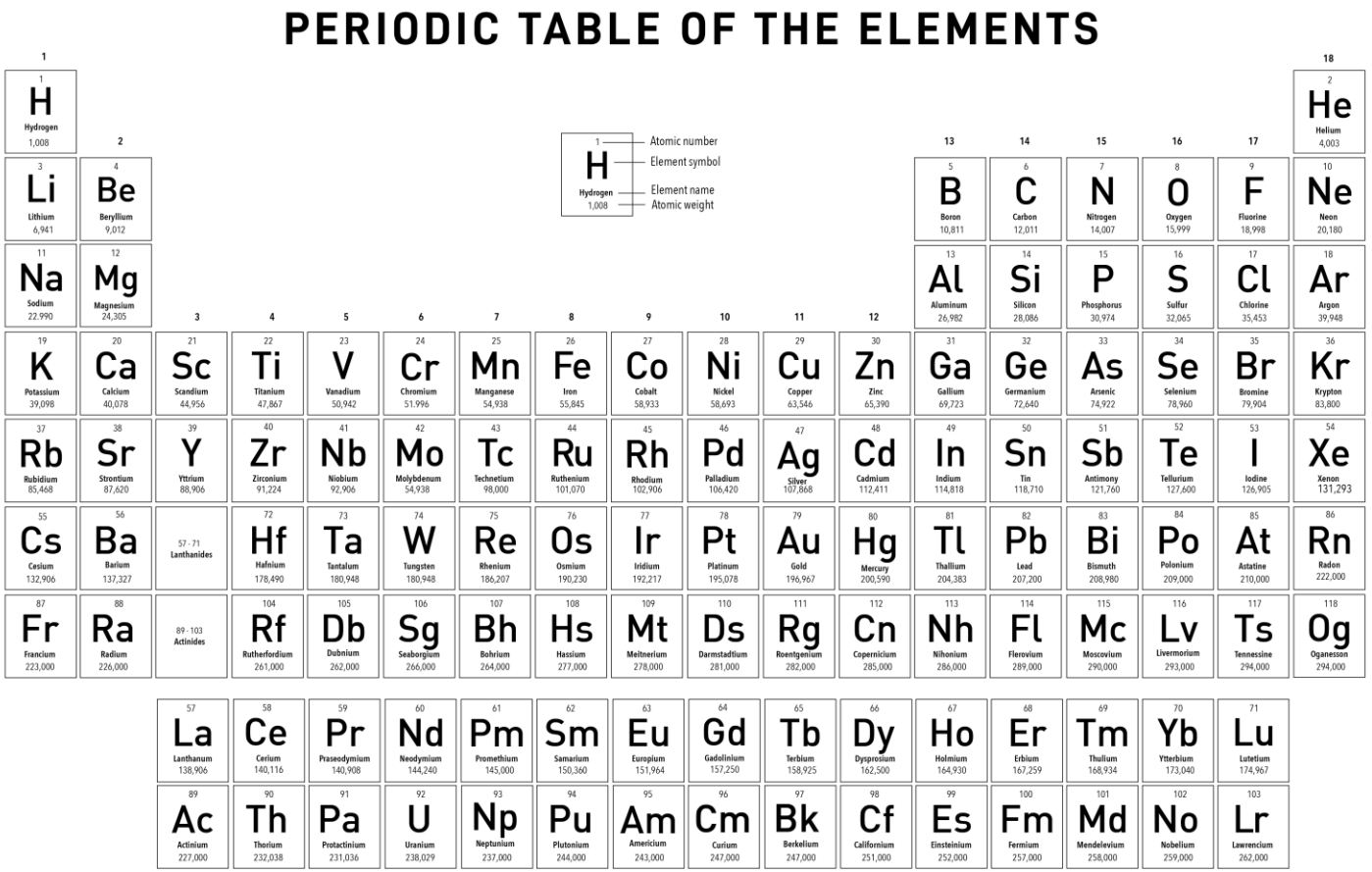

Safety
Anode
Increase of energy density
Increase of power density


Coatings
New materials
Cathode
Materials with higher capacity
High voltage cathode materials

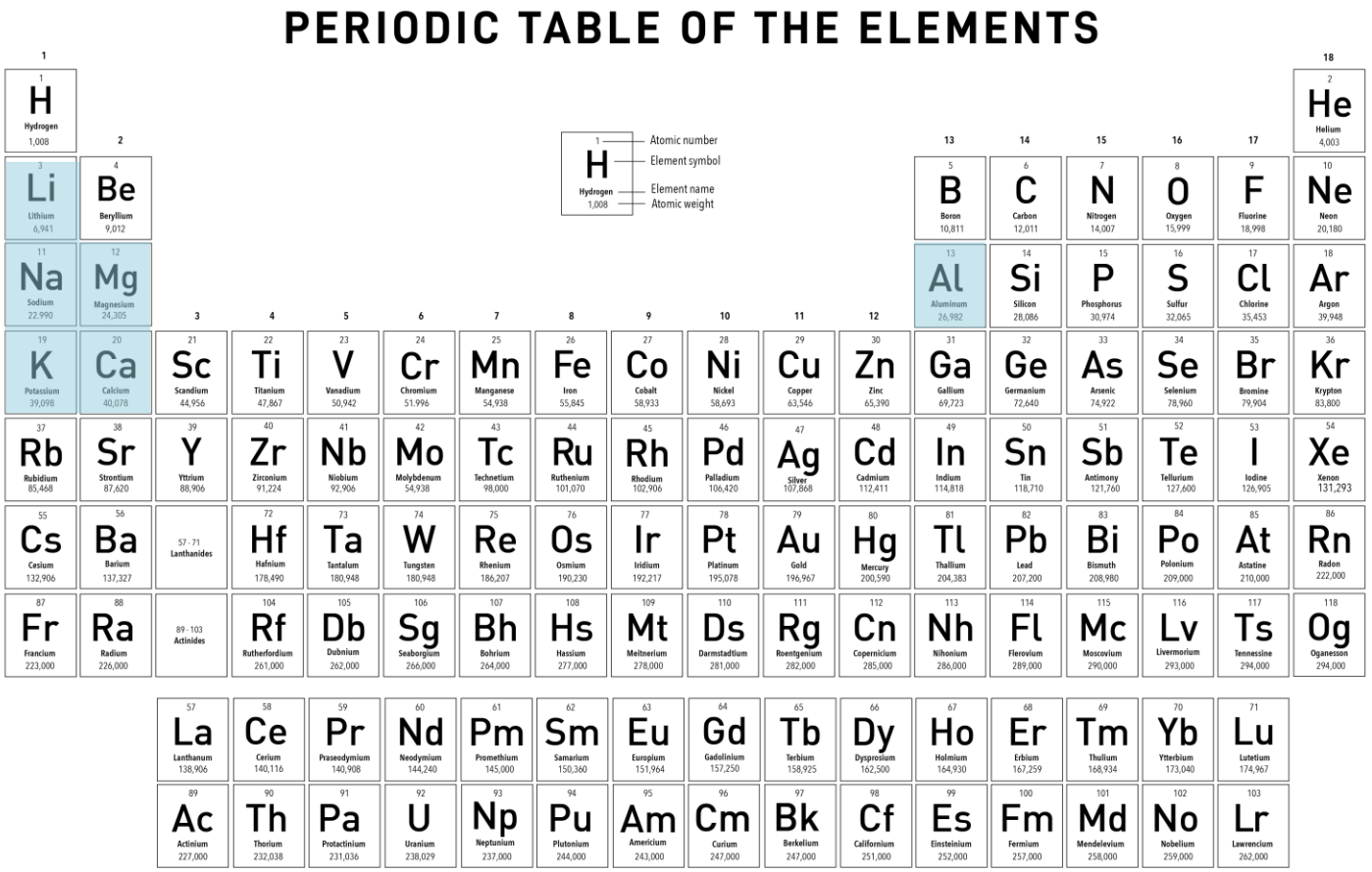

Solid electrolyte
Safety
Ionic liquids
Electrolyte
Low temperature electrolyte
High voltage electrolyte

"Classic" approach

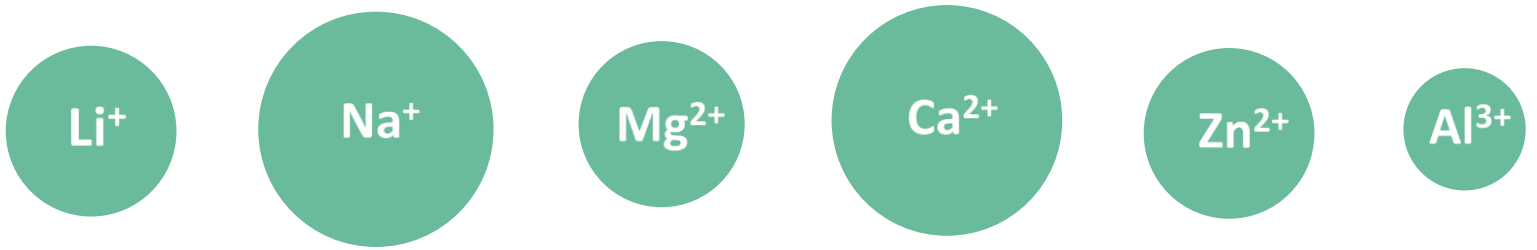
"Classic" approach



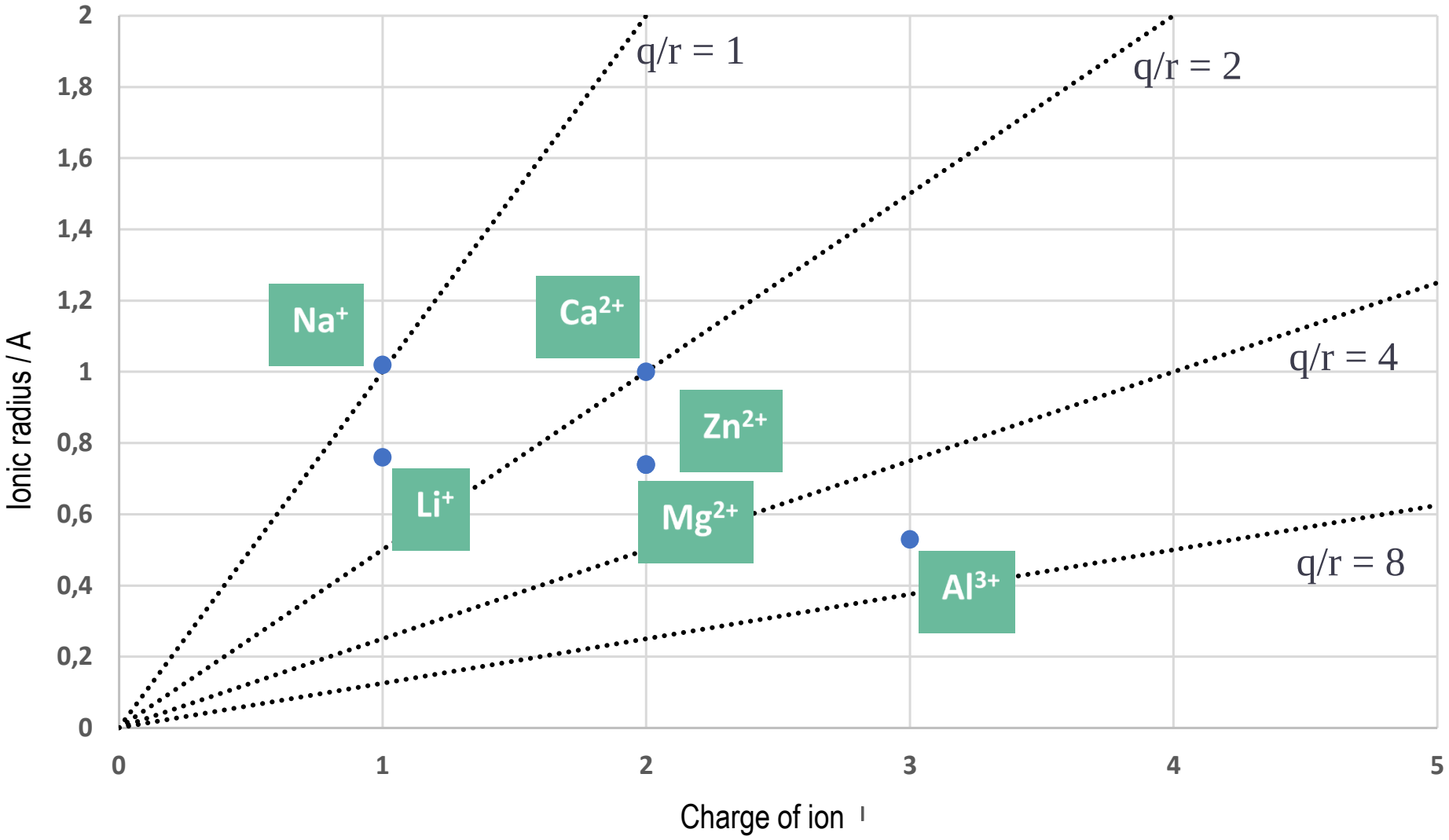
"Classic" approach



Ionic radius for c.n.=6 according to Shannon's – Prewitt's



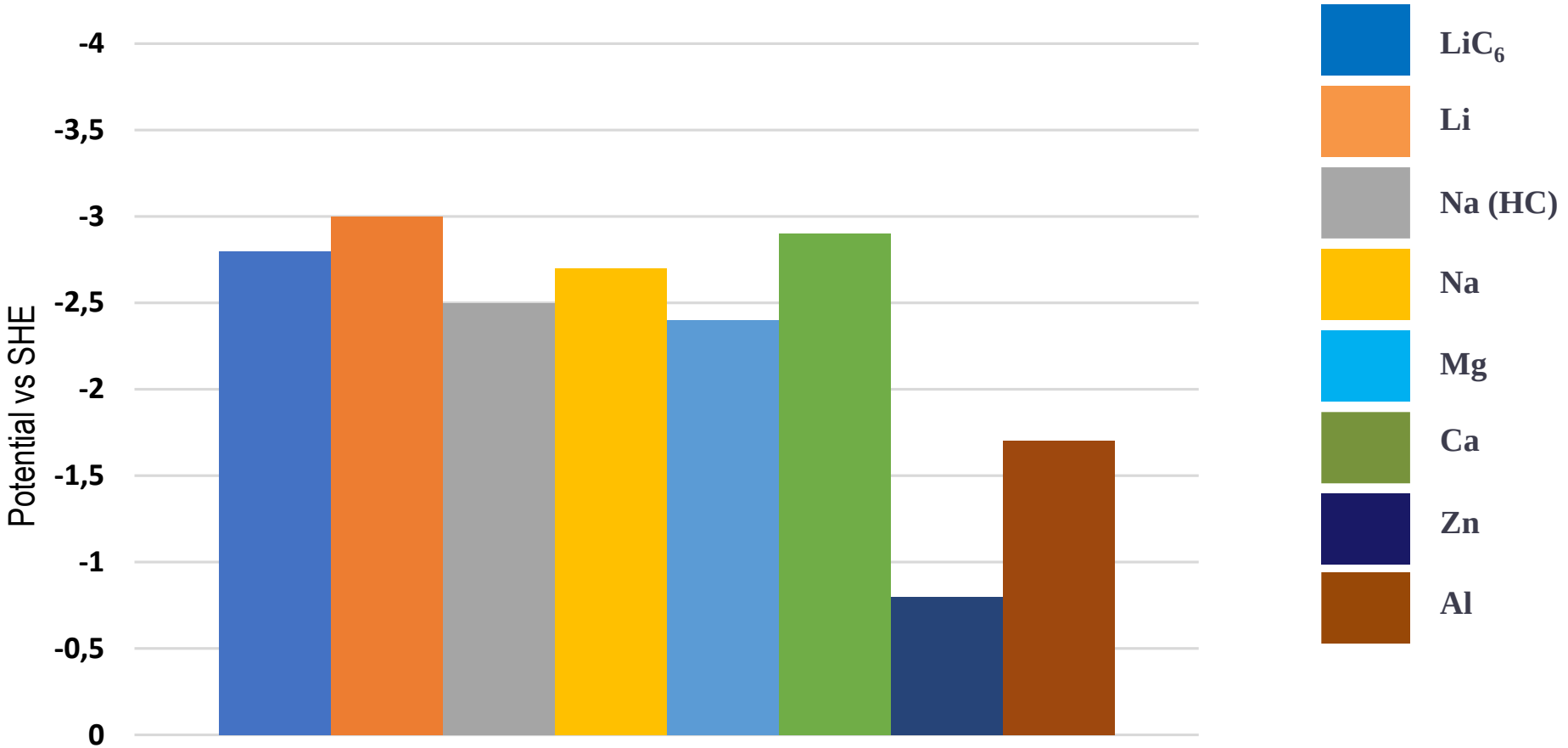
Li^{+}	Na^{+}	Mg^{2+}	Ca^{2+}	Zn^{2+}	Al^{3+}
0,74 Å	1,02 Å	0,72 Å	1,00 Å	0,74 Å	0,53 Å


q/r = 1
q/r = 2
q/r = 4
q/r = 8
Na+
Ca2+
Zn2+
Li+
Mg2+
Al3+
Ionic radius / A
Charge of ion
0
0,2
0,4
0,6
0,8
1
1,2
1,4
1,6
1,8
2
0
1
2
3
4
5

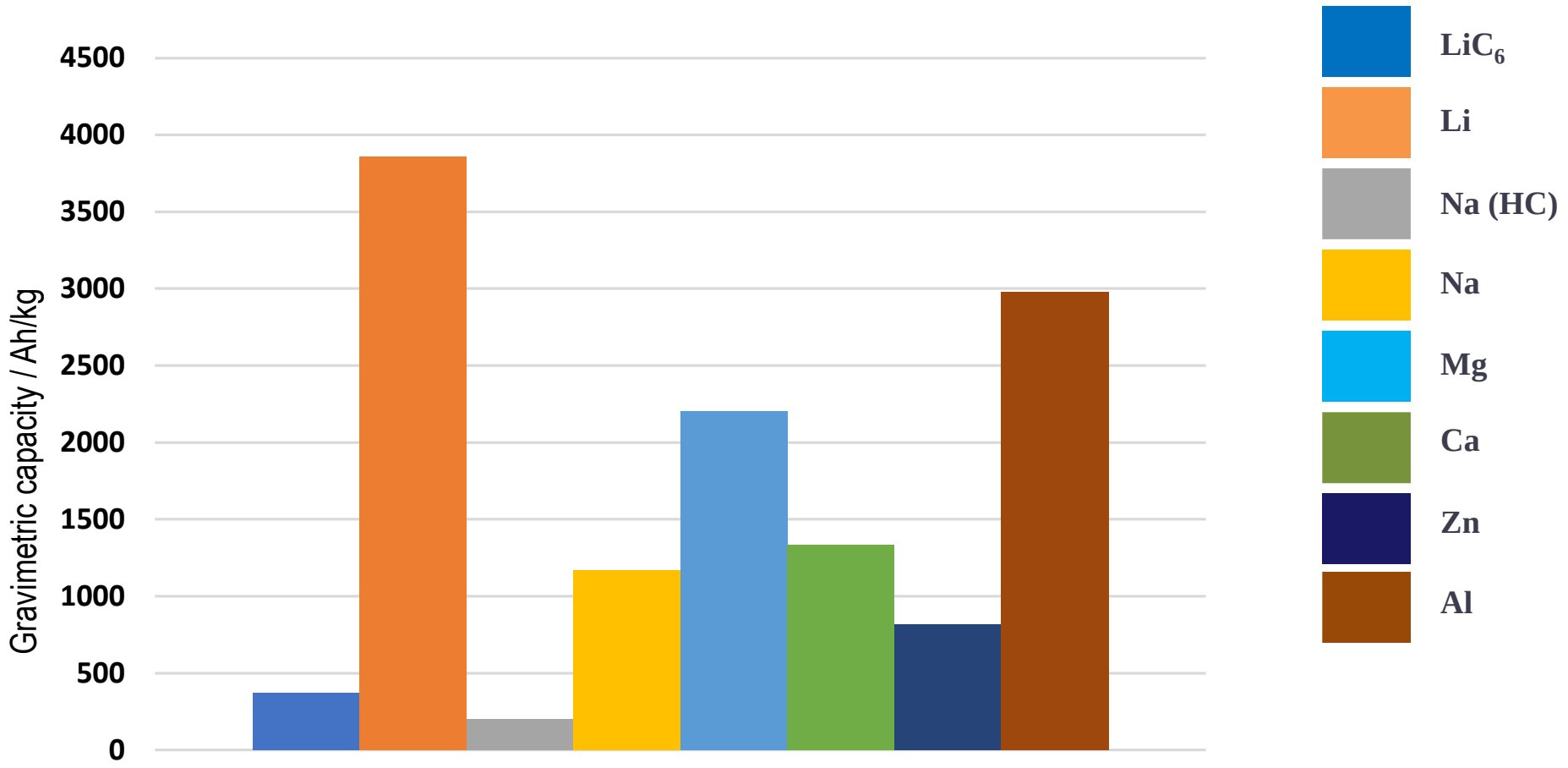
Elemental abundance in the Earth's crust W_{sz} [mg/kg] and price in USD/t

W_{sz}	20	23600	23300	41500	70	82300
Price	7000-8000	150-200	300-1000	200-500	1500-2500	1000-2500

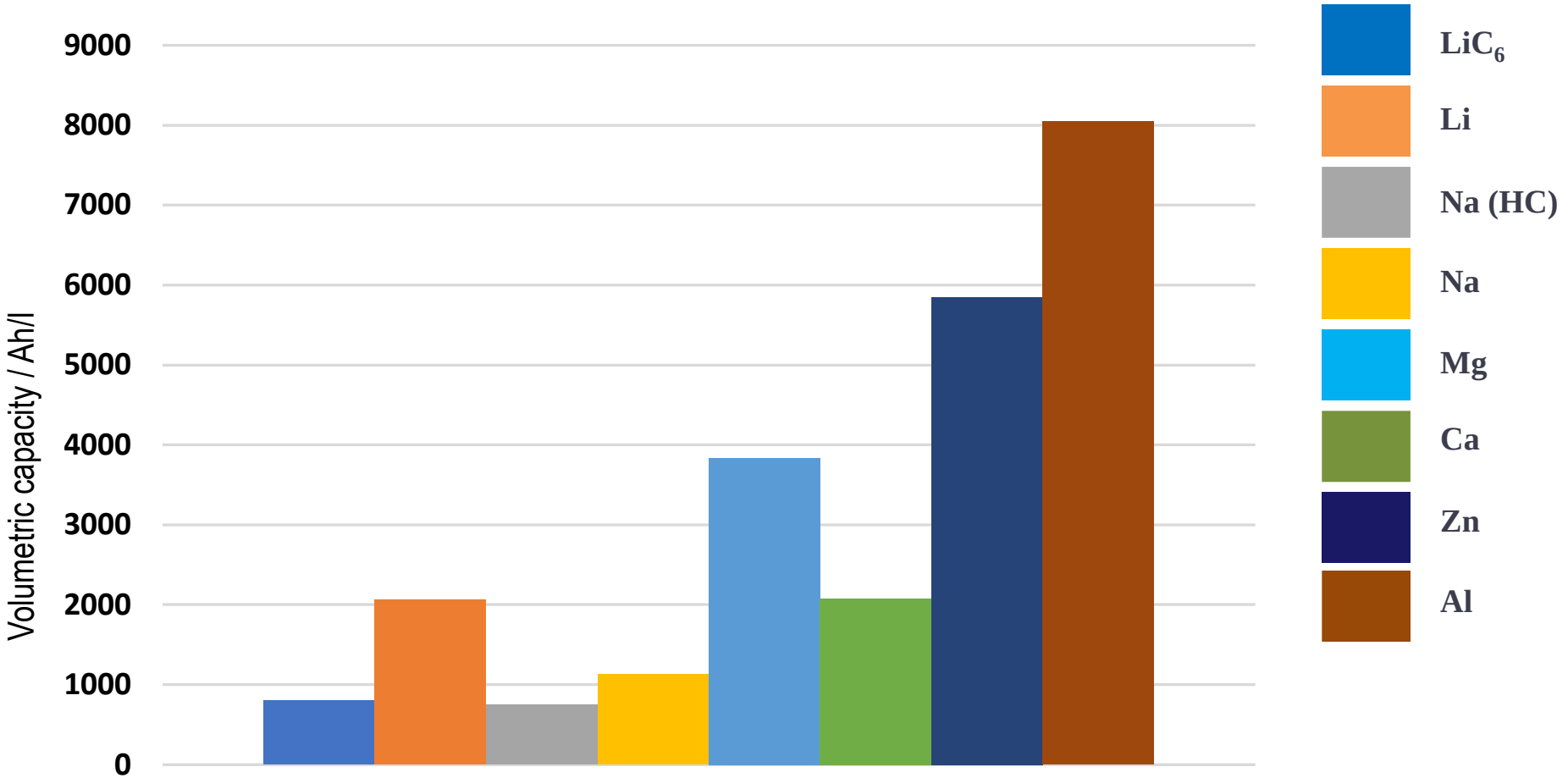
Electrochemical properties – potential vs SHE



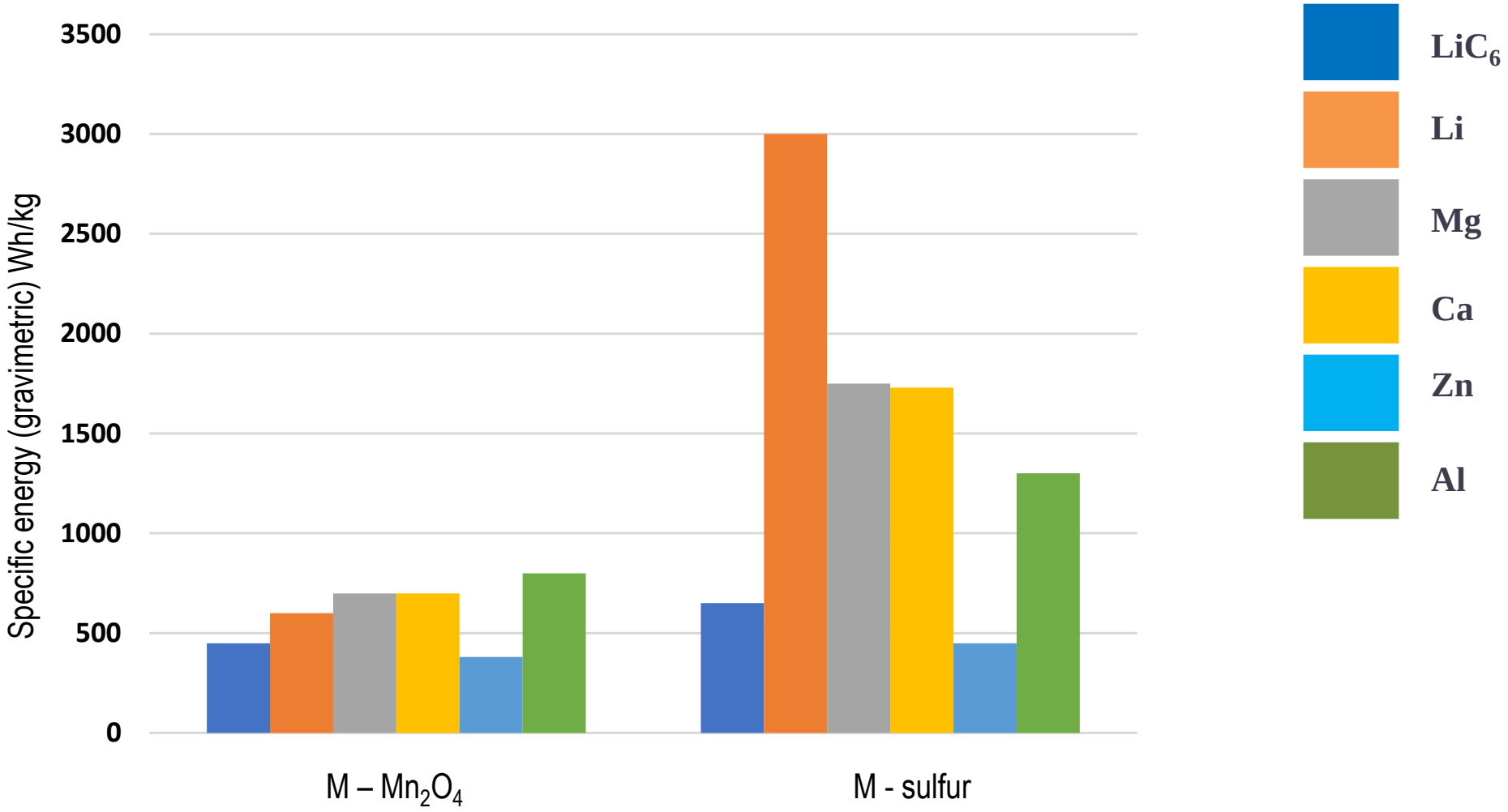
Electrochemical properties – gravimetric capacity



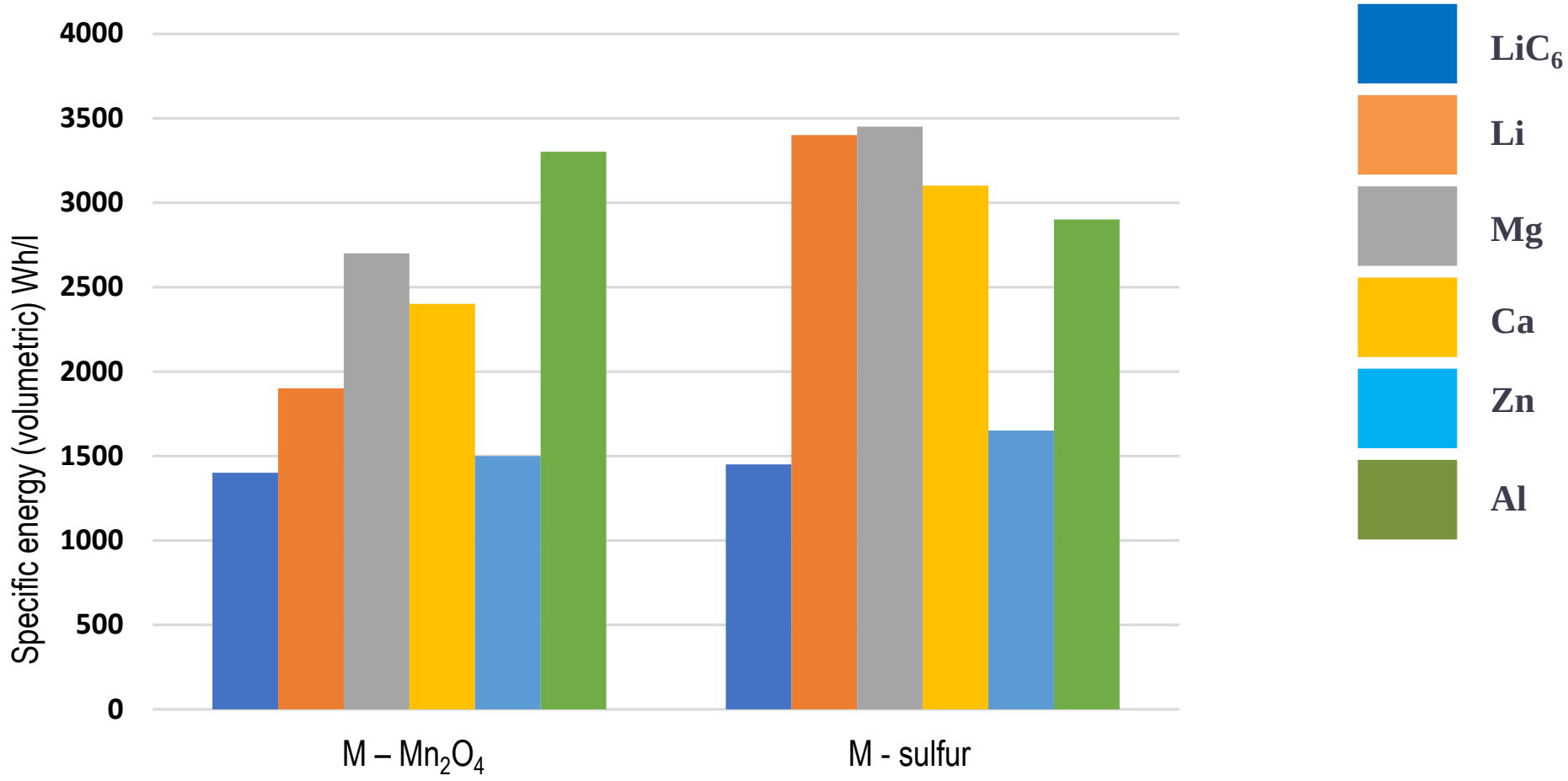
Electrochemical properties – volumetric capacity

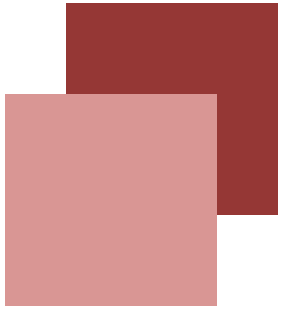


Electrochemical properties – specific energy (gravimetric)



Electrochemical properties – specific energy (volumetric)

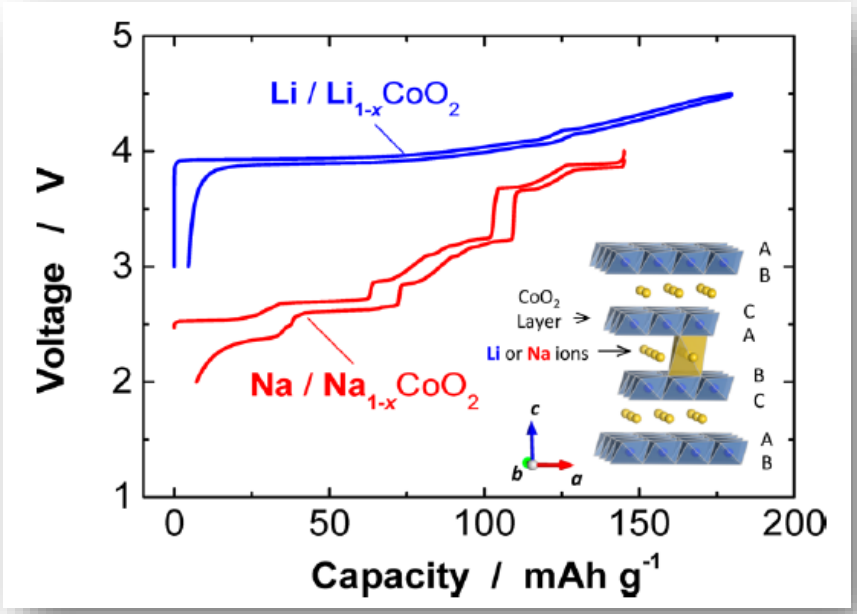


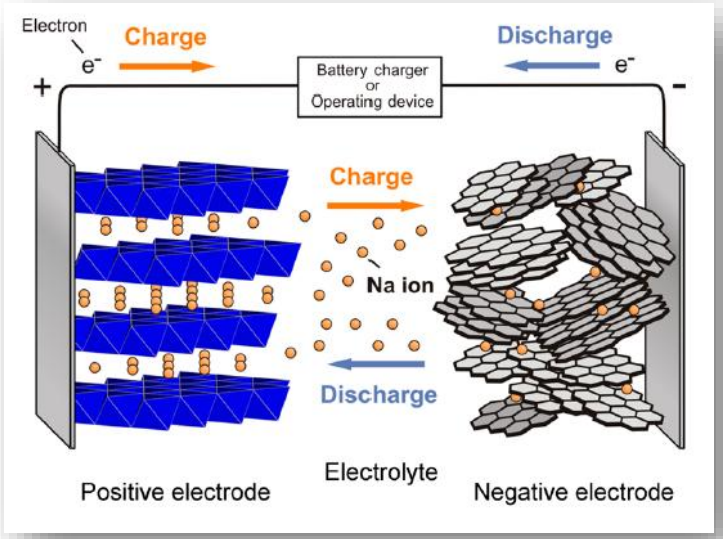


NIB - Sodium Ion Batteries

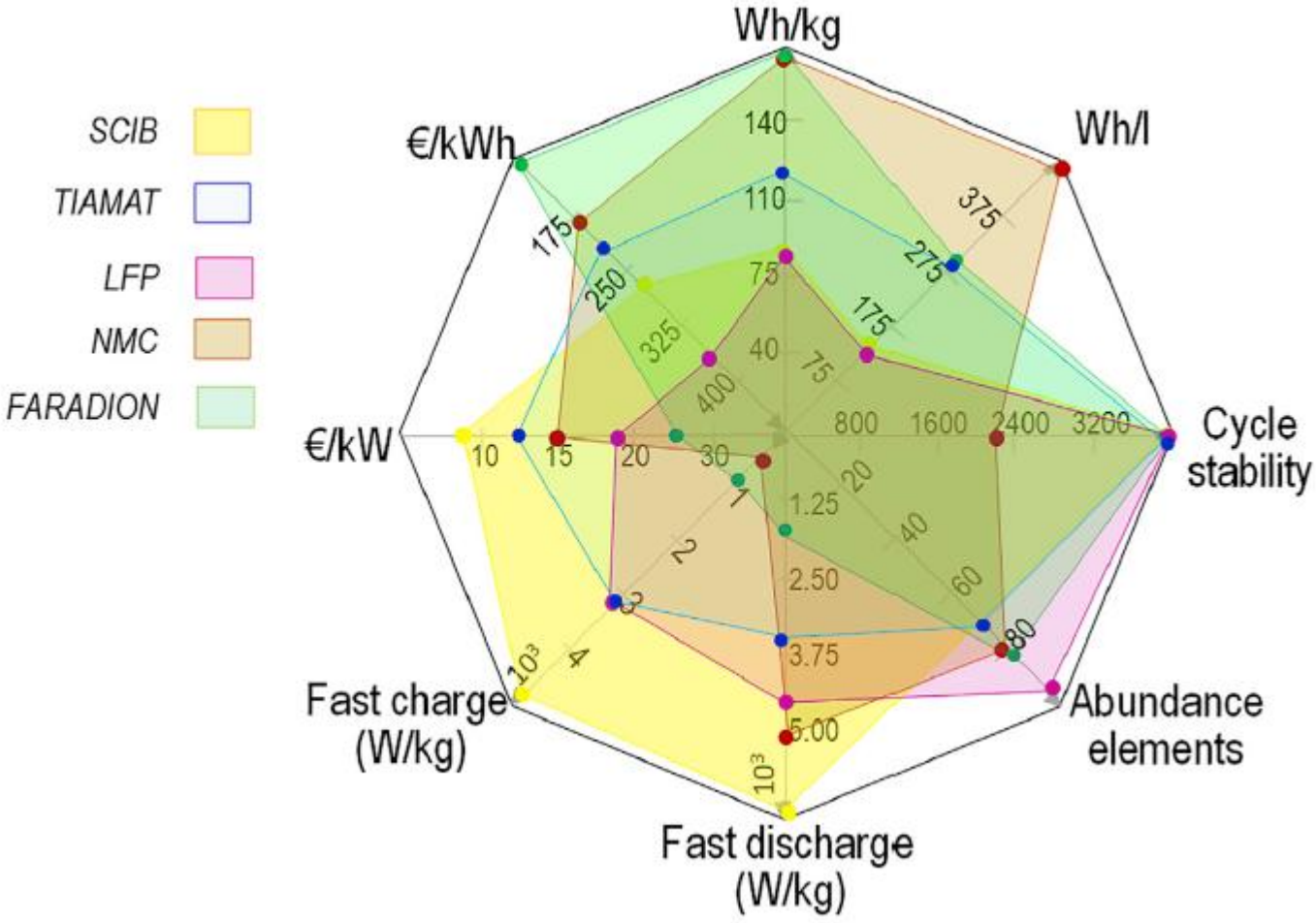
Electrochemistry For Renewable Energy

NIB





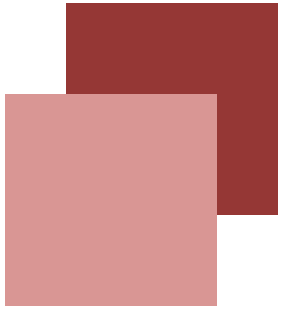
NIB



Tentative comparison between High-Power Cells Relying on Na-Ion Technology either in 18650 format from **TIAMAT** [Na_3V_2 $(PO_4)_2F_3$ (NVPF)/Hard Carbon] or Pouch Cells [$Na_xM_{1-y-z}M'_yM''_zO_2$/Hard carbon] from **FARADION** and on Li-Ion Technology in 18650 format [$LiFePO_4$(LFP)/Graphite and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/Graphite] and Pouch Cells [NMC/$Li_4Ti_5O_{12}$] firmy SCIB. (Jean-Marie Tarascon, Joule, 4, 1613–1620, 2020)

NIB

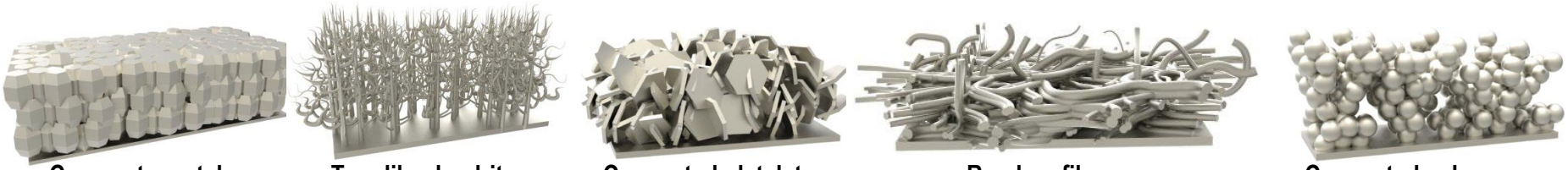
Parameter	Cell Technology				
	SIB		LIB		
Cell format	18650	Pryzmatic	18650	18650	Pryzmatic
Cathode material	$Na_3V_2(PO_4)_2F_3$ (NVPF)	$Na_xM_{1-y-z}M'_yM''_zO_2$	$LiFePO_4$(LFP)	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	NMC
Anode material	Hard carbon	Hard carbon	Graphite	Graphite	$Li_4Ti_5O_{12}$
Specific energy/ Wh/kg	120	80	170	170	80
Specific energy/ Wh/l	280	280	130	475	130
No. of cycles	4800	4800	4800	2000	4800
€/kW	13	25	19	15	8
€/kWh	210	100	375	175	275



Multivalent batteries

R&D – anode

Typical plating morphologies of multivalent metal-ion metals



Compact crystals | Tree-like dendrites | Connected platelets | Random fibers | Connected spheres

Compact crystals are desirable and have established the reputation of multivalent metals as safe anodes.

Tree-like dendrites are directional structures that infamously penetrate separators and cause shorts, thus are actively avoided.

Other morphologies such as **connected platelets**, **random fibers** and **connected spheres** do not cause shorts as quickly as dendrites do, but the impact of their large volume and surface area on coulombic efficiency and long-term stability deserves monitoring.

R&D – anode

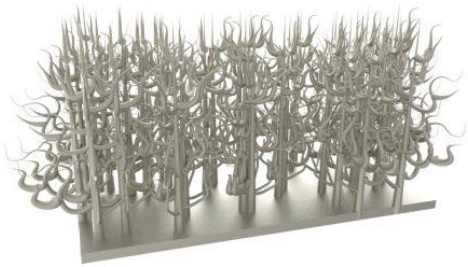
Typical plating morphologies of multivalent metal-ion metals

Compact crystals:

- **Mg**
- **Ca**
- **Al**

Connected platelets:

- **Zn**
- **Al**

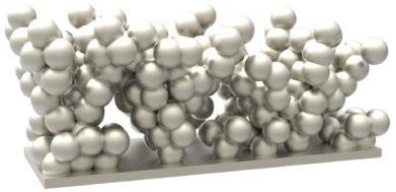


Tree-like dendrites:

- **Li**
- **Ca**
- **Zn**
- **Al**

Random fibers:

- **Zn**
- **Al**



Connected spheres:

- **Ca**
- **Al**

R&D – anode

Lithium:
Dendritic/mossy in most electrolyte solutions; improvement via Surface modifications being explored.

Magnesium:
Dendrite-free plating is widely documented in efficient electrolyte solutions.

Calcium:
Surface typically covered by electrolyte decomposition products, but non-dendritic deposition morphology seems plausible.

Zinc:
Dendritic in both non-aqueous and aqueous electrolyte solutions; suppression via electrode architecture and surface film design being explored.

Aluminium:
Depending on electrolyte solution composition and plating condition, morphologies of all sorts have been observed.

R&D – electrolyte

1. When developing an electrolyte, its electrochemical stability is very important

2. The possibility of reversible and stable cycling of the cell is important

3. In the case of cells based on multivalent metal cations, an important issue is the overpotential of deposition and dissolution of cations

R&D – electrolyte

Lithium:
Ethereal electrolyte solutions with fluorinated additives show high efficiency.

Magnesium:
Relatively established; some more reversible ones may be expensive, synthetically challenging, and of limited anodic stability.

Calcium:
Compositions mimicking magnesium ones have shown decent reversibility albeit not as stable as their magnesium counterparts.

Zinc:
Common zinc salts in common organic solvents show high efficiency.

Aluminium:
$AlCl_3$-based ionic melts are the only options so far; they are corrosive, and the Al−Cl bonds are hard to break.

R&D – cathode

1. It is important in what form the cations penetrate the electrode material - whether they are bound to an anion, in a solvated form by solvent molecules, or in an ionic form.

2. It is important to determine the mechanism of cation diffusion in the structure of the cathode material

R&D – cathode

Lithium:
Established.

Magnesium:
Chevrel phase Mo_6M_8 is finally being challenged by more common chalcogenides, sulfur and organic carbonyl polymers, though most of the newcomers need to improve on cycling stability.

Calcium:
Viable options not yet available.

Zinc:
Reversible intercalation in high-potential oxides in non-aqueous electrolyte solutions; more options in aqueous electrolyte solutions but need stability improvement and scrutiny of the mechanism.

Aluminium:
Al^{3+}-storing cathodes deliver low energy, efficiency and cyclability.

Multivalent - Mg

Parameter	Cell Technology					
	Mg					
Cell format	R&D @ TRL4					
Cathode material	Mo_6S_8	VS_4	MoS_2	Organic	Sulphur	Vanadium oxide
Anode material	Mg	Mg	Mg	Mg	Mg	Mg
Specific energy/ Wh/kg	**60-90** LIB 170 SIB 120	**100-180** LIB 170 SIB 120	**120-180** LIB 170 SIB 120	**90-180** LIB 170 SIB 120	**140-350** LIB 170 SIB 120	**200-300** LIB 170 SIB 120
Specific energy/ Wh/l	**150-300** LIB 475 SIB 280	**180-380** LIB 475 SIB 280	**250-540** LIB 475 SIB 280	**200-380** LIB 475 SIB 280	**250-580** LIB 475 SIB 280	**380-580** LIB 475 SIB 280
No. of cycles	Up to 200/300					
€/kW	Lower then SIB					
€/kWh	Lower then SIB					

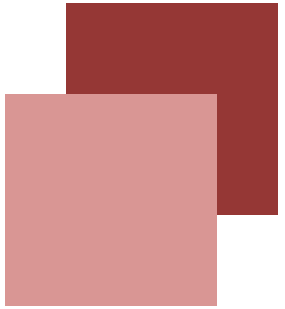
R&D – summary

1. Cells based on multivalent metal cations are a promising addition to the energy storage market.

2. At the moment, the theoretical values of performance parameters planned for these cells have not been achieved or even come close.

3. New materials dedicated to use in these cells should continue to be developed and researched.

„Other" approach



Li – S batteries

Li – S batteries

Principle of lithium - sulfur batteries is based on the reduction of sulfur (which is the cathode material) to polisulfides, which by interacting with lithium cations form the lithium sulfide - Li_2S

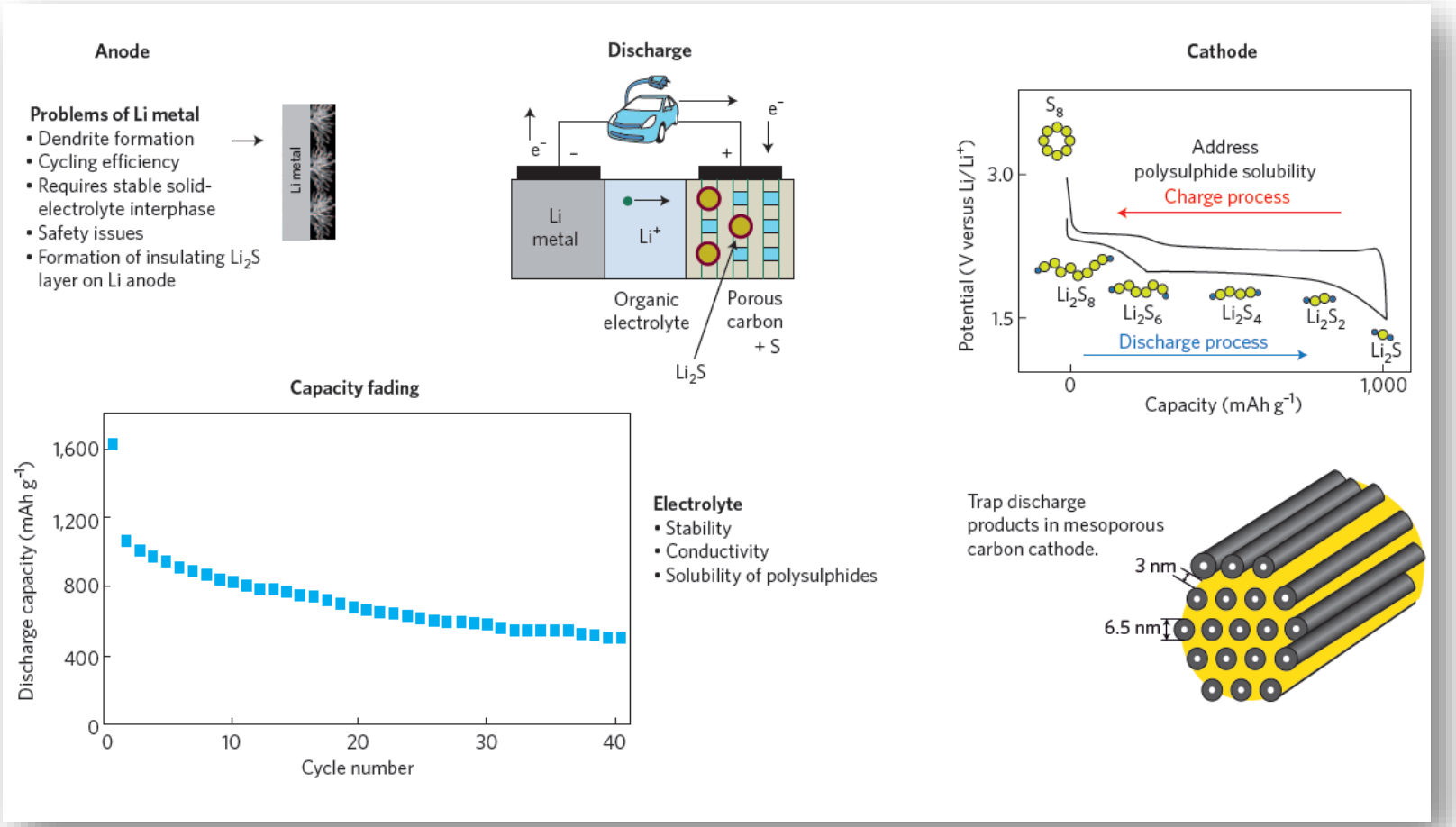
- during discharge of the battery on the anode (built with metallic lithium) a process of oxidation of lithium is taking place: $Li = Li^+ + e^-$
- at the same time on the cathode the reduction of the sulfur is taking place: $S + 2e^- = S^{2-}$

The overall reaction is as follows: **$2Li + S = Li_2S$**.
Because sulfur in nature exists in a form of octasulfur (S_8) it necessary to modify the overall reaction equation to following form: **$16Li + S_8 = 8Li_2S$**

Such cells have many attractive features, including:

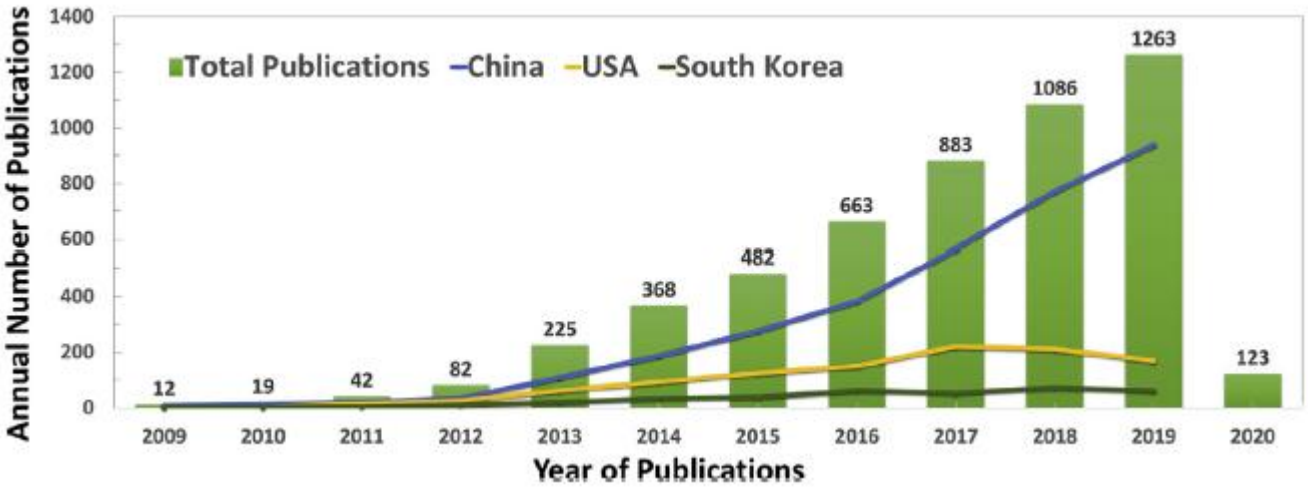
- the natural abundance and low cost of S
- high theoretical energy storage

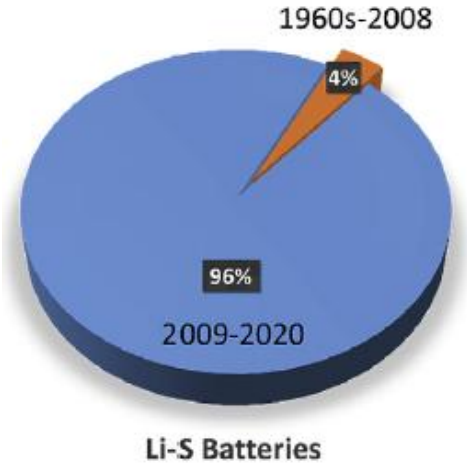
Li – S batteries



Li – S batteries

Publications on Li-S batteries

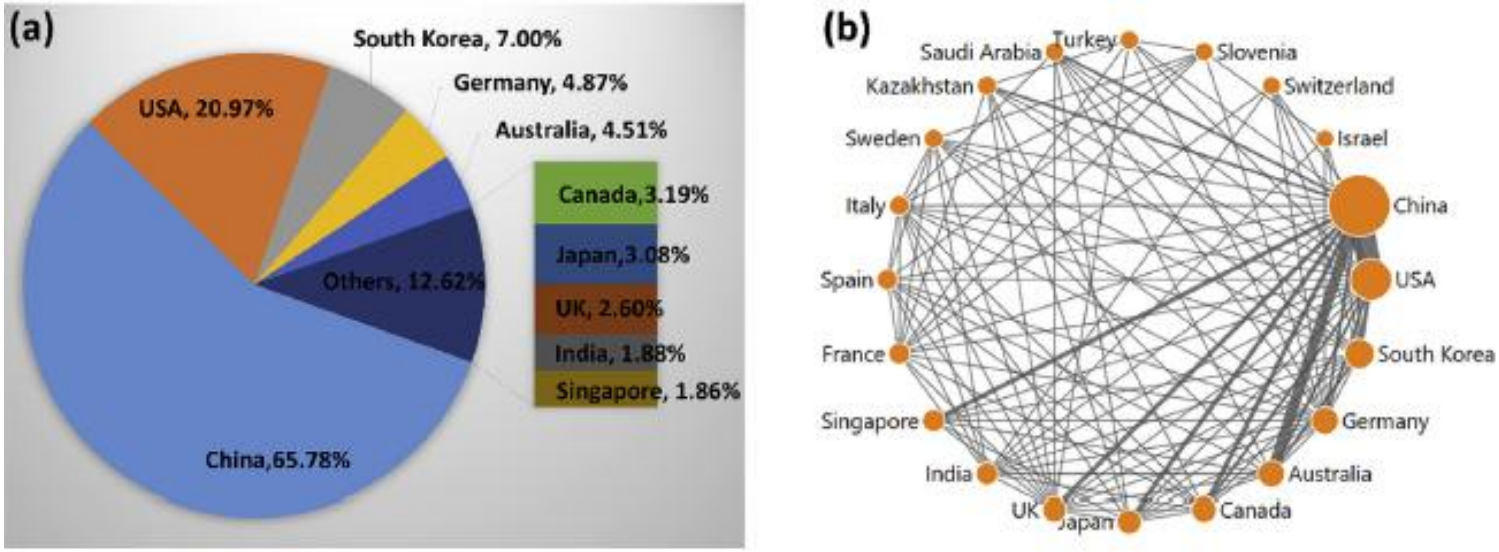




T. Liu, H. Hu, X. Ding, H. Yuan, C. Jin, J. Nai, Y. Liu, Y. Wang, Y. Wan, X. Tao, Energy Storage Materials, 2020, 30, 346

Li – S batteries

Publications on Li-S batteries

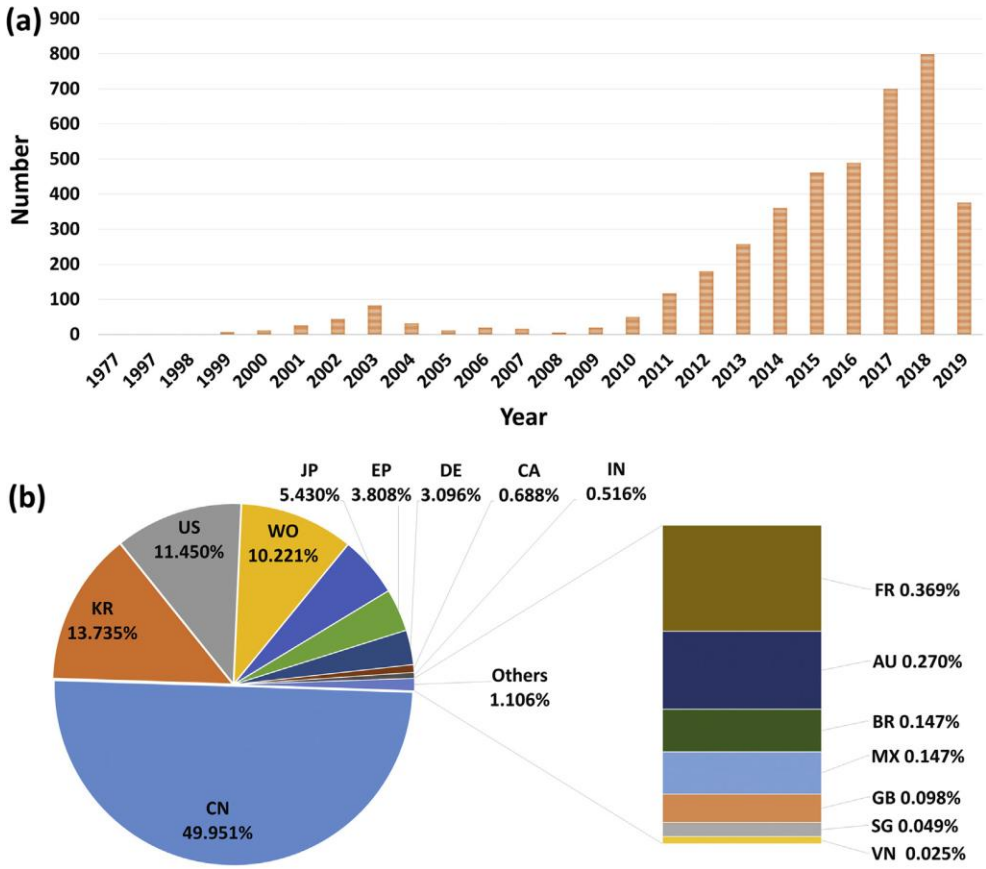


(a) Contribution and impact of the top 10 most productive countries in Li-S batteries and (b) Collaboration matrix map among the top 20 most productive countries.

T. Liu, H. Hu, X. Ding, H. Yuan, C. Jin, J. Nai, Y. Liu, Y. Wang, Y. Wan, X. Tao, Energy Storage Materials, 2020, 30, 346

Li – S batteries

Patent applications for Li-S batteries



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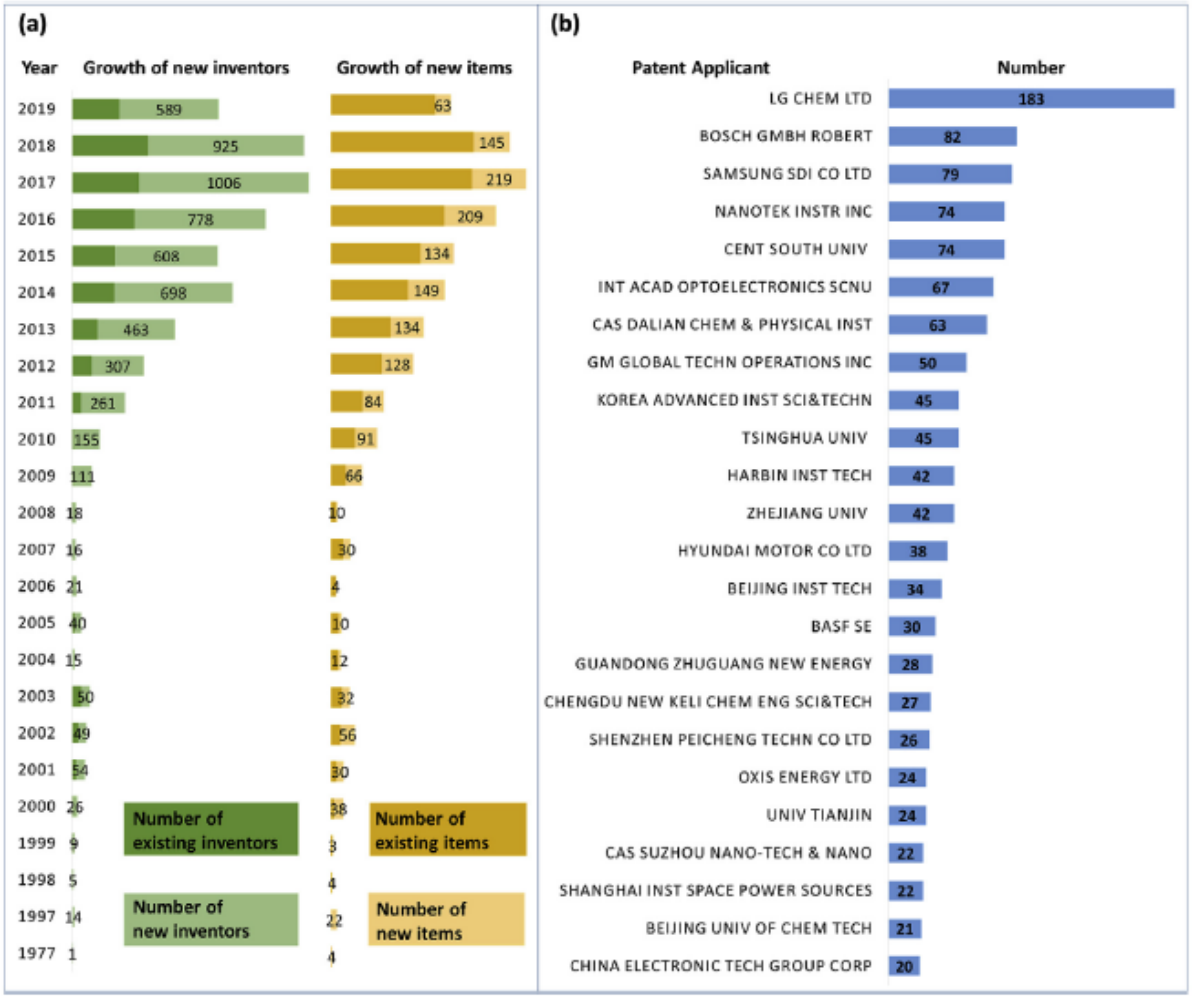
Li – S batteries

Patent applications for Li-S batteries



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Li – S batteries

Electrolyte

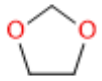
- **high ionic conductivity** (in the range between 10^{-3} Scm^{-1} to 10^{-2} Scm^{-1} at room temperature)
- **high lithium ion mobility**
- **the required stability window** (is less stringent since Li-S batteries operation window is between 1.5 to less than 3 V, therefore oxidative stability is not an issue as in the case of Li-ion batteries)
- **the stability with lithium is a prerequisite**
- **low flammability**
- **low toxicity for**
- **the electrolyte in a Li-S cell should have a good stability in the presence of polysulfide anions and their radicals**

Marczewski Maciej, W: Designing Electrolytes for Lithium-Ion and Post-Lithium Batteries / Wieczorek Władysław, Płocharski Janusz (red.), 2021, New York, Taylor & Francis Group, s.293-318, ISBN 978-981-4877-16-9

Li – S batteries

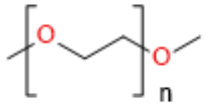
Electrolyte - solvent

Ethers



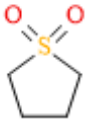
DIOX, DOL

THF

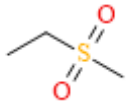


DME (n=1); Gn (n≥2)

Sulfones

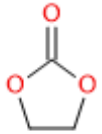


TMS

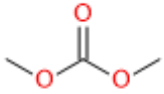


EMS

Carbonates



EC

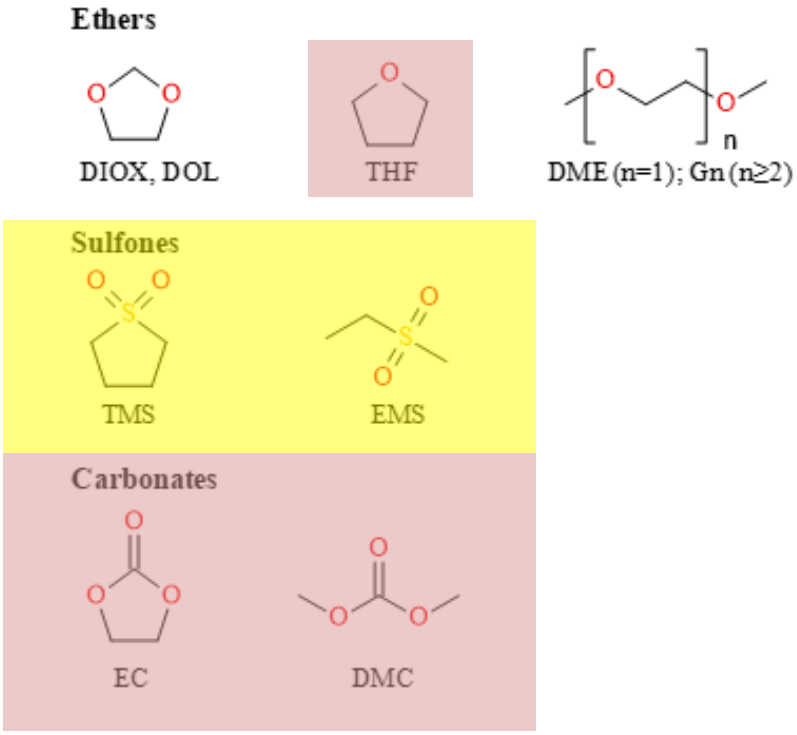


DMC

Marczewski Maciej, W: Designing Electrolytes for Lithium-Ion and Post-Lithium Batteries / Wieczorek Władysław, Płocharski Janusz (red.), 2021, New York, Taylor & Francis Group, s.293-318, ISBN 978-981-4877-16-9

Li – S batteries

Electrolyte - solvent



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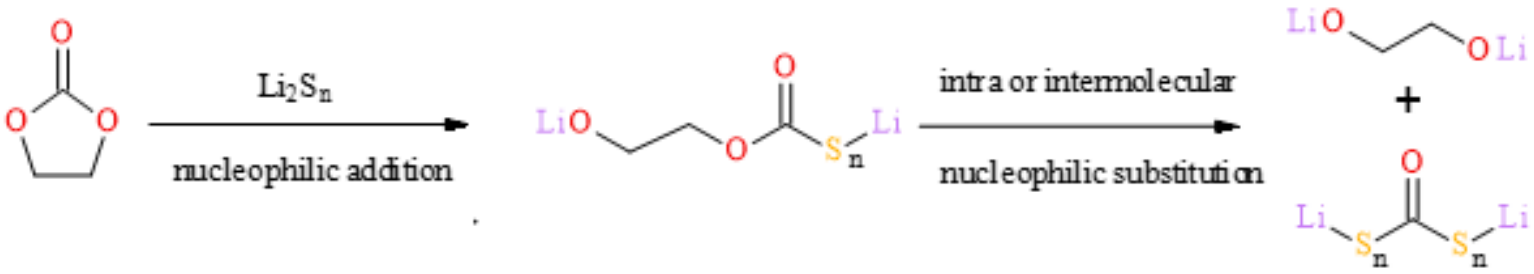
Li – S batteries

Electrolyte - solvent



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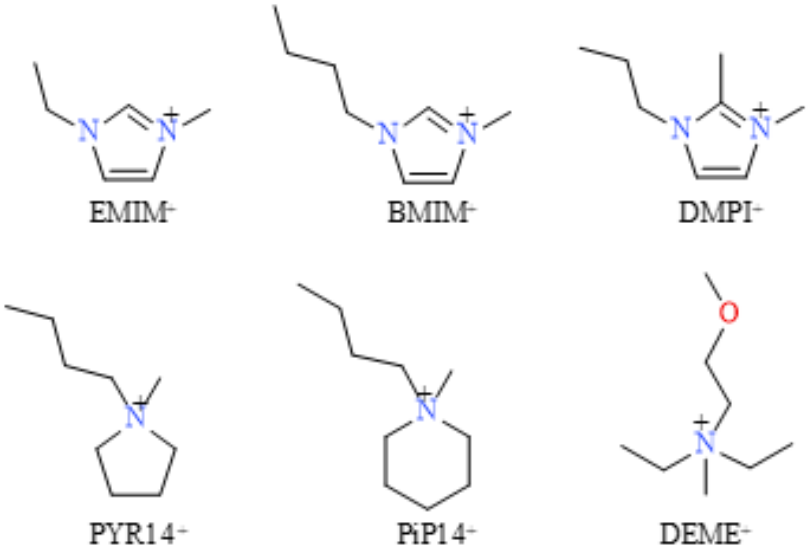
Electrolyte - solvent



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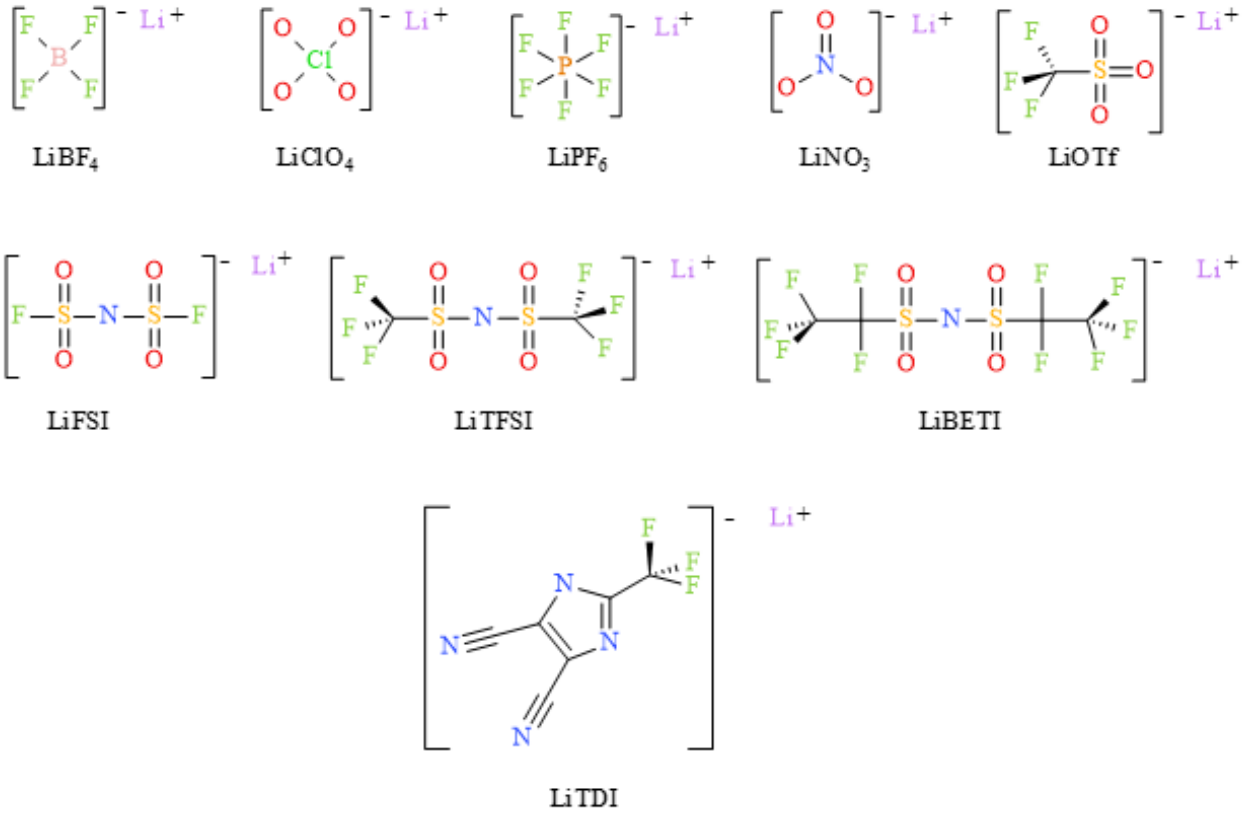
Li – S batteries

Electrolyte - salts



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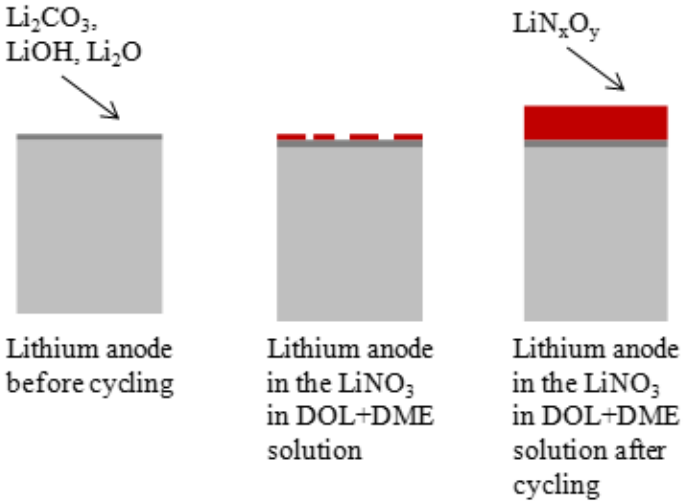
Li – S batteries

Electrolyte - additives

- $LiNO_3$
- Sulfones
- Phosphorous pentasulfide and polysulfides



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Li – S batteries

Electrolyte

- Liquid
- Solid
  - Gel
  - Polymer
  - Ceramic
- Highly Concentrated Electrolyte (HCE)

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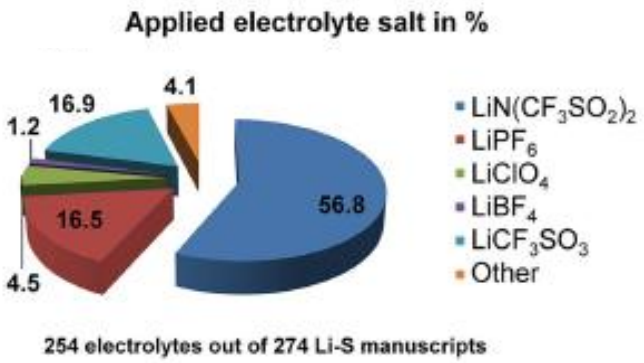
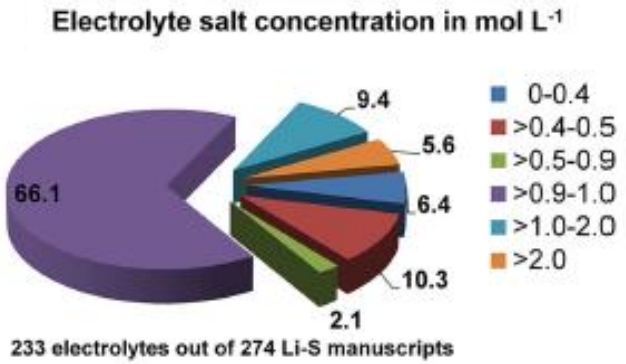
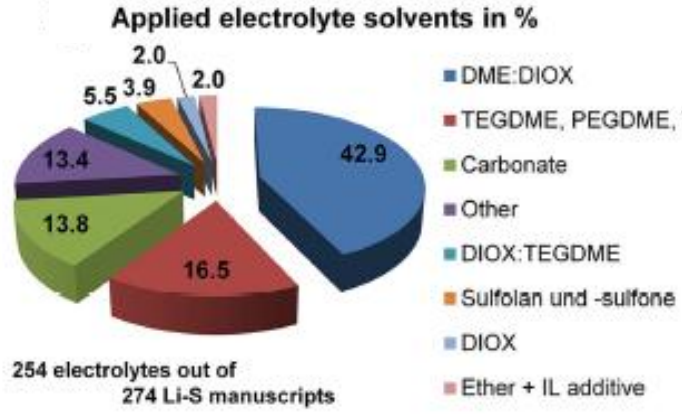
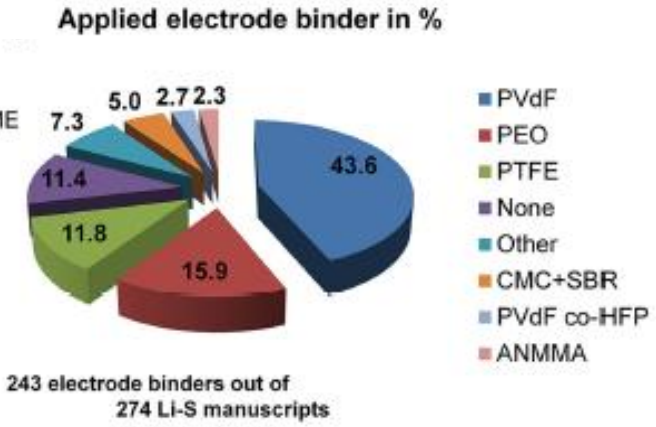
Li – S batteries

Electrolyte





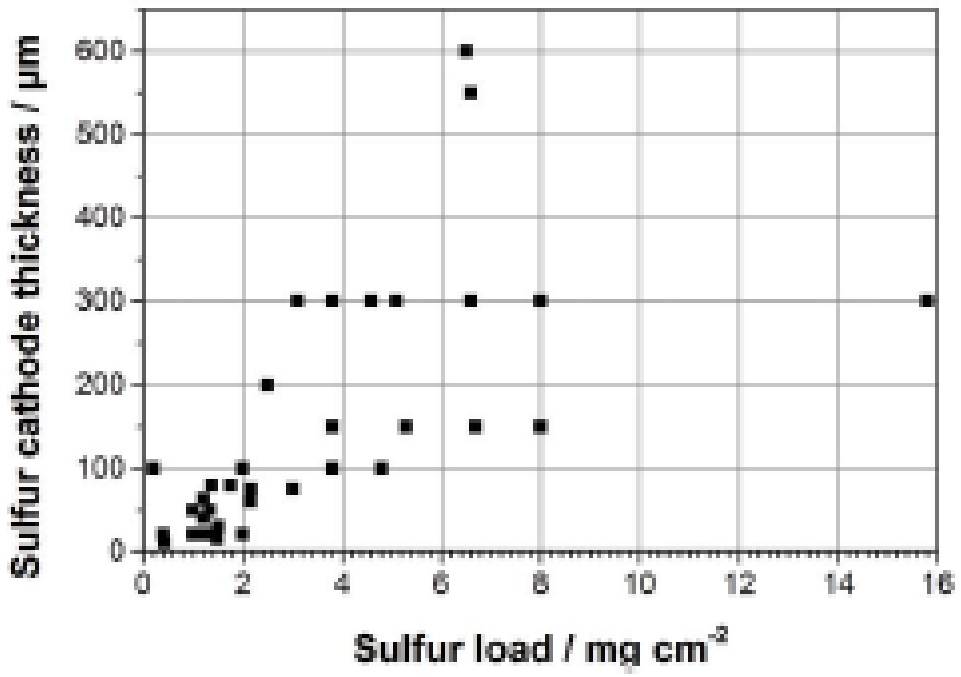




M. Hagen, D. Hanselmann, K. Ahlbrecht, R. Maça, D. Gerber, J. Tübke, Adv. Energy Mater. 2015, 5, 1401986

Li – S batteries

Electrolyte



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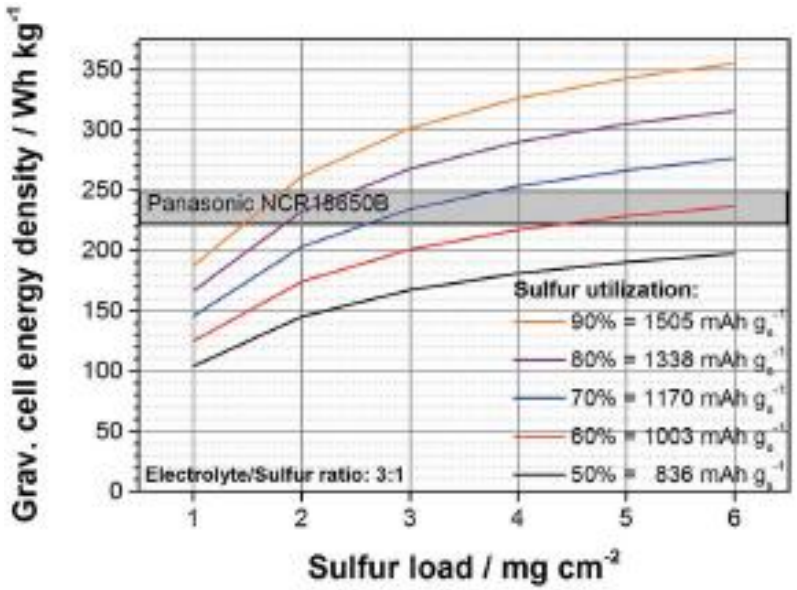
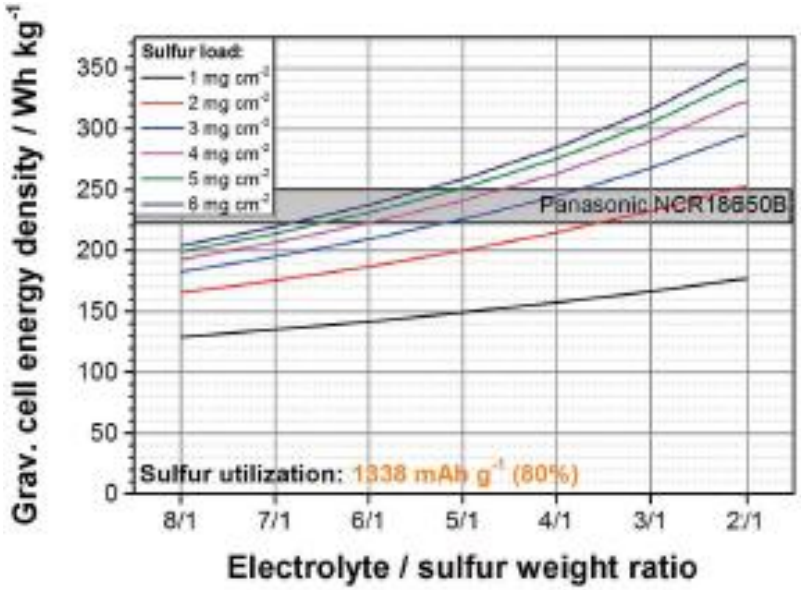
Li – S batteries

Electrolyte





M. Hagen, D. Hanselmann, K. Ahlbrecht, R. Maça, D. Gerber, J. Tübke, Adv. Energy Mater. 2015, 5, 1401986

Electrochemistry For Renewable Energy

Metal – air batteries

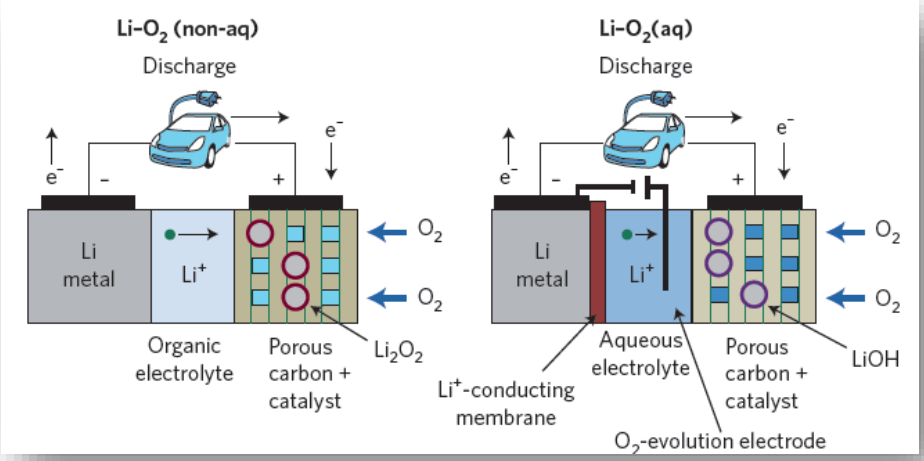
Metal – air batteries

- metal–air batteries have much higher specific energies than most currently available primary and rechargeable batteries
- a significant amount of work was carried out on metal–air batteries in the 1960s and early 1970s however, efforts in the field decreased considerably in the 1980s because of problems associated with the air electrode, thermal management, and the reversibility of the system
- recent advances in electrode materials and electrolytes, as well as new designs for metal–air batteries, have led to the renewal of intensive efforts, especially in the development of lithium–air batteries
- metal–air batteries are unique in that the active cathode material (oxygen) is not stored in the battery, instead, oxygen can be absorbed from the environment and reduced by catalytic surfaces inside the air electrode

Metal – air batteries

Metal/O_2 couple	Specific capacity based on metal alone ($Ah\ g^{-1}$)	Theoretical voltage (V)	Practical voltage (V)	Specific energy based on metal alone ($Wh\ kg^{-1}$)	Specific energy based on metal and all reactants H_2O (aqueous only) ($Wh\ kg^{-1}$)	Specific energy based on reaction ($Wh\ kg^{-}$)
In nonaqueous electrolytes						
$Li + 1/4\ O_2 \rightarrow 1/2\ Li_2O$	3.862	2.91	2.80	10 813	10 813	5023
$Li + 1/2\ O_2 \rightarrow 1/2\ Li_2O_2$	3.862	3.10	3.00	11 586	11 586	3505
In aqueous electrolytes						
$Li + 1/4\ O_2 + 1/2\ H_2O \rightarrow LiOH^a$	3.862	3.45	3.00	11 586	5044	3359
$Zn + 1/2\ O_2 \rightarrow ZnO$	0.820	1.65	1.10	902	902	725
$Al + 3/4\ O_2 + 1\,1/2\ H_2O \rightarrow Al(OH)_3$	2.980	2.71	1.30	3874	1936	1340
$Mg + 1/2\ O_2 + H_2O \rightarrow Mg(OH_2)$	2.205	2.93	1.30	2867	1647	1195
$Fe + 1/2\ O_2 + H_2O \rightarrow Fe(OH)_2$	0.960	1.30	1.00	960	726	597
$Ca + 1/2\ O_2 + H_2O \rightarrow Ca(OH)_2$	1.337	3.12	2.00	2675	1846	1447

Lithium – O_2 batteries

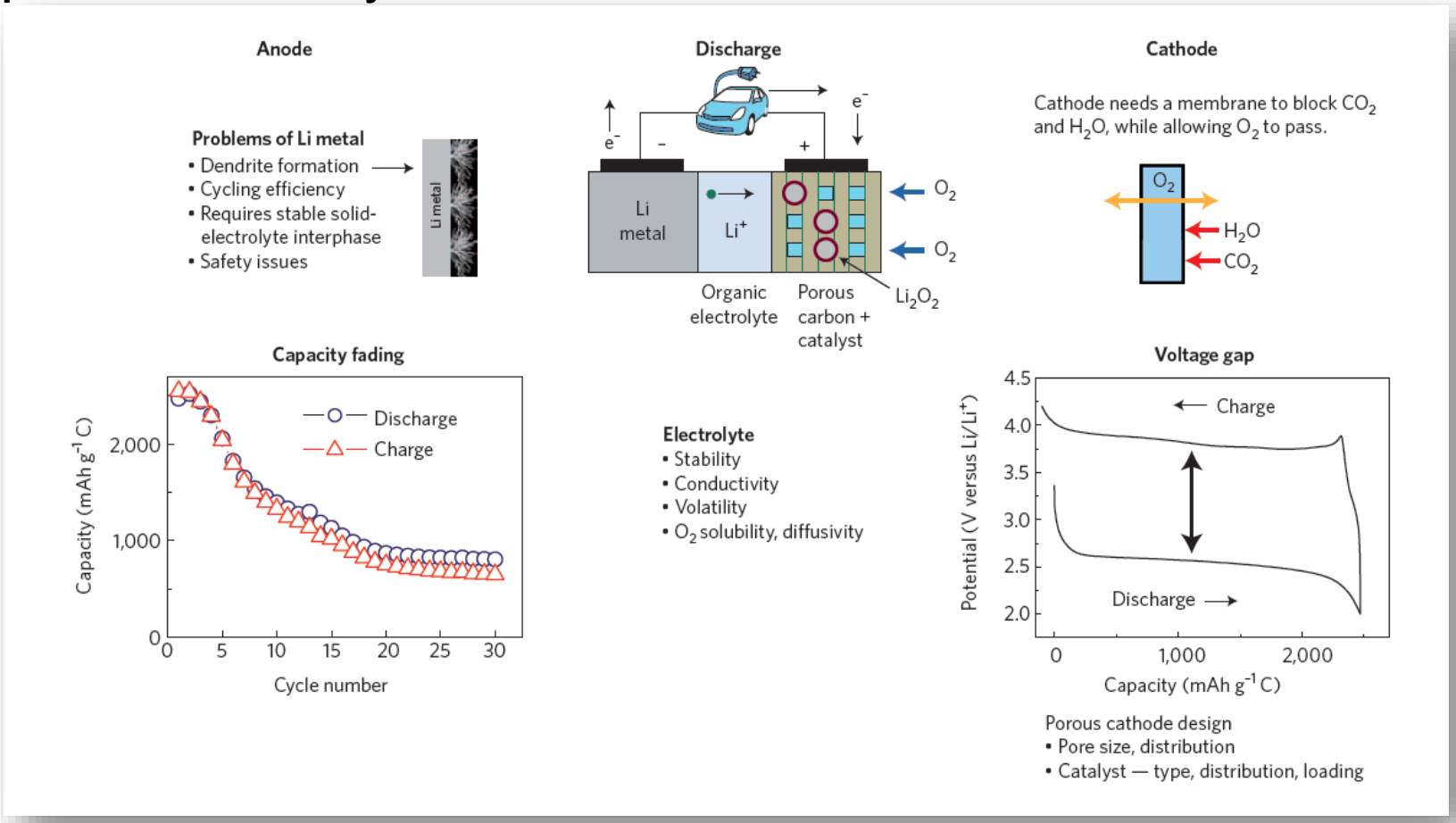


- on discharge, the Li-metal anode is oxidized, releasing Li^+ into the electrolyte, and the process is reversed on charge
- at the positive electrode, O_2 from the atmosphere enters the porous cathode, dissolves in the electrolyte within the pores and is reduced at the electrode surface on discharge

- when a suitable non-aqueous electrolyte is employed, O_2^{2-} is formed, which, along with Li^+ from the electrolyte, forms Li_2O_2 as the final discharge product
  - the peroxide is then decomposed on charging: $2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$
- aqueous electrolytes involve the formation of OH^- and then LiOH at the cathode on discharge
  - according to the equation: $2Li^+ + O_2 + H_2O + 2e^- \leftrightarrow 2LiOH$, with LiOH being oxidized on charge

Lithium – O_2 batteries

the non-aqueous Li–O2 battery



Lithium – O_2 batteries

the aqueous Li–O2 battery

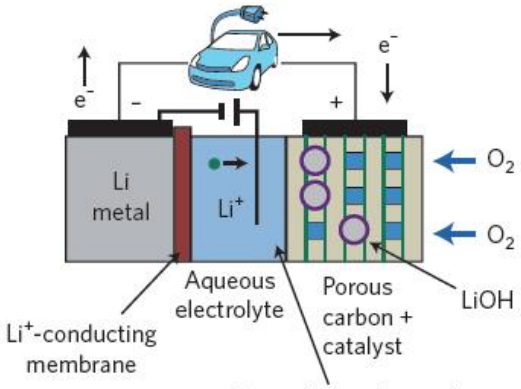
Anode

Problems of Li metal
- Cycling efficiency
- Li/ceramic interface
- Safety issues

Requires Li^+-conducting membrane (such as LISICON) to protect Li.

Precipitation of LiOH on LISICON membrane and membrane instability in strong acidic and basic electrolyte.

Discharge

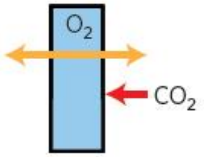


O_2-evolution electrode
Requires cheap, efficient O_2-evolution catalyst.

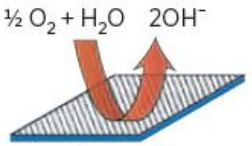
Electrolyte
Limited LiOH solubility in H_2O: precipitation of LiOH, blocking electrode pores.

Cathode

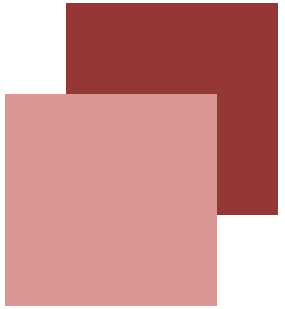
Cathode needs membrane blocking CO_2, while allowing O_2 to pass



Optimize gas-diffusion electrode for Li–O_2 cell.



Requires cheap, efficient oxygen-reduction catalyst.



Capacitors & Super Capacitors

Capacitors & Super Capacitors

Electrical energy can be basically stored in two different ways:

- First, electrical energy can be stored as chemical energy which becomes available through the faradaic reaction of the active material. **This type of energy storage device is called a battery.**
- Second, electrical energy can be stored as electrostatically adsorbed positive and negative charges, that is, to say non-faradaic reaction occurs on the electrode. **Conventional capacitors use non-faradaic reaction to store the electrical energy.**

Non-faradaic reactions involve no chemical reaction on the electrodes, but faradaic reactions involve chemical reactions including phase transition of active materials.

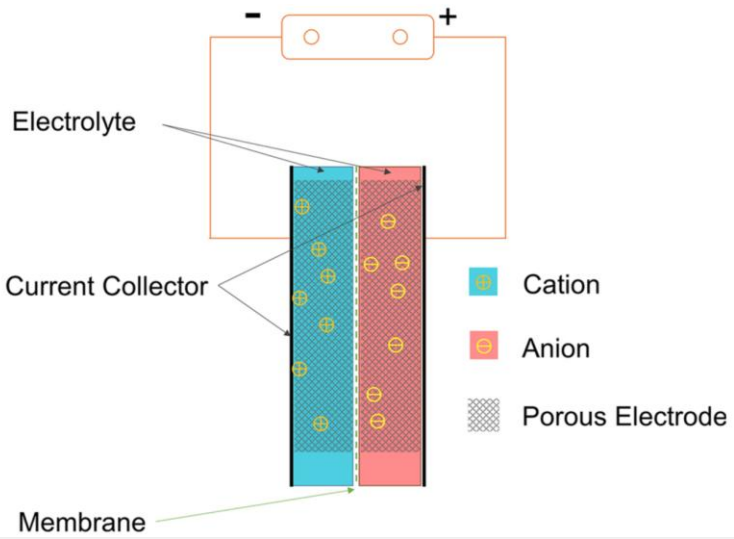
Therefore, the cycle life of battery reactions is limited **to several thousand cycles or less**, due to irreversible chemical reactions and irreversible phase changes of active materials. The cycle life of capacitors **is over 10^5 10^6 cycles**.

Capacitors & Super Capacitors

Classification of Capacitors

Super Capacitors, Table 1 Classification of capacitors

Name	Mechanism	Type	Classification
Electrostatic capacitor	Electrostatic	Non-faradaic	Conventional capacitor
Electrolytic capacitor	Electrostatic	Non-faradaic	Conventional capacitor
Electrical double-layer capacitor	Electrical double layer	Non-faradaic	Super capacitor
Pseudo capacitor	Redox reaction	Faradaic	Super capacitor
Hybrid capacitor	Redox reaction	Faradaic	Super capacitor



Wikipedia

Capacitors & Super Capacitors

Comparison with Secondary Battery

- From the view point of charge/discharge capacity, super capacitors are positioned between electrostatic capacitors and secondary batteries. That is, the charge/discharge capacity (energy density) of super capacitors is greater than electrostatic capacitors but smaller than secondary batteries.
- The operation voltage of super capacitors is almost same as secondary batteries, but charging/discharging speed is much faster than secondary batteries.
- The power density of super capacitors is greater than secondary batteries.
- Turning to the cycle characteristics of super capacitors, electrical double-layer capacitors are possible which cycle an infinite time – at least – in principle. On the other hand, pseudocapacitors have better cycle characteristics than secondary batteries but poorer cycle characteristics than electrical double-layer capacitors.

Capacitors & Super Capacitors

Commercially Available Super Capacitor

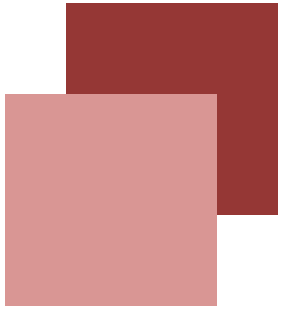
- The electrochemical double-layer capacitor is already commercially available from several companies, and their energy densities are about 10 Wh L^{-1}.
- Lithium-ion capacitor is one of the most promising commercially available super capacitor due to its high energy density and high specific power. As the negative electrode, a conventional graphite electrode for lithiumion battery is used and activated carbon electrode is used as positive electrode. Thus, the lithium ion capacitor belongs to the group of hybrid capacitor. The cell voltage of lithium-ion capacitors is 3.8 V with fully charged state and 2.2 V with fully discharged state. The lithium-ion capacitor is already commercially available, and Japanese companies, including JM Energy Corp., Asahi Kasei FDK Energy, and TAIYO YUDEN Co., Ltd, took initiative to develop the practical lithium-ion capacitor. Commercial lithium ion capacitor shows the energy density about 20 Wh L^{-1}.

Capacitors & Super Capacitors

Application of Super Capacitors

Super capacitors have different characteristics with rechargeable batteries as mentioned above, so super capacitors are used in different applications with rechargeable batteries.

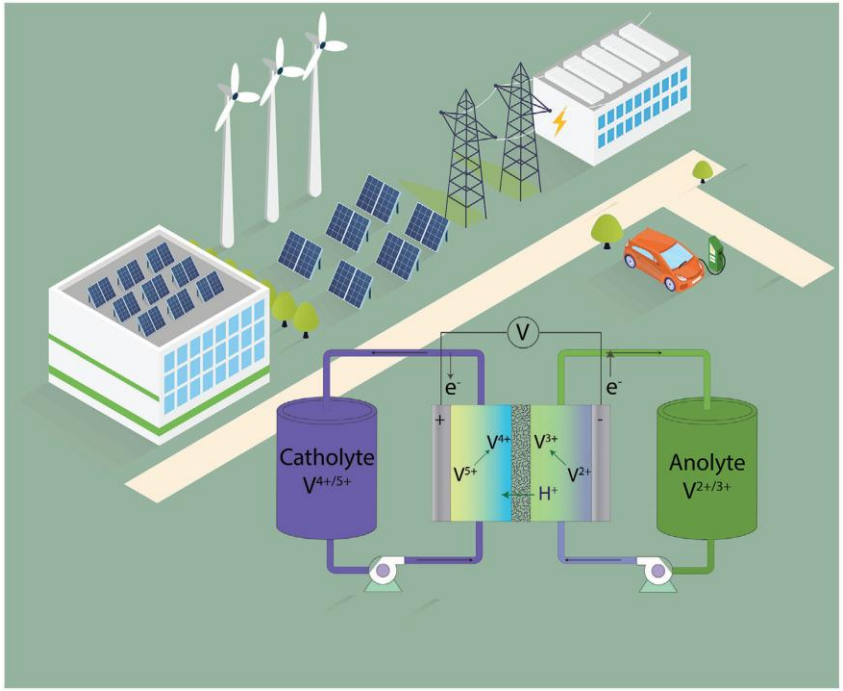
- The major applications for super capacitors are high-pulse power and short-term power hold.
- There are several applications for super capacitors like memory backup, portable power supplies, electric vehicles, and hybrid electric vehicles.
- Recent attracting applications are load leveling of renewable energy applications like photovoltaic or wind energy. Rechargeable batteries for such applications need to be replaced every 1–3 years. On the other hand, life duration of super capacitors in such application is around 20 years, which is similar to the life span of the photovoltaic panels.



Redox Flow Batteries (VRFBs)

VRFBs

A vanadium redox battery consists of an assembly of power cells in which two electrolytes are separated by a proton-exchange membrane. The electrodes in a VFRB cell are carbon based. Both electrolytes are vanadium-based. The electrolyte in the positive half-cells contains V^{4+} and V^{5+} ions, while the electrolyte in the negative half-cells consists of V^{3+} and V^{2+} ions. The electrolytes can be prepared by several processes, including dissolving vanadium pentoxide (V_2O_5) in sulfuric acid (H_2SO_4).



Adv. Energy Mater. 2024, 14, 2400721

VRFBs – cell architecture

The main drawback to lithium batteries for large-scale projects, is that hundreds of thousands of cells are needed. This is an inefficient way of storing energy and uses far more materials than a VFRB battery, since each of these individual Li-on battery cells can only store a relatively small amount of energy. There is a limit to the amount of active materials that one can hold inside the electrodes, since thick electrodes result in poor performance and shorter lifetimes.

In contrast, VRFBs store their energy in two electrolyte tanks, which are connected to a stack of cells. The electrolyte is the fluid that stores the active materials dissolved in the liquid, and is pumped from the two tanks through the cell stack during charging and discharging process. The energy capacity of a VFRB battery can easily be expanded by adding more solution to the tank. This battery design makes it much easier to adapt VRFBs to industrial-scale operations without adding much costs since the tanks can be any size desired. In other words, as the energy capacity of a VRFB battery increases, the price per kilowatt hour decreases.

VRFBs outperform Li-on batteries and are a far superior energy storage option for stationary applications, where their feature of storing chemicals in external tanks enables large-scale energy storage from a renewable source during peak-production times and consistent supply when energy production drops below demand.

VRFBs – Energy capacity

Lithium batteries decay over time and lose capacity; a well-designed VRFB System can run at 100% capacity forever.

To make up for their capacity loss, lithium batteries are built to be oversized at the time of installation, which increases costs to the end user. The average age of a substation transformer is 42 years.

According to Battery University, the capacity of lithium-ion cells can drop to a 50 percent level after 1,200 to 1,500 discharges while VRFBs retain 100% capacity up to 14,000 discharges.

VRFBs – Safety

All energy-storage systems have safety concerns. VRFBs are inherently safer than Li-on batteries, since the energy is stored separately from the conversion device (i.e., the cell stacks).

- Li-ion batteries use flammable electrolytes, are prone to “thermal runaway” during charging, and are never truly “off” since all of the materials are connected at all times.

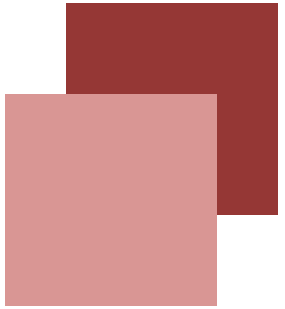
- VRFBs use aqueous electrolytes, which are not flammable. VRFBs are also well equipped for emergency power delivery, which has to remain off for long periods of time to be kept in reserve for powering a grid. The self-discharge rates of VFRBs are very low due to the energy being stored separately where it cannot react during idle periods.

VRFBs – Lifespan

VRFBs have inherently much longer lifetimes than Li-on batteries. This is because Li-ion electrodes undergo significant physical changes with each charge-discharge cycle in order to accommodate the insertion and removal of the Li ions in the intercalation electrodes.

These changes are greater for deeper discharge cycles. In contrast, VRFBs electrodes do not have to undergo changes during cycling, since they are simply sites for the electrochemical reactions of the V ions, which remain dissolved in the electrolytes. A VRFBs lifetime does not depend on the number of cycles or the depth of the charge each cycle.

VRFBs have an avg. lifespan of 25 years or longer, more than double the 7 to 10 years of a typical lithium battery. Li-on battery life span can vary significantly depending on the number and depth of the charge-discharge cycles.



Fuel Cells

Fuel Cells

Through fuel cells we can convert chemical energy to electrical energy directly where fuel and oxidant are supplied from the outside of a cell. Fuel cells are the energy conversion systems rather than the energy storage devices such as primary or secondary batteries. Fuel cel was invented by Schoenbein or Sir William Grove in 1839. This invention was before those of a lead acid battery and a manganese dry cell.

Fuel Cells - principles

Fuel cells can produce electricity and heat simultaneously through an electrochemical reaction using a fuel and an oxidant. Fuel cells can produce electric energy through an electrochemical system composed of two electrodes (anode and cathode) and an electrolyte. Electrodes are electronic conductors and should have a good electrochemical catalytic activity for the oxidation of fuels and/or the reduction of oxidants. An electrolyte is an ionic conductor.

Normally, hydrogen is used for a fuel and air (oxygen) is used for an oxidant. When a fossil fuel is used as a primary fuel, it has to be converted to hydrogen through a steam reforming or a partial oxidation. Since hydrocarbons are not electrochemically active at room temperature, they have to change to hydrogen for fuel cells. In a fuel cell system, an oxidation reaction of a fuel (hydrogen) takes place at the anode and a reduction reaction of an oxidant (oxygen, air) takes place at the cathode.

Fuel Cells - principles

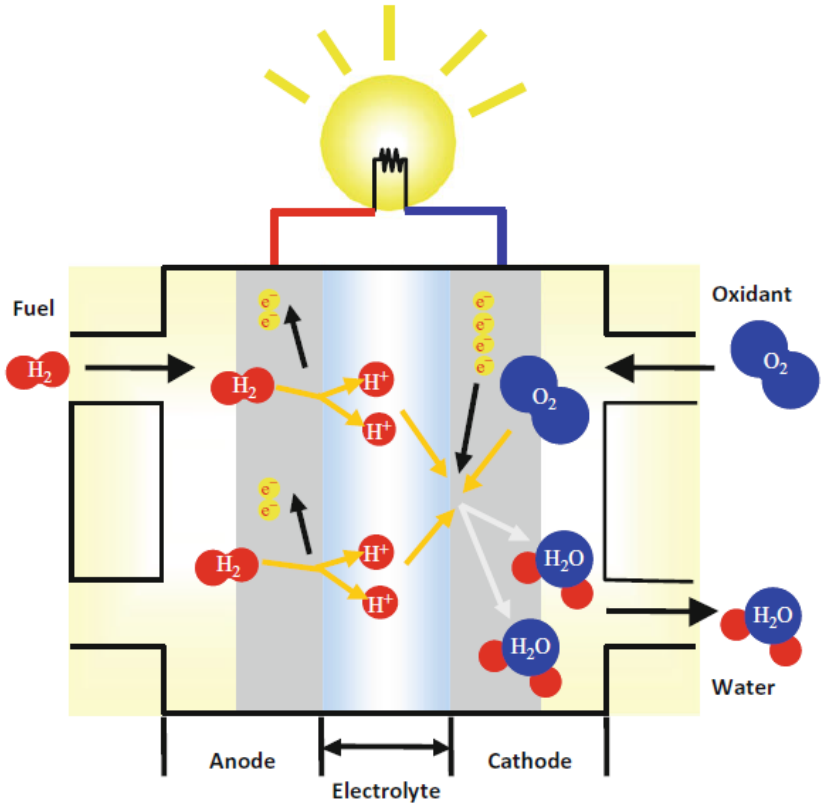
The electrochemical reactions which take place at an anode and a cathode for hydrogen-oxygen can be expressed as follows:

Anode (hydrogen): $H_2 = 2H^+ + 2e^-$

Cathode (oxygen): $½\ O_2 + 2H^+ + 2e^- = H_2O$

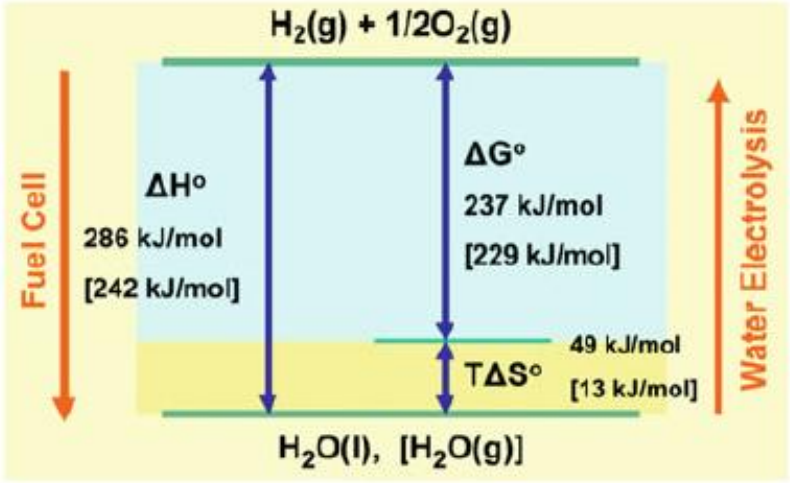
Total: $H_2 + ½\ O_2 = H_2O$

Fuel Cells, Principles and Thermodynamics,
Fig. 1 Schematic drawing of fuel cell

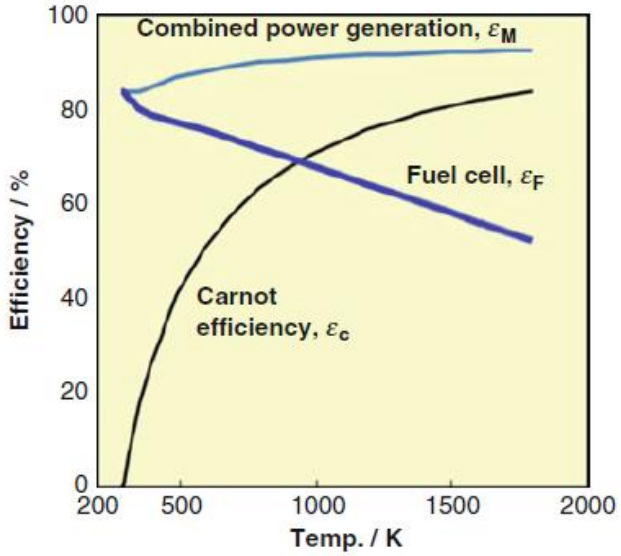


Fuel Cells - principles

Figure 2 shows the energy change of the water formation reaction at 25 °C. The total Energy change is expressed in ΔH which is - 286 kJ/mol when the formed H_2O is liquid water (HHV). If water vapor is formed, the total energy changed to - 242 kJ/mol (LHV). In this paper the HHV value is used unless otherwise expressed. The total energy can be divided into work and heat. The work which is expressed in Δ G is -237 kJ/mol. This value is the theoretical amount of the electrical energy that can be obtained through the water formation reaction at 25 °C. The theoretical energy conversion efficiency of a fuel cell can be calculated by Δ G/ Δ H. This value becomes 83 % for hydrogen–oxygen fuel cell at 25 °C.



Fuel Cells, Principles and Thermodynamics, Fig. 2 Energy conversion of fuel cell reaction



Fuel Cells, Principles and Thermodynamics, Fig. 3 Theoretical efficiency of hydrogen–oxygen fuel cell and Carnot efficiency

Fuel Cells - principles

Fuel	Reaction	ΔH° (kJ/mol)	ΔG° (kJ/mol)	EMF (V)	Eff. (%)
Hydrogen	$H_2(g) + 1/2O_2(g) => H_2O(I)$	−286	−237	1.23	83
Methane	$CH_4(g) + 2\ O_2(g) => CO_2(g) + 2\ H_2O(I)$	−890	−817	1.06	92
CO	$CO(g) + 1/2\ O_2(g) => CO_2(g)$	−283	−257	1.33	91
Carbon	$C(s) + O_2(g) => CO_2(g)$	−394	−394	1.02	100
Methanol	$CH_3OH(I) + 1/2O_2(g) => CO_2(g) + 2H_2O(I)$	−727	−703	1.21	97
Ethanol	$C_2H_5OH(I) + 3O_2(g) => 2CO_2(g) + 3H_2O(I)$	−1,367	−1,325	1.18	96
Hydrazine	$N_2H_4(I) + O_2(g) => N_2(g) + 2H_2O(I)$	−622	−623	1.61	100
Ammonia	$NH_3(g) + 4/3O_2(g) => 3/2H_2O(I) + 1/2\ N_2(g)$	−383	−339	1.17	89
DME	$CH_3OCH_3(g) + 3O_2(g) => 2CO_2(g) + 3H_2O(I)$	−1,460	−1,390	1.20	95

Fuel Cells - characteristic

1. Theoretical efficiency is very high especially at low temperatures.
2. The output voltage of a unit cell is 1 V or less. In order to get a high power, a large current is needed. In another words, the large quantity of reactants should react at the electrode/electrolyte interface smoothly.
3. The system efficiency does not depend on the size of the system. The fuel cell system is suitable for the smaller size power generation system compared to engines and turbine systems.
4. A fuel cell is an environmentally friendly system with no NOx emission, no noise, and no vibration.

Fuel Cells - types

advantages	disadvantages	comments
	Alkaline (AFC)[a]	
mechanically rechargeable	limited activated life	original development > 30 years ago
low-cost KOH electrolyte	intolerant of impurities in gas streams CO_2 and CO	Apollo fuel cell
	pure H_2 only suitable fuel	operates at room temp to 80 °C
		demo in vehicles in the 1970s
	Polymer Electrolyte Membrane Fuel Cell (PEMFC)	
nonvolatile electrolyte	expensive catalysts required	operates best at 60–90 °C
few materials problems	CO a strong poison	originally developed for space by GE
CO_2 rejecting electrolyte	H_2O management essential	hydrogen fuel (re-formed hydrocarbons, pure H_2, MH storage)
pressure differential between anode and cathode	high-cost electrolyte	
	pure H_2 only suitable fuel	main development efforts for automotive and stationary applications
polymer electrolyte	oxygen kinetics are slow	
	intolerant of impurities	
	limited life	
	water management essential	
	Direct Methanol Fuel Cell (DMFC)	
direct fuel conversion	stable reaction intermediates	operates best at 60 to 90 °C)
slow electrode kinetics	high catalyst loadings	same construction as PEMFC
improved wt and vol	water management essential	methanol fuel eliminates reformer
polymer electrolyte	low overall efficiency	lower current capability
	methanol hazardous	methanol crossover reduces efficiency
		needs new membrane, higher efficiency
		high catalyst loadings
		main effort for portable electronic devices

Fuel Cells - types

advantages	disadvantages	comments
	Phosphoric Acid Fuel Cell (PAFC)	
CO_2 rejecting electrolyte high fuel efficiency	H_2 only suitable fuel anode CO catalyst poison O_2 kinetics hindered low conductivity electrolyte high-cost catalysts limited life	operates best at ~200 °C stationary energy storage (nominal units, 250 kW) available commercially
	Molten Carbonate Fuel Cell (MCFC)	
fast electrode kinetics high efficiency CO/CH_4 usable fuel direct reforming feasible high-grade heat available	materials problems and life low sulfur tolerance high ohmic electrolyte low tolerance to sulfur need to recycle CO_2 limited life	operates best at 550 °C nickel catalysts, ceramic separator membrane hydrocarbon fuels re-formed in situ several large demonstration units significant government support
	Solid Oxide Fuel Cell (SOFC)	
high grade heat available fast electrode kinetics in situ reforming feasible no electrolyte management high system efficiency tolerant of impurities	high fabrication costs severe materials constraints high electrolyte conductivity	operates at 900 °C conducting ceramic oxide electrodes hydrocarbon fuels re-formed in situ least sensitive to sulfur, etc.

Fuel Cells - characteristic

Considering the world climate change due to a large consumption of fossil fuels, we have to move to a clean energy system as soon as possible. The hydrogen energy is a clean energy system. If hydrogen is obtained from water using renewable energies, we can reach an ultimate clean energy system. Fuel cells would be the most suitable device to use hydrogen since it has high conversion efficiency. In order to create an ultimate clean energy system for the sustainable growth of human beings, the hydrogen-fuel cell system is inevitable and should be promoted.

Electrochemistry For Renewable Energy