Challenges and Opportunities of Next-generation Rechargeable Batteries

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MINISTRY OF BUSINESS, INNOVATION & EMPLOYMENT
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ROYAL SOCIETY TE APĀRANGI

NZ Product Accelerator

Outline

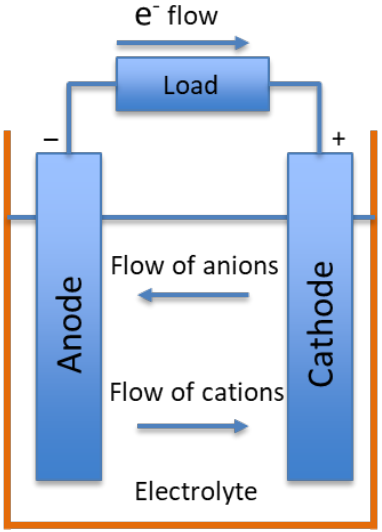
1) Battery and Electrochemical cells
2) Next-generation rechargeable batteries
   - ❖All solid-state batteries
   - ❖Na-ion batteries
   - ❖……
3) Mg-based batteries
4) Summary

Battery & Electrochemical cell

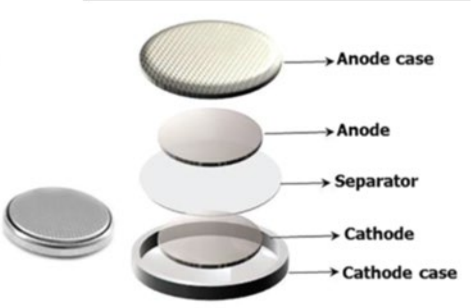
Battery: a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction.

- Cell: the basic electrochemical unit
- A battery consists of one or more of cells

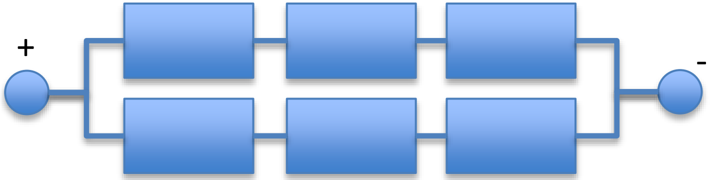
1) Primary batteries: discharge once and discard
    - Convenient, usually cheap, lightweight
2) Secondary or rechargeable batteries
    - High efficiency, long cycle life



Single battery cell



Coin-cell battery

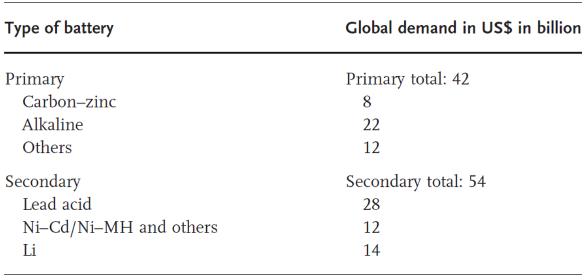


A battery with several cells

Battery

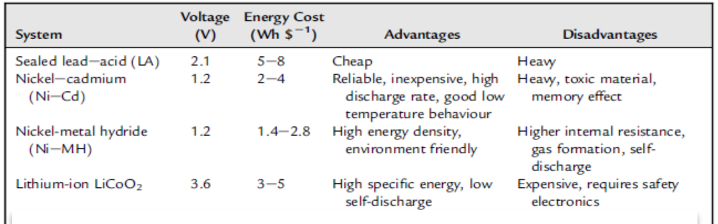
- ❑ Primary batteries
  - ○ Alkaline battery
  - ○ Lithium primary
  - ○ ……
- ❑ Secondary batteries
  - ○ Lead-acid batteries
  - ○ Ni-batteries (NiCd, Ni/MH)
  - ○ **Li ion batteries (LIBs)**

Global battery market for 2010



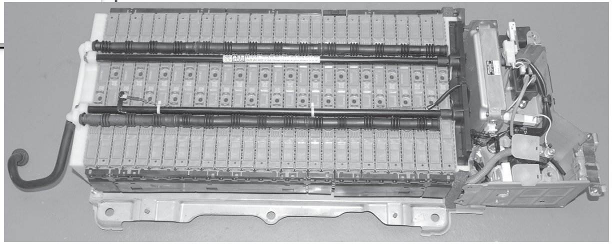
Type of battery	Global demand in US$ in billion
Primary	Primary total: 42
Carbon–zinc	8
Alkaline	22
Others	12
Secondary	Secondary total: 54
Lead acid	28
Ni–Cd/Ni–MH and others	12
Li	14

- ❑ 1st Rechargeable battery: Lead-acid battery was invented in 1859.
- ❑ First car with combustion engine 1885 (Karl Benz)
- ❑ First electric car 1881
- ❑ Around 1900, competing options electric versus combustion



System	Voltage (V)	Energy Cost (Wh $^{-1})	Advantages	Disadvantages
Sealed lead–acid (LA)	2.1	5–8	Cheap	Heavy
Nickel–cadmium (Ni–Cd)	1.2	2–4	Reliable, inexpensive, high discharge rate, good low temperature behaviour	Heavy, toxic material, memory effect
Nickel-metal hydride (Ni–MH)	1.2	1.4–2.8	High energy density, environment friendly	Higher internal resistance, gas formation, self-discharge
Lithium-ion LiCoO$_2$	3.6	3–5	High specific energy, low self-discharge	Expensive, requires safety electronics

2008 Toyota Prius NiMH battery pack



1899, Camille Jenatzy reached a speed record of 109 km/h with his cigar-shaped electric car powered with lead-acid batteries.

N. M. Johnson, Battery technology for CO2 reduction, 2014, 10.1533/9780857097422.3.582
https://www.iihs.org/ratings/vehicle/toyota/prius-4-door-hatchback/2008

Li-ion Batteries (LIBs)

Nobel Prize Invention:
“This lightweight, rechargeable and powerful battery is now used in everything from cell phones to laptops and electric vehicles. It can also store significant amounts of energy from solar and wind power, making possible a fossil fuel-free society.” --- Nobel Prize in Chemistry 2019


1995
Toshiba T3400CT


1998
Motorola GC87C


2000
Canon D30


Tesla Model S


Tesla Power wall


Tesla Powerpack 100MW (megawatts)
2017 South Australia

1980s
LIBs prototype

2000s
3C products

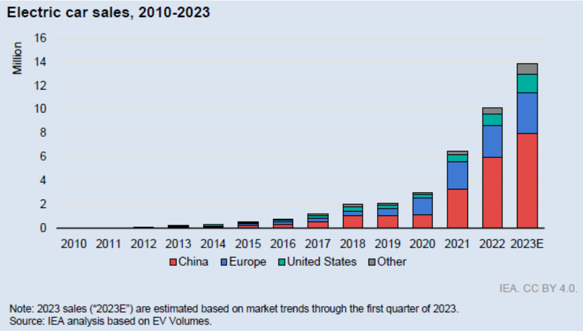
2020s
PEDs, smart grid storage

https://www.tesla.com/

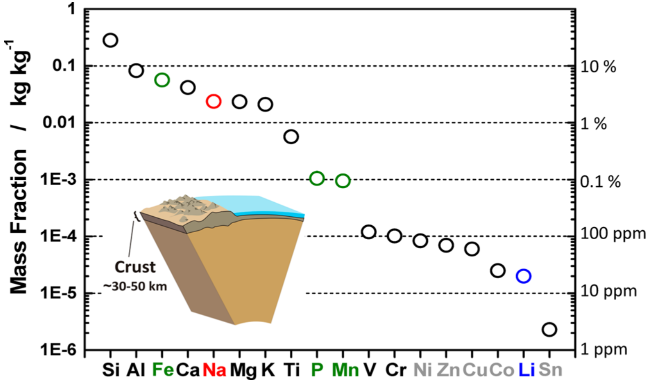
Challenges

Current LIBs have very good properties and widely used for small, medium and large portable electronic devices.

Electric car sales, 2010-2023



Note: 2023 sales ("2023E") are estimated based on market trends through the first quarter of 2023.
Source: IEA analysis based on EV Volumes.



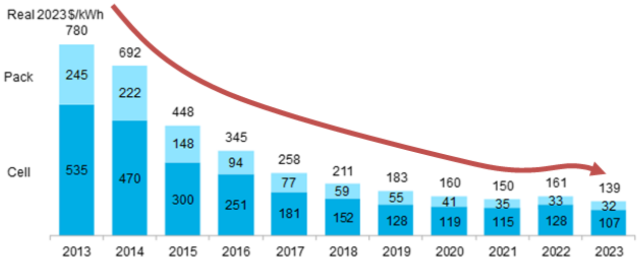
Elemental abundance in the Earth's crust

Lithium and cobalt are rare and expensive resources, making up 20ppm and 25ppm of the earth's crust.

However, the rapid growth of battery demand brings substantial challenges:

- ☐ Raw materials:
  - The critical metals in LIBs, including Li, Co, Ni and Mn, is geographically limited. For example, two thirds of global Li reserves are distributed in Chile and Australia, whilst 51% of global Co reserves are found in the Congo.
- ☐ LIBs are very difficult to recycle
- ☐ Low Cost (Cost< $100/kWh)
- ☐ *High energy density > 500 Wh/kg*
- ☐ *Very long cycle life (>2000, Calendar life: 10 years)*

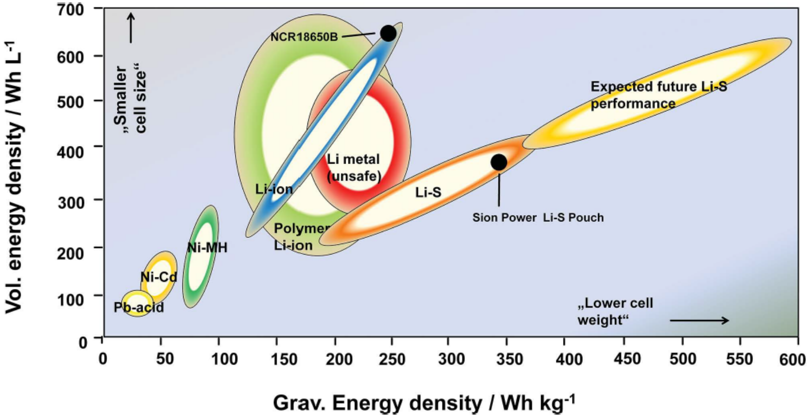
Figure 1: Volume-weighted average lithium-ion battery pack and cell price split, 2013-2023

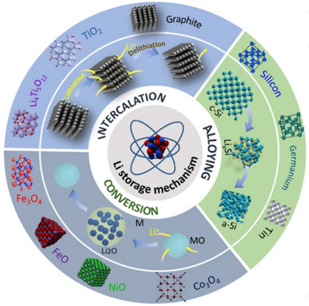


Source: BloombergNEF. Historical prices have been updated to reflect real 2023 dollars. Weighted average survey value includes 303 data points from passenger cars, buses, commercial vehicles, and stationary storage.

Next-generation Batteries

a) Post Lithium-ion batteries





Reaction mechanisms	Anode materials	Scapacity/mAh g^{-1}
Insertion	C	372
	$Li_4Ti_5O_{12}$	175
Conversion	Fe_3O_4	924
	FeO	744
	Co_3O_4	890
	NiO	718
Alloying	Si	4200
	Sn	994
	Ge	1600

Replace graphite with high energy density anode materials, such as Sn or Si

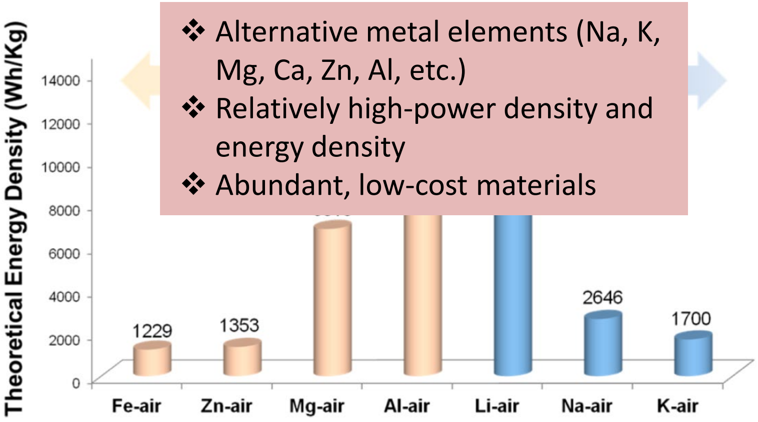
b) All solid-state batteries

- Make Li metal as anode
- Replace liquid electrolyte with solid electrolyte
- Design SEI (solid-electrolyte interface)

Theoretical capacities, reduction potential and effective ionic radius of various metals

Species	Volumetric capacity (mA h mL^{-1})	Specific capacity (mA h g^{-1})	Reduction potential (*V vs.* SHE)	Effective ionic radius (Å)
Li	2026	3861	– 3.04	0.76
Na	1128	1165	– 2.71	1.02
K	591	685	– 2.93	1.38
Mg	3833	2205	– 2.37	0.72
Ca	2073	1337	– 2.87	1.00
Zn	5851	820	– 2.20	0.74
Al	8040	2980	– 1.67	0.54

c) Non-Li batteries/Metal-air batteries



- Alternative metal elements (Na, K, Mg, Ca, Zn, Al, etc.)
- Relatively high-power density and energy density
- Abundant, low-cost materials

Z.-L. Xu et al. Prog. in Mater. Sci 90 (2017) 1–44
Y. Li and J. Lu, ACS Energy Lett. 2017, 2, 1370–1377

All solid-state battery

Li metal anode:

☐ An ideal battery anode

☐ extremely high theoretical specific capacity (3,860 mAh/g), low density (0.534 g/cm^3)

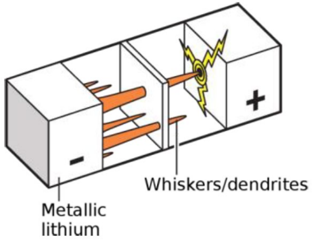
☐ the lowest negative electrochemical potential (-3.040 vs standard hydrogen electrode)

☐ Extensive attempts have been made to use Li as an anode in rechargeable Li batteries since the 1970s

However,

☐ Dendrite growth which can cause short circuiting and cause the battery to catch fire.

☐ Poor cycle life



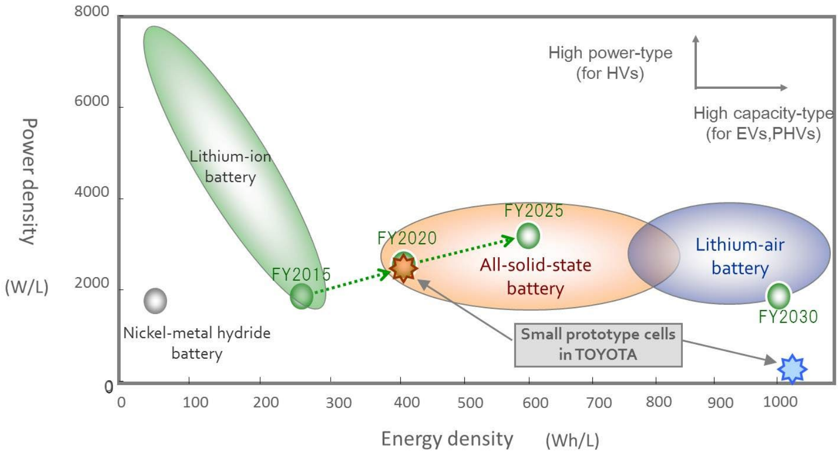
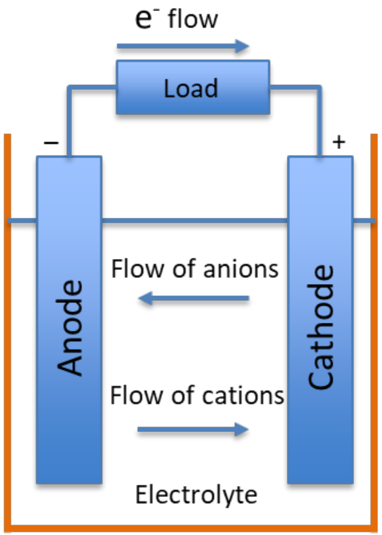


Figure 1. Ragone plots for various battery systems

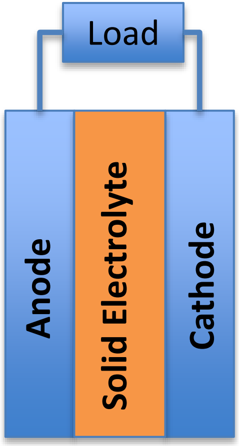
H.Iba and C. Yada’s presentation: Innovative Batteries for Sustainable Mobility

All-Solid-State Battery

Conventional Li-ion Battery



All-Solid-State Battery



Challenges: Solid electrolyte needs to satisfy:

- high ionic conductivity
- Interface stability
- Air & moisture stability
- Mechanical property
- Low-cost & scalable synthesis, processing and cell fabrication

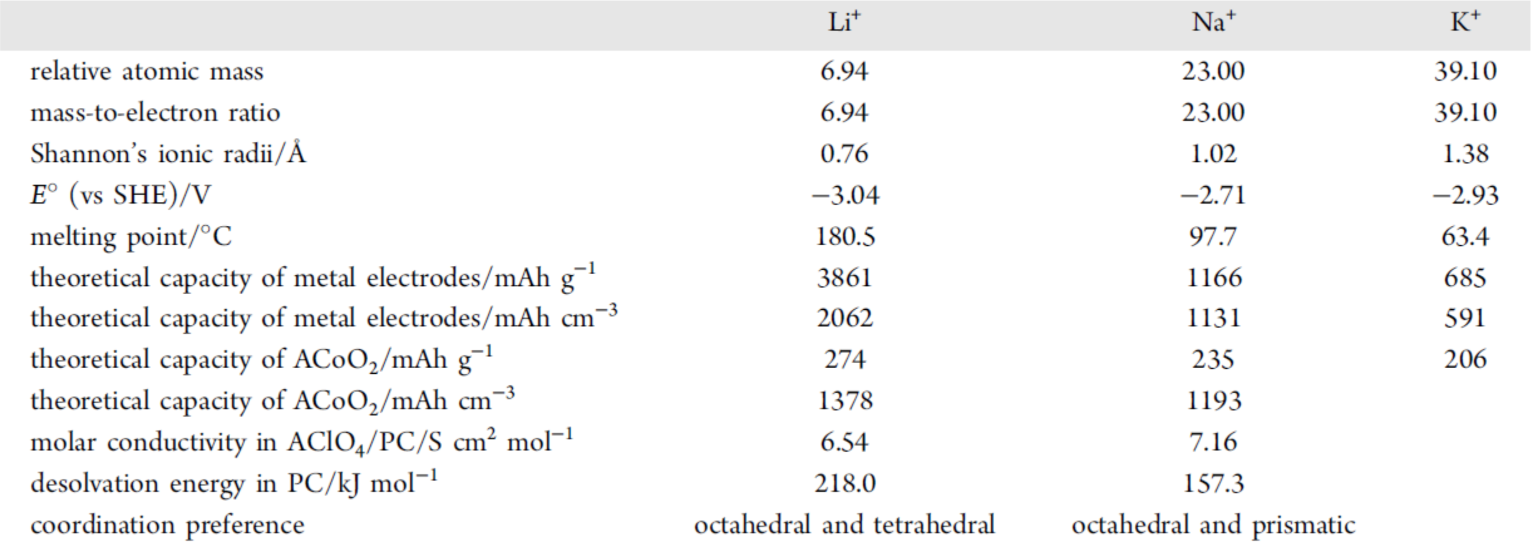
Solid-state batteries

- Improved safety: non-flammable ceramic electrolyte
- High energy density: Li metal anode and/or high-voltage cathode
- High power, long cycle life, charge quicker, and wider temperature range.

H.Iba and C. Yada's presentation: Innovative Batteries for Sustainable Mobility

Na-ion Battery

Comparison of Physical Properties for “Lithium” and “Sodium” as Charge Carriers for Rechargeable Batteries

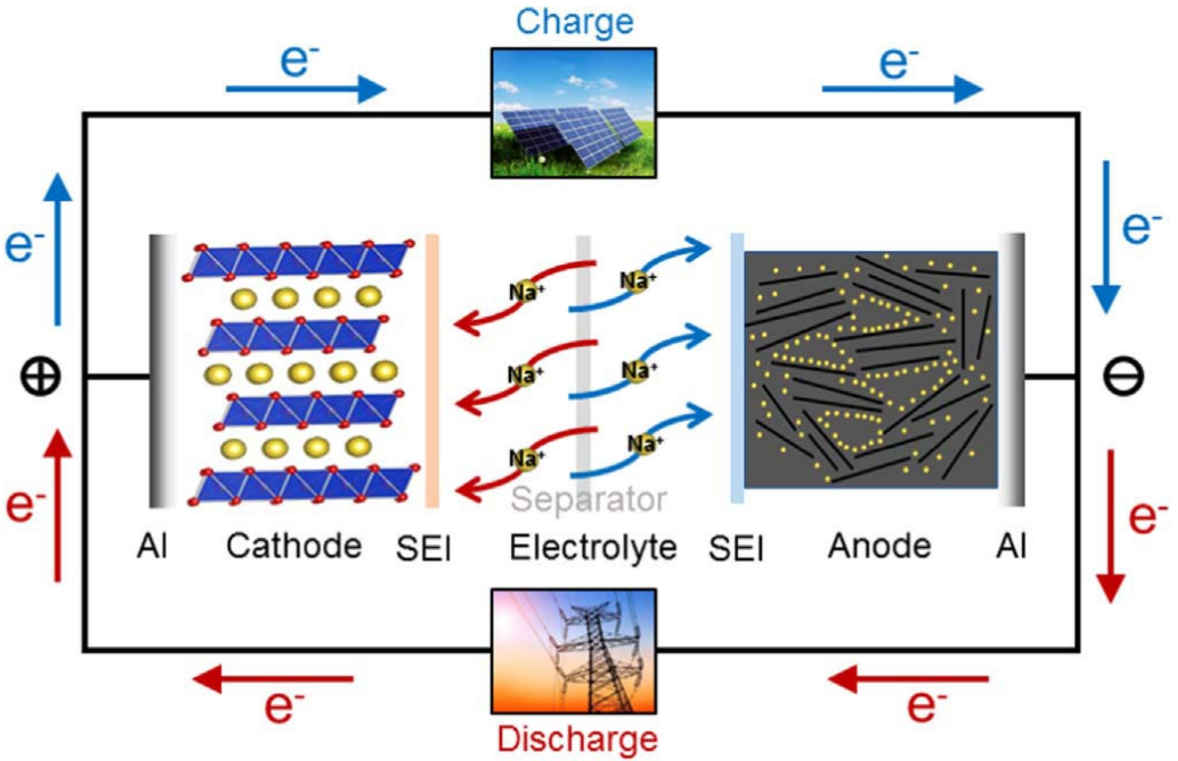


	Li^+	Na^+	K^+
relative atomic mass	6.94	23.00	39.10
mass-to-electron ratio	6.94	23.00	39.10
Shannon’s ionic radii/Å	0.76	1.02	1.38
E° (vs SHE)/V	−3.04	−2.71	−2.93
melting point/°C	180.5	97.7	63.4
theoretical capacity of metal electrodes/mAh g^{-1}	3861	1166	685
theoretical capacity of metal electrodes/mAh cm^{-3}	2062	1131	591
theoretical capacity of $ACoO_2$/mAh g^{-1}	274	235	206
theoretical capacity of $ACoO_2$/mAh cm^{-3}	1378	1193	
molar conductivity in $AClO_4$/PC/S cm^2 mol^{-1}	6.54	7.16	
desolvation energy in PC/kJ mol^{-1}	218.0	157.3	
coordination preference	octahedral and tetrahedral	octahedral and prismatic	

Average voltage (V_{ave}) and energy density (Wh kg−1) versus gravimetric capacity (mAh g−1) for selected positive electrode materials for NIBs. Energy density was calculated with the hard carbon (reversible capacity of 300 mAh g−1 with Vave = 0.3 V vs Na metal) as negative electrode materials.

Chem. Rev. 2014, 114, 11636−11682

Working principle of Na-ion Batteries



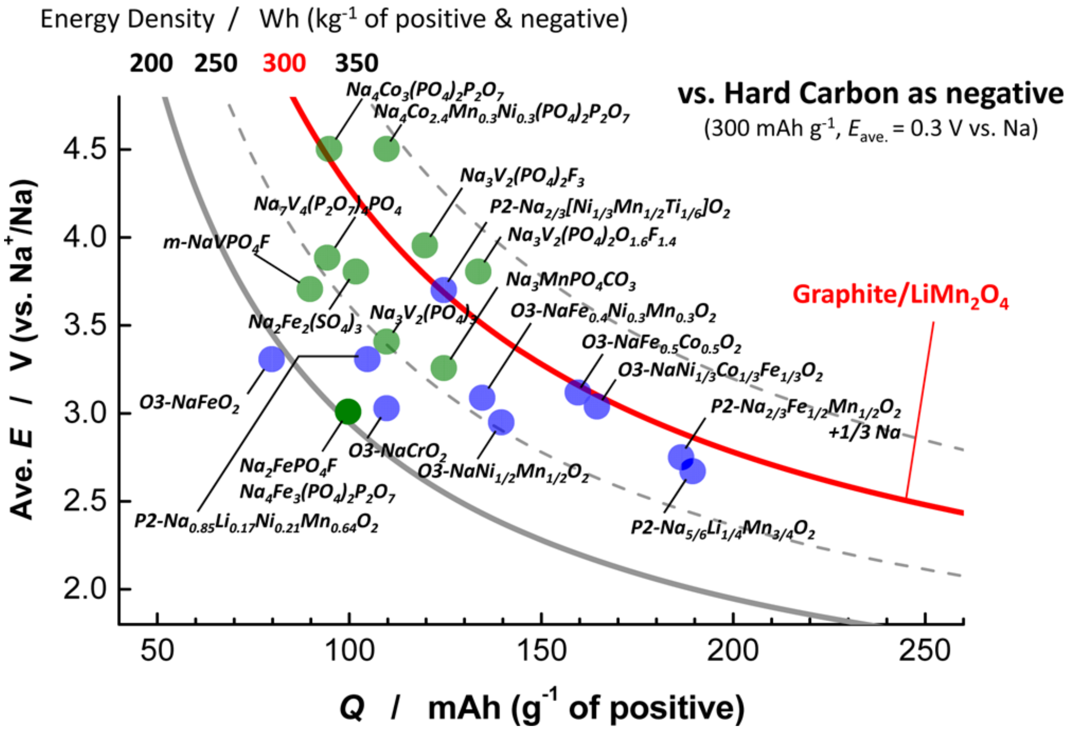
Compared with LIBs, SIBs shall have a lower energy density due to the relatively heavier and larger Na atom.

- Structure damage
- Slow diffusion
- Complicated reaction

Similar mechanism to Li-ion batteries (LIBs)
Similar process to manufacture Na-ion batteries (SIBs)

Energy Storage Materials 7 (2017) 130–151

Na-ion Battery R&D



CATL: First generation of Na-ion battery:

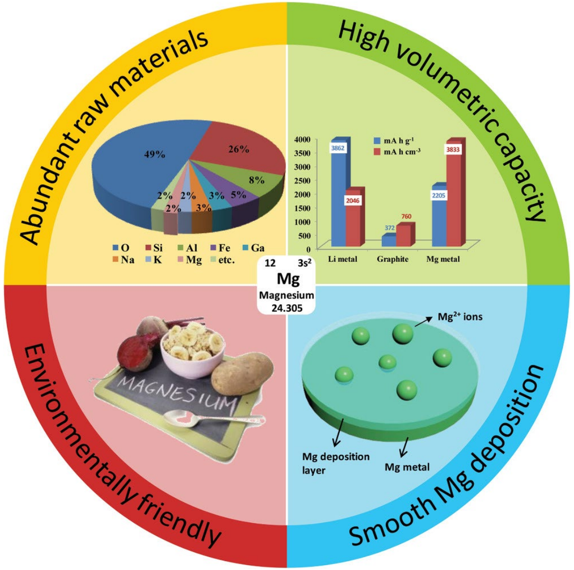
- Energy density: 160Wh/kg
- Fast charge in 15 minutes to 80% SOC at room temperature.
- Wide operation temperature: -20°C
- Has a capacity retention rate >90%.

Average voltage (V_{ave}) and energy density (Wh kg−1) versus gravimetric capacity (mAh g−1) for selected positive electrode materials for NIBs. Energy density was calculated with the hard carbon (reversible capacity of 300 mAh g−1 with V_{ave} = 0.3 V vs Na metal) as negative electrode materials.

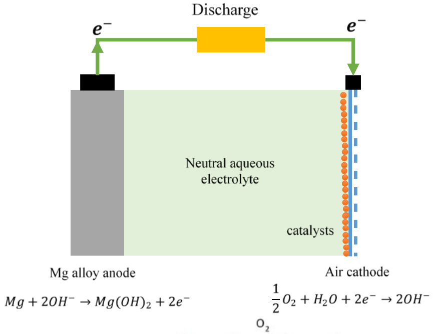
Chem. Rev. 2014, 114, 11636–11682

Mg-based Batteries – Dr. Wei's Lab

- ☐ High theoretical capacity
- ☐ Environmentally friendly
- ☐ Abundance of elements – low cost
  - Mg: 2.33% and 7th most overall
  - Li: 0.002% and 33rd most overall
- ☐ Safe (no dendrite growth)



Mg-Air aqueous battery



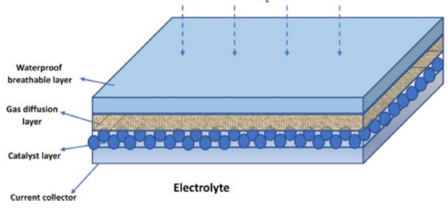
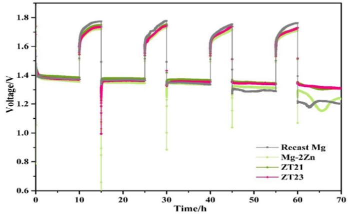
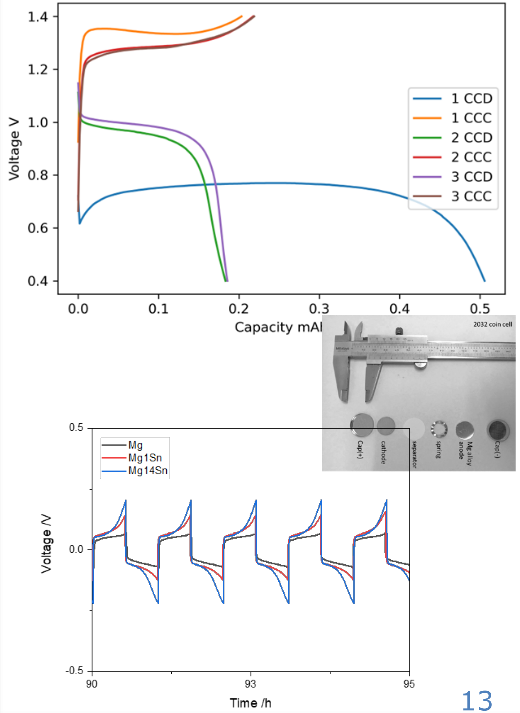


Fig. 2. Schematic of the typical structure of air cathode [10]

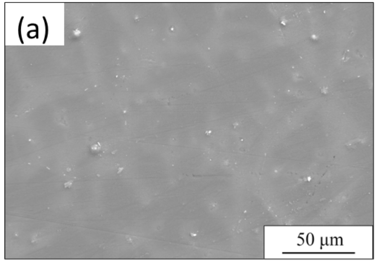


Mg-ion rechargeable battery

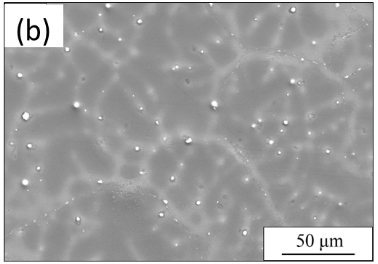


F. Tong, S. Wei, X. Chen et al. / Journal of Magnesium and Alloys 9 (2021) 1861–1883
Chen, X., Wei, S., Tong, F., Taylor, M.P., Cao, P.,, Electrochimica Acta (2021), 398, 139336.*
Niu, J., Zhang, Z., & Aurbach, D.. Advanced Energy Materials, 2020, 2000697.

Mg-air Battery – Dr. Wei's Lab

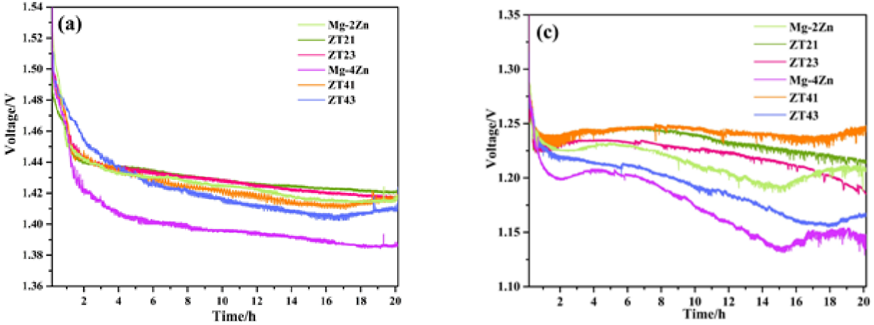


Mg-2Zn-1Sn (ZT21)

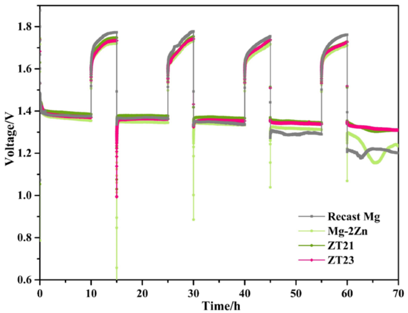


Mg-2Zn-3Sn (ZT23)

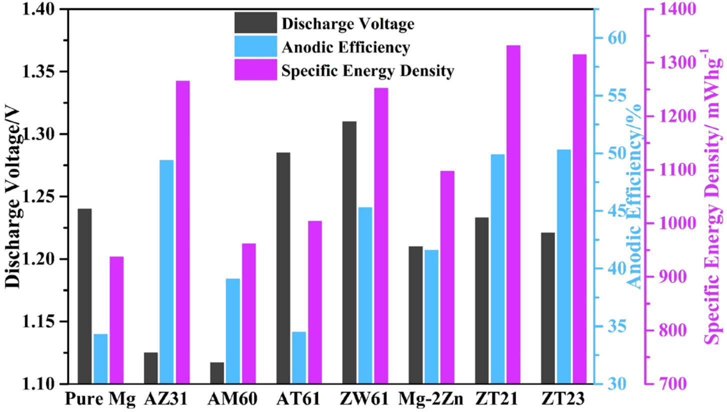
WattSatt Mg-air battery



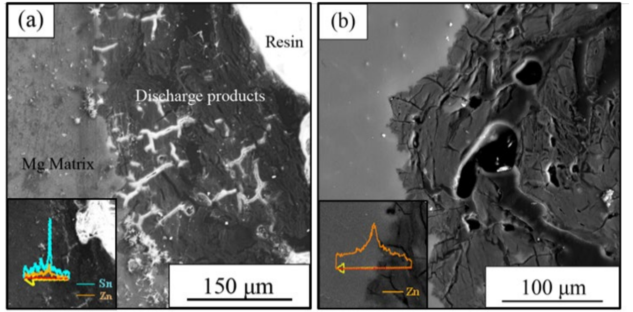
Discharge curves of alloy anodes at current densities: (a) 1 mA·cm^{-2}; and (c) 5 mA·cm^{-2} in 3.5 wt.% NaCl solution.



Intermittent discharge of Mg-air battery at 2 mA·cm^{-2} in 3.5 wt.% NaCl solution.



Battery discharge performance of ZT anodes comparing with pure Mg and commercial alloys anodes at the current density 5 mA·cm^{-2}



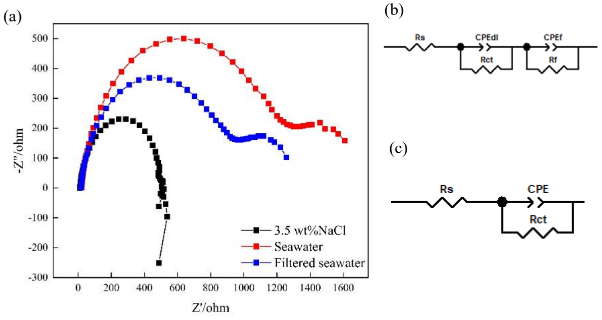
Cross-section of (a) ZT21 and (b) Mg-2Zn alloy anodes discharge at 2 mA·cm^{-2} for 20 h with discharge products.

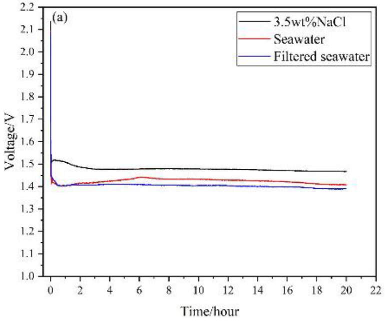
Tong, F., Chen, X., Wei, S., Malmstrom, J., Vella, J., Gao, W., Microstructure and battery performance of Mg-Zn-Sn Alloys as anodes for magnesium-air battery, Journal of Magnesium and Alloys, 2021*

Seawater battery – Dr. Wei's Lab

THE UNIVERSITY OF AUCKLAND
Te Whare Wānanga o Tāmaki Makaurau
NEW ZEALAND
ENGINEERING

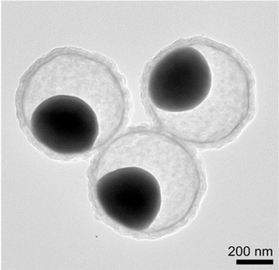
- Several alloys have been designed and studied as anodes for MSWBs.
- Achieved very good battery performance at low current densities (≤1mA/cm2).

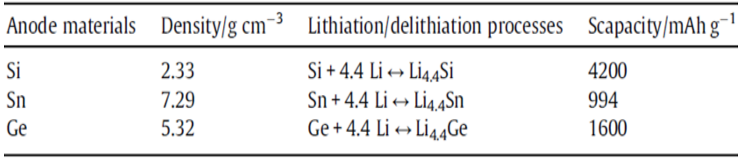




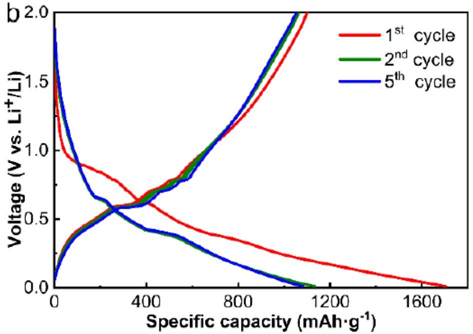
Post Li-ion batteries – Dr. Wei's Lab

Sn-based anode material:
Yolk-shelled Sn@void@NxCS nanosize spherics
(Nitrogen doped carbon hollow structure)

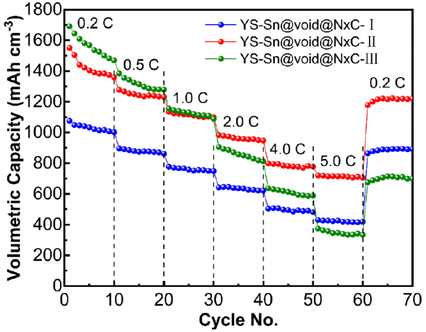




Anode materials	Density/g cm^{-3}	Lithiation/delithiation processes	Scapacity/mAh g^{-1}
Si	2.33	Si + 4.4 Li ↔ Li$_{4.4}$Si	4200
Sn	7.29	Sn + 4.4 Li ↔ Li$_{4.4}$Sn	994
Ge	5.32	Ge + 4.4 Li ↔ Li$_{4.4}$Ge	1600

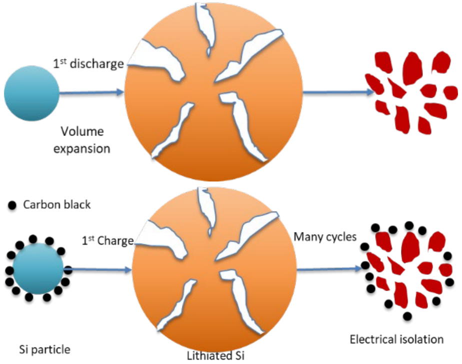


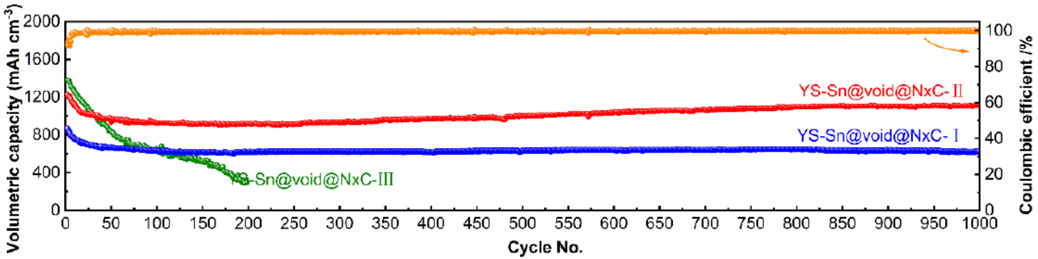
Galvanostatic charge/discharge profiles of nanostructure materials as electrodes



Rate performance of nanostructure electrodes

Main failure mechanisms





Volumetric capacity-based long cycling performance

Achieved high specific capacity at a high charge rate

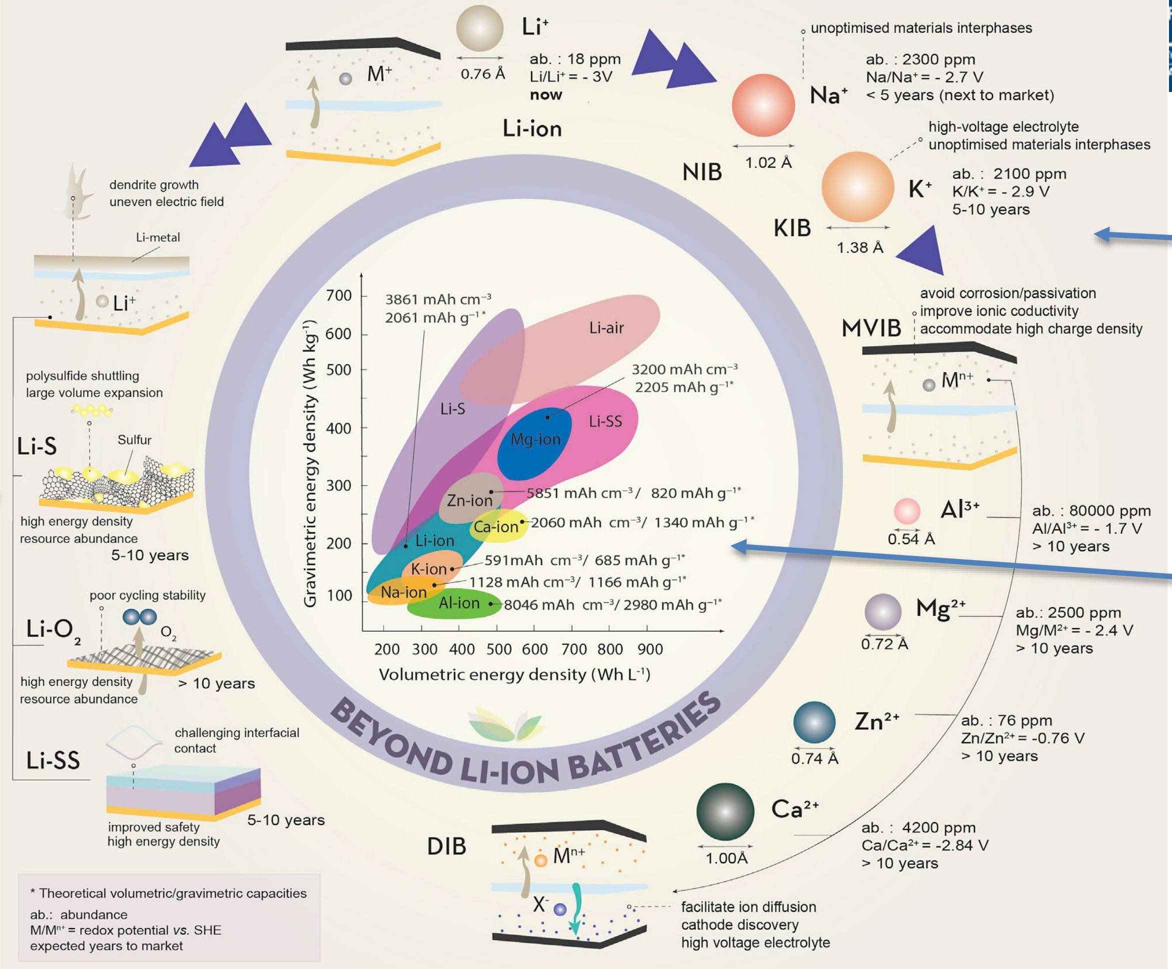
Li, B., Zhang, W., Zhang, T., Wei, S., Gao, W., Accurately tailoring yolk-shell spheres to balance cycling stability and volumetric capacity of lithium storage, J. Alloy. Comp., (2022), 917, 165548.

NZ Battery R&D

Some of the key points:

- Sustainability and supply chain issues over time for existing battery chemistries;
- New battery chemistries and and use-specific battery design and chemistry;
- recycling and re-use battery
- the value of establishing shared national research facilities and infrastructure aligned with national research priorities;
- The potential for the use of NZ biomass in new technology batteries.
- Workforce development & training to ensure we have people qualified to work on, maintain and develop next generation battery systems.

Current status and challenges in beyond LIBs



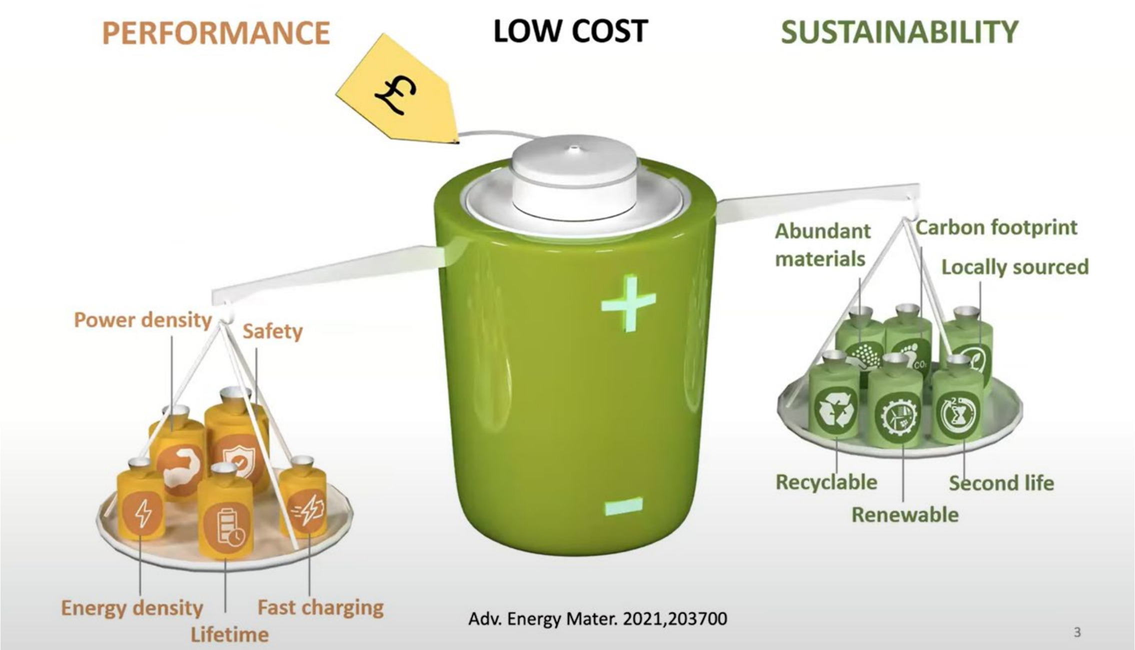
The substituting Li ions (Na, K, Al, Mg, Zn, Ca), with their global abundance, standard redox potential, and expected years to market.

The main advantages and challenges are outlined alongside their currently achievable volumetric/gravimetric energy densities and theoretical capacities.

chemistries deploying Li-metal anodes (Li-S, Li-O2, Li-SS)

H. Au, M. Crespo-Ribadeneyra, M.M. Titirici, Beyond Li-ion batteries: performance, materials diversification, and sustainability, One Earth, 3(2022) 07-211,

Summary



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Thank you for your attention!