Unlocking the potential of metal air batteries through materials development

Nagore Ortiz-Vitoriano

Gandía, October 17, 2023

ESAM 2023

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1.
The energy problem

> The energy problem solution relies on the use of renewable sources

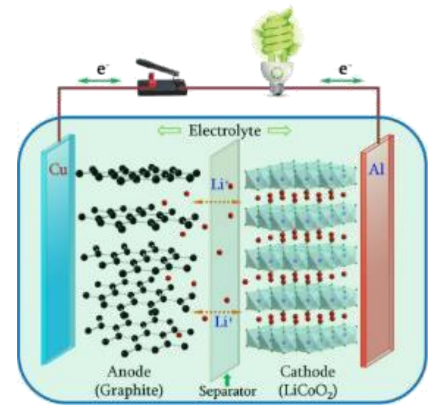
THE ENERGY CRISIS IS A RESULT OF MANY DIFFERENT STRAINS ON OUR NATURAL RESOURCES

India Gate – New Delhi

Current Energy Outlook

- **Advanced electronic devices** have evolved rapidly, contributing to an ever-increasing **demand** for power sources with **high energy density** & high **power density**.
- **Li-ion technologies**, i.e. electric cars, are actually the **hope** for fulfilling many of these **demands**.

  - **However, Li-ion batteries are actually limited by:**
    - **The intercalation chemistry of the electrodes;**
    - **Energy density;**
    - **Use of EU-listed Critical Raw Materials (CRMs).**



DOI: 10.1016/j.mattod.2015.10.009

2020 Critical Raw Materials (new as compared to 2017 in bold)		
Antimony	Hafnium	Phosphorus
Baryte	Heavy Rare Earth Elements	Scandium
Beryllium	Light Rare Earth Elements	Silicon metal
Bismuth	Indium	Tantalum
Borate	Magnesium	Tungsten
Cobalt	Natural Graphite	Vanadium
Coking Coal	Natural Rubber	**Bauxite**
Fluorspar	Niobium	**Lithium**
Gallium	Platinum Group Metals	**Titanium**
Germanium	Phosphate rock	**Strontium**

Tesla

Beyond Li-ion Batteries

BATTERIES EUROPE

BATTERIES EUROPE
EUROPEAN **TECHNOLOGY**
AND **INNOVATION** PLATFORM

European Technology and Innovation Platform on Batteries - Batteries Europe

Battery Generation	Electrodes active materials	Cell Chemistry / Type	Forecast market deployment
Gen 1	• Cathode: LFP, NCA • Anode: 100% carbon	Li-ion Cell	current
Gen 2a	• Cathode: NMC111 • Anode: 100% carbon	Li-ion Cell	current
Gen 2b	• Cathode: NMC523 to NMC 622 • Anode: 100% carbon	Li-ion Cell	current
Gen 3a	• Cathode: NMC622 to NMC 811 • Anode: carbon (graphite) + silicon content (5-10%)	Optimised Li-ion	2020
Gen 3b	• Cathode: HE-NMC, HVS (high-voltage spinel) • Anode: silicon/carbon	Optimised Li-ion	2025
Gen 4a	• Cathode NMC • Anode Si/C • Solid electrolyte	Solid state Li-ion	2025
Gen 4b	• Cathode NMC • Anode: lithium metal • Solid electrolyte	Solid state Li metal	>2025
Gen 4c	• Cathode: HE-NMC, HVS (high-voltage spinel) • Anode: lithium metal • Solid electrolyte	Advanced solid state	2030
Gen 5	• Li|O_2 – lithium air / metal air • Conversion materials (primarily Li|S) • new ion-based systems (Na, Mg or Al)	New cell gen: metal-air/ conversion chemistries / new ion-based insertion chemistries	>2030

2.

Introduction to Batteries

> Electrochemical Energy Storage

INTRODUCTION TO BATTERIES

A battery is 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.
In 1800, Alessandro Volta invented the first modern battery.

Primary

- ✓ Irreversible oxidation-reaction reaction
- ✓ Also called non-rechargeable or throw away

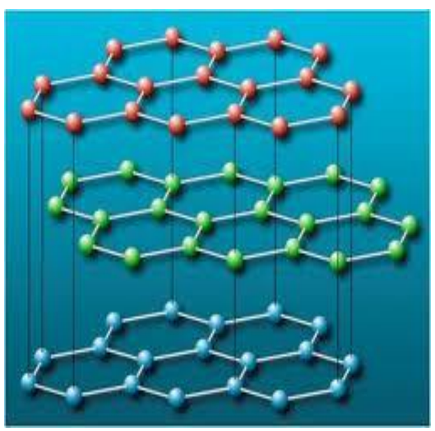
Secondary

- ✓ The battery is recharged by a reversal of the process
- ✓ Involves the transfer of electrons from one material to another through an electric circuit

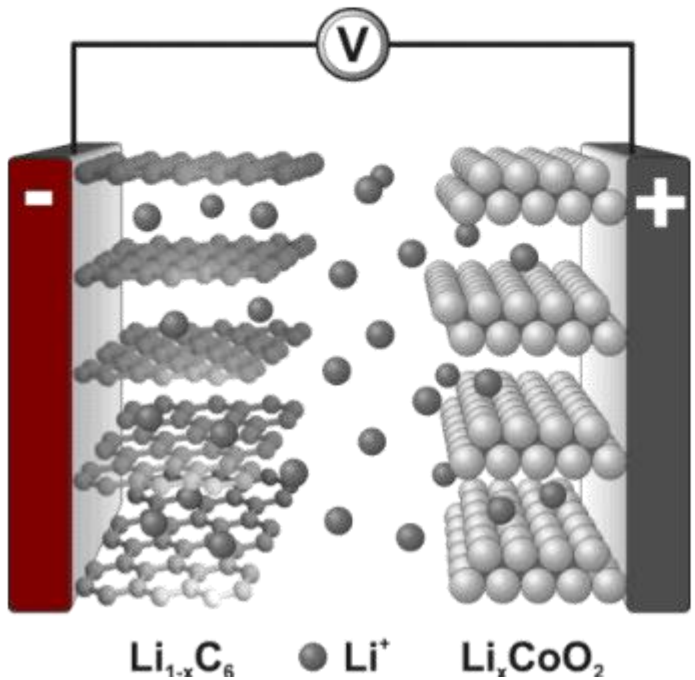
> Electrochemical Energy Storage

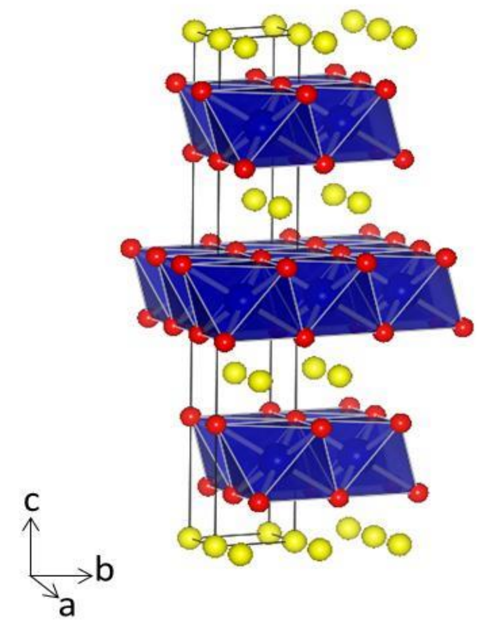
First commercial Lithium-ion battery

- In 1991 by Sony. $LiCoO_2$ cathode material (still used in the majority of commercial Li-ion batteries). Graphite anode material.



C graphite





$LiCoO_2$

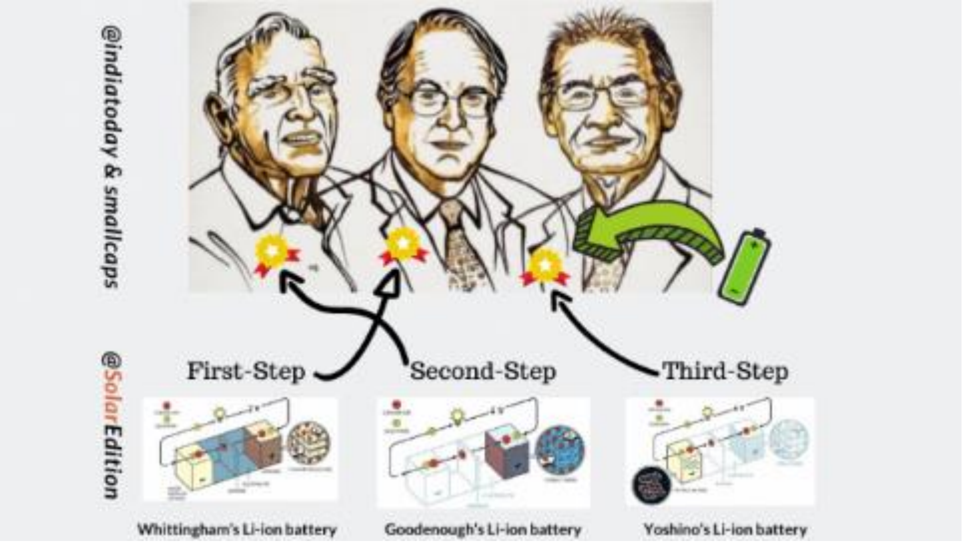
However, there are issues with $LiCoO_2$ material; e.g. cost and toxicity of Co, capacity not high enough.

> Electrochemical Energy Storage

INTRODUCTION TO BATTERIES

The Nobel Prize in Chemistry 2019 rewards the development of Li-ion Battery

- **Early 1970s**, *Dr. Whittingham* figured out that Li would make a good anode because it releases electrons easily → first functional lithium battery.
- **Around 1980**, *Dr. Goodenough* predicted that lithium-ion batteries would have greater potential if the cathode were made with different materials, for example, cobalt oxide.
- **Finally**, *Dr. Yoshino* followed Goodenough's step and showed that more complicated carbon-based electrodes could eliminate pure lithium from the battery entirely. Instead, the battery used only lithium-ions which it causes to become safer.



> Electrochemical Energy Storage

BEGINNING OF LI-ION

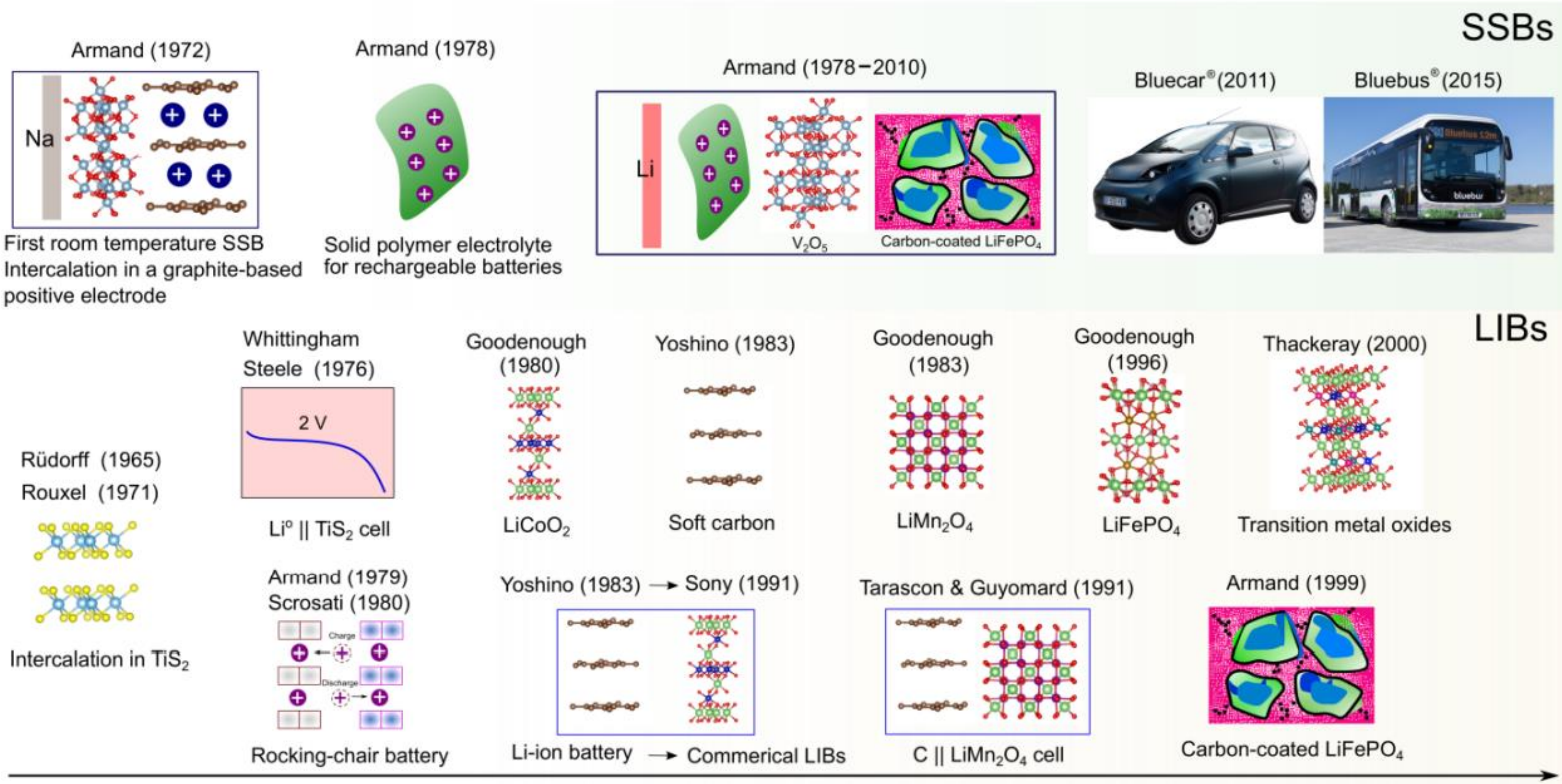


Figure 1. The evolution of battery chemistry and key findings of lithium-ion batteries (LIBs) and solid state batteries (SSBs) over the past 40 years. The crystal structures of the electrode materials are obtained from the Materials Project[6] and are visualized with VESTA software[7]. The photographs of Bluecar® and Bluebus® are provided here by courtesy of Bollore Group.

H. Zhang, AngewChemInternational Ed 10.1002/anie.201913923

> Electrochemical Energy Storage

MECHANISMS IN ELECTRODE MATERIALS

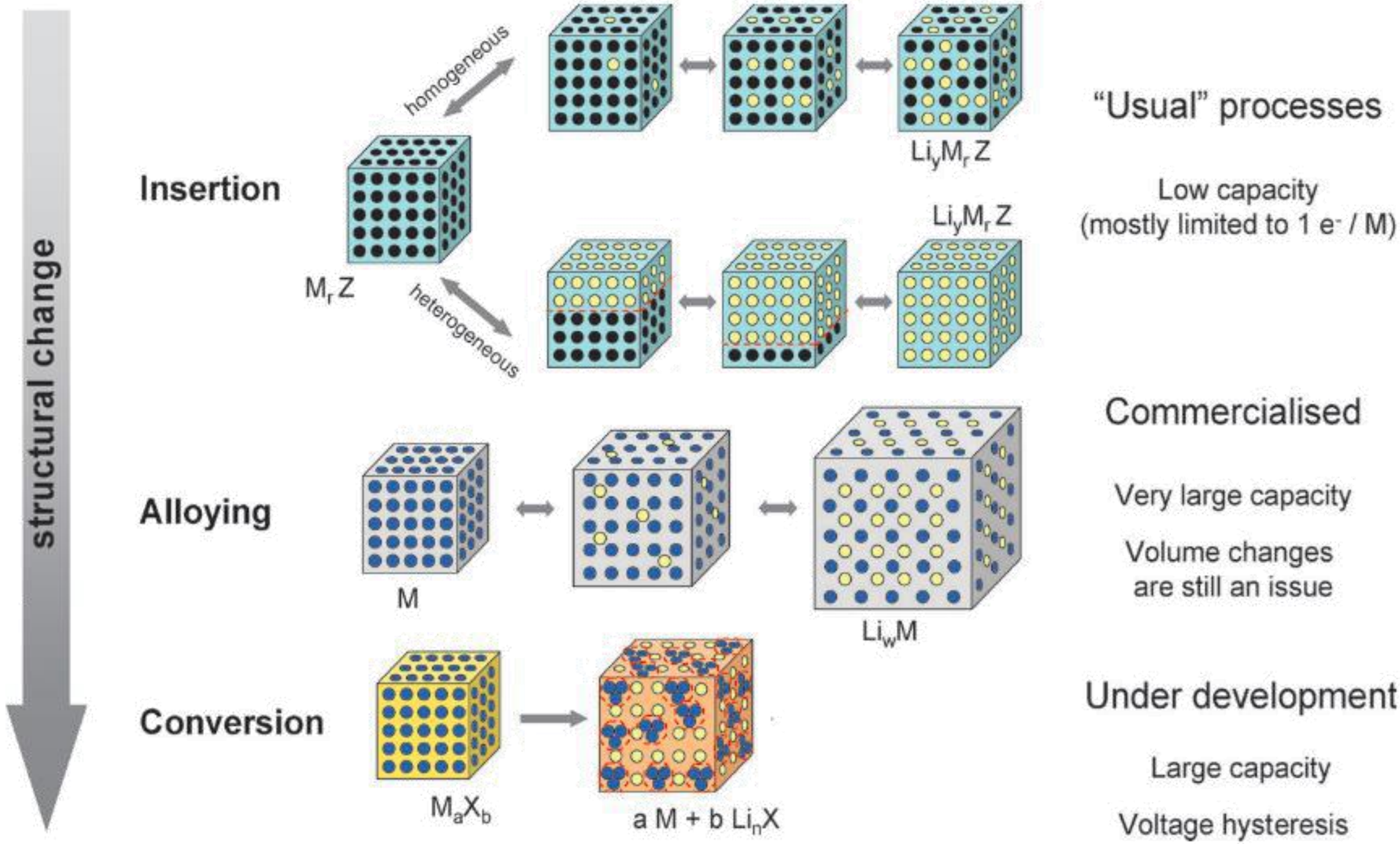


Fig. 5 A schematic representation of the different reaction mechanisms observed in electrode materials for lithium batteries. Black circles: voids in the crystal structure, blue circles: metal, yellow circles: lithium.

M. Rosa Palacín., Chem. Soc. Reviews 2009, 38, 2565

3.

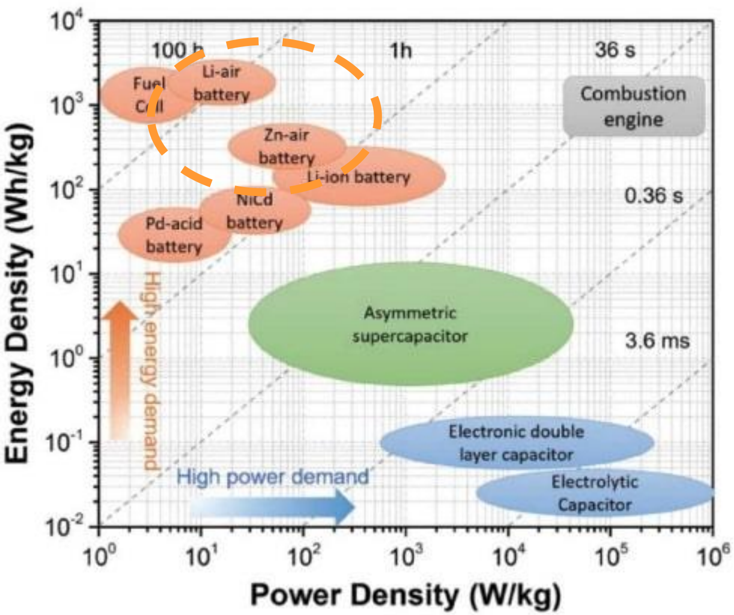
Metal-air batteries

> Beyond Li-ion batteries

PROMISING BATTERY TECHNOLOGY

- **Metal-air** battery technologies: **holy grain of battery research & theoretically** could store **11 times more energy** than Li-ion

"Horizon technology" but big companies interested (Tesla, Toyota, IBM)



https://www.nextbigfuture.com/2021/04/battery-technology-2021.html

United States Patent 9,559,532
Hermann , et al. January 31, 2017

Charge rate modulation of metal-air cells as a function of ambient oxygen concentration

Abstract

A method for charging a metal-air battery pack at the maximum possible rate while maintaining an ambient oxygen concentration below a preset concentration is provided, thereby minimizing the risks associated with generating oxygen during the charging cycle.

Inventors: Hermann; Weston Arthur (Palo Alto, CA), Straubel; Jeffrey Brian (Menlo Park, CA), Beck; David G. (Tiburon, CA)
Applicant: Name City State Country Type
Tesla Motors, Inc. Palo Alto CA US
Assignee: TESLA MOTORS, INC. (Palo Alto, CA)
Family ID: 43928284
Appl. No.: 13/967,501
Filed: August 15, 2013

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)
(19) World Intellectual Property Organization
International Bureau
(43) International Publication Date
15 January 2015 (15.01.2015)
WIPO | PCT
(10) International Publication Number
WO 2015/004069 Al
(51) International Patent Classification:
AGUIRRE, Patricio; Tecnalia, Mikeletegi Pasealekua, 2,

350 - 400 Wh/kg_{cell} (Li ion)
3505 Wh/kg_{cell} (Li_2O_2)
1086 Wh/kg_{cell}, (ZnO)
1108 Wh/kg_{cell}, (NaO_2)
2567 Wh/kg_{cell} (Li_2S)

Electrochemical cell that uses an anode made from pure metal and an external cathode of ambient air, typically with an aqueous or aprotic electrolyte.

> Aqueous and non-aqueous (aprotic) metal-air batteries

A CENTURY OLD TECHNOLOGY

Concept reported by Smee

First comercial products

Non-aqueous

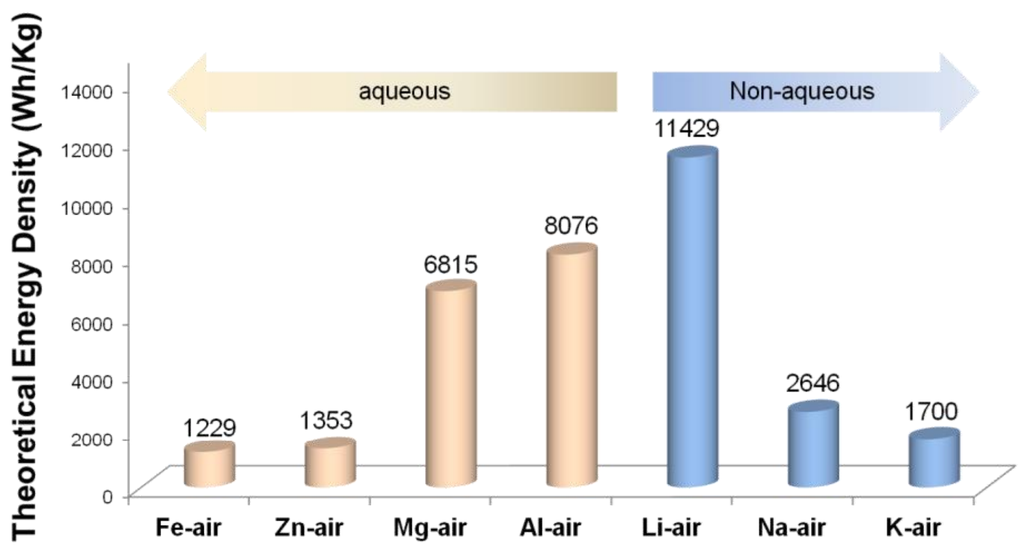
Li | Na | K | ...

1840 | 1878 | 1932 | 1960s | 1996 | 2013 | 2022

Primary Zn-air by Maiche

Aqueous Fe/Al/Mg-air

porous platinized carbon cathode



doi.org/10.1021/acsenergylett.7b00119

Figure 1. Theoretical energy densities for different types of metal-air batteries.

> What is a metal-air battery?

OXYGEN AS FUEL

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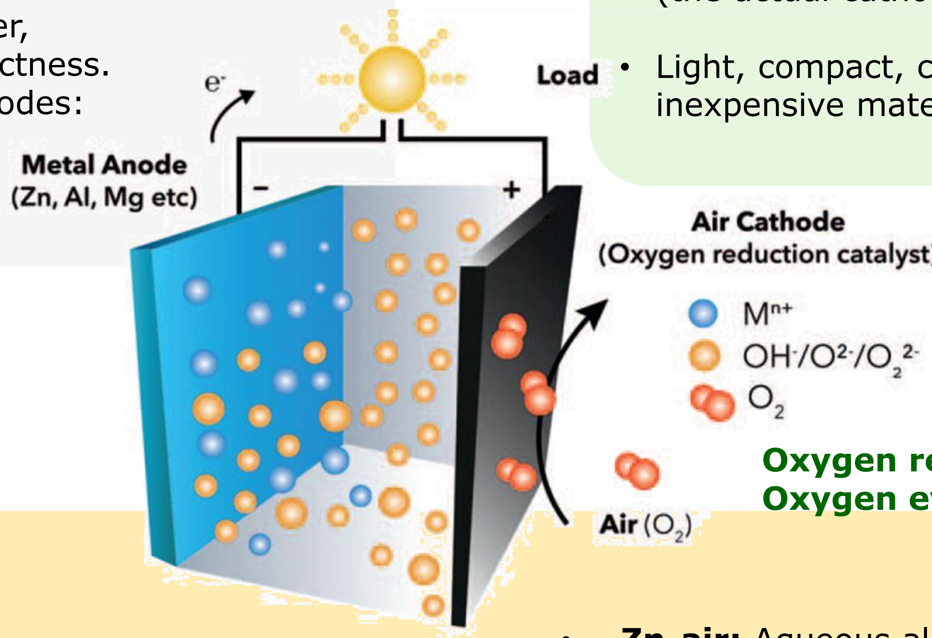
COMPONENTS

Metal anode

- Strong reducing power, lightness, and compactness.
- Other negative electrodes: metal hydride, alloys, organic materials

Air electrode

- Film where oxygen diffuses and is reduced (the actual cathode is O_2)
- Light, compact, corrosion resistive and inexpensive materials → Carbon materials



Oxygen reduction reaction (ORR)
Oxygen evolution reaction (OER)

Electrolyte

- Good ionic conductivity
- Electrically insulating nature
- Stability against the reducing potential of the negative metal
- Stability against the oxidizing potential of oxygen.

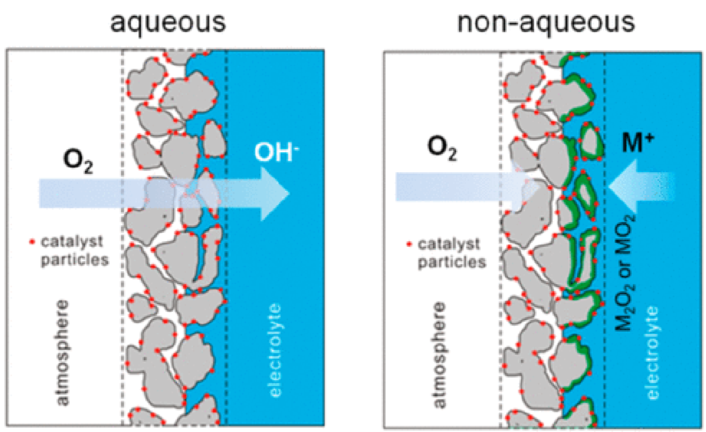
- **Zn-air:** Aqueous alkaline electrolyte, gel electrolytes
- **Li-air,Na-air:** Non-aqueous: organic liquids, polymers, inorganic solid electrolytes, ionic liquids.

Hajime Arai,Jurgen Garche, Luis Colmenares. Electrochemical Power Sources: Fundamentals, Systems, and Applications Metal-Air Batteries: Present and Perspectives. Elsevier 2021

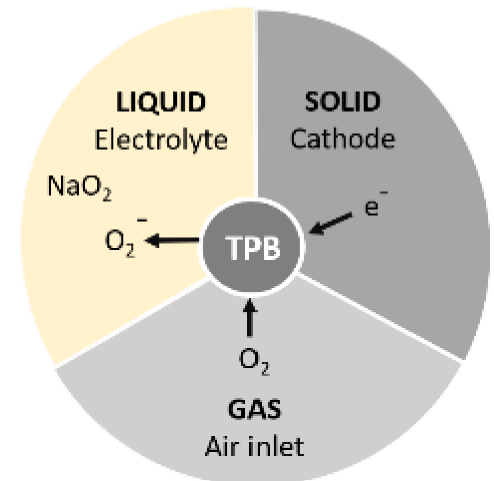
> Reaction mechanism – oxygen electrochemistry

THREE PHASE REACTION

Oxygen Reduction Reaction (ORR)



TRIPLE PHASE BOUNDARY (TPB)

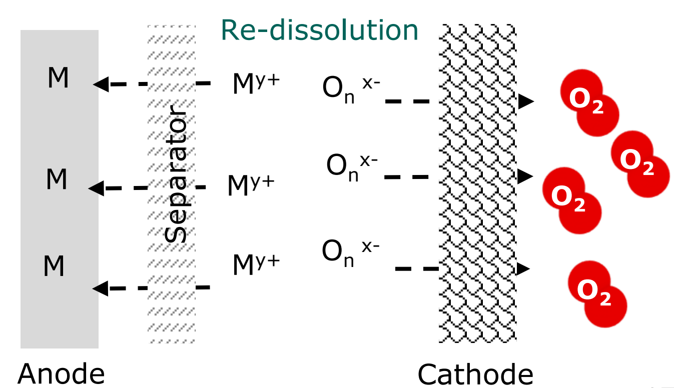


Electronic conduction
Diffusion of O_2 gas
Electrolyte wettability/Flooding

Oxygen Evolution Reaction (OER)

Limiting process for rechargeability

$M_x(O_n)_y$: metal oxides or hydroxides in the electrolyte or cathode surface



Oxygen reduction reaction (ORR)

$O_2 + 1e^-$ or $2e^- \longrightarrow O_2^-$ (superoxide) / O_2^{2-} (peroxide)

Oxygen evolution reaction (OER)

$O_2^- / O_2^{2-} \longrightarrow O_2 + 1e^-$ or $2e^-$

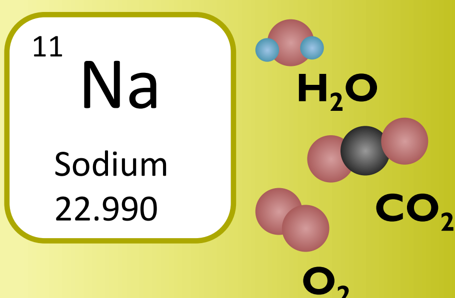
10.1021/acsenergylett.7b00119

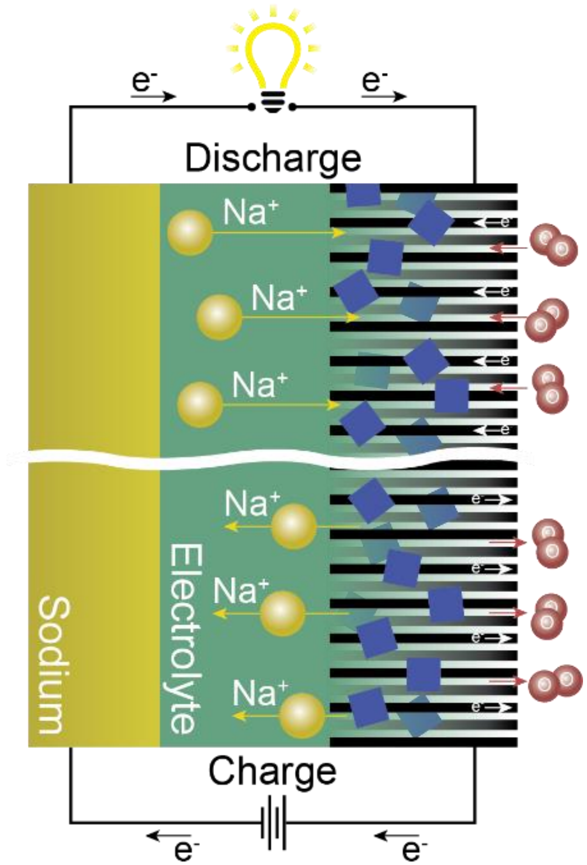
4. Aprotic-air batteries (Na)

Electrodeposition of Na
Na dendrites

Energy Technol. 2017, 5, 2265–2274

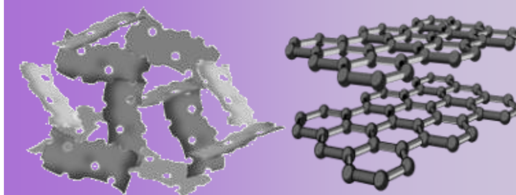
Contamination: H_2O, air (O_2) – Protected Na



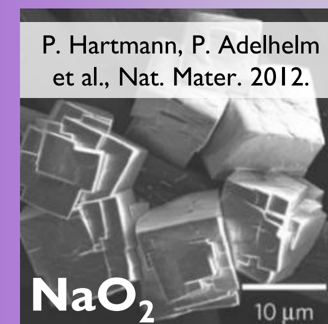


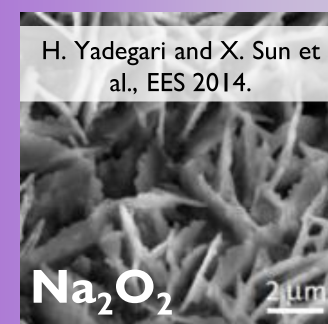
high volatility
low solvent stability/oxygen solubility
reactivity with superoxide
contamination (e.g. air, H_2O)

Cathode design



Cell chemistry

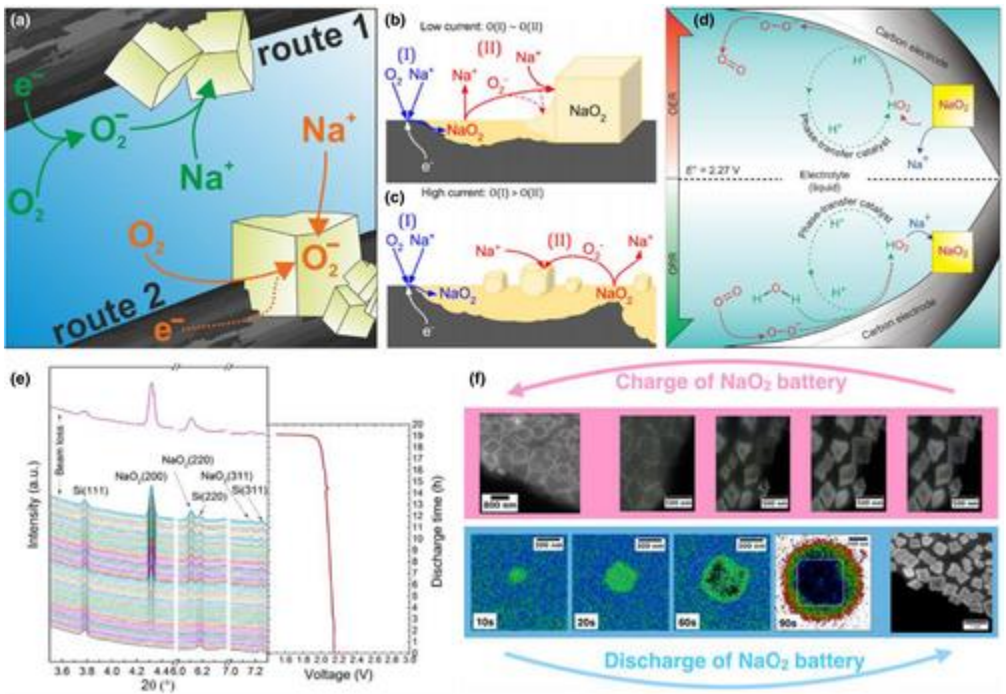




> Sodium-oxygen batteries

DISCHARGE PRODUCT NUCLEATION & GROWTH

Solution vs surface mechanisms



J. Phys. Chem.
C 2015, 119, 22778.
J. Phys. Chem. C 2017, 121, 85.
Nat. Chem. 2015, 7, 496.
ACS Energy Lett. 2017, 2, 2440.
Nano Lett. 2018, 18, 1280.
Energy Environ. Mater.2021,4,
158–177158.

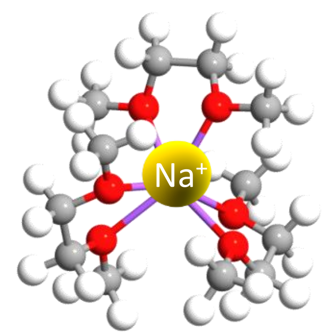
Air cathode development

- The oxygen doesn't need to be store within the battery
- Lightweight, and widely available

Electrolyte development

Rate-limiting processes in batteries are controlled by solvation

- Novel formulations
- SEI formation

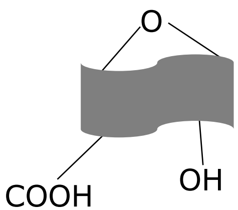


> Sodium-oxygen batteries

GRAPHENE PROCESSING

Graphite oxide route

Graphene oxide
(GO)

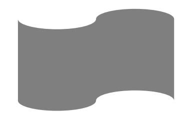


CHEMICAL OR THERMAL REDUCTION

Reduced graphene oxide (rGO)
Defects in lattice/edges of the sheets.

Electrochemical exfoliation

Graphene (GNs)

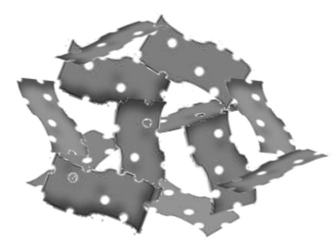


NO DISPERSIBILITY

USE OF SYNTHETIC SURFACTANTS

RESTACKING!!! Loss of the excellent properties

3D reduced graphene oxide structures prevent sheet restacking



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> Sodium-oxygen batteries

ENGINEERING 3D GRAPHENE AIR CATHODES

ROYAL SOCIETY OF CHEMISTRY

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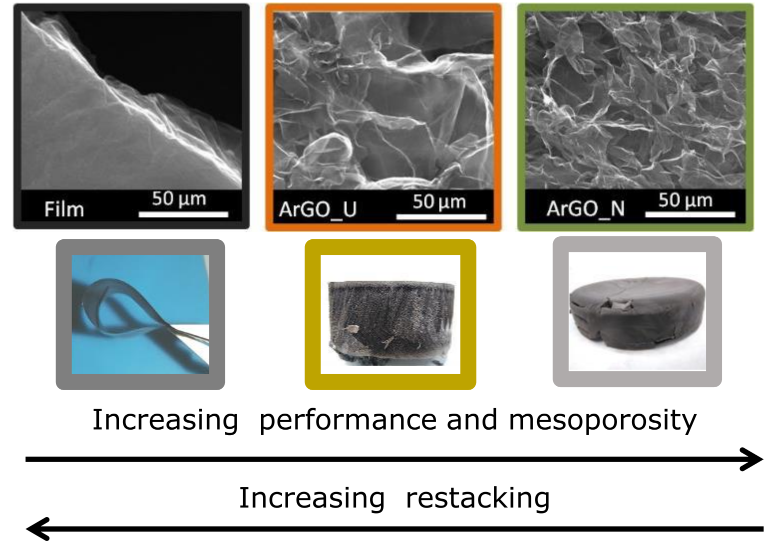
DOI: 10.1039/C8TA07273F (Paper) J. Mater. Chem. A, 2018, 6, 20778-20787

Pathways towards high performance Na–O_2 batteries: tailoring graphene aerogel cathode porosity & nanostructure†

Marina Enterría [a], Cristina Botas [a], Juan Luis Gómez-Urbano [a], Begoña Acebedo [a], Juan Miguel López del Amo [a], Daniel Carriazo [ab], Teófilo Rojo [*ac] and Nagore Ortiz-Vitoriano [*ab]



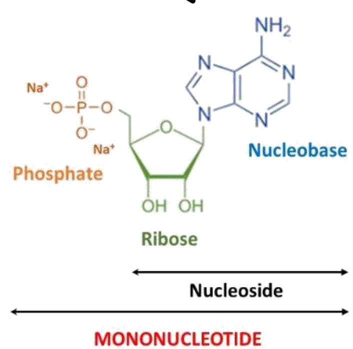
NANO · MICRO small

Full Paper | Open Access

Boosting the Performance of Graphene Cathodes in Na–O_2 Batteries by Exploiting the Multifunctional Character of Small Biomolecules

Marina Enterría, Juan Luis Gómez-Urbano, Jose María Munuera, Silvia Villar-Rodil, Daniel Carriazo, Juan Ignacio Paredes, Nagore Ortiz-Vitoriano

First published: 16 December 2020 | https://doi.org/10.1002/smll.202005034 | Citations: 1

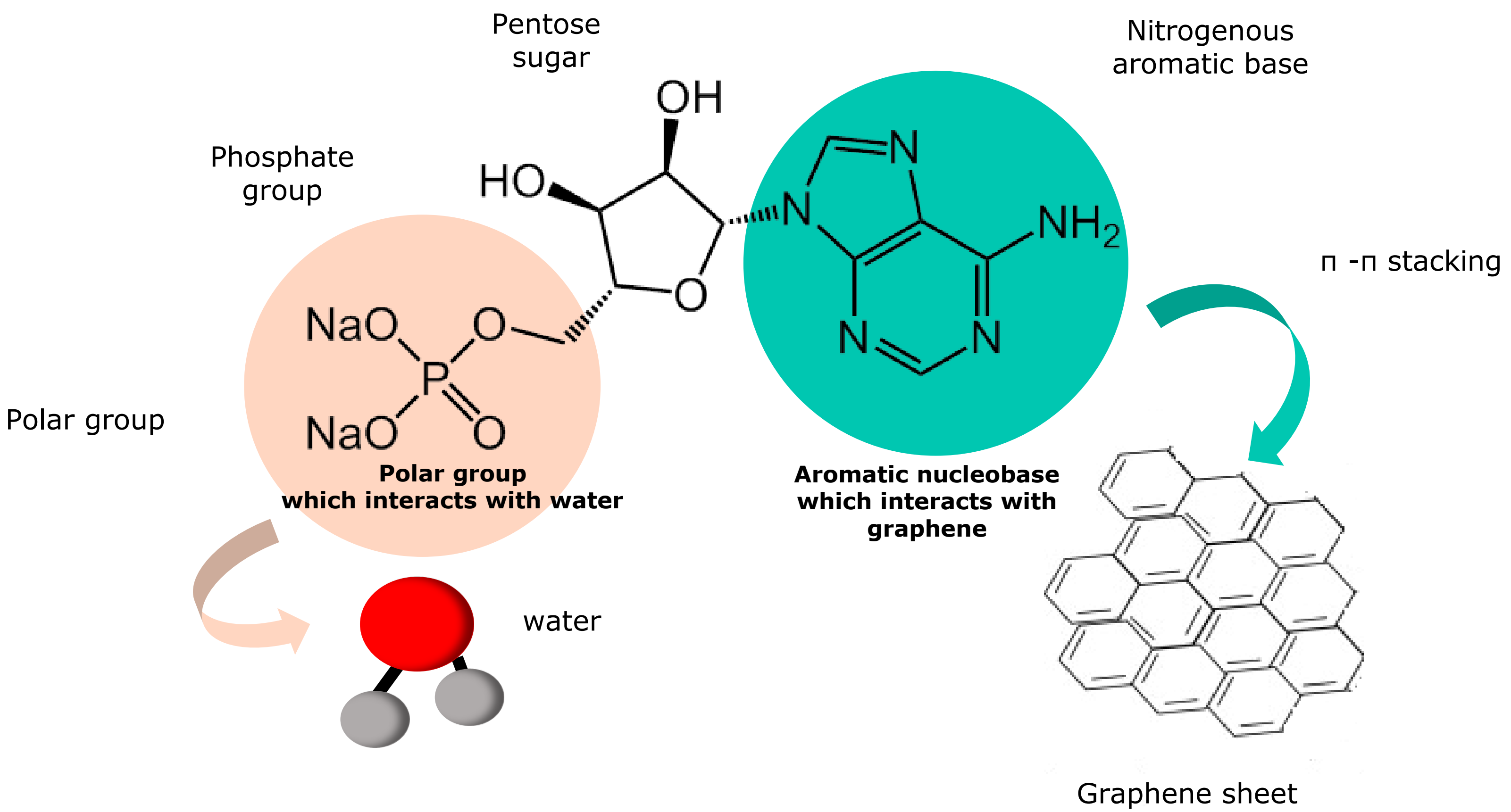


1. **Ribose** moiety **doesn't enhance performance** of the cathode.
2. **Nucleobase** probably **catalyses ORR/OER.**
3. **Phosphates** are able to **bind oxygen species** involved in discharge/charge.

> Engineering 3D Graphene Air Cathodes for $Na\text{-}O_2$ Batteries

BIOMOLECULE-ASSISTED ELECTROCHEMICAL EXFOLIATION OF GRAPHITE

Nucleotides: small innocuous biomolecules - adenosine monophosphate (AMP)

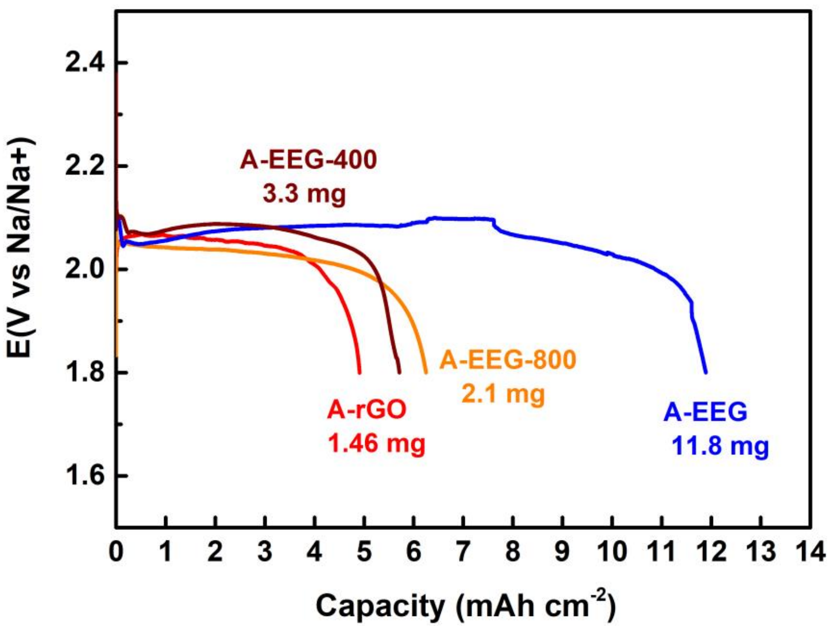


Dual functionality: exfoliating electrolyte/ colloidal stabilizer which could facilitate graphene processing in water

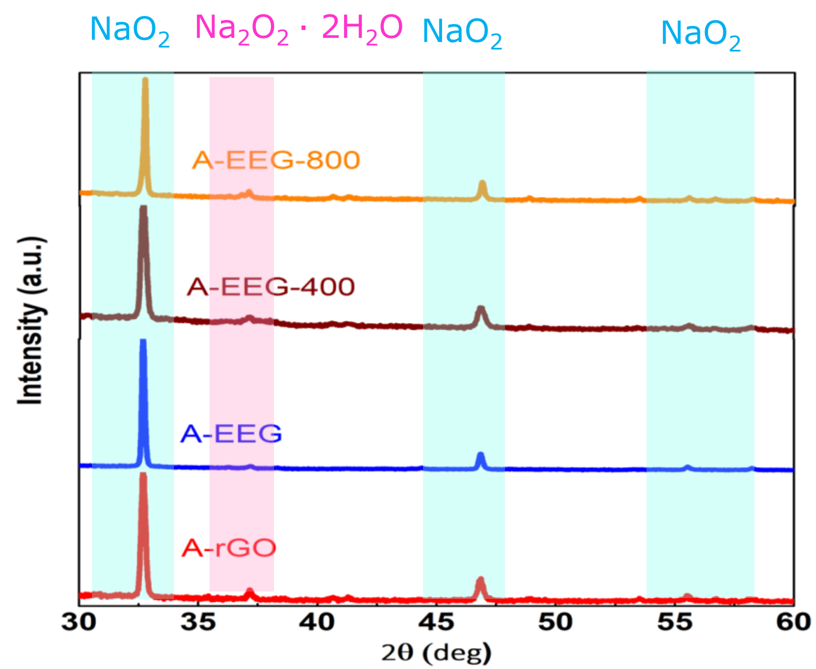
ACS Applied Materials & Interfaces 12 (1) (2019), 494-506/ Small 17 (2) (2021), 2005034

> Na-O_2 cell assembly and full discharge experiment

Current density: 0.2 mA cm^{-2}



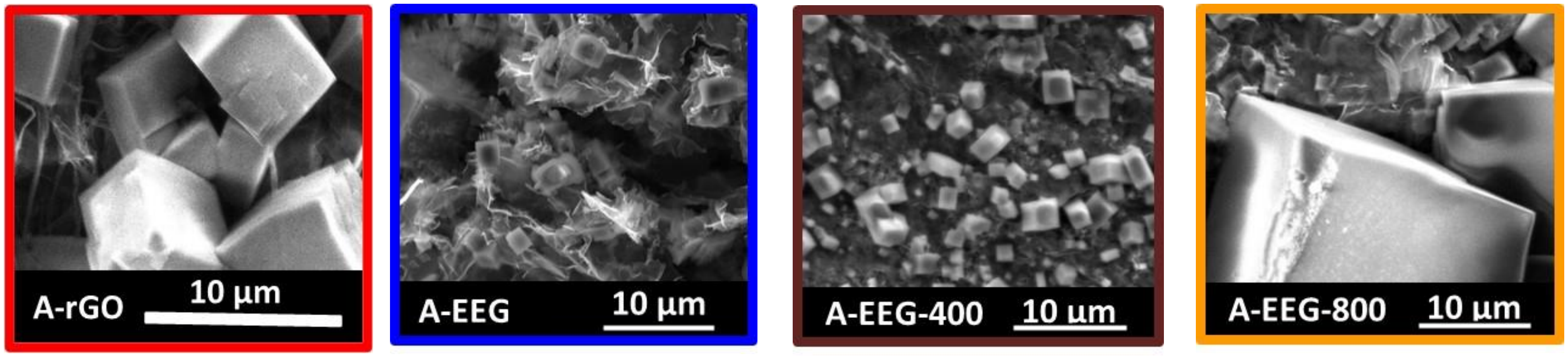
Characterization of the discharge products (XRD)



- The nucleotide does play a role on the cathode performance as the decomposition of the molecule leads to a significant decrease of the discharge capacity.

- Main discharge product NaO_2 for all the graphene cathodes (✓ rechargeability)

> Characterization of the discharge products (SEM)



~ 5 µm cubes

0.7–1.25 µm cubes

Cube size

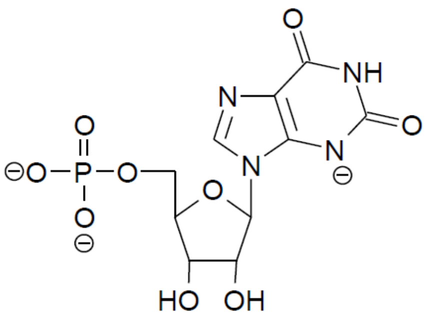
Temperature of the thermal treatment (i.e. AMP decomposition)

- **AMP favors the nucleation of the NaO_2 on the surface** of the graphene electrode, leading to a good dispersion of the discharge products.
- The **removal of the AMP** leads to the formation of bigger cubes suggesting a change in the mechanism whereby **discharge products nucleate/growth in the electrolyte** rather than on the surface.

> Potential bifunctional catalysts

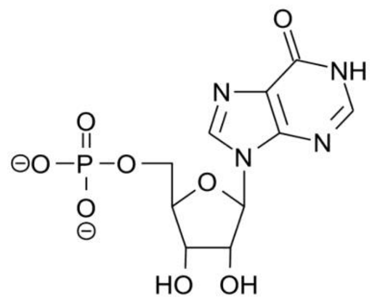
Nucleotides, biomolecules to be studied

XMP



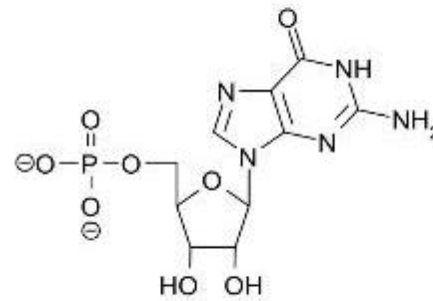
Xanthosine monophosphate

IMP



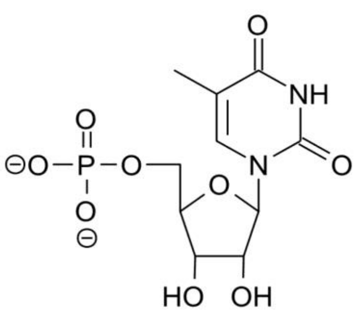
Inosine monophosphate

GMP



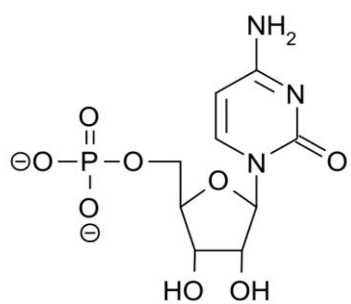
Guanosine monophosphate

TMP



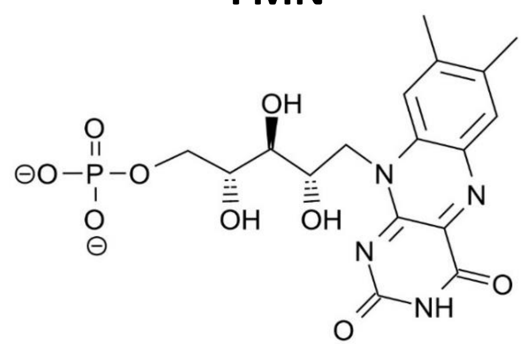
Thymidine monophosphate

CMP



Cytidine monophosphate

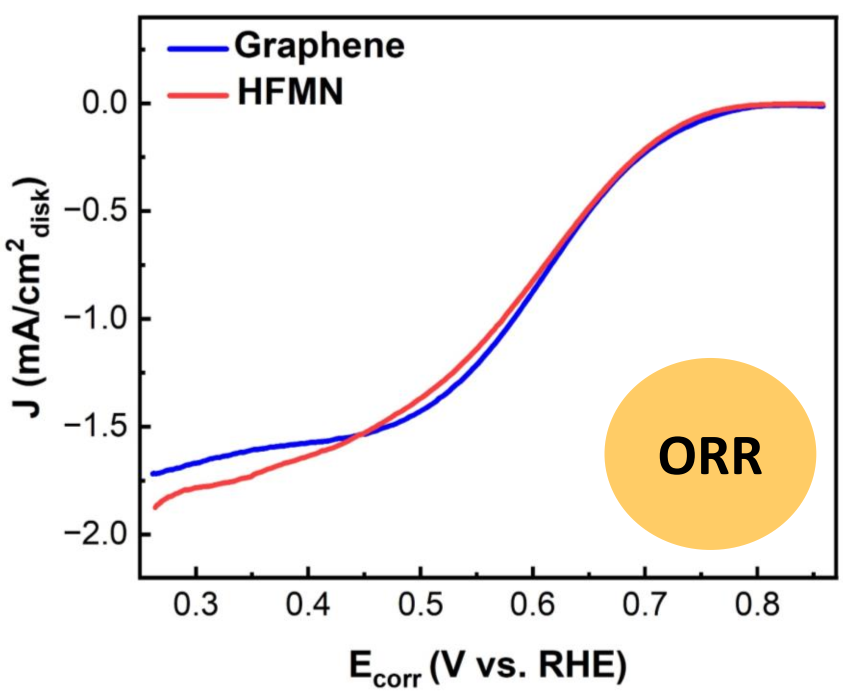
FMN

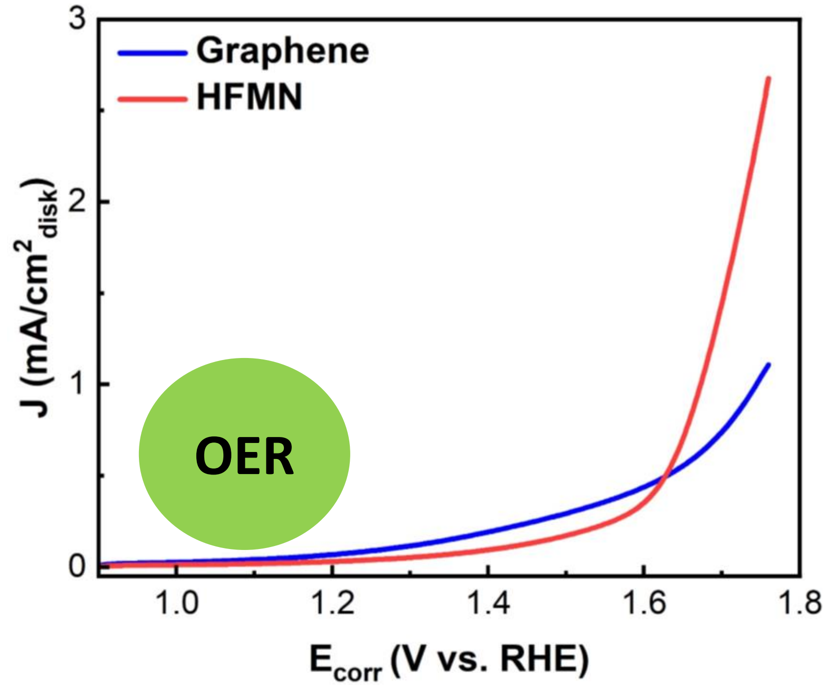


Flavin monophosphate

> Evaluation of the electrocatalytic activity towards ORR and OER

Proof of concept with flavine/graphene hybrid (HFMN)

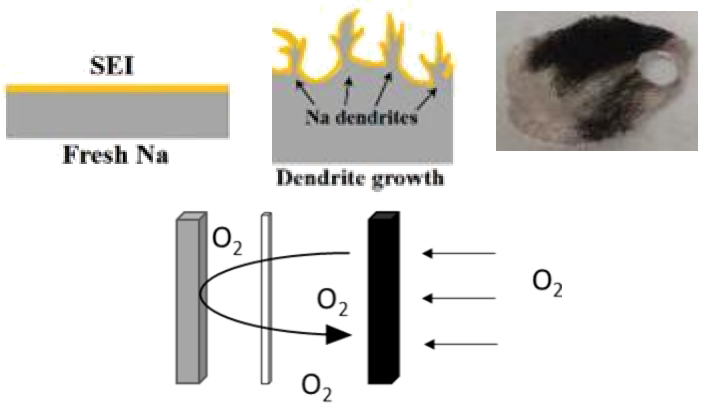


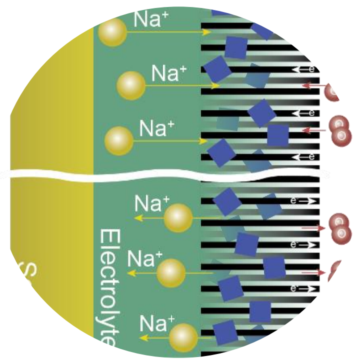


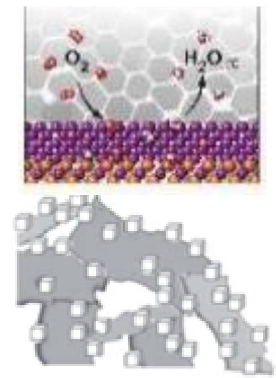
	ORR		OER	
	E_{onset} (-0.1 $mAcm^{-2}$)	Tafel slope (mV/dec)	E_{onset} (+0.5 $mAcm^{-2}$)	Tafel slope (mV/dec)
Graphene	0.7392	60	1.630	295
HFMN	0.7296	65	1.627	151

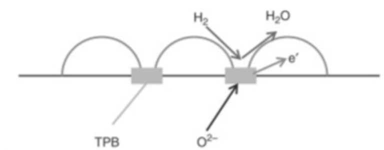
> Sodium-oxygen batteries

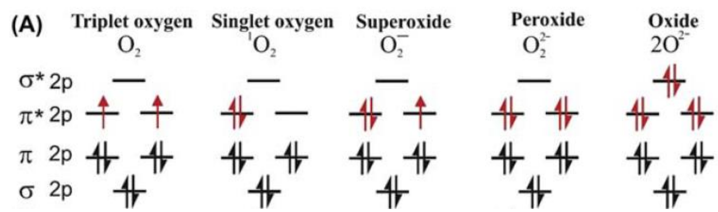
FUTURE OUTLOOK

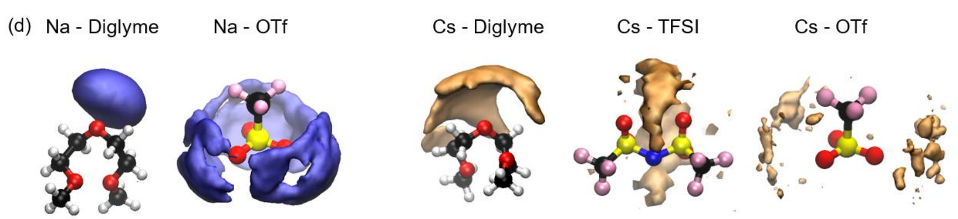












CIC energiGUNE activity is focused on cathode and electrolyte materials development; moving towards solid electrolytes and bio-based separators.

C. Pozo-Gonzalo & N. Ortiz-Vitoriano; Current Opinion in Electrochemistry 2022, 36:101120

4. Aqueous-air batteries (Zn)

Zn dissolution

shape changes
&
dendrite growth

$Zn \rightarrow Zn^{2+} + 2e^-$

$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-}$

$(E^o = -\ 1(25\ V\ vs.\ NHE)$

$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^-$

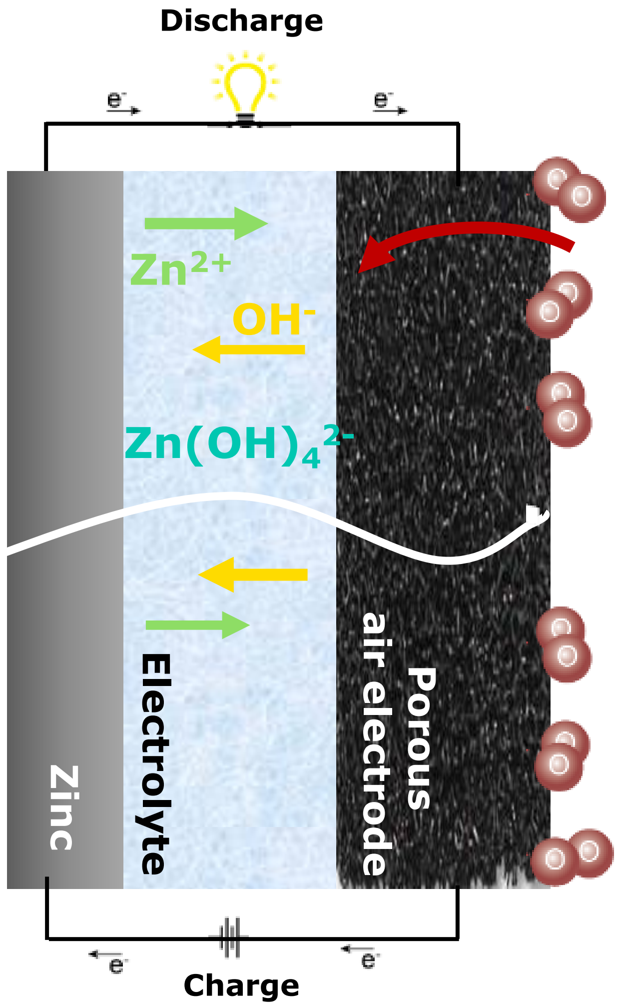
$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \uparrow$ [114]

Zn passivation

ZnO deposition

Zn corrosion

H_2 production



Sluggish oxygen reactions

ORR & OER

Bifunctional catalysts

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (E^0 = 0.40\ V)$

$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (E^0 = -0.07\ V)$

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (E^0 = 0.87\ V)$

$2HO_2^- \rightarrow 2OH^- + O_2$

$M^{m+} - O + OH^- \rightarrow M^{(m-1)+} - O - OH + e^-$

$M^{(m-1)+} - O - OH + OH^- \rightarrow M^{m+} - O - O^{2-} + H_2O + e^-$

$2M^{m+} - O - O^{2-} \rightarrow 2M^{m+} - O^{2-} + O_2$

Carbon corrosion

during OER

Electrolyte/Cathode interphase

Wettability, porosity, conductivity

Vulnerability to CO_2
Evaporation and leakage problems
Cycling stability

In practise working **voltages < 1.2 V**; **< 60 % round-trip** energy efficiency.
Rechargeable Zn-air battery still a great **challenge.**

Zinc air batteries

CONFIGURATIONS

High chemical instability and parasitic reactions by the use of alkaline electrolytes lead to electrochemical irreversibility.

Zn-air primary

- **MnO_2 cathode**
  - Low activity & stability
- **Aqueous electrolyte**
  - Alkaline
- **Zn anode**

Zn-air secondary

- **Cathode**
  - Two cathodes
  - **Bifunctional cathode**
- **Electrolyte**
  - Aqueous
  - Non-aqueous
  - **Semi-solid**
  - Solid
- **Anode**
  - Structure (fibers, sponge, etc.)
  - Surface modifications

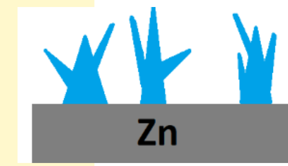
Rechargeability depends on the combined improvements of all cell components

Liquid electrolyte evaporates in the open system

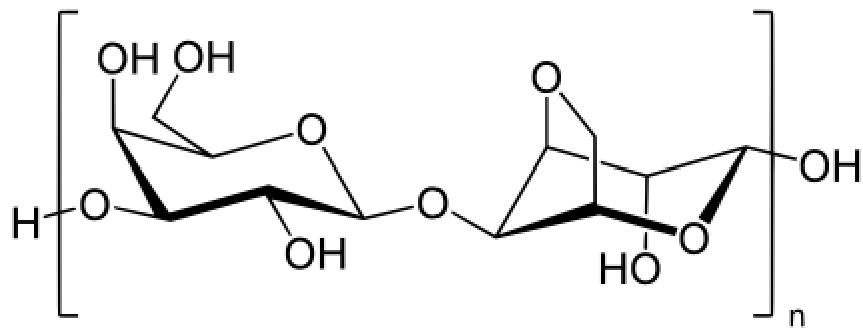
GEL POLYMER ELECTROLYTE

CHALLENGES

Leakage
Dendrites
Evaporation
Carbonate precipitation



Our Approach: GELATION

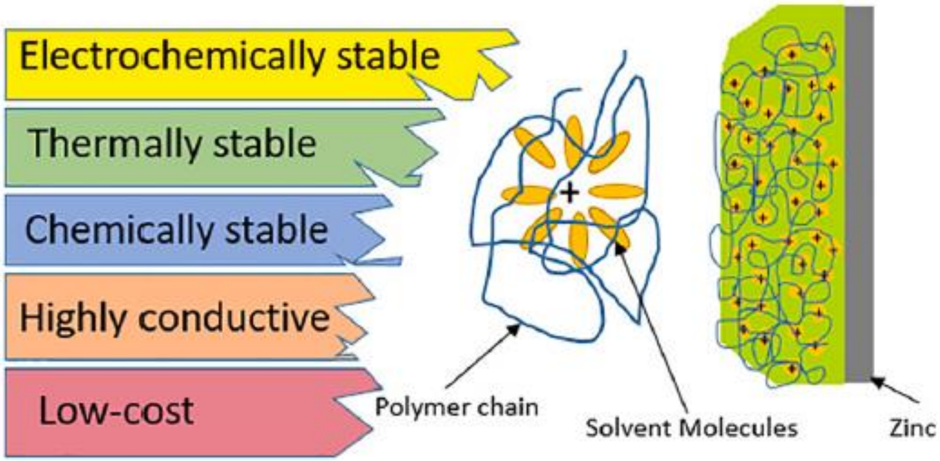


Patent nº WO2022189566A1

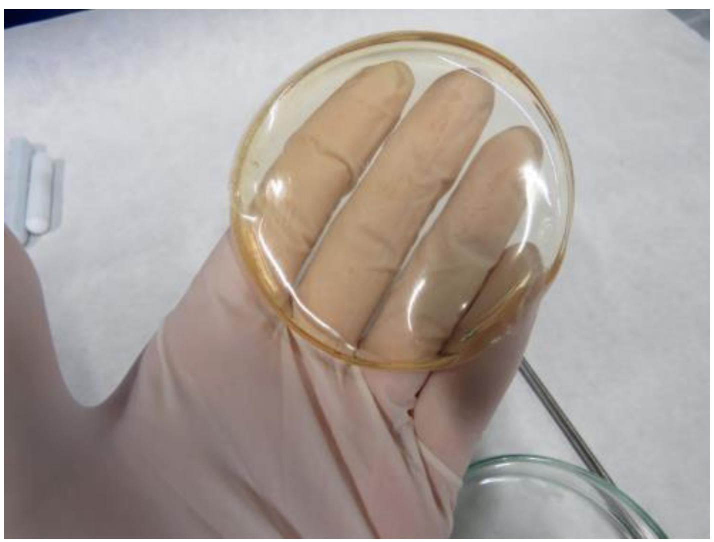
Zinc air batteries

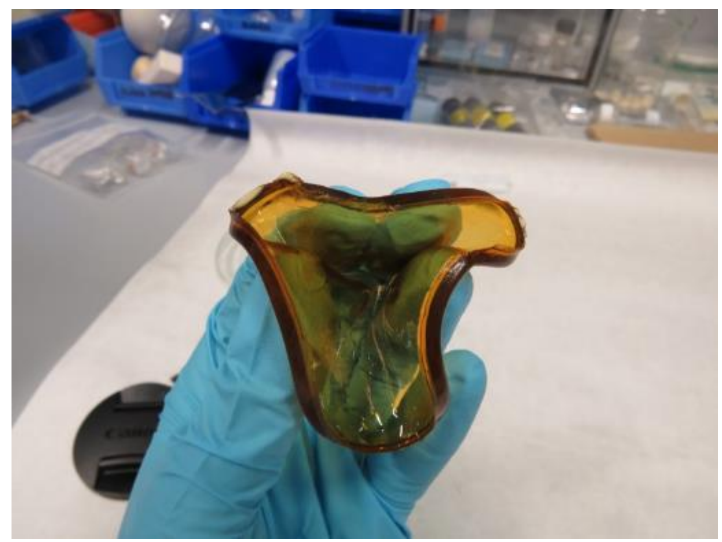
GEL POLYMER ELECTROLYTE

- Consisting of a polymer host and a liquid electrolyte.
- High conductivity, flexibility, interfacial contact.



Chemical Engineering Journal 408 (2021) 127241



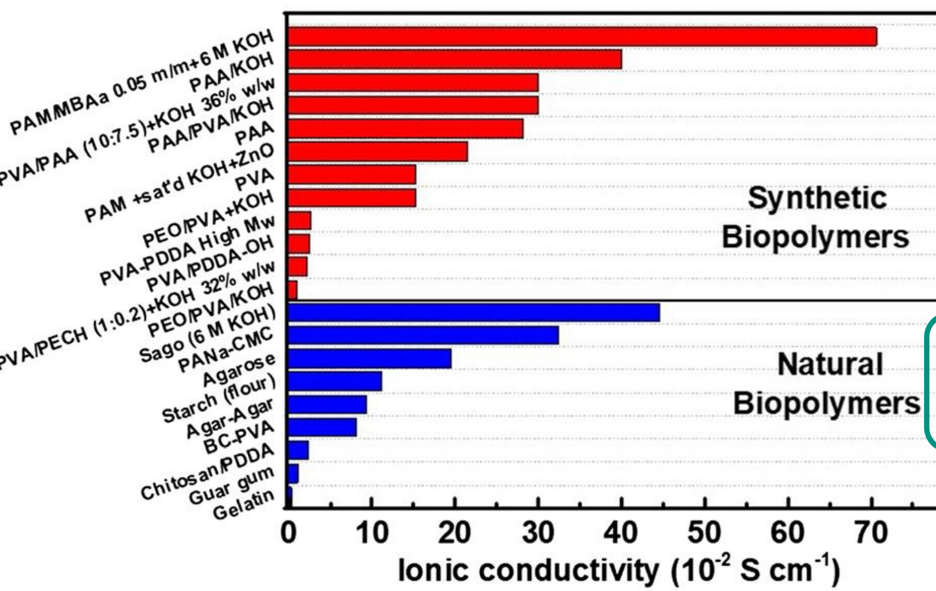


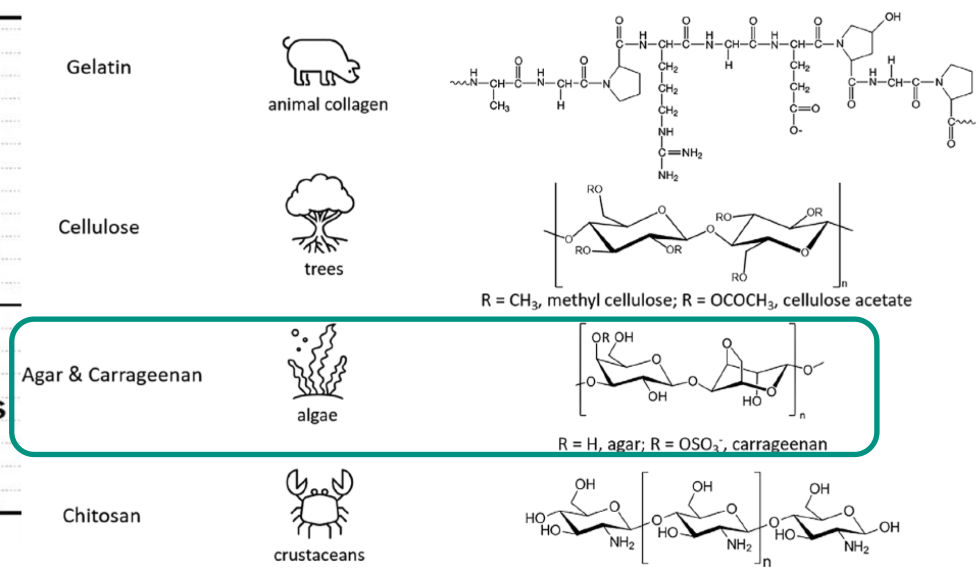
> Biopolymers in EES devices

WHICH BIOPOLYMER FOR MY ZAB?

Synthetic or natural biopolymer?

- Polymer matrices generally proposed in the literature include polyvinyl alcohol (PVA), polyethylene oxide (PEO), polyacrylamide (PAM), polyacrylic acid (PAA), and other synthetic (bio)polymers (higher ionic conductivity).



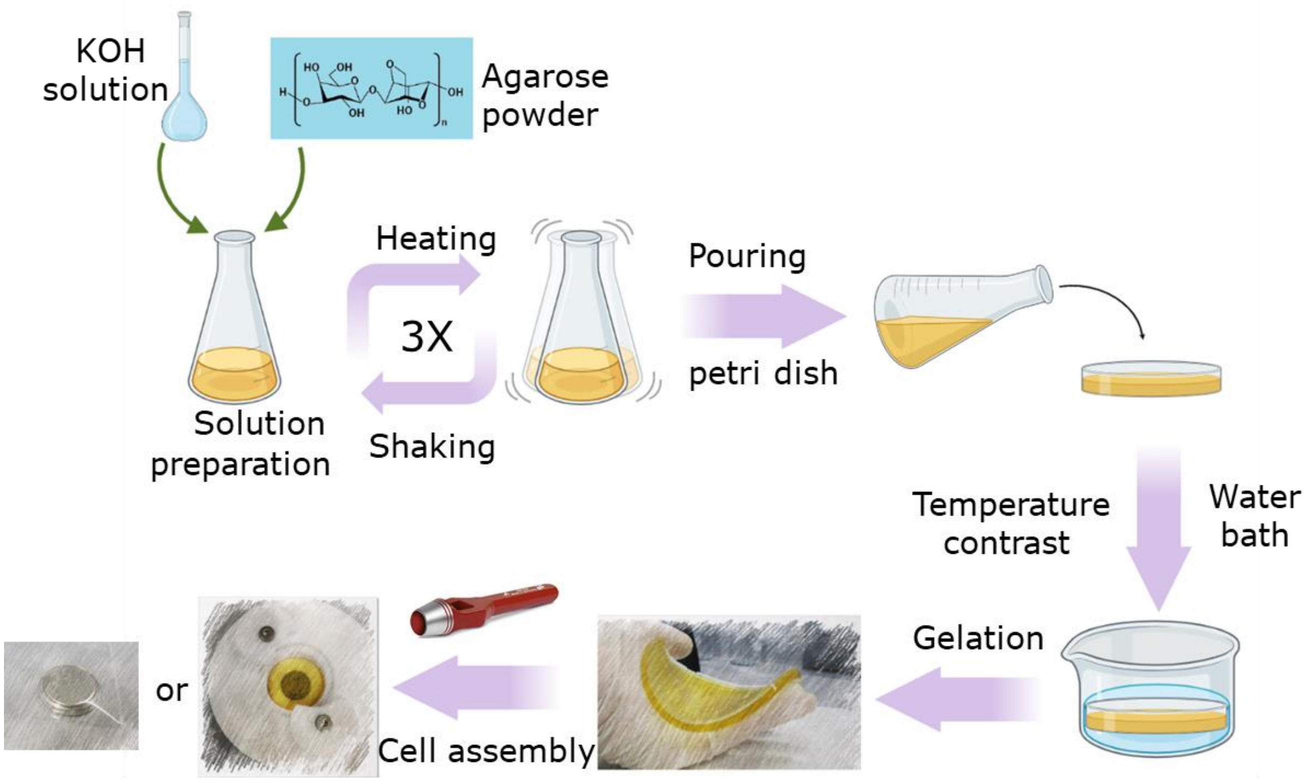


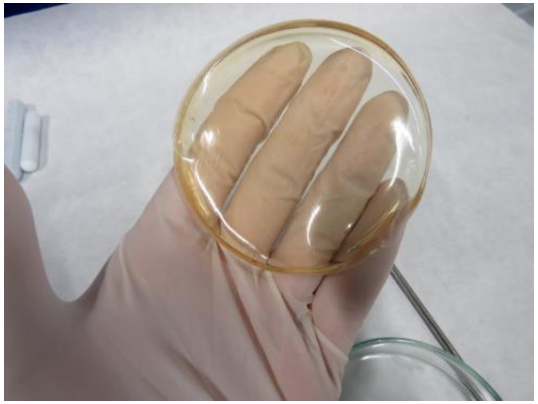
D. Frattini, N. Ortiz-Vitoriano et al., Energy & Environmental Science 2022 - 10.1039/D2EE02421G

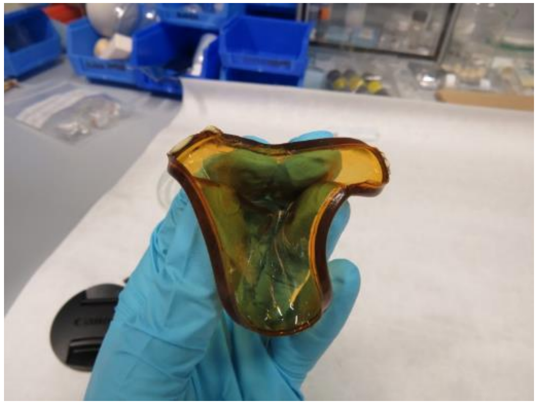
> Electrolyte development

AGAROSE BASED ALKALINE GEL ELECTROLYTE

Simple preparation



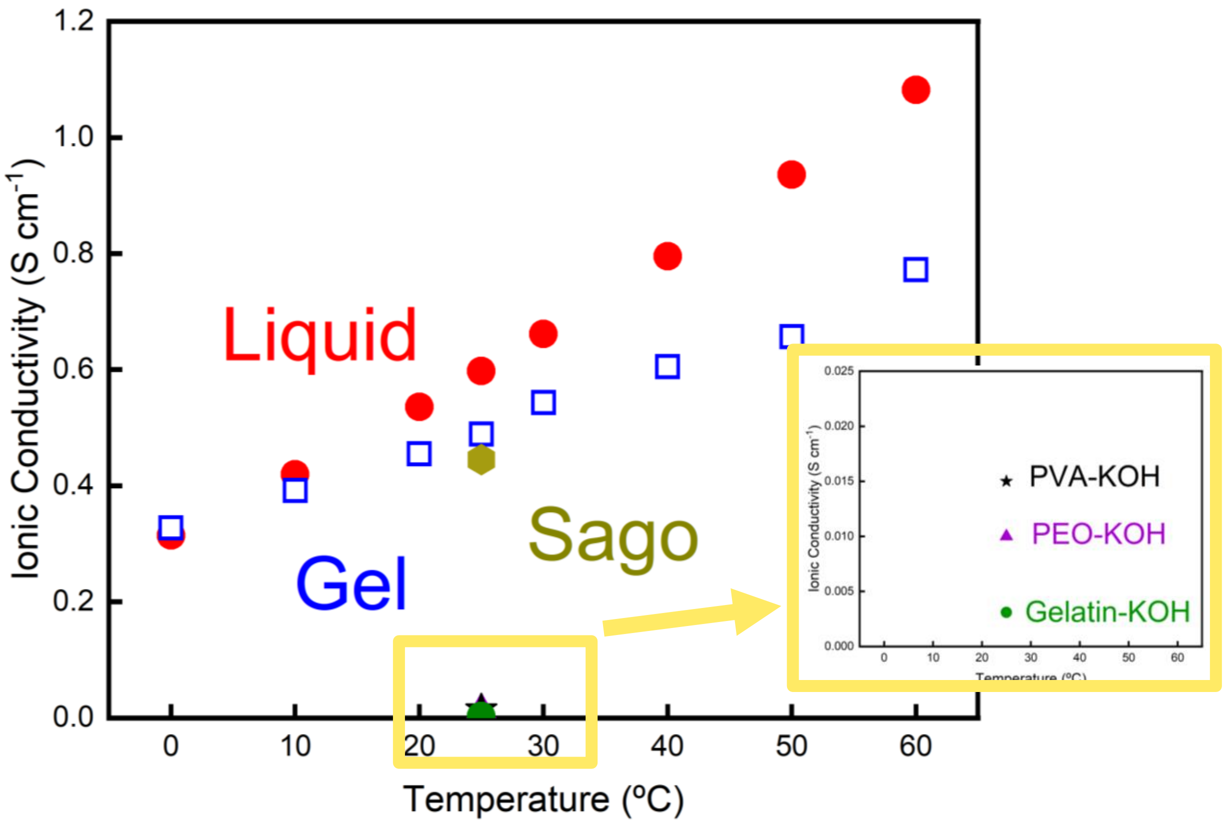




POLYSACCHARIDE ELECTROLYTES, Patent No. WO2022189566A1

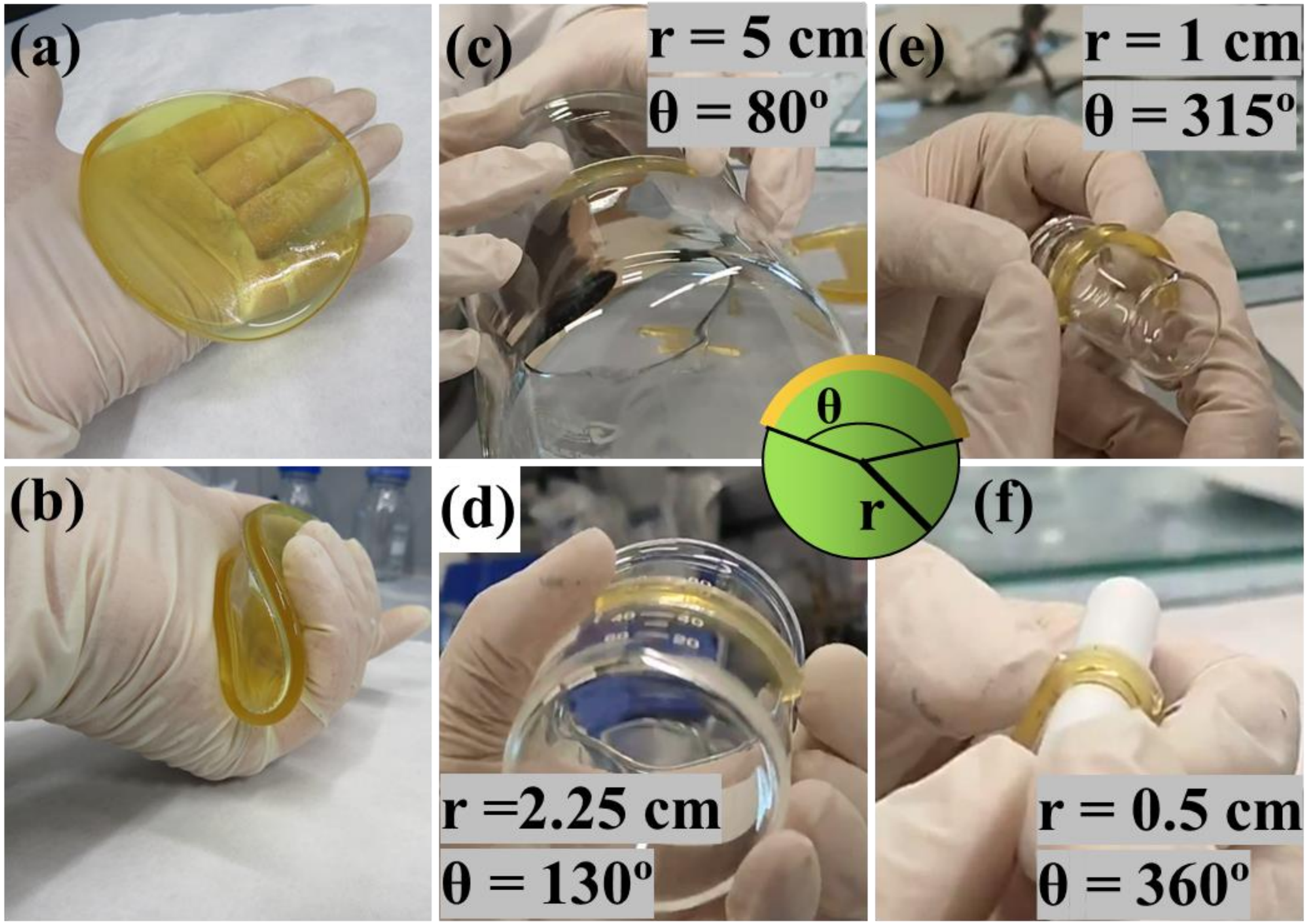
Ionic conductivity at different temperatures

GEL BEHAVES SIMILAR TO LIQUID ELECTROLYTE



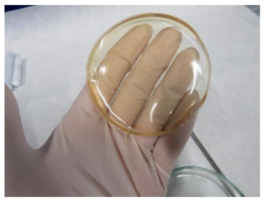
> Compression key to enabling a good contact in the battery

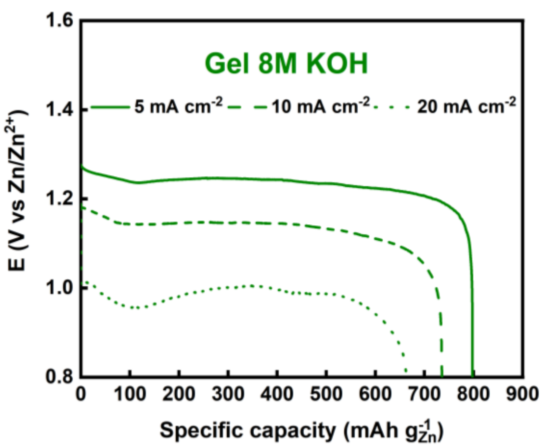
GEL STABLE UPON CYCLING

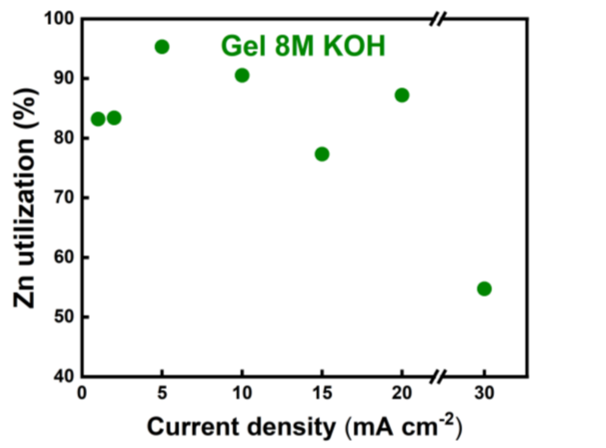


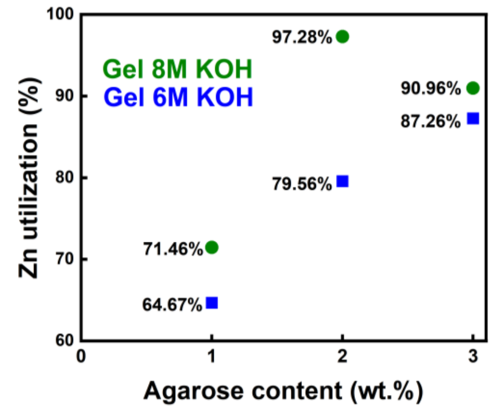
> Primary Zn-air Battery

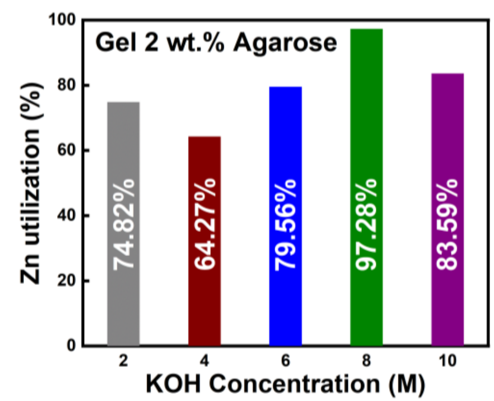
HIGH ZN UTILIZATION









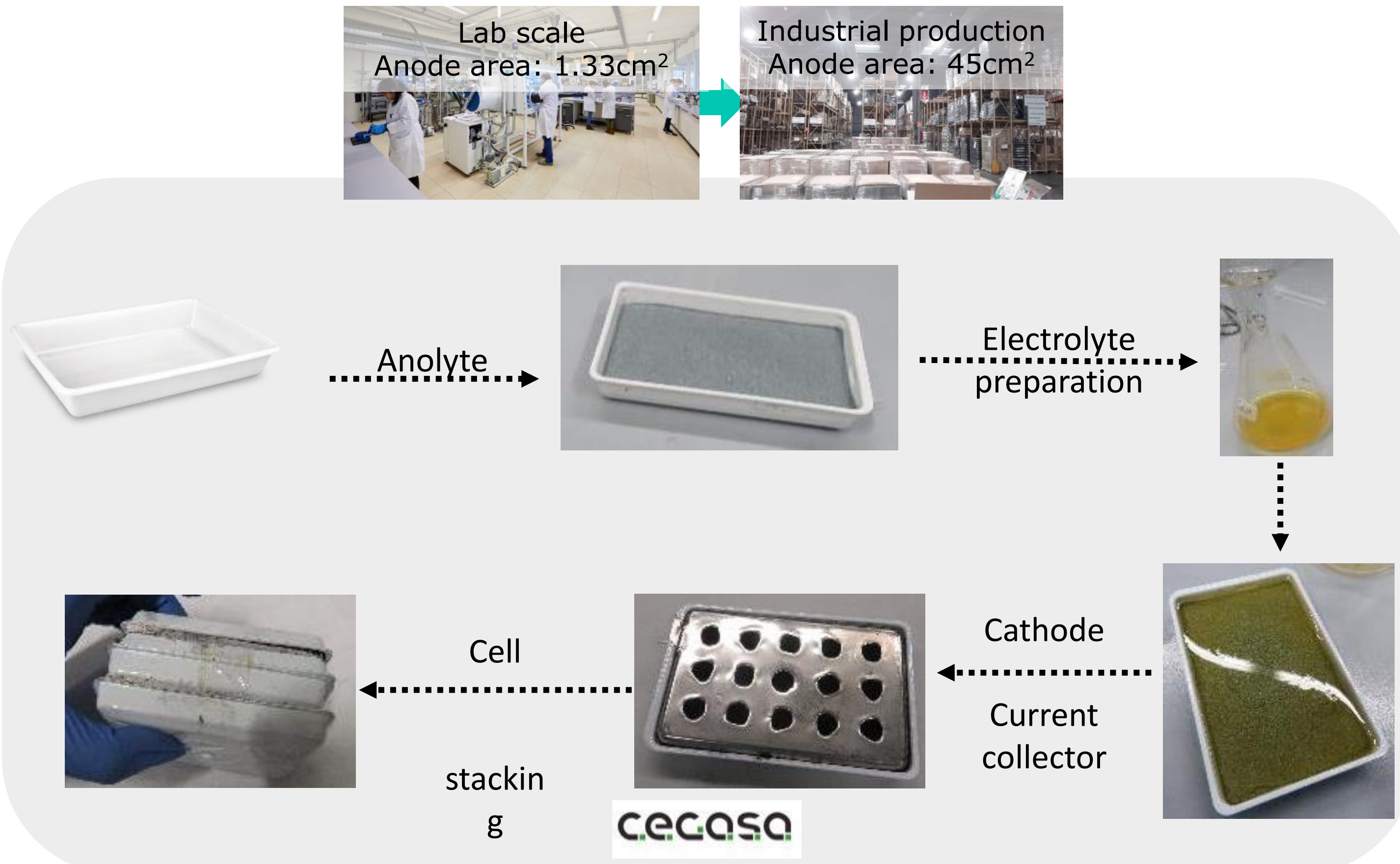


> Towards Industrialization

AGAR-AGAR BASED GEL ELECTROLYTE UPSCALING

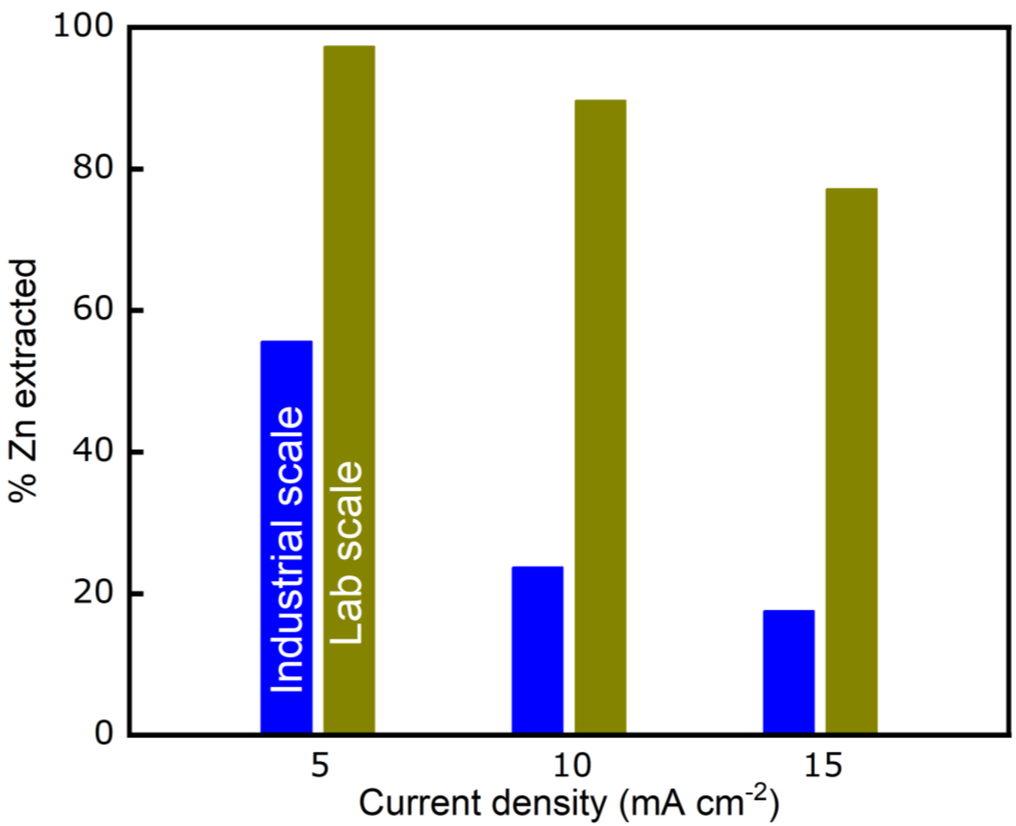
> Zinc-air batteries

AGAR-AGAR BASED GEL ELECTROLYTE UPSCALING



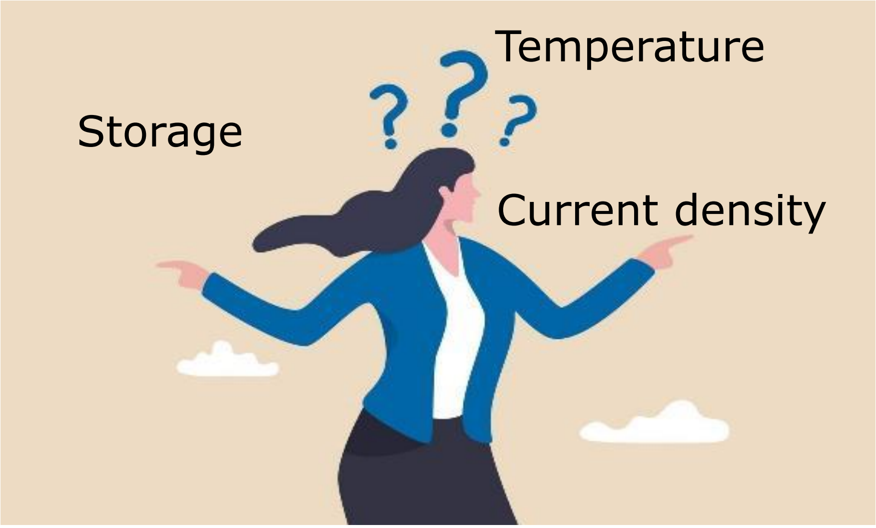
> Towards Industrialization

UP-SCALING DECREASES ZN UTILIZATION

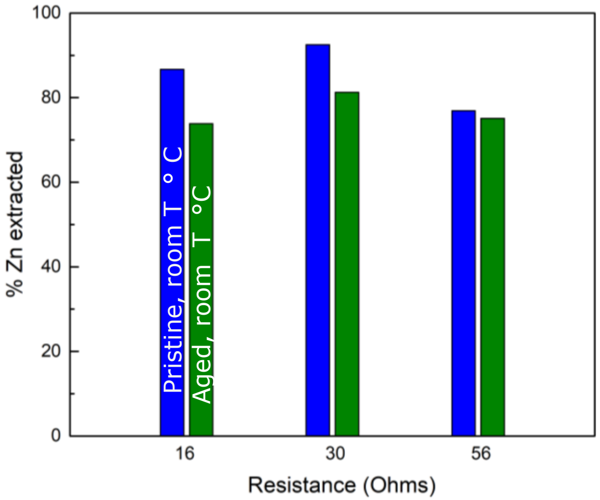


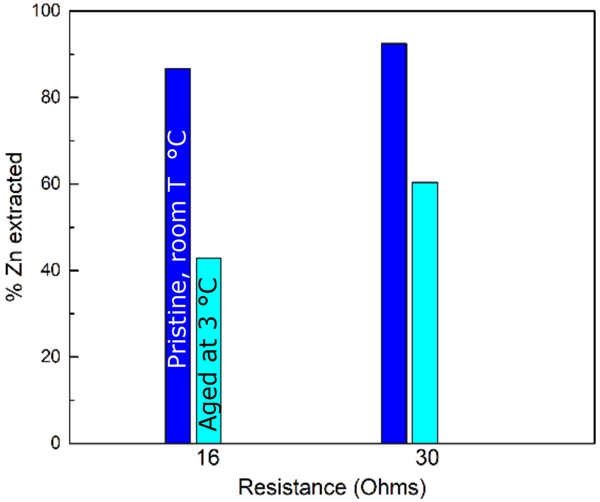
> Zinc air batteries

AGAR-AGAR BASED GEL ELECTROLYTE UPSCALING



Does the storing & temperature affect (6M)?





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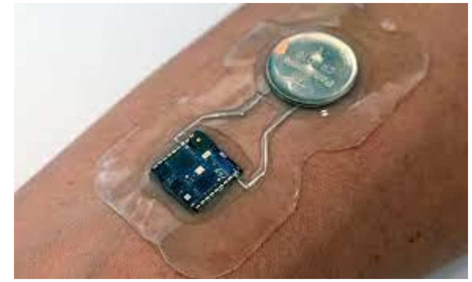
Railway Signalling

Hearing aids



Wearable electronics

Primary ZABs
Portable, small devices, low consumption, long duration

Electrical rechargeability bottleneck

Secondary (electrically rechargeable) ZABs
Centralized/Remote stationary, grids, high energy/power

Renewables' storage

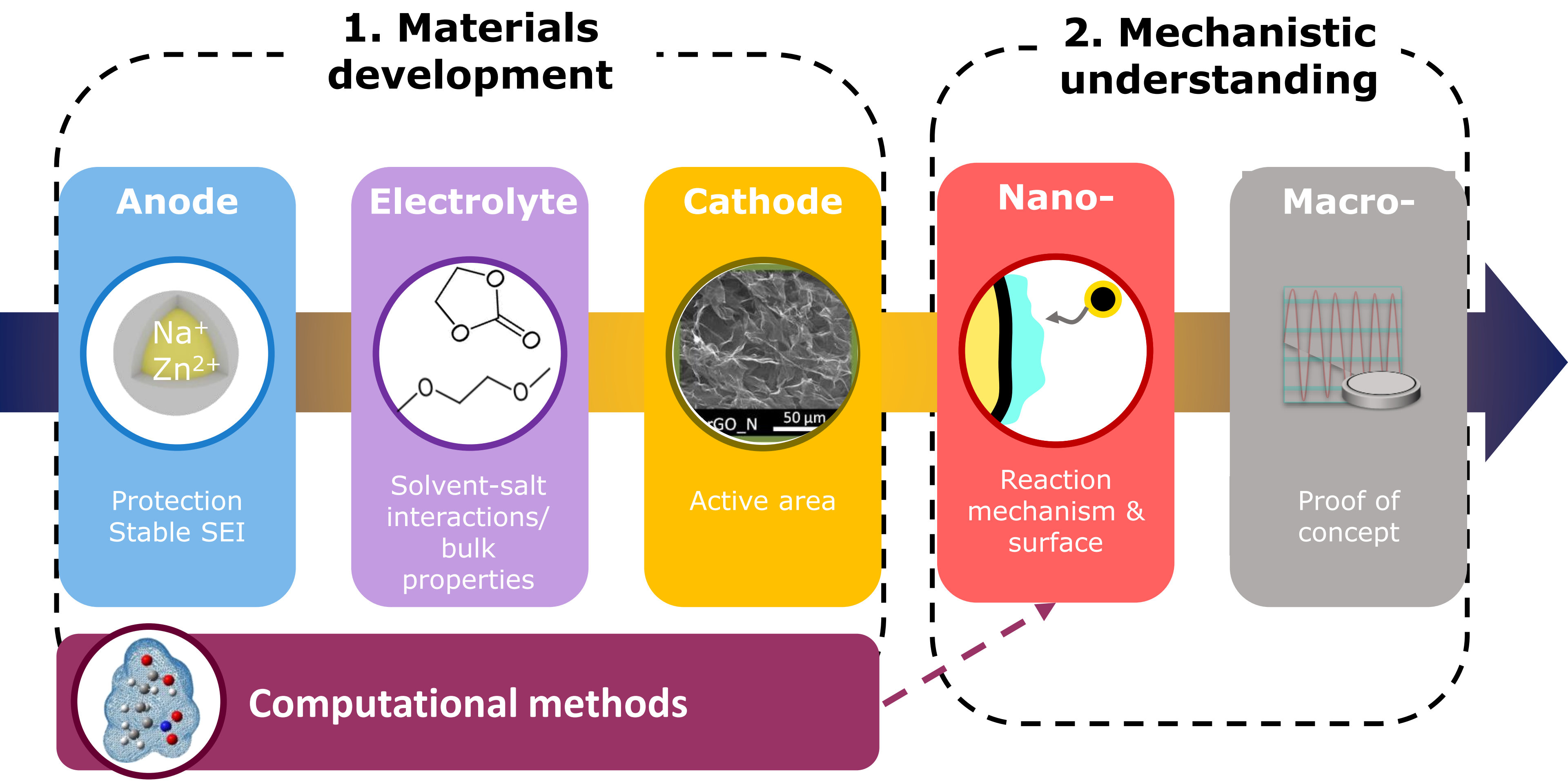
Navigation Aids

Smart Microgrids

https://www.cegasa.com/ez8

Metal-air batteries

MATERIALS DEVELOPMENT AND INTEGRATION



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CIC energiGUNE

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Making sustainability real

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