

Next-Generation Batteries

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Fellow – Royal Society of Chemistry**

Outline of this Seminar

This seminar will introduce some of the new rechargeable battery systems being developed for the energy sector. Topics that will be touched upon include:

- Global energy outlook & the need for renewables
- Challenges around renewable energy storage at scale
- Current rechargeable battery systems and their limitations
 - Lead-acid batteries
 - Li-ion batteries
- Emerging battery technologies
 - Metal-air batteries
 - Redox flow batteries

I'm particularly interested in how these emerging batteries technologies could be used alongside Green Hydrogen to **decarbonization of the global energy sector.**



Bio – Geoffrey Waterhouse

I was born in Auckland, completed all my primary, secondary, and tertiary education (BSc, MSc and PhD) in Auckland, postdoc'd at Massey University (2004-2007), before returning to the University of Auckland in 2008 (where I have been firmly entrenched ever since!)

I was awarded the 2023 MacDiarmid Medal from the Royal Society Te Apārangi for discovering low-cost nanocatalysts critical to global decarbonisation efforts and creating energy infrastructures based around renewables.

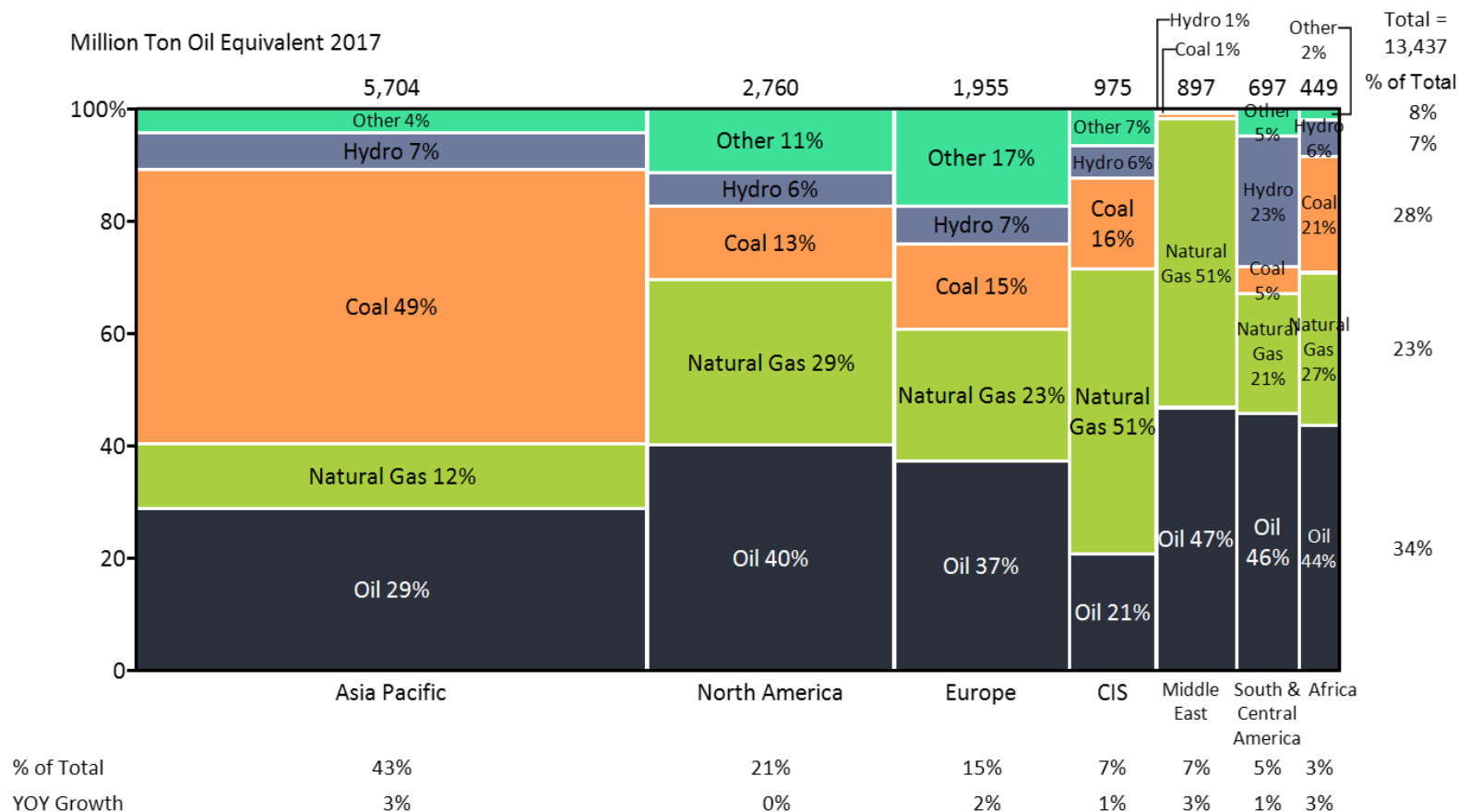


Prof. Waterhouse receiving the MacDiarmid Medal from the Governor General of New Zealand, Dame Cindy Kiro, at Government House, Wellington, November 23, 2023

Powering the Planet – Energy Challenges

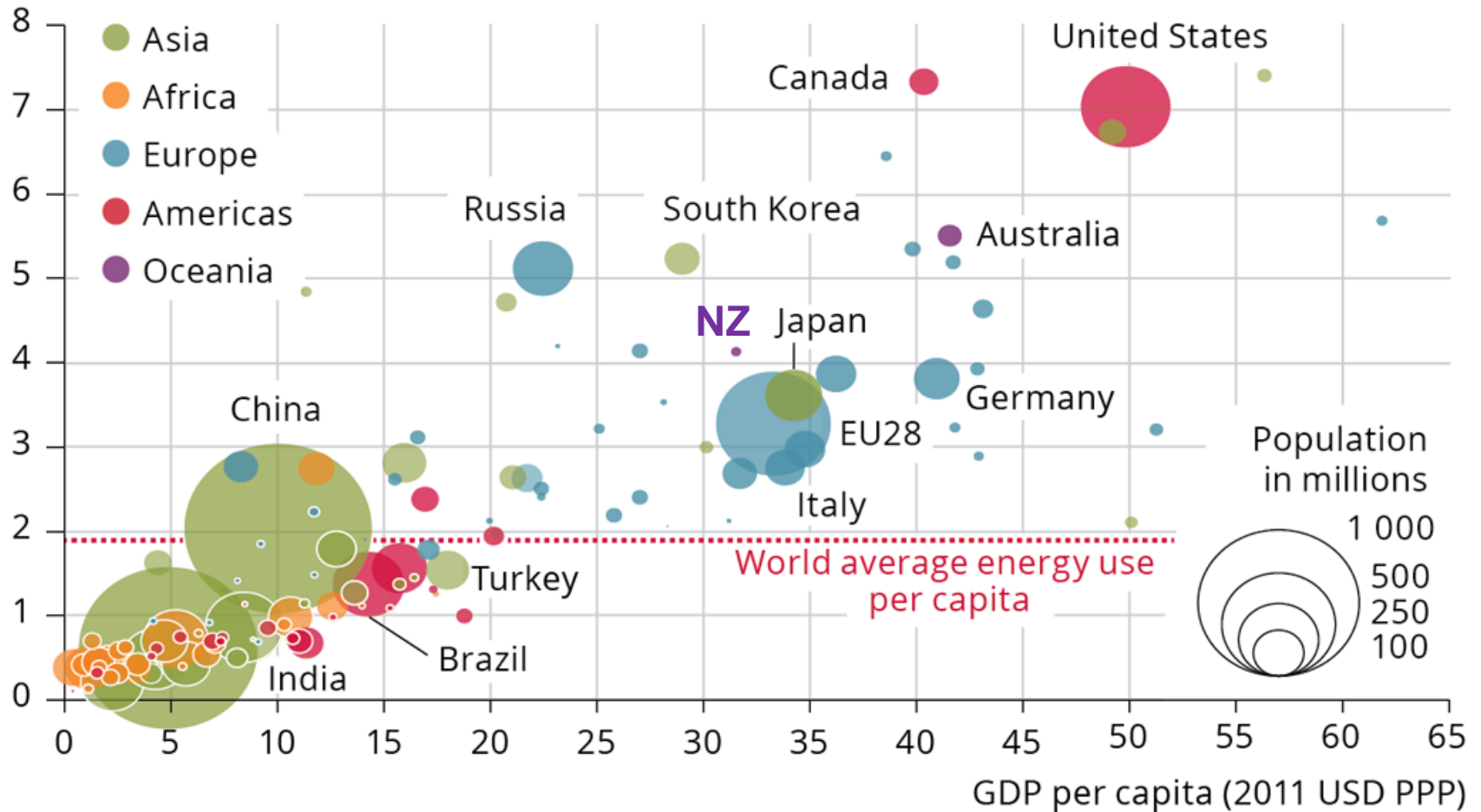
Modern societies remain heavily dependent on **fossil fuel energy**, in spite of the strong link between fossil fuel use and global warming.

The **Asia-Pacific Region** consumes 43% of energy resources (half of which is coal) and consumption is growing at 3% year-on-year (<https://www.mekkgographics.com>)



Powering the Planet – Energy Challenges

Energy use in tonnes of oil equivalent per capita

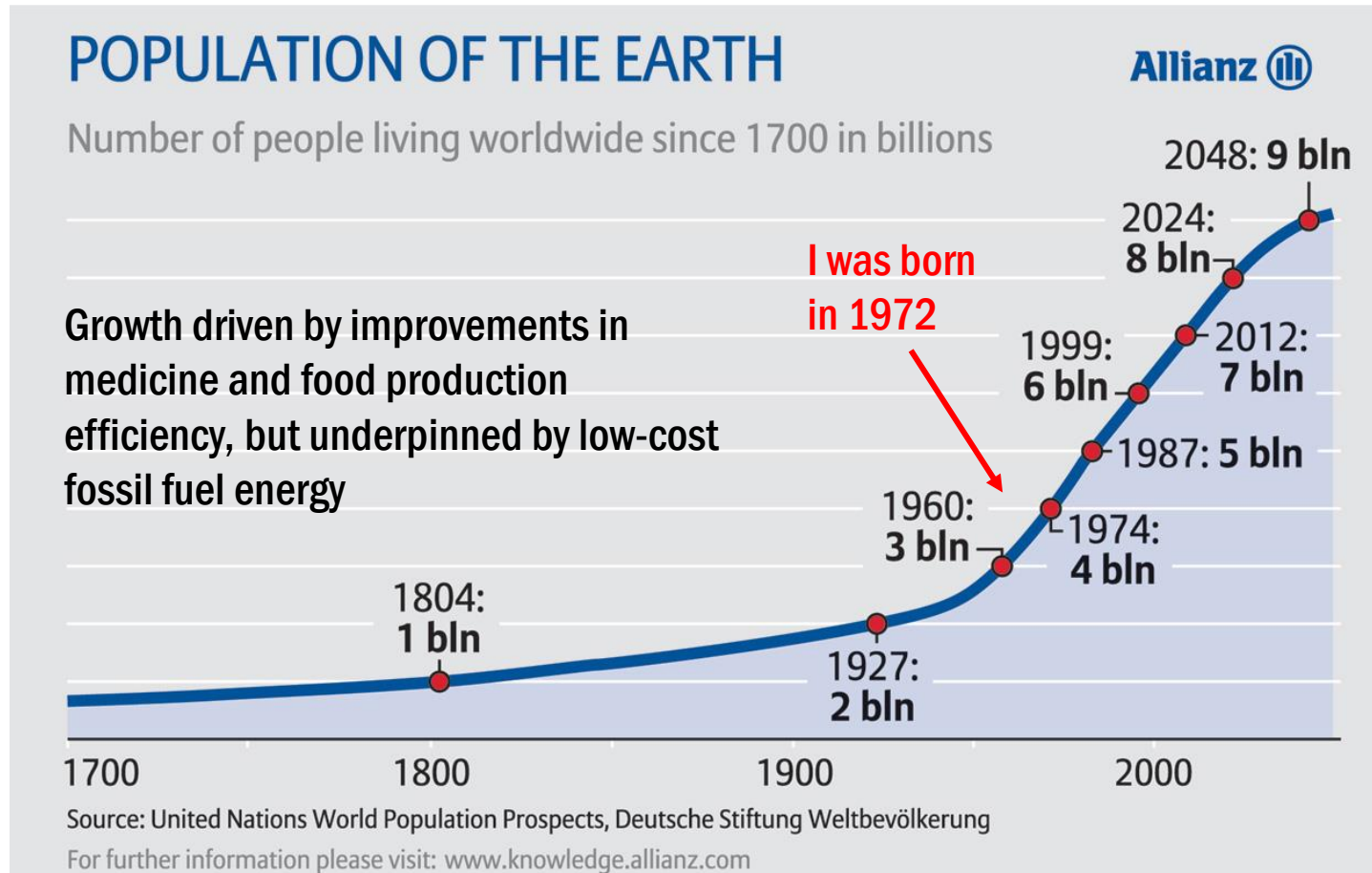


Total energy consumption: 13.5 TW in 2001, 16 TW currently, 28 TW by 2050, 43 TW by 2100

China's GDP per capita now 12,621 USD and New Zealand's GDP per capita now 47,000 USD

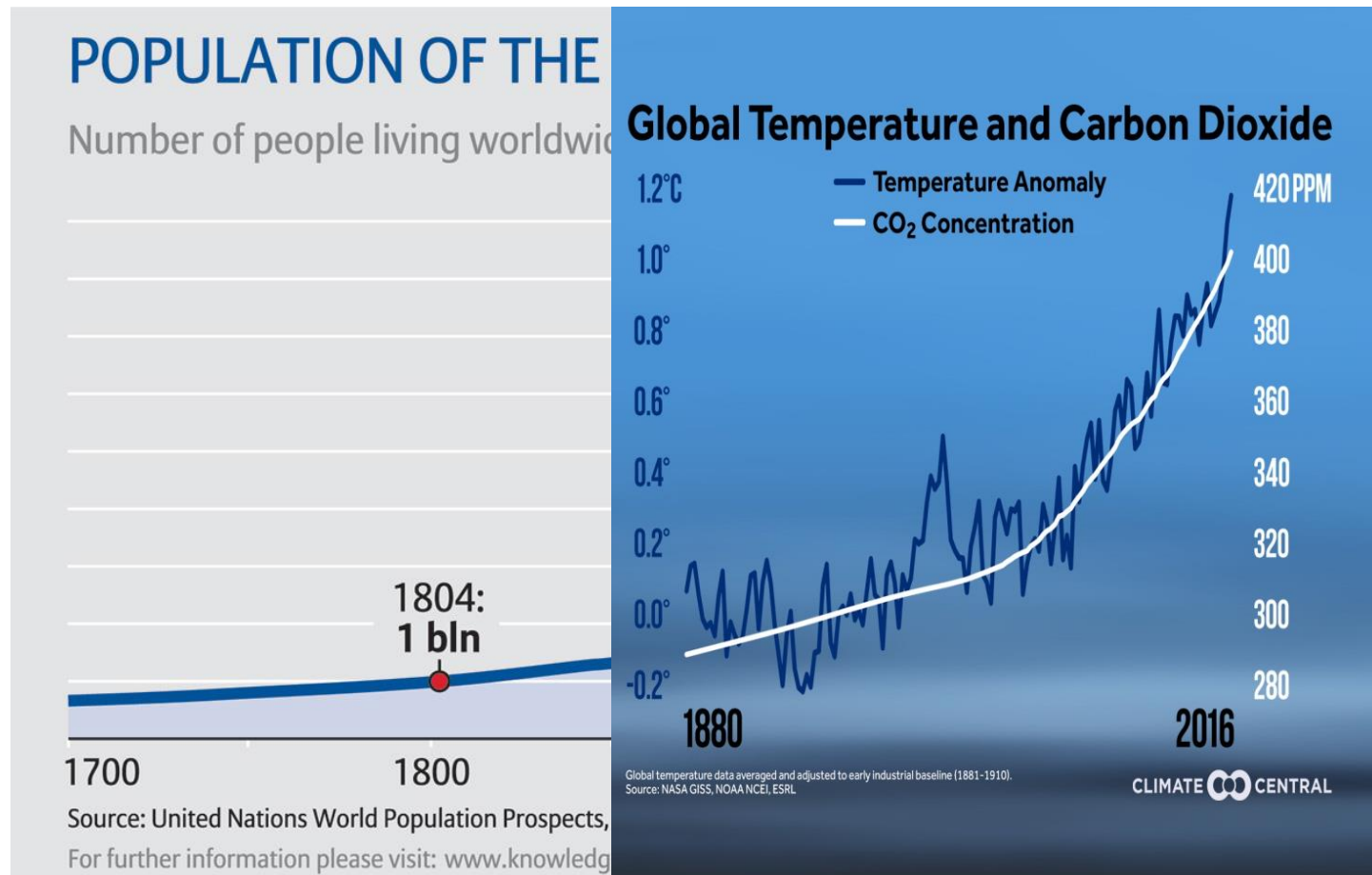
Population Growth

- Since 1960, the human population on Earth has increased by ~1 billion every 12 years.
- Over the same period the average temperature on Earth has increased by ~1 °C.



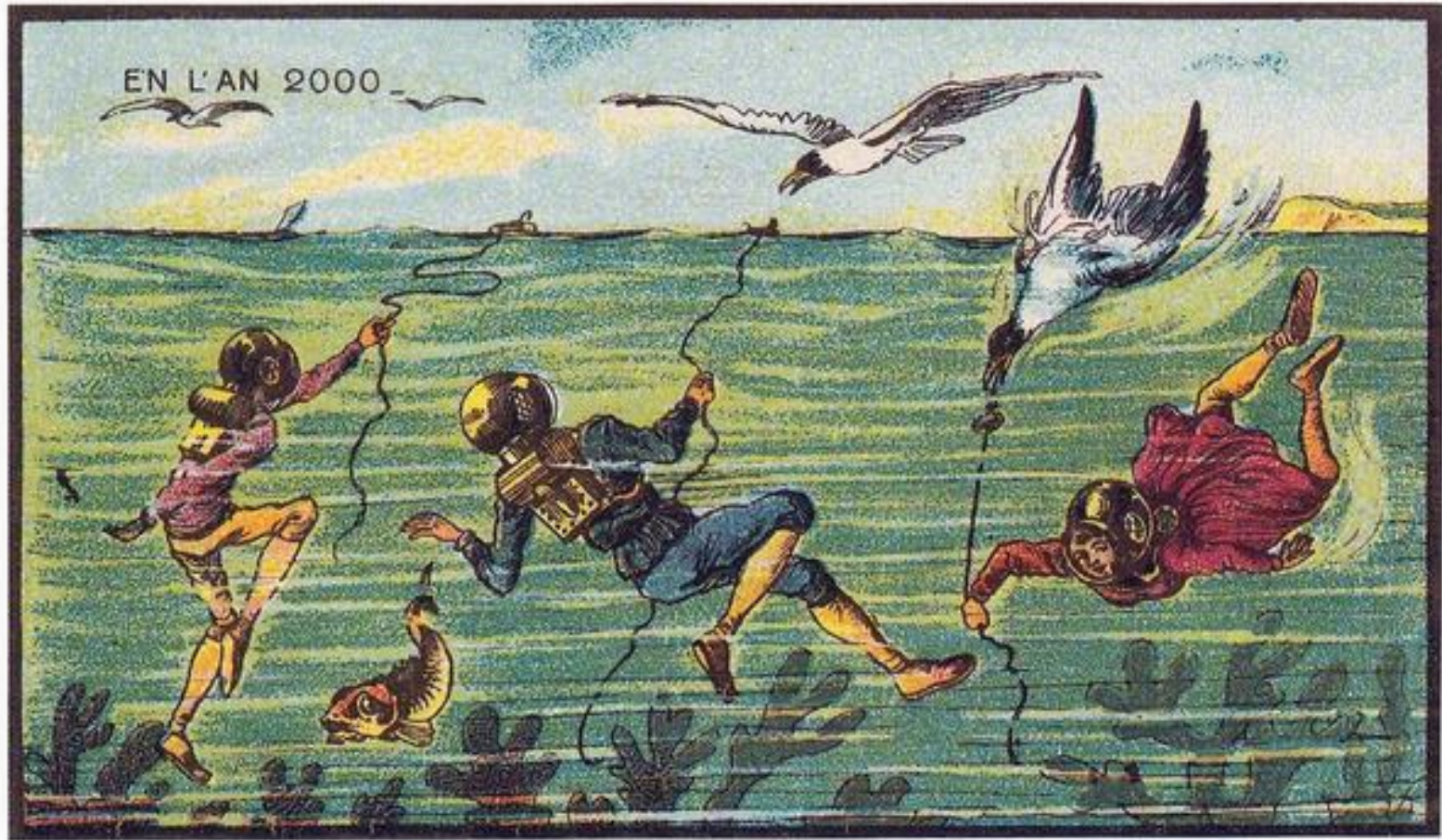
Is Global Warming Real?

Increasing global temperatures are leading to increased incidences of extreme weather events (floods, droughts, typhoons, etc.) and losses in biodiversity.



Urgent action is needed to avoid the worst impacts of global warming. Decarbonization of the global energy sector is an imperative.

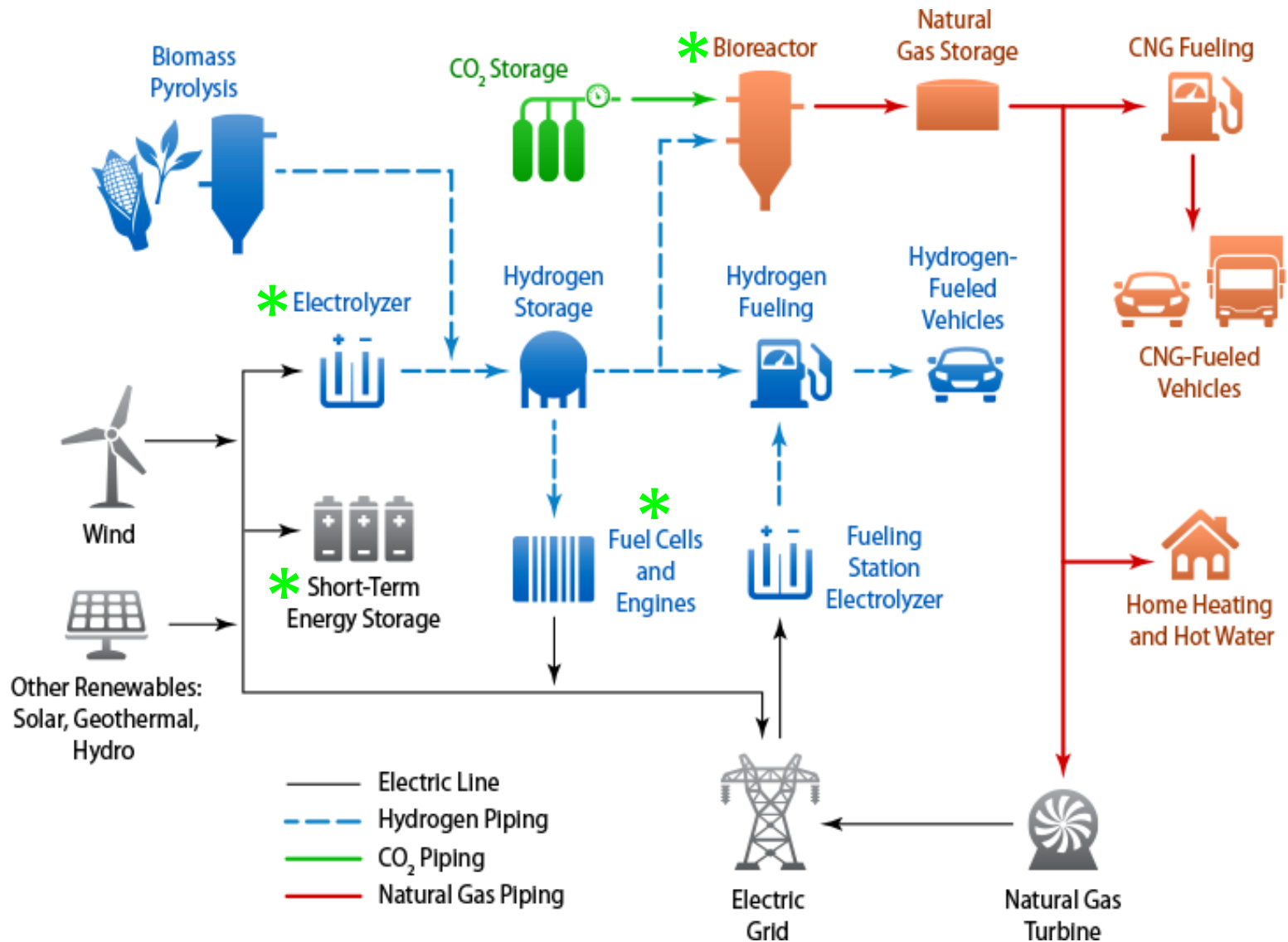
What Will the World Look Like in 2050 or 2100?



Fishing for Seagulls

A vision of the future from 1899 (Jean-Marc Cote and other artists). A futuristic postcard presented at the 1900 World Exhibition in Paris, showing how nineteenth century artists envisioned France in the year 2000.

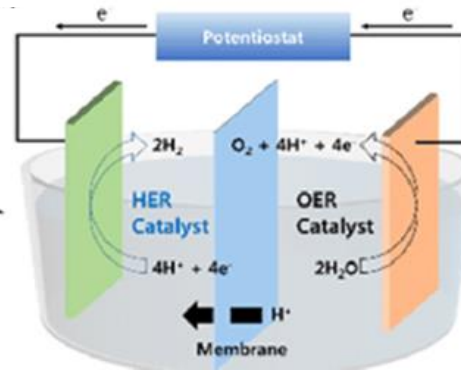
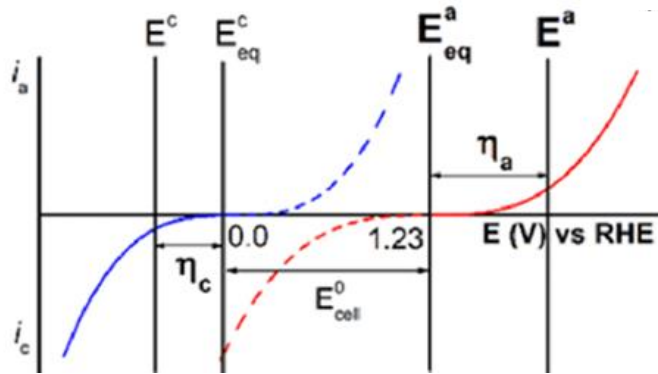
Decarbonizing using Batteries and Green Hydrogen



* My group seeks low-cost catalysts for batteries, water electrolyzers, fuel cells and CO₂ hydrogenation.

Key Technologies in a Green Hydrogen Economy

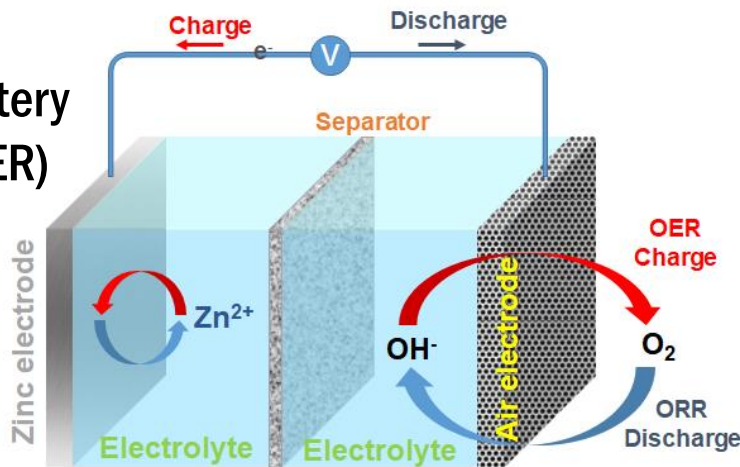
Energy efficient water electrolyzers, high energy density rechargeable batteries and low-cost fuel cells are needed for a hydrogen economy to be a reality. These devices utilize the **oxygen evolution reaction (OER)** and/or the **oxygen reduction reaction (ORR)**.



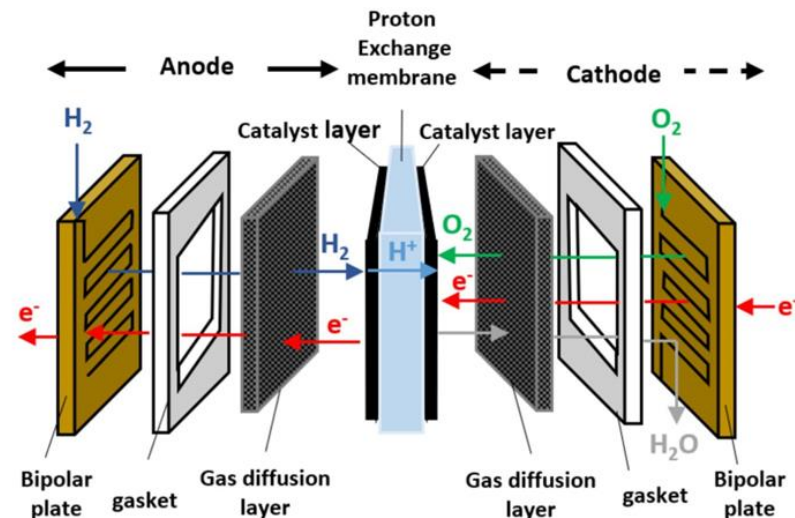
Water electrolyzers (HER + OER)

Rechargeable Batteries

Zn-air battery (ORR + OER)



PEM fuel cells (HOR + ORR)

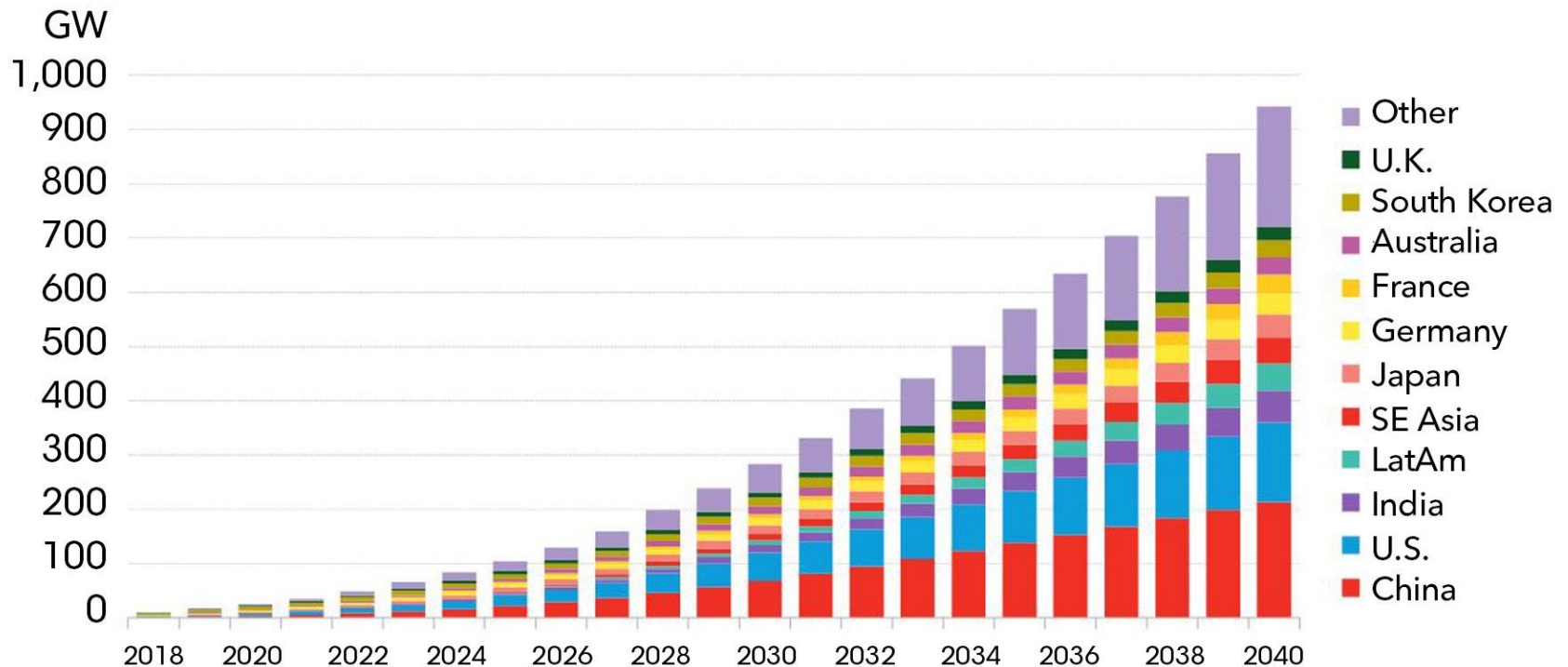


Global Energy Storage

The global energy storage market [1] will grow to a cumulative 942GW/2,857GWh by 2040, attracting \$620 billion in investment over the next 22 years. Cheap batteries and low-cost hydrogen generation are key to storing renewably-generated electricity at scale.

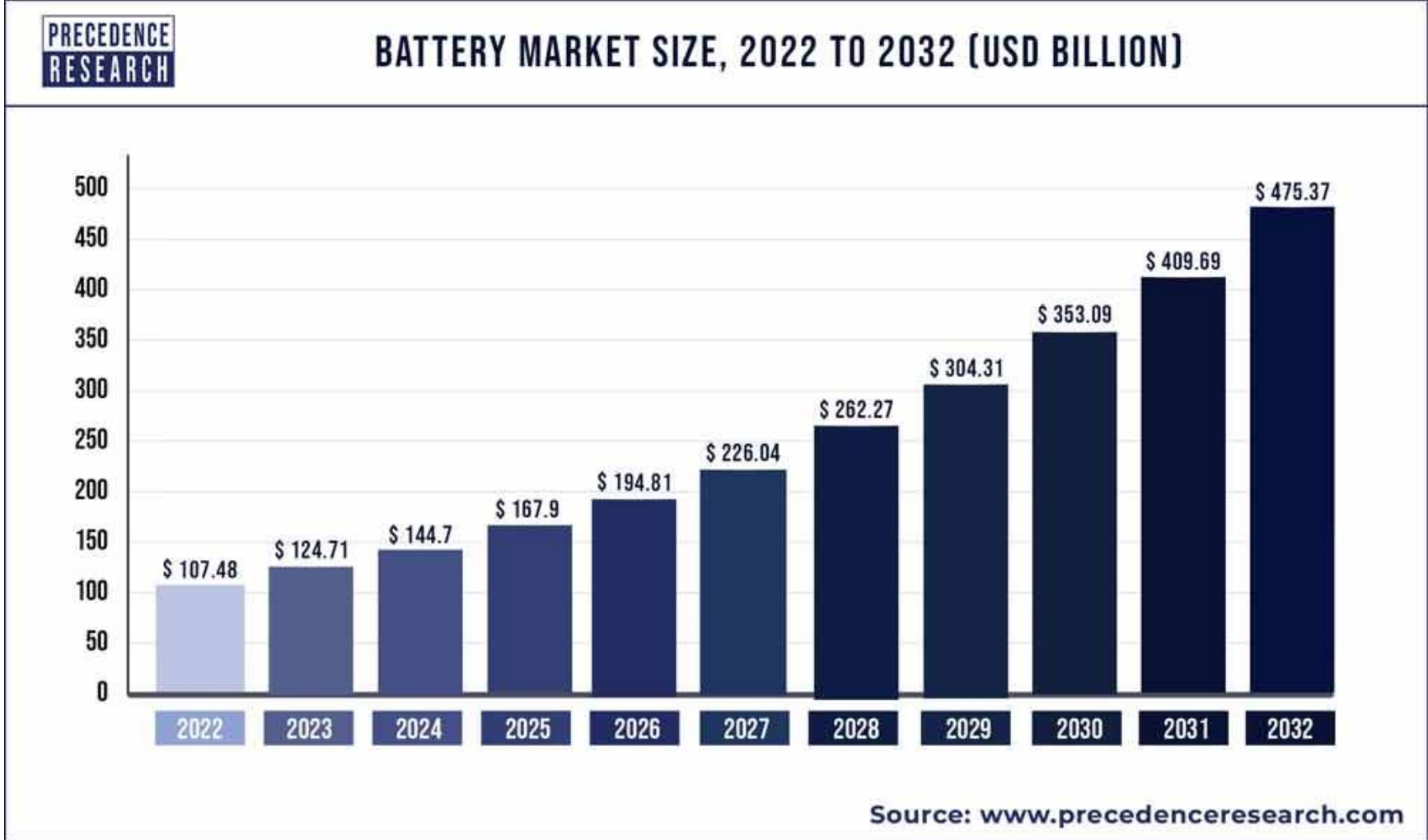
<https://about.bnef.com/blog/energy-storage-620-billion-investment-opportunity-2040/>

Global cumulative storage deployments



Source: BloombergNEF

The global battery market size was estimated at USD 107.48 billion in 2022 and it is expected to hit around USD 475.37 billion by 2032, poised to grow at a CAGR of 16.03% over the forecast period 2023 to 2032.



<https://www.precedenceresearch.com/battery-market>

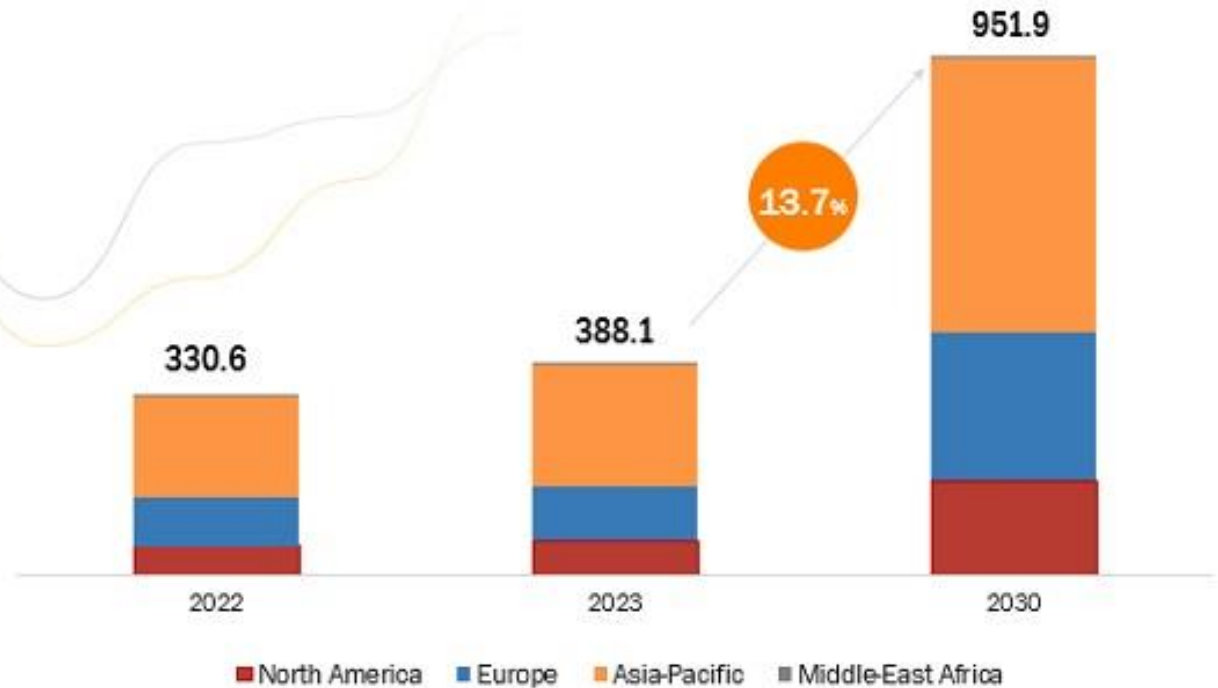
The growth in the battery market is driven by renewable energy storage and rising demand for electric vehicles.

ELECTRIC VEHICLE MARKET GLOBAL FORECAST TO 2030 (USD BILLION)



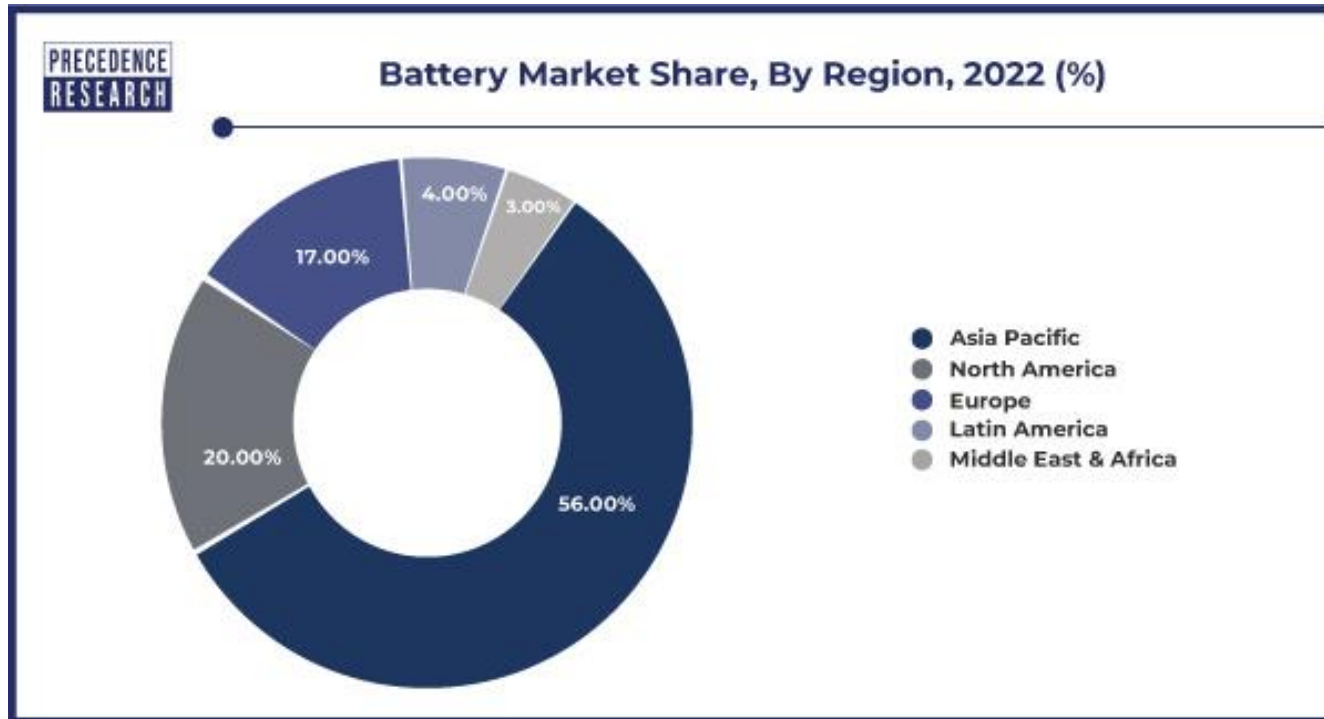
CAGR OF
13.7%

The EV market is expected to be worth USD 951.9 billion by 2030, growing at a CAGR of 13.7% during the forecast period.



<https://www.marketsandmarkets.com/Market-Reports/electric-vehicle-market-209371461.html>

Regional Insights: The Asia Pacific region is the world's major battery market and accounts for a high share of global battery sales.



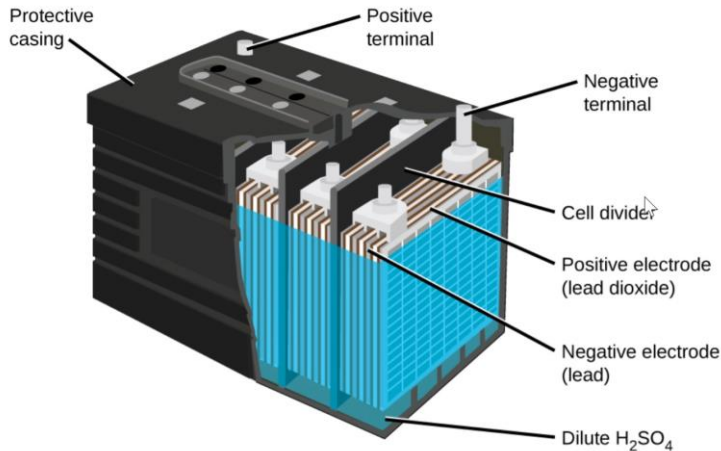
Key Takeaways:

- Asia Pacific region generated more than 56% of the revenue share in 2022.
- By Type, the lithium-ion battery segment has dominated the global market with revenue share of 40.8% in 2022.
- By End-Use, the automotive sector contributed for the largest market share of around 32.4% in 2022.
- By Application, the industrial batteries segment has held revenue share of 35.9% in 2022.
- By Application, the automotive batteries segment has held revenue share of 34.7% in 2022.

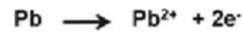
Rechargeable Batteries you will be Very Familiar With

There are many types of rechargeable batteries in use today. Very common battery types include the **lead-acid battery** and **Li-ion batteries**. The batteries are named after their components and the ways charge is stored in the batteries.

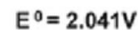
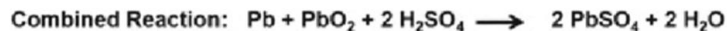
LEAD-ACID BATTERY



Negative Electrode:



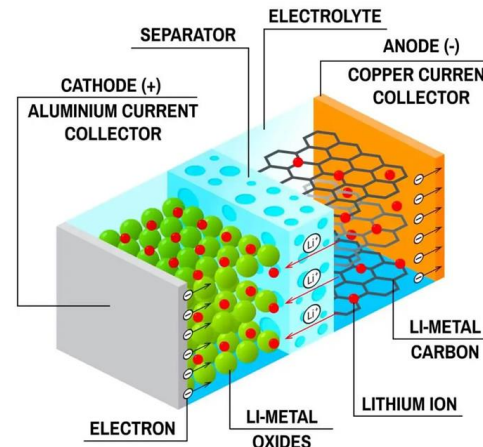
Positive Electrode :



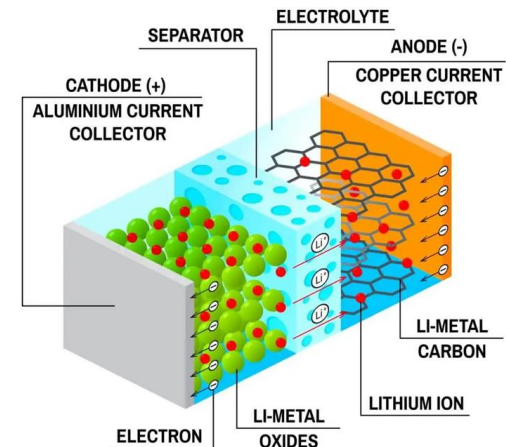
LITHIUM-ION BATTERY

InstrumentationTools.com

DISCHARGE



CHARGE



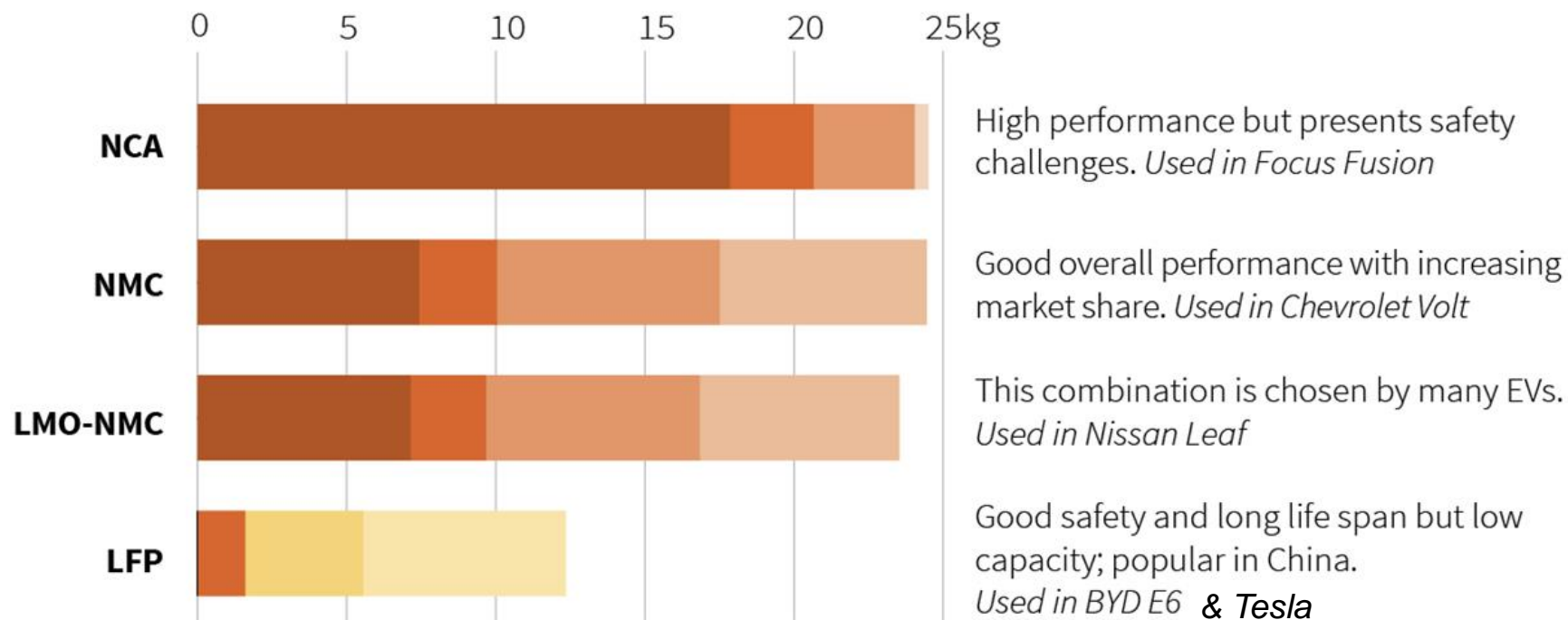
Types of Lithium-ion battery and their makeup

Lithium-ion batteries containing nickel are used to fuel electric cars made by many manufacturers. As the sales of electric vehicles are projected to grow, the demand for nickel is likely to grow over coming years.

WEIGHT OF CATHODE METAL CONTENT PER BATTERY

In plug-in hybrid electric vehicles with driving range of 40 miles using only battery power































■ Nickel ■ Lithium ■ Cobalt ■ Manganese ■ Aluminum ■ Iron ■ Phosphate



Notes: NCA stands for lithium nickel cobalt aluminum oxide; NMC stands for lithium nickel manganese cobalt oxide; LMO stands for lithium ion manganese oxide; LFP stands for lithium iron phosphate.

Sources: Argonne National Laboratory; GFMS, Thomson Reuters; The Boston Consulting Group; Bank of America, Merrill Lynch

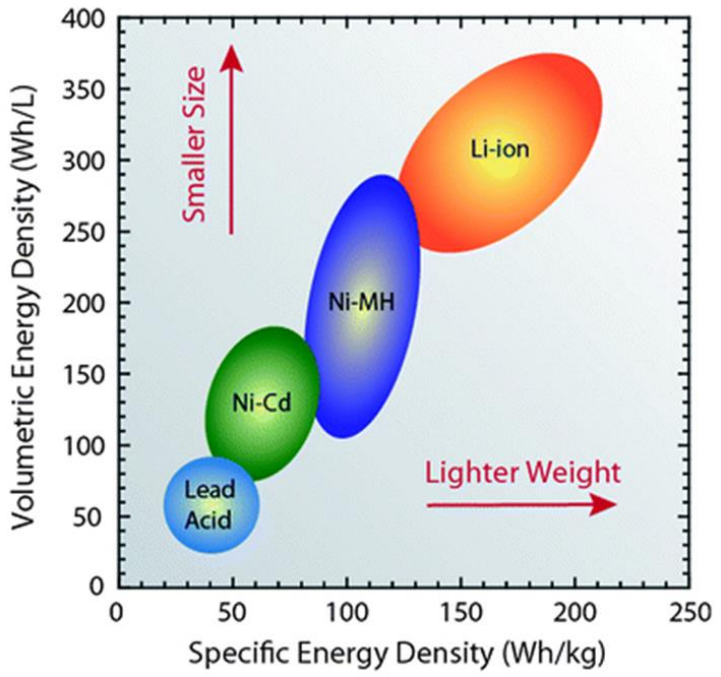
The table below compares different lithium-ion battery types in terms of features such as energy density, power density, battery performance, safety, lifespan, cost and more.

Key Active Material	Lithium-Iron Phosphate	Lithium Nickel Manganese Cobalt Oxide	Lithium Manganese Oxide	Lithium Nickel Cobalt Aluminum	Lithium Titanate
Technology Short Name	LFP	NMC	LMO	NCA	LTO
Cathode	LiFePO_4	$\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$	LiMn_2O_4 (spinel)	LiNiCoAlO_2	variable
Anode	C (graphite)	C (graphite)	C (graphite)	C (graphite)	$\text{Li}_4\text{Ti}_5\text{O}_{12}$
Safety					
Power Density					
Energy Density					
Cell Costs Advantage					
Lifetime					
BESS Performance					


Energy Density: Amount of energy that can be stored in a given volume or mass of a battery. It is typically measured in watt-hours per liter (Wh/L) or watt-hours per kilogram (Wh/kg). A higher energy density indicates that the battery can store more energy.

Power Density: Rate at which energy can be delivered or extracted from a battery. It is measured in watts per liter (W/L) or watts per kilogram (W/kg). Fast discharging/charging is important for EVs.

Battery Performance Comparison



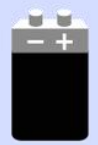
Measuring capacity by watt-hours lets us compare any type of battery



1
12 V car battery

1 battery
× (12 V × 50 Ah)

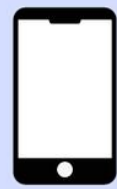
600 Wh



133
9 V batteries

133 batteries
× (9 V × .5 Ah)

600 Wh



67
3.6 V smartphones

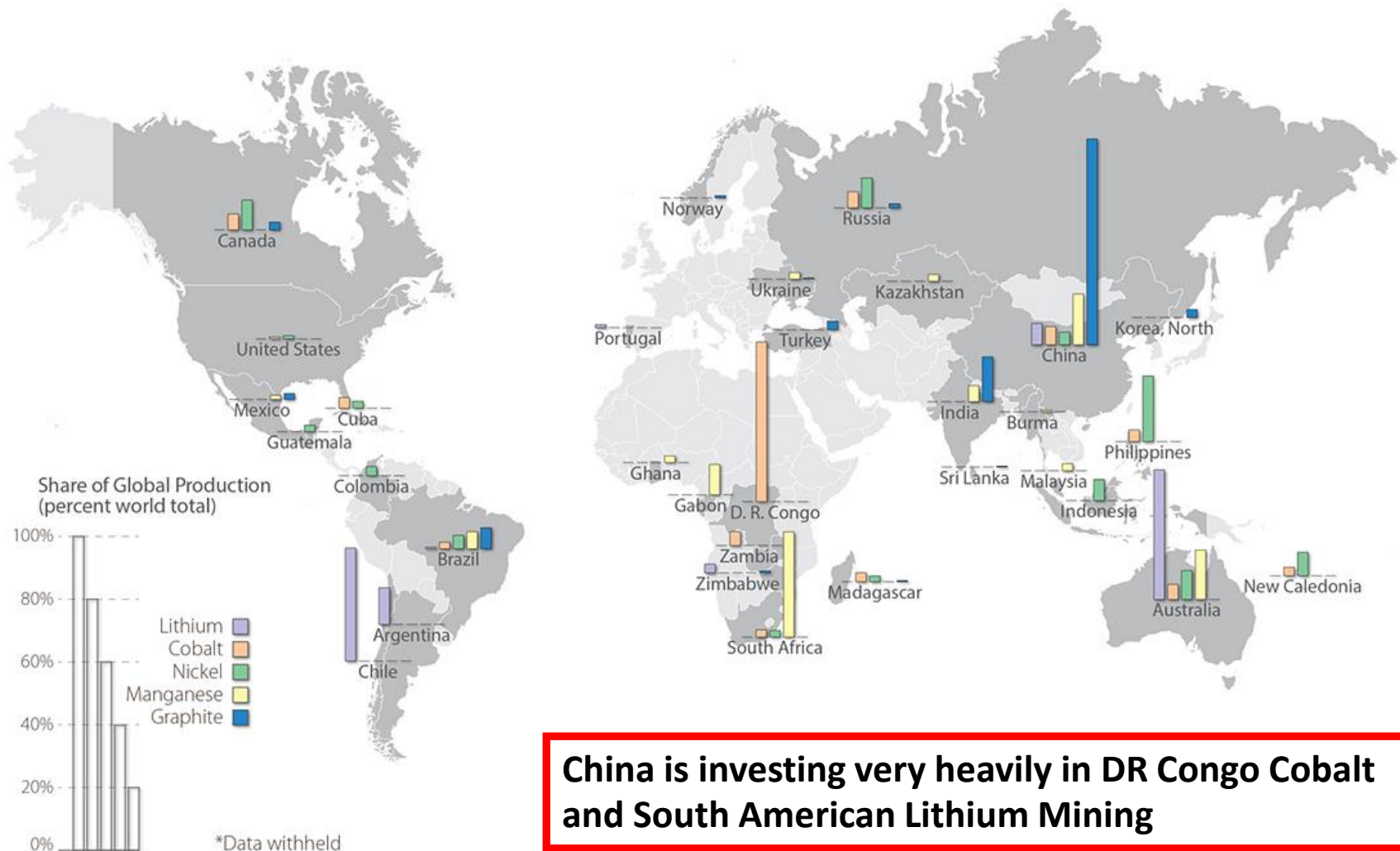
67 smartphones
× (3.6 V × 2.5 Ah)

600 Wh

Specifications	Lead Acid	NiCd	NiMH	Li-ion		
				Cobalt	Manganese	Phosphate
Specific Energy Density (Wh/kg)	30-50	45-80	60-120	150-190	100-135	90-120
Internal Resistance (mΩ)	<100 12V pack	100-200 6V pack	200-300 6V pack	150-300 7.2V	25-75 per cell	25-50 per cell
Life Cycle (80% discharge)	200-300	1000	300-500	500-1,000	500-1,000	1,000-2,000
Fast-Charge Time	8-16h	1h typical	2-4h	2-4h	1h or less	1h or less
Overcharge Tolerance	High	Moderate	Low	Low. Cannot tolerate trickle charge		
Self-Discharge/month (room temp)	5%	20%	30%	<10%		
Cell Voltage (nominal)	2V	1.2V	1.2V	3.6V	3.8V	3.3V
Charge Cutoff Voltage (V/cell)	2.40 Float 2.25	Full charge detection by voltage signature		4.20	3.60	
Discharge Cutoff Voltage (V/cell, 1C)	1.75	1.00		2.50-3.00		2.80
Peak Load Current Best Result	5C 0.2C	20C 1C	5C 0.5C	>3C <1C	>30C <10C	>30C <10C
Charge Temperature	-20 to 50°C -4 to 122°F	0 to 45°C 32 to 113°F		0 to 45°C 32 to 113°F		
Discharge Temperature	-20 to 50°C -4 to 122°F	-20 to 65°C -4 to 149°F		-20 to 60°C -4 to 140°F		
Maintenance Requirement	3-6 Months (topping charge)	30-60 days (discharge)	60-90 days (discharge)	Not required		
Safety Requirements	Thermally stable	Thermally stable, fuse protection common		Protection circuit mandatory		
In Use Since	Late 1800s	1950	1990	1991	1996	1999
Toxicity	Very High	Very High	Low	Low		

Ready for the “White Petroleum” War?

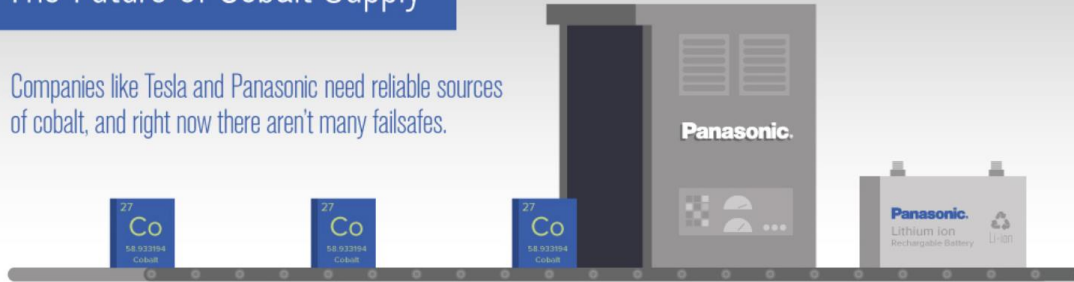
Lithium prices have increased ~5-fold in the last decade, peaking in 2022, driven by demand for lithium-ion batteries needed to power electric vehicles, laptops and cell phones.



Cobalt, the Congo and Underage Child Labour

The Future of Cobalt Supply

Companies like Tesla and Panasonic need reliable sources of cobalt, and right now there aren't many failsafes.

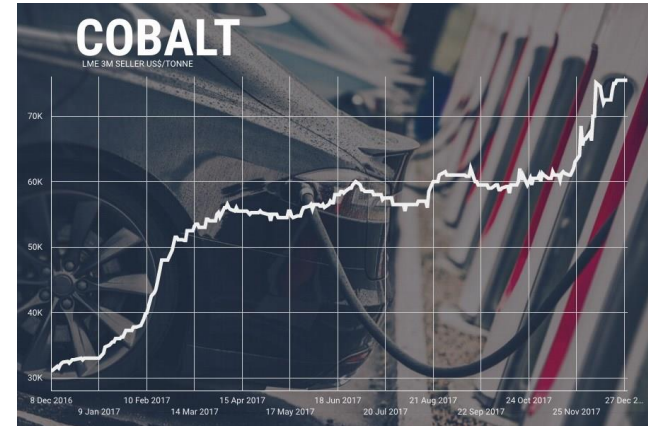


The U.S. hasn't mined cobalt in significant volumes since 1971, and the USGS reports that the United States only has 301 tonnes of the metal stored in stockpiles.

Here's where cobalt is found throughout the world:
(2014 identified deposits, thousands of tonnes)

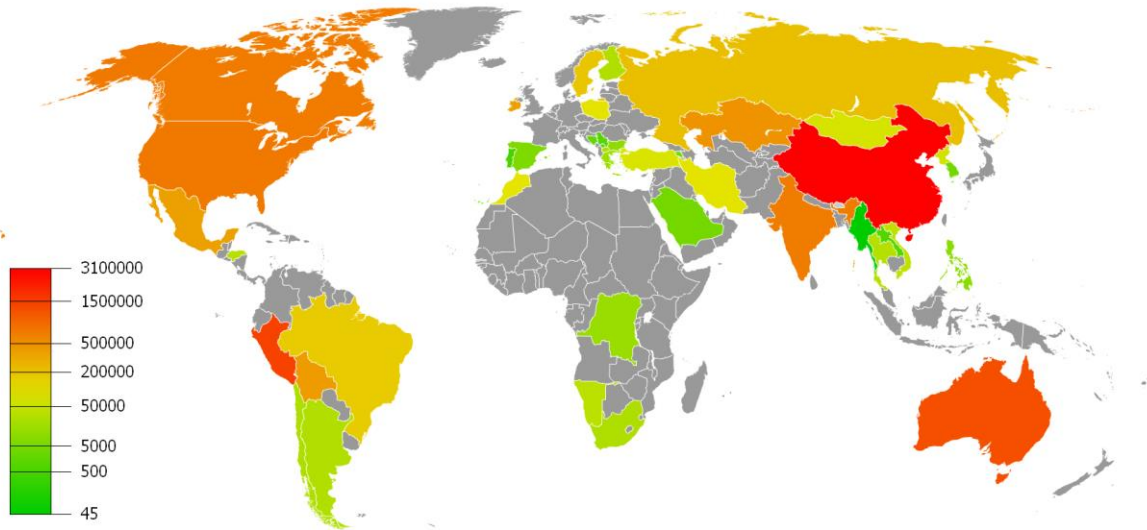


Main cobalt containing minerals include cobaltite (CoAsS), safflorite (CoAs_2), glaucodot ($(\text{Co,Fe})\text{AsS}$), and skutterudite (CoAs_3).



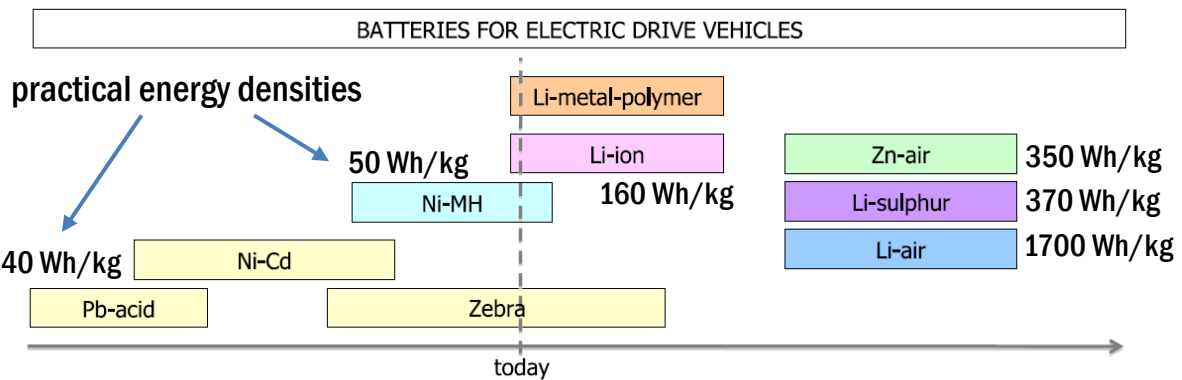
Time for a Rethink With Zinc?

https://en.wikipedia.org/wiki/List_of_countries_by_zinc_production



Rank	Country/Region	Zinc production 2009 (tonnes)
—	World total	11,200,000
1	China	3,100,000
2	Peru	1,509,129
3	Australia	1,290,000
4	United States	736,000
5	Canada	698,901
6	India	695,000
7	Kazakhstan	480,000
8	Bolivia	421,721
9	Mexico	390,000
10	Ireland	385,670
11	Russia	225,000
12	Sweden	192,538
13	Brazil	174,000
14	Iran	160,000
15	Poland	100,000

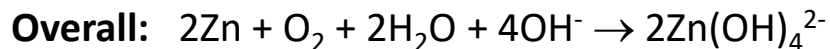
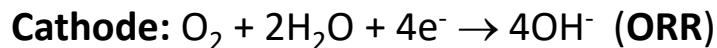
Zinc has a higher earth abundance than Cobalt and is distributed across all continents.



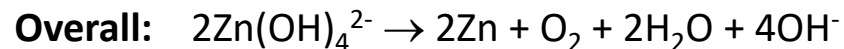
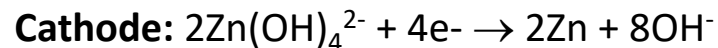
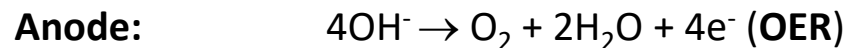
Rechargeable Zinc-air Batteries

Rechargeable zinc-air batteries (ZABs) are very attractive for the short-term storage of electrical energy owing to their low cost, safety and very high specific energy densities.

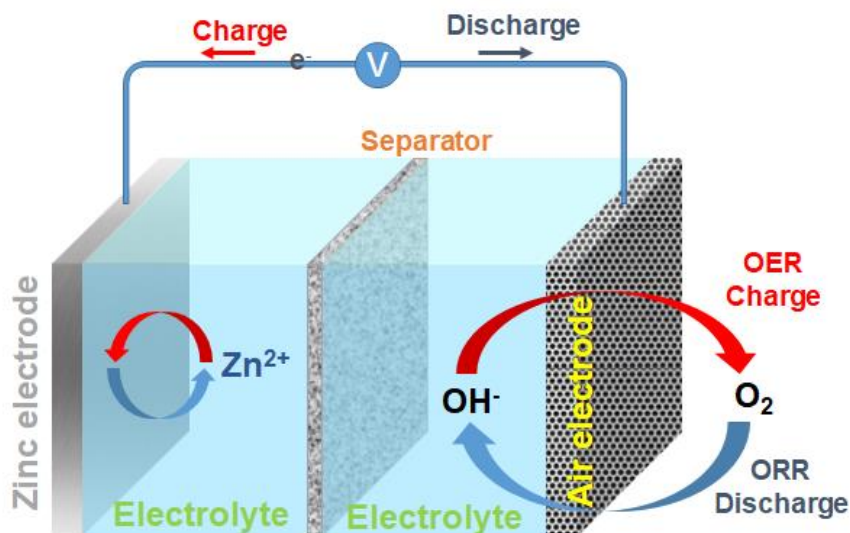
Zinc-air battery **discharge** reactions



Zinc-air battery **charge** reactions



Theoretical voltage: 1.65 V, Actual voltage: 1.4 V



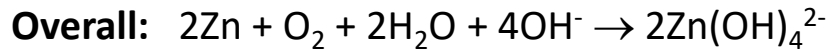
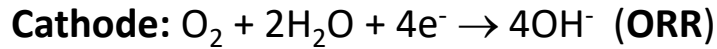
Chemistry	Theoretical specific energy ^a , Wh/kg
Li/O ₂	5,200
Al/O ₂	4,304
Ca/O ₂	2,990
Mg/O ₂	2,789
Na/O ₂	1,677
Zn/O ₂	1,090

Chemistry	Practical specific energy, Wh/kg
Li ion	265
Pb acid	30

Rechargeable Zinc-air Batteries

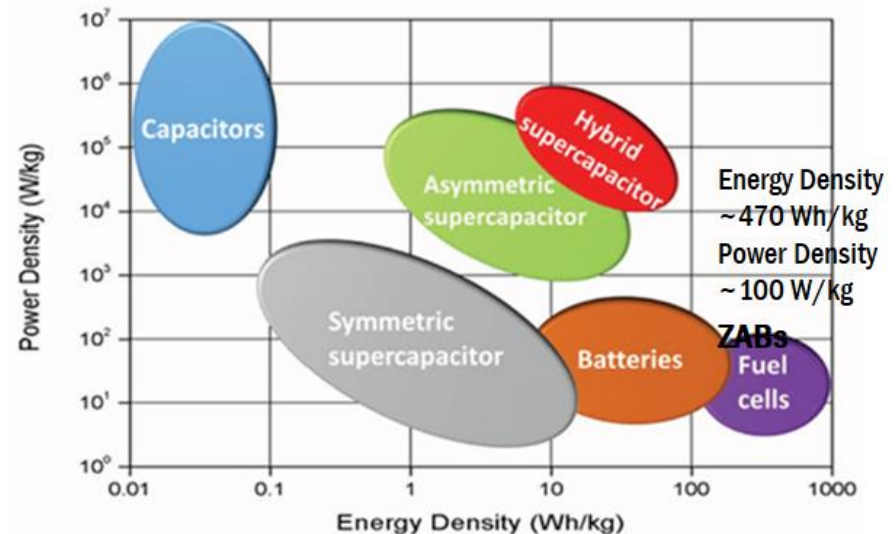
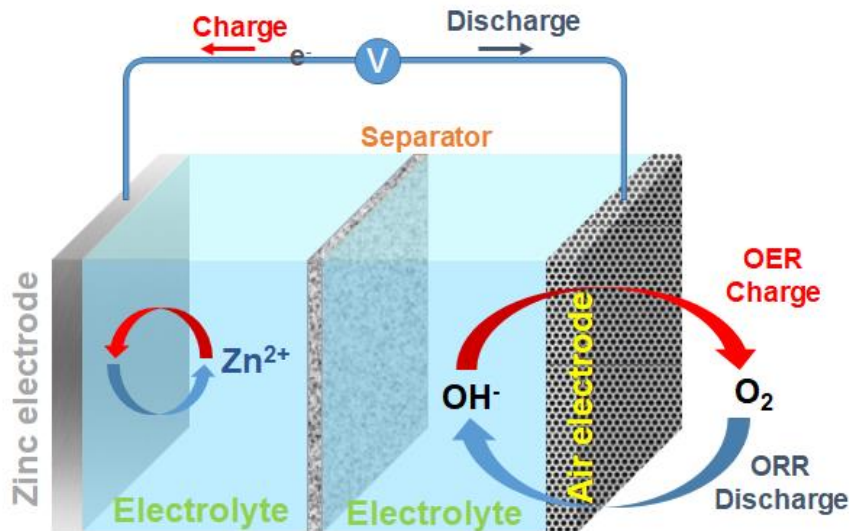
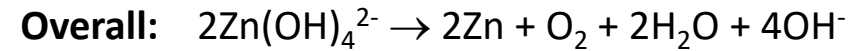
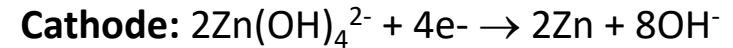
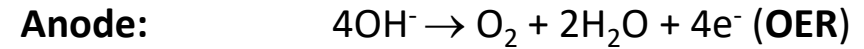
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Zinc-air battery **discharge** reactions



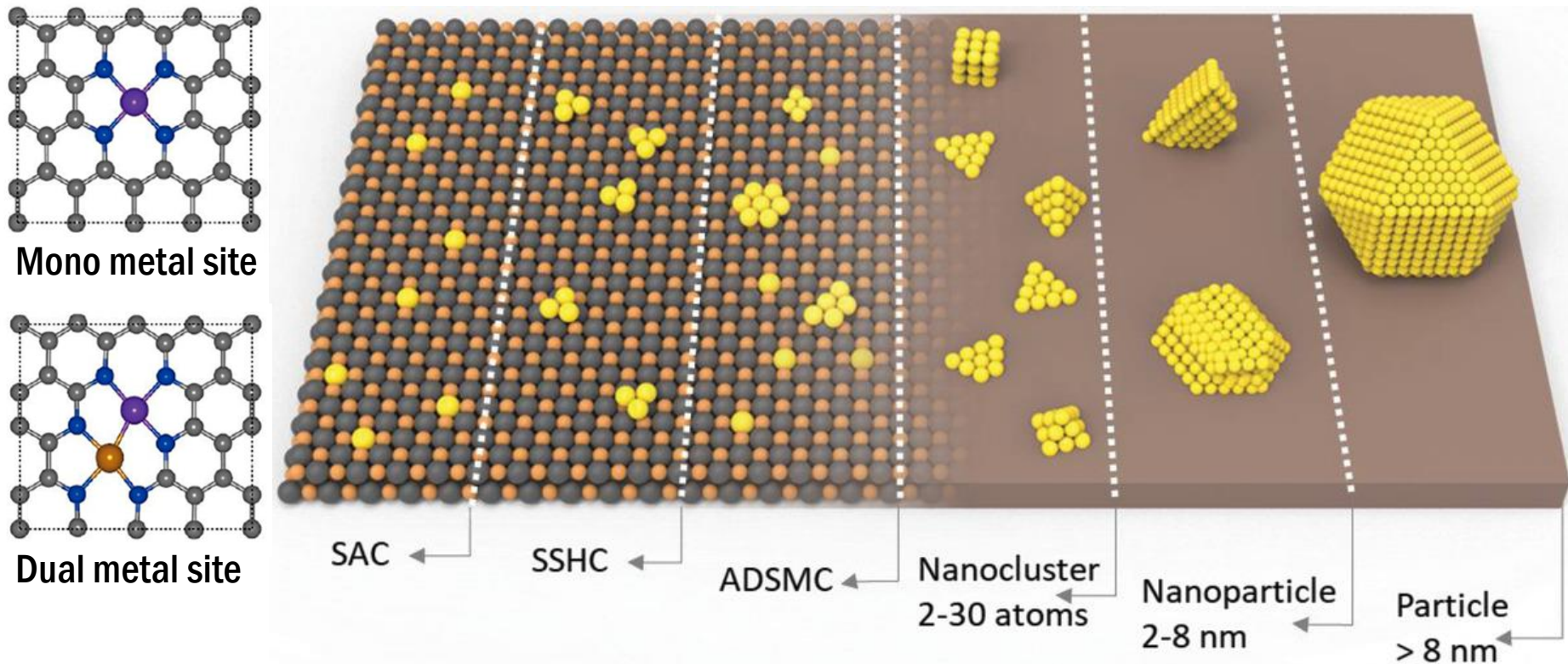
Theoretical voltage: 1.65 V, Actual voltage: 1.4 V

Zinc-air battery **charge** reactions



Metal Single Atom Catalysts (SACs) for ORR/OER

Traditionally, supported metal nanoparticle catalysts have been used for HER, HOR, and ORR (e.g. 10-20 wt.% Pt/C), and RuO_2 or IrO_2 for OER. This results in poor metal atom utilization since only surface metal atoms participate in catalysis. **SACs offer ~100% metal utilization.**

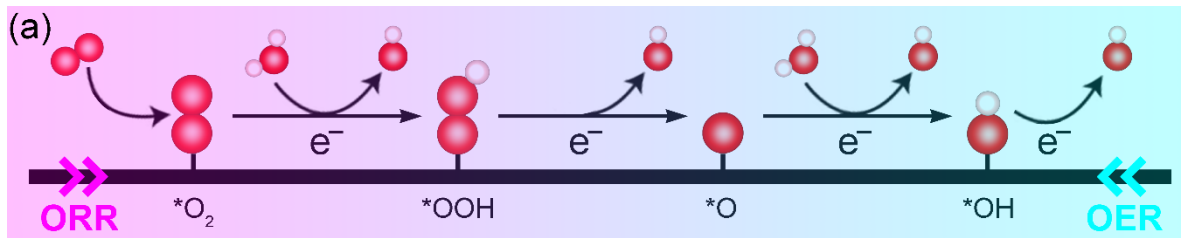


SAC = single atom catalyst, **SSHC** = single site heterogeneous catalyst, **ADSMC** = atomically dispersed supported metal catalyst (Wu et al. *Small Methods* (2020), 4, 19005-40)

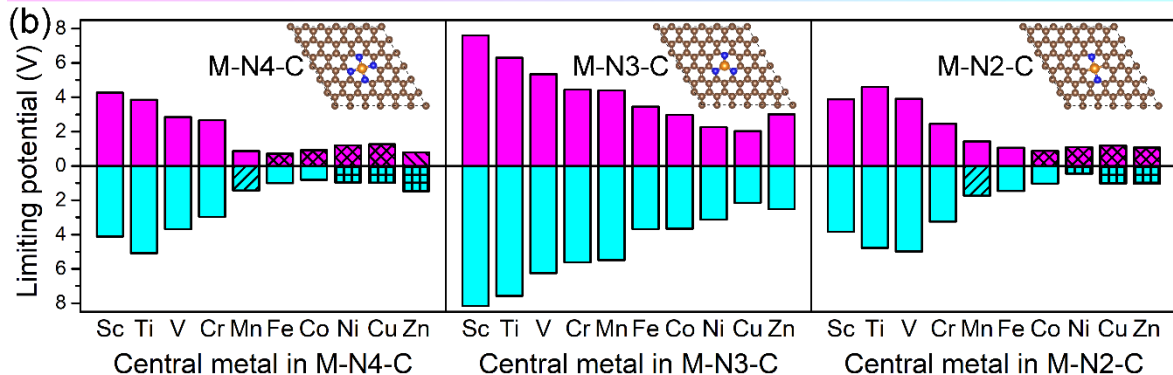
Computational Screening of SACs for ORR/OER

Computational methods are very useful for screening SACs for particular reactions.

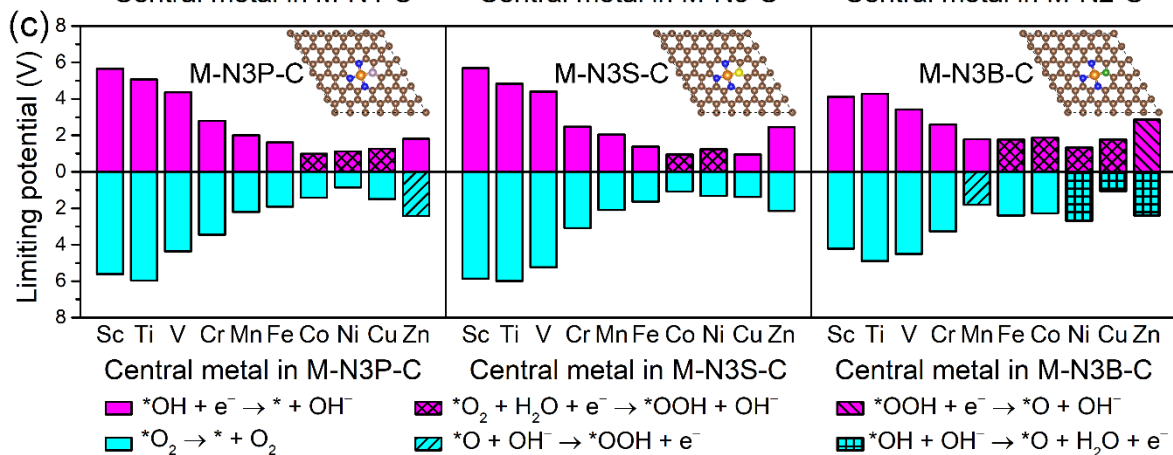
Chemical Engineering Journal (2021), 427, 132038.



(right) (a) Scheme for four-electron ORR (forward reaction) and OER (reverse reaction) via an associative pathway. White and red spheres represent H and O atoms, respectively.



(b,c) Limiting potentials of ORR (pink bars) and OER (aqua bars) on 3d-TM-SACs in six different configurations at $U = 0.402$ V vs NHE.



Results reveal that FeN_4-C , CoN_4-C and NiN_4-C SACs are the best for ORR and OER, respectively, whilst $Ni-N_2-C$, $Fe-N_4-C$, $Co-N_4-C$, $Co-N_2-C$, and $Ni-N_3P-C$ SACs are the best bifunctional ORR/OER catalysts.

Rechargeable ZAB based on a Fe-N₄-C/Fe₃C Catalyst

Recently we discovered a Fe single atom seed-mediated strategy for the fabrication of novel Fe-N₄-C/Fe₃C catalysts with outstanding bifunctional ORR/OER performance in alkaline media.

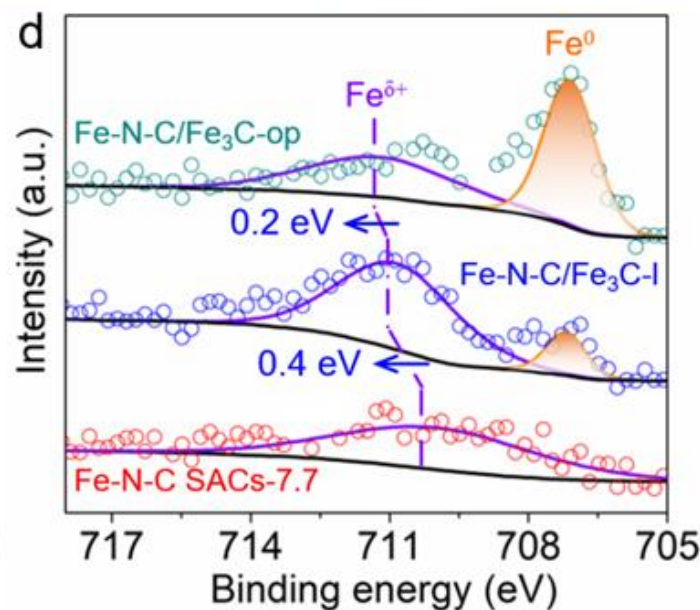
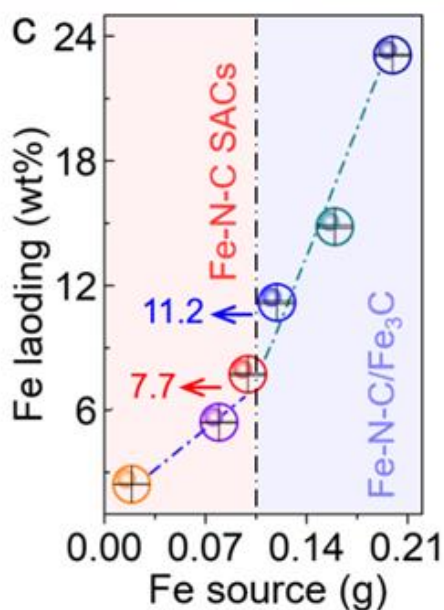
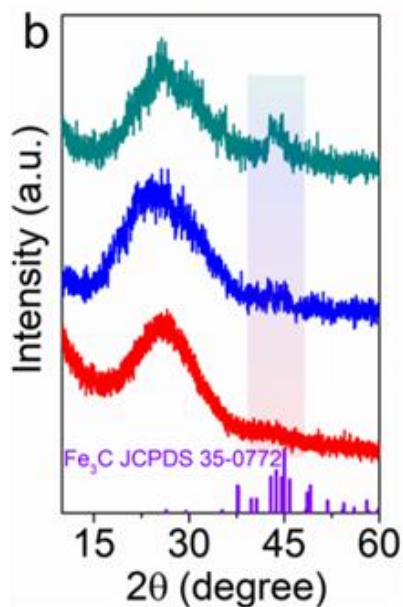
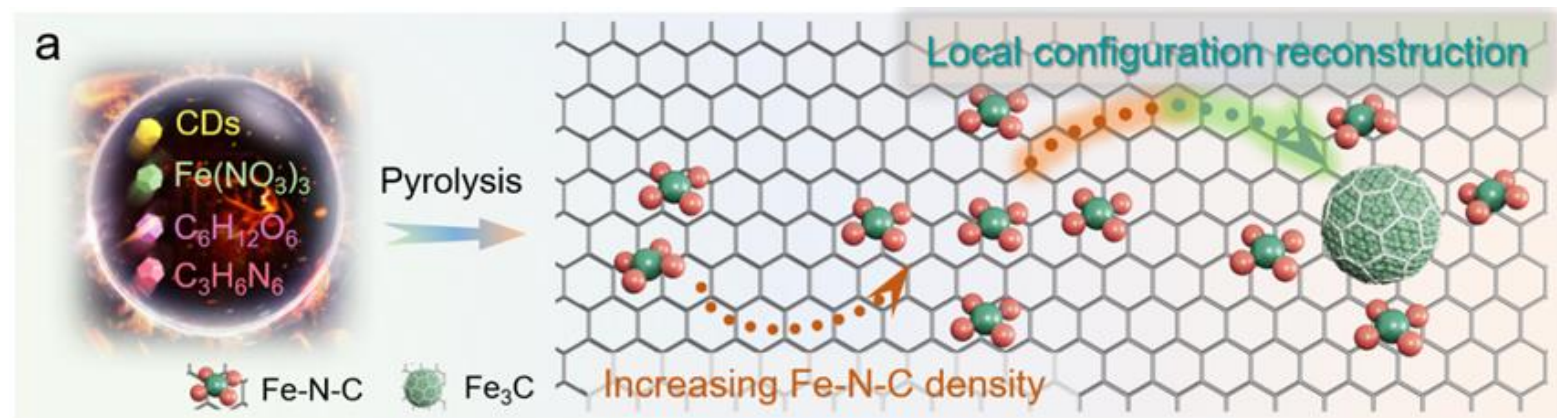
The introduction of Fe₃C species near iron single atom (Fe-N₄-C) sites allows optimization of the adsorption energies of oxygen intermediates formed during ORR and OER, resulting in superior ORR/OER activities and kinetics.

A zinc-air battery constructed with Fe-N-C/Fe₃C-op as the air-cathode catalyst delivered a remarkable **specific capacity (818.1 mAh g_{Zn}⁻¹)** and a **power density (1013.9 mWh g_{Zn}⁻¹)**, along with excellent long-term durability (>450 h). The open circuit voltage was 1.568 V. This work demonstrates that metallic Fe₃C can be used to modulate FeN₄-C single atom sites for improved bifunctional oxygen electrocatalysis.

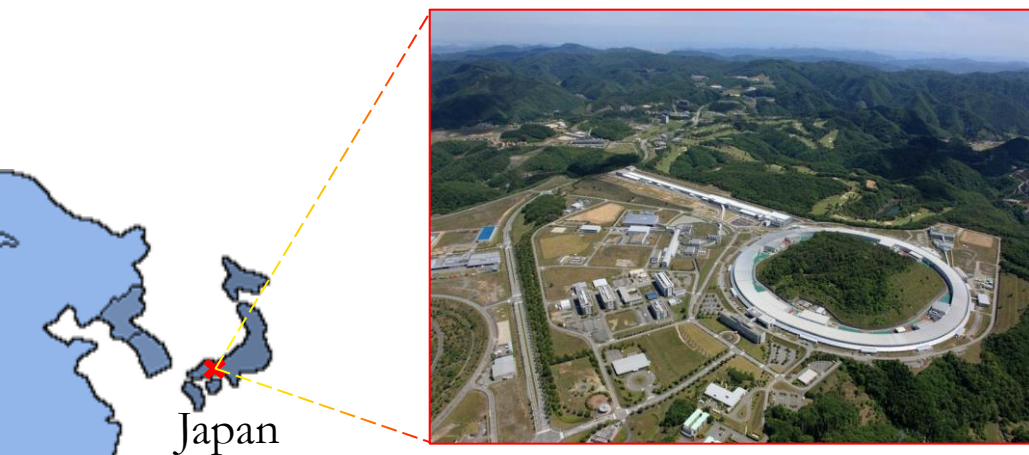
Advanced Science (2023), 10(22), 2301656

Rechargeable ZAB based on Fe-N₄-C/Fe₃C Catalyst

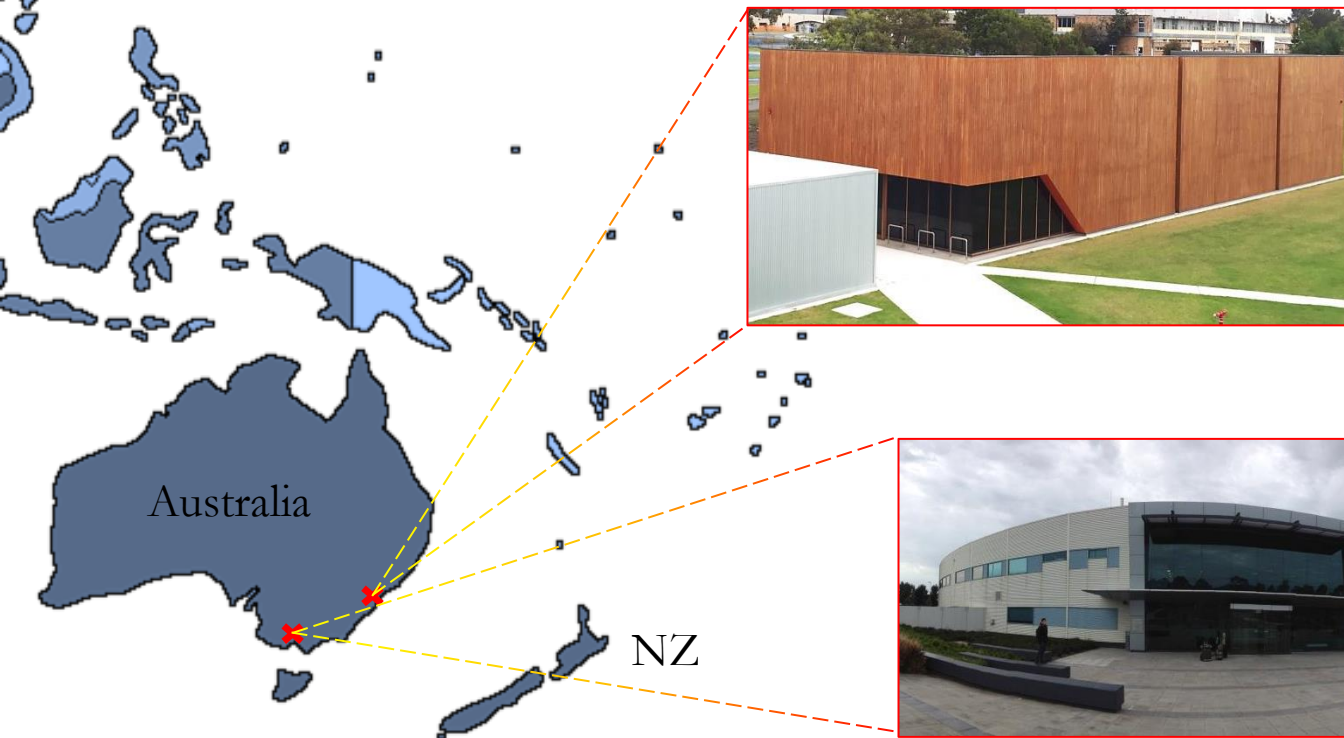
A Fe-N₄-C/Fe₃C catalyst was synthesized by the pyrolysis of carbon dots, Fe(NO₃)₃, glucose and melamine. *Advanced Science* (2023) 2301656



Catalyst Characterisation is Fun



- SPring-8 Synchrotron, Hyogo
- 8 GeV Ring, 1.4 km circumference
- 100 mA current, 10^9 - 10^{11} photons/s
- 56 Beamlines
- *In-situ* XANES/EXAFS



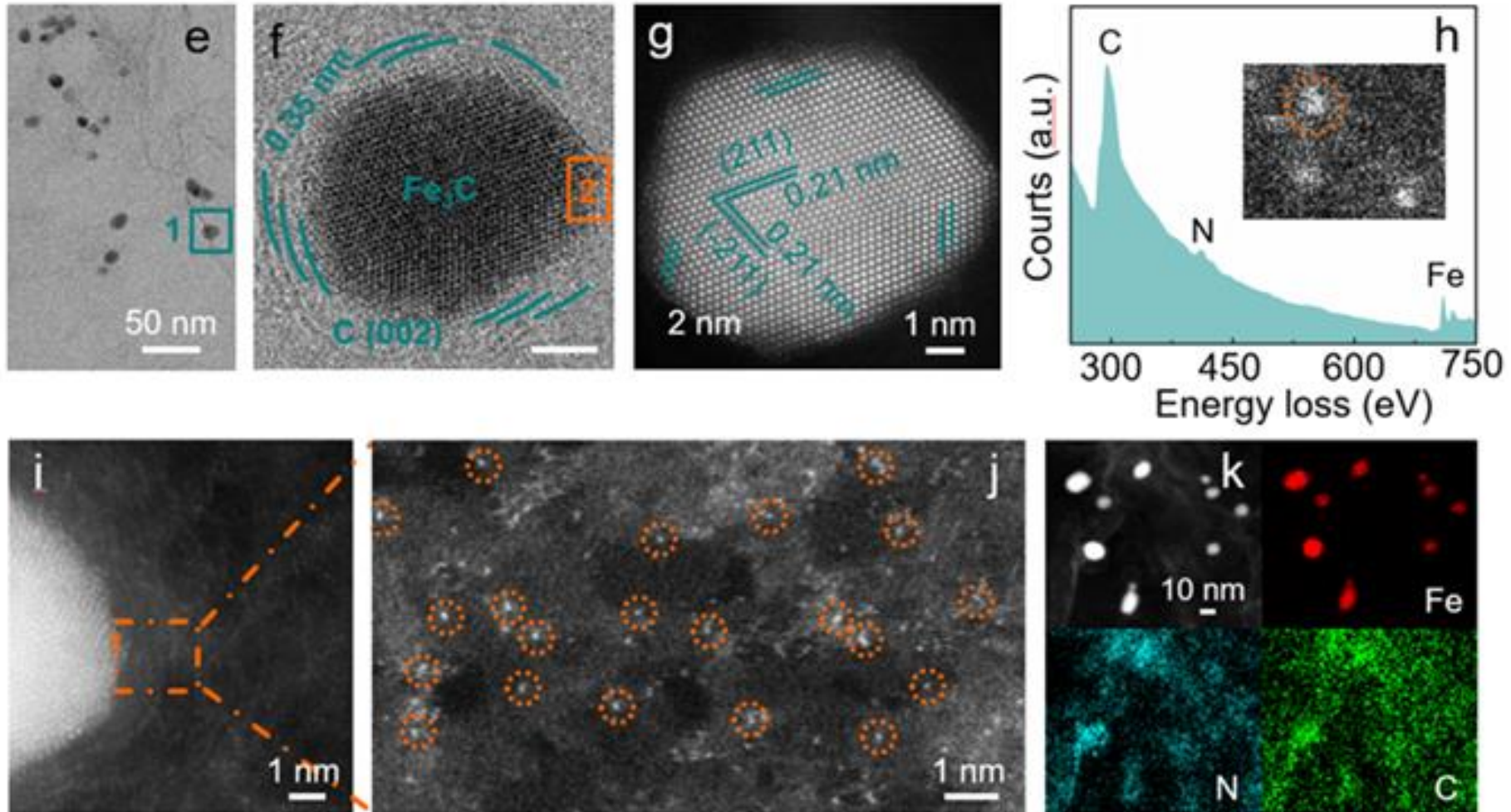
- ANSTO, Sydney
- HR-TEM, 200 kV
- STEM/HAADF
- EDS

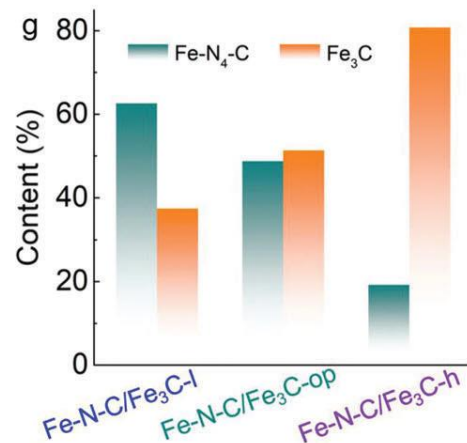
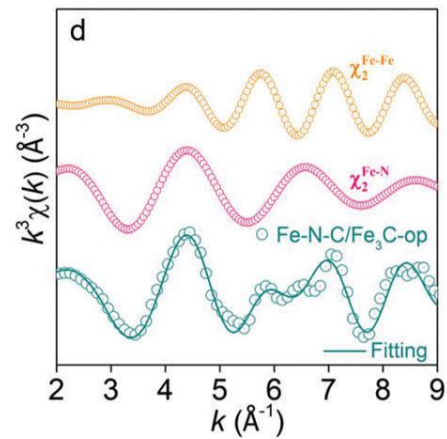
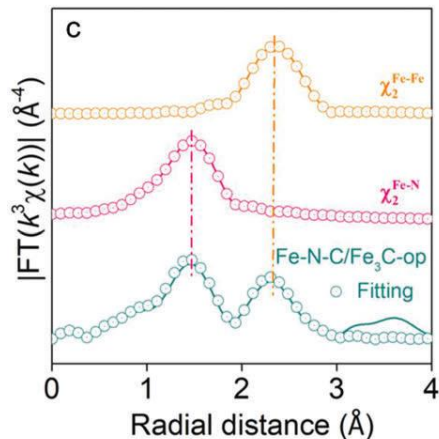
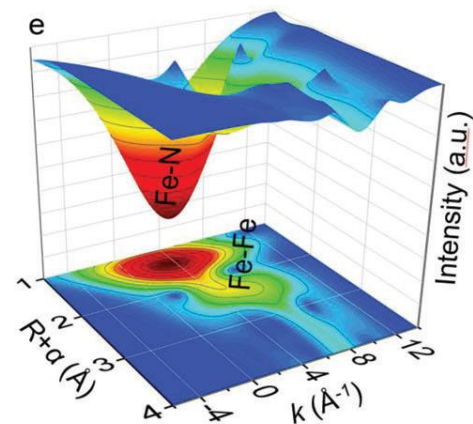
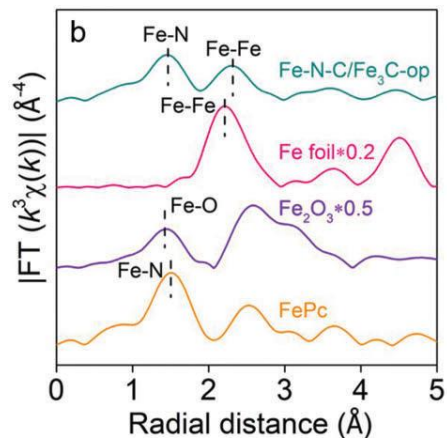
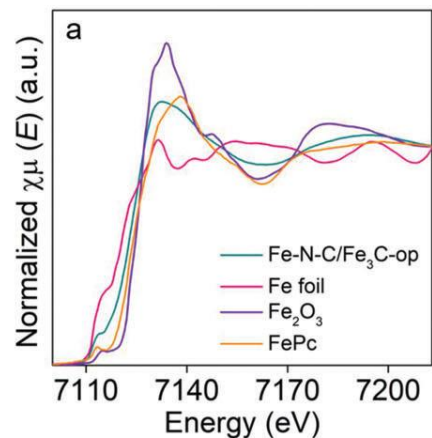


- Australian Synchrotron, Melbourne
- 3 GeV Ring
- XPS/NEXAFS

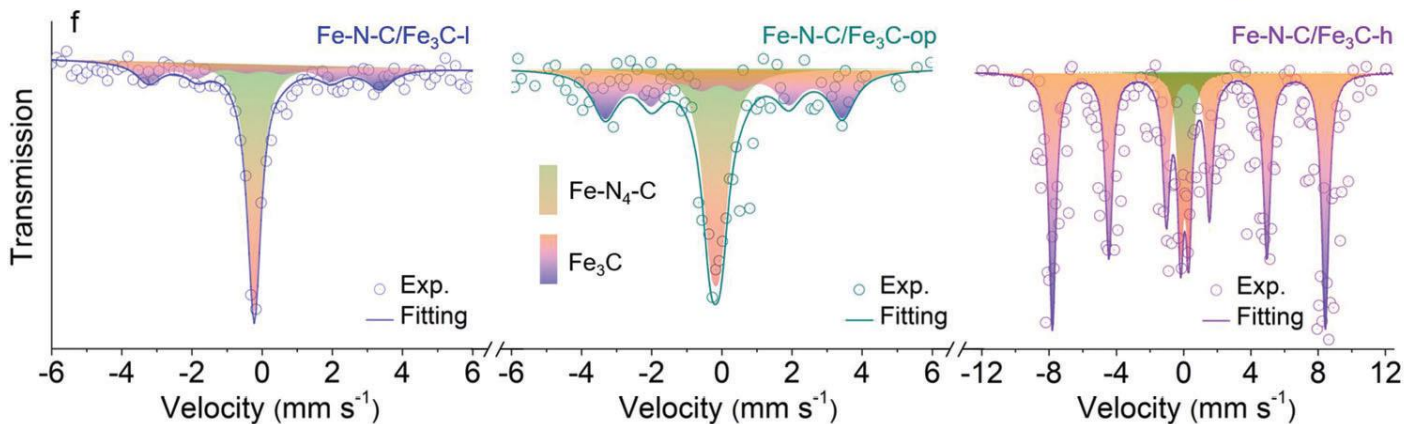
Rechargeable ZAB based on Fe-N₄-C/Fe₃C Catalyst

A Fe-N₄-C/Fe₃C catalyst was synthesized by the pyrolysis of carbon dots, Fe(NO₃)₃, glucose and melamine.



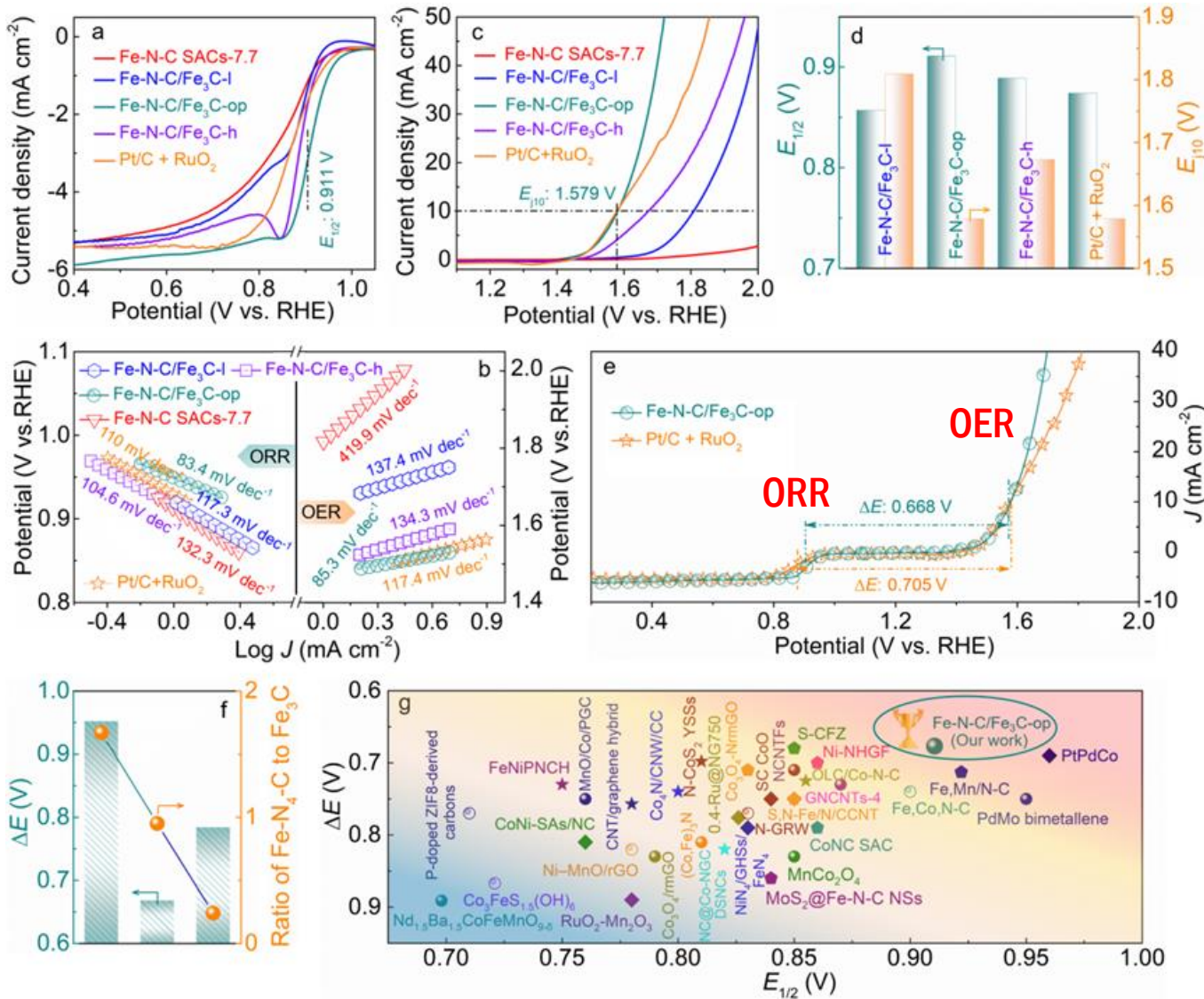


Optimizing the FeN₄-C to Fe₃C ratio important.



Rechargeable ZAB based on Fe-N₄-C/Fe₃C Catalyst

The Fe-N₄-C/Fe₃C catalyst delivered state-of-the-art bifunctional ORR/OER activity.

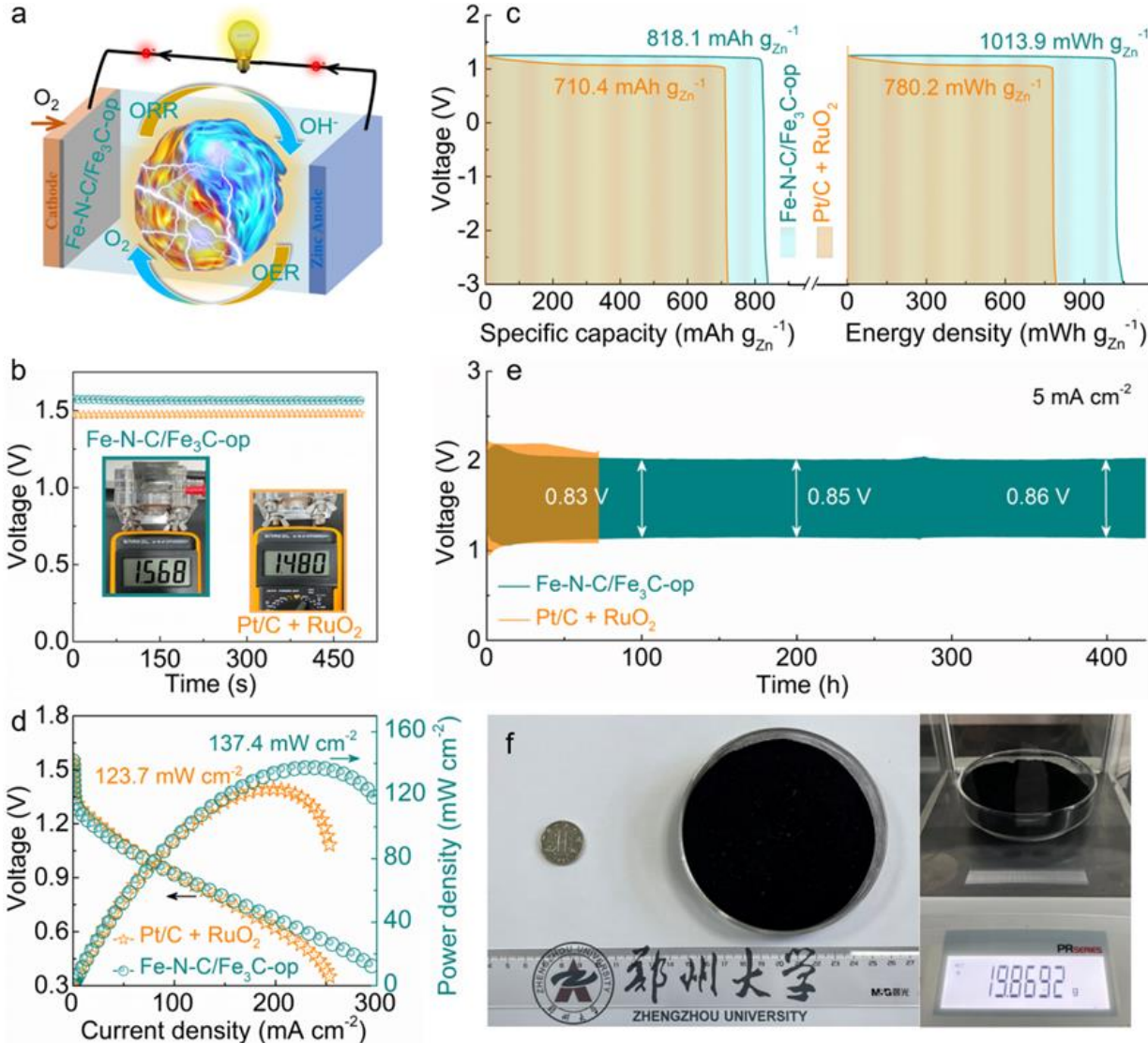


Bifunctional ORR/OER activity evaluation.

- a) ORR LSV curves.
- b) Tafel plots for ORR and OER on different electrocatalysts.
- c) OER LSV curves.
- d) $E_{1/2}$ and E_{j10} of different electrocatalysts.
- e) Bifunctional LSV curves tested in a 0.10 M KOH solution.
- f) Correlation between the value of ΔE and Fe-N₄-C/Fe₃C ratio, revealing the optimal ratio in Fe-N-C/Fe₃C-op.
- g) Comparison of the bifunctional ORR/OER activity of Fe-N-C/Fe₃C-op and other electrocatalysts.

Rechargeable ZAB based on Fe-N₄-C/Fe₃C Catalyst

The Fe-N₄-C/Fe₃C catalyst delivered state-of-the-art bifunctional ORR/OER activity.



Performance of rechargeable ZABs. **a)** Schematic diagram of the Fe-N₄-C/Fe₃C-op-based ZAB.

b) Open-circuit voltage test. The inset shows the VOC of the assembled ZABs.

c) Specific capacity and energy-density curves of ZABs fabricated with Fe-N₄-C/Fe₃C-op and Pt/C + RuO₂

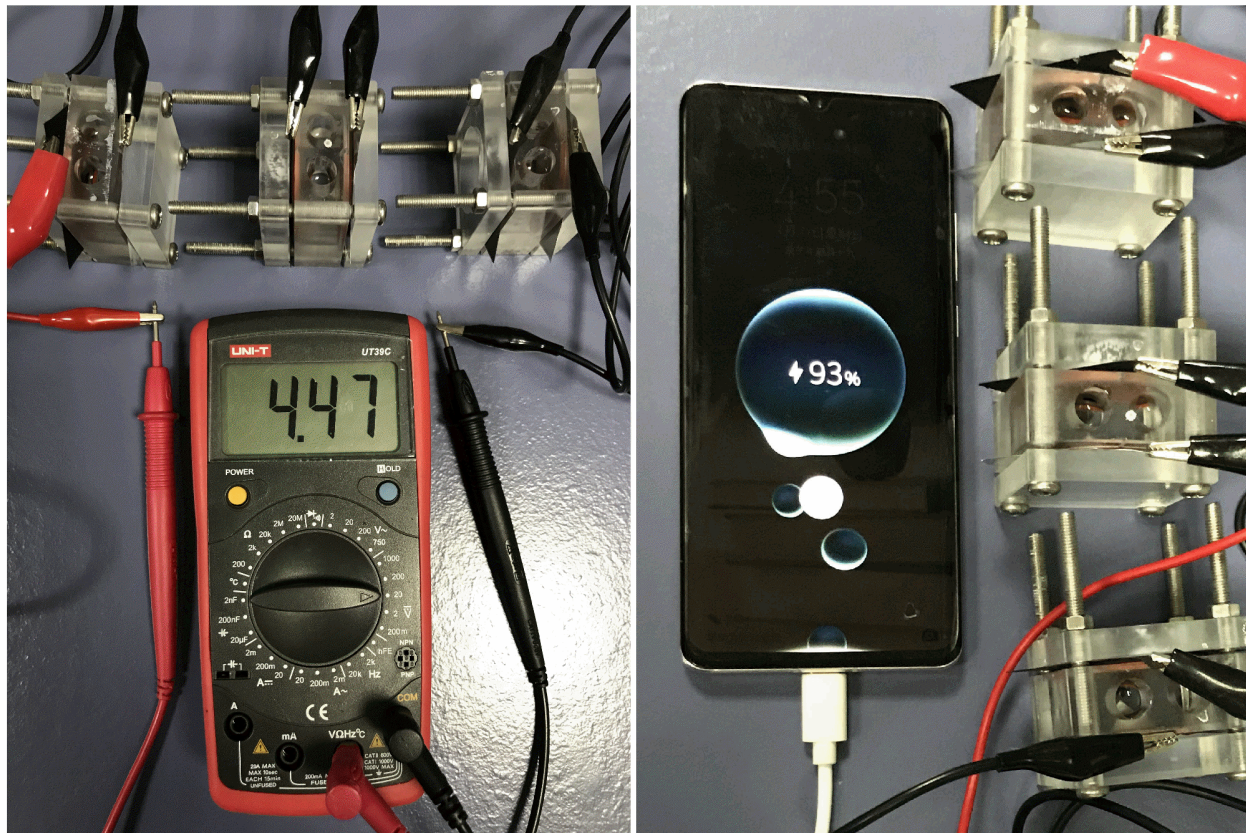
d) LSV profiles and power density curves of the ZABs with Fe-N₄-C/Fe₃C-op and Pt/C + RuO₂

e) Charge-discharge cycling curves of rechargeable ZABs with Fe-N₄-C/Fe₃C-op and Pt/C + RuO₂ electrocatalysts at a constant current density of 5 mA cm⁻².

f) Photograph of a 20 g batch of the Fe-N₄-C/Fe₃C-op electrocatalyst.

Journey from Lab to Real Batteries

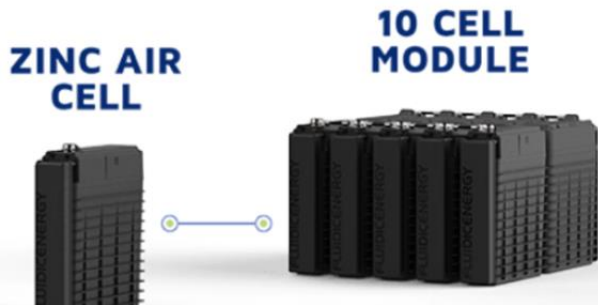
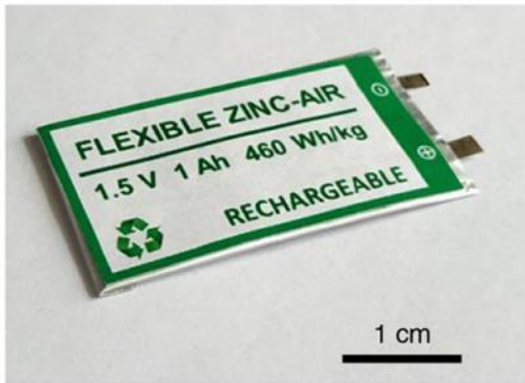
Having designed excellent ORR/OER catalysts for zinc-air batteries, we now need to work on building larger, space efficient modular battery systems.



Open circuit voltages (OCV) for three zinc-air batteries in series, and a demonstration of smart phone (Huawei) charging by three zinc-air batteries linked in series.

Journey from Lab to Real Batteries

Aim to fabricate cells that can be assembled into modules, as well as pouch type flexible batteries. Market needs batteries operating below the \$100 per kWh mark.



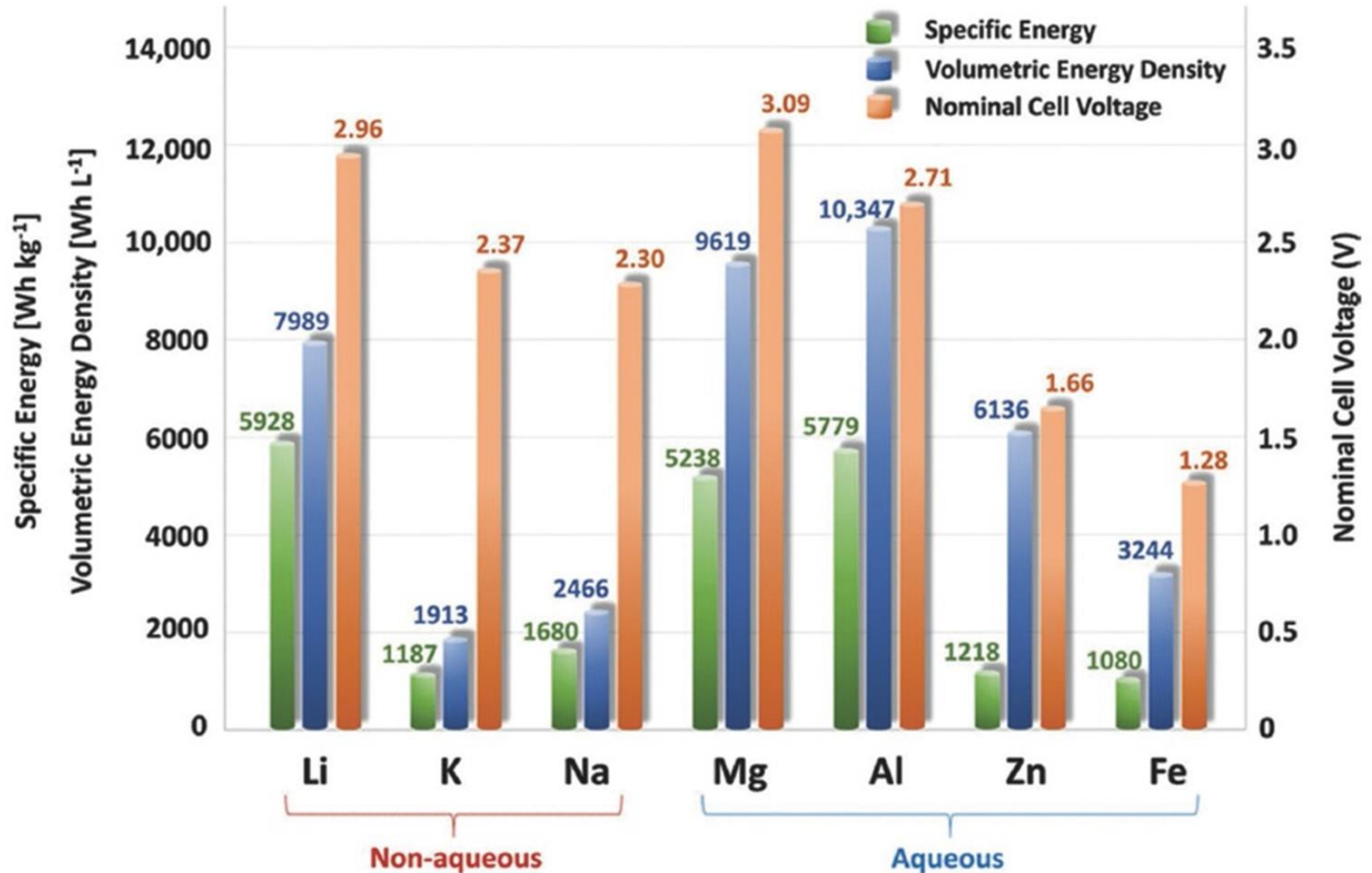
4 MODULE SYSTEM



EV enthusiasts Kathryn and Greg Trounson who fund our zinc-air battery research.

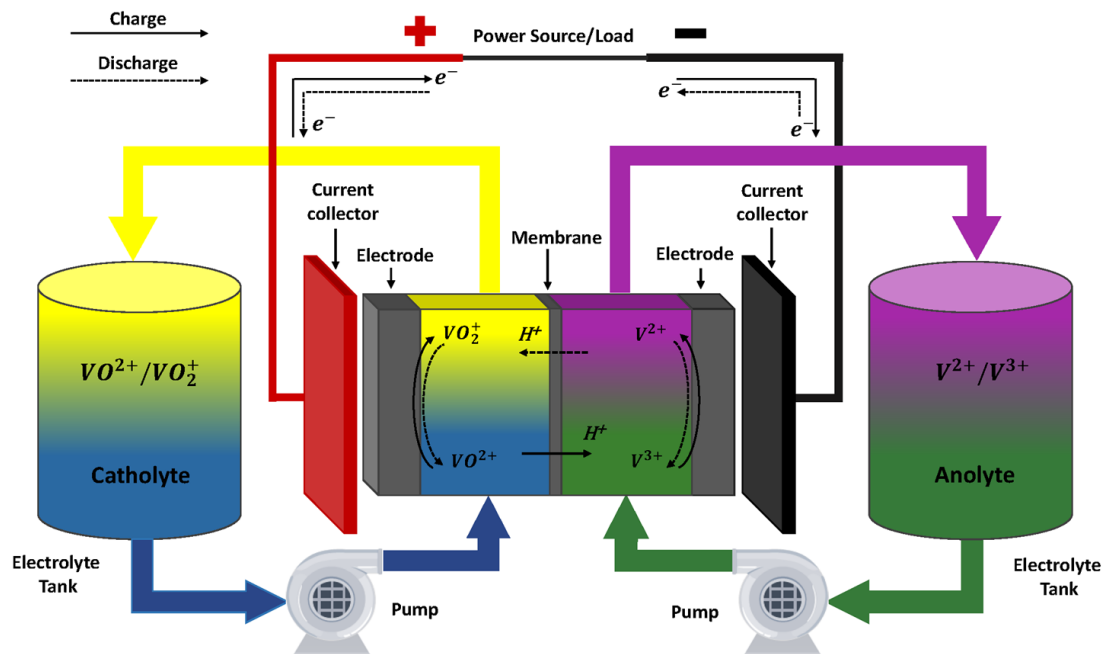
Other Rechargeable Metal-air Batteries

The same catalyst is now being used in the development of other types of metal-air battery with higher energy densities.



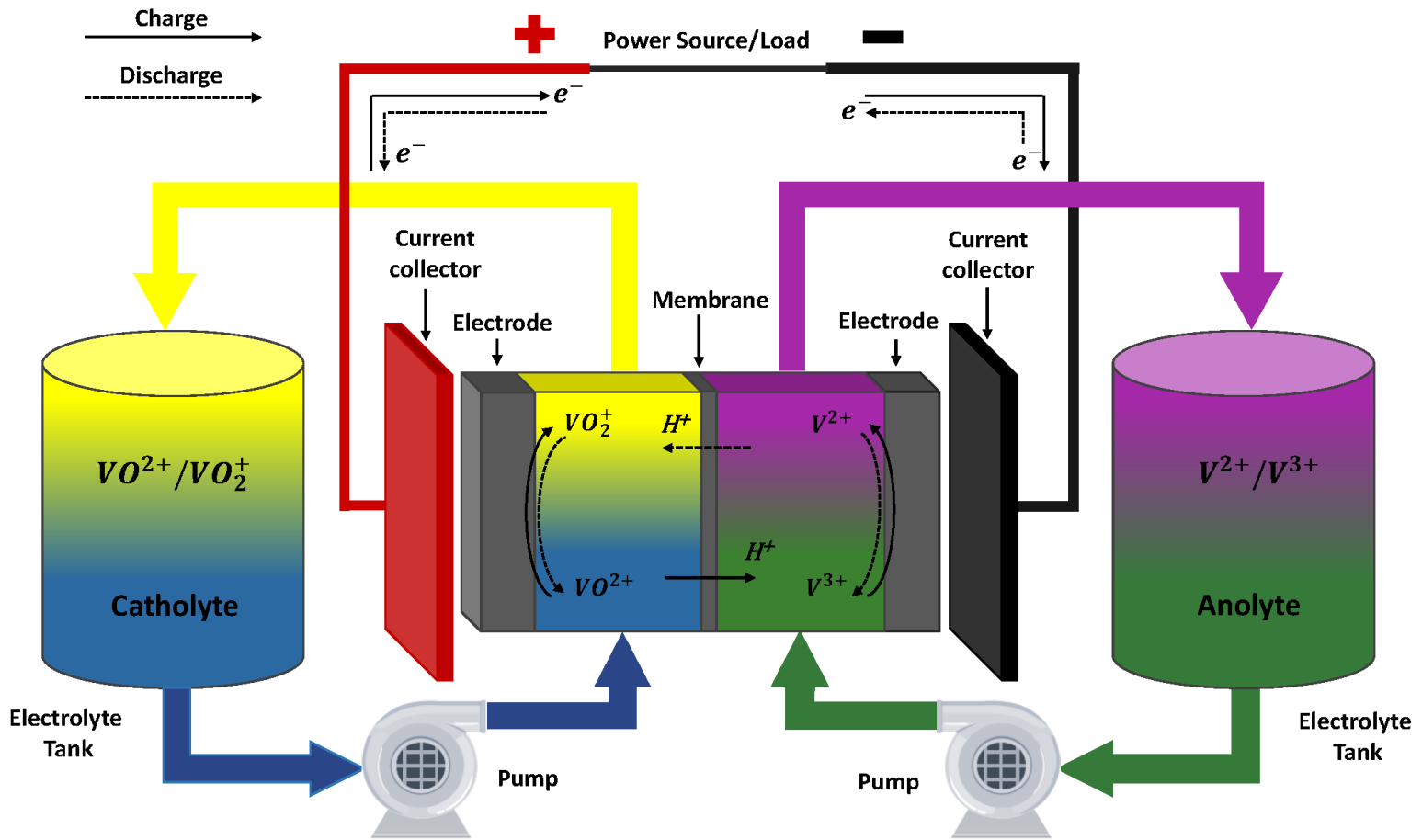
Vanadium Redox Flow Batteries

Vanadium redox flow batteries hold great promise for large-scale stationary electricity storage.

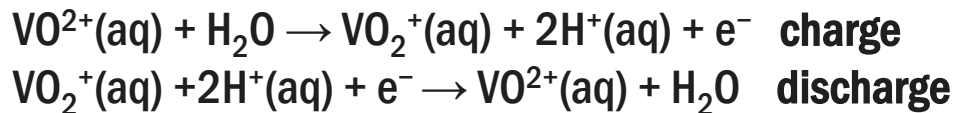


Under standard conditions, the overall cell potential is 1.26 V at 25 °C, but for an electrolyte composition of 2 M vanadium in 5 M sulfuric acid open-circuit potentials of 1.4 and 1.6 V can be measured at 50% and 100% state-of-charge (SOC), respectively .

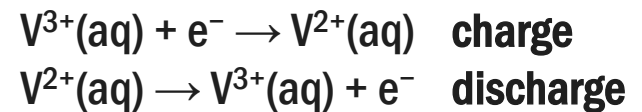
<https://www.youtube.com/watch?v=TSsqCazP1V0>



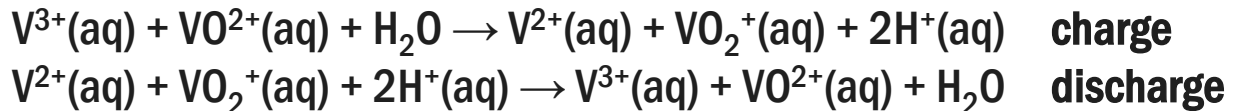
Positive electrode reactions:



Negative electrode reactions:



Overall cell reactions:



Vanadium redox flow batteries (VRBs) are ideal for medium- and large-scale energy storage.

An **all-vanadium redox flow battery (VRB)** that was pioneered at the University of New South Wales in Australia is currently considered one of the most promising battery technologies that will be able to meet the growing global need for stationary energy storage. It has been extensively field tested in a range of applications, including wind and solar energy storage, load leveling, peak shaving, and emergency backup systems with kW to MW power rating, and has demonstrated overall energy efficiencies of up to 80% and more than 200,000 cycles.



Summary

- Decarbonisation of the global energy sector will require massive investment in technologies for electricity generation from renewables and in efficient electrical energy storage technologies.
- Both hydrogen and rechargeable batteries will play important roles in energy storage.
- The battery market is growing rapidly, driven by the renewable energy sector and the EV sector.
- Current rechargeable battery technologies, such as Li-ion batteries, are good but rely on certain critical elements (Li, Co, Mn, Ni) which are not geographically well-distributed.
- Metal-air batteries hold great promise for EVs and portable electronic devices due to their extremely high energy densities (>> Li-ion batteries), whilst redox flow batteries are attractive for long-term stationary electricity storage.

Thanks for your attention! g.waterhouse@auckland.ac.nz

Metal/air battery	Calculated OCV, V	Theoretical specific energy, Wh/kg	
		Including oxygen	Excluding oxygen
Li/O ₂	2.91	5200	11140
Na/O ₂	1.94	1677	2260
Ca/O ₂	3.12	2990	4180
Mg/O ₂	2.93	2789	6462
Zn/O ₂	1.65	1090	1350

