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Another look at Zinc-Air

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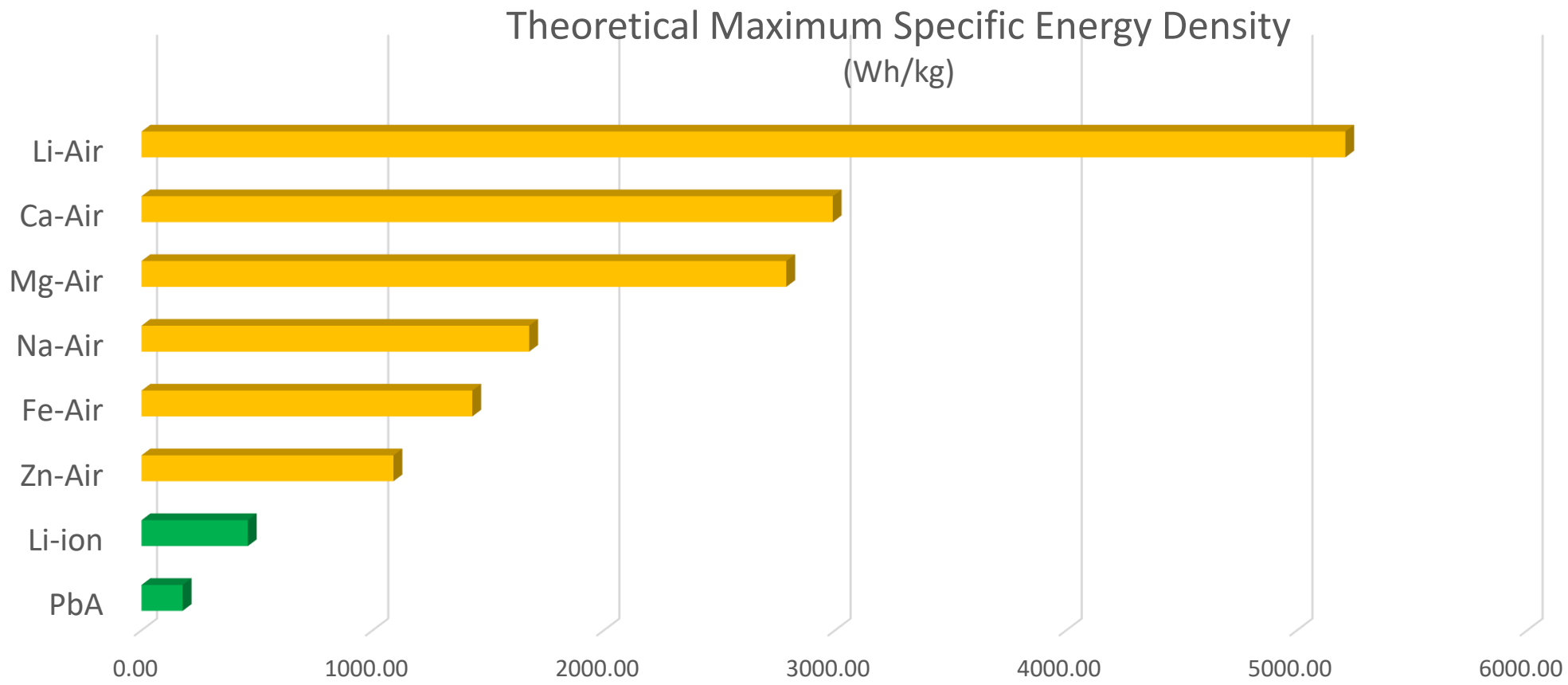
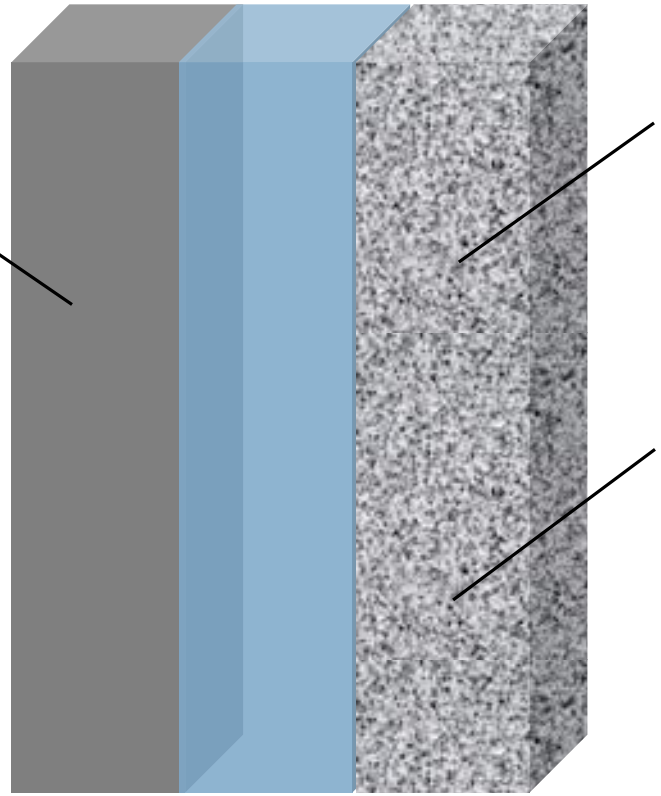
Metal-Air Batteries (MABs) offer tantalizing potential….



….because half of a MAB's chemistry is O_2 from air

Metal anode:
Oxidized on discharge
$M + O_2 \rightarrow MO_x$
Reduced on charge
$MO_x \rightarrow M + O_2$



Gas Diffusion Electrode (GDE):
Takes O_2 from air on discharge
Returns O_2 to air on discharge

Electrolyte, aqueous, ionic liquid and/or polymer

Simplified Generic Layout

But which metal to use?

Let’s start with alkali and alkaline earth metals

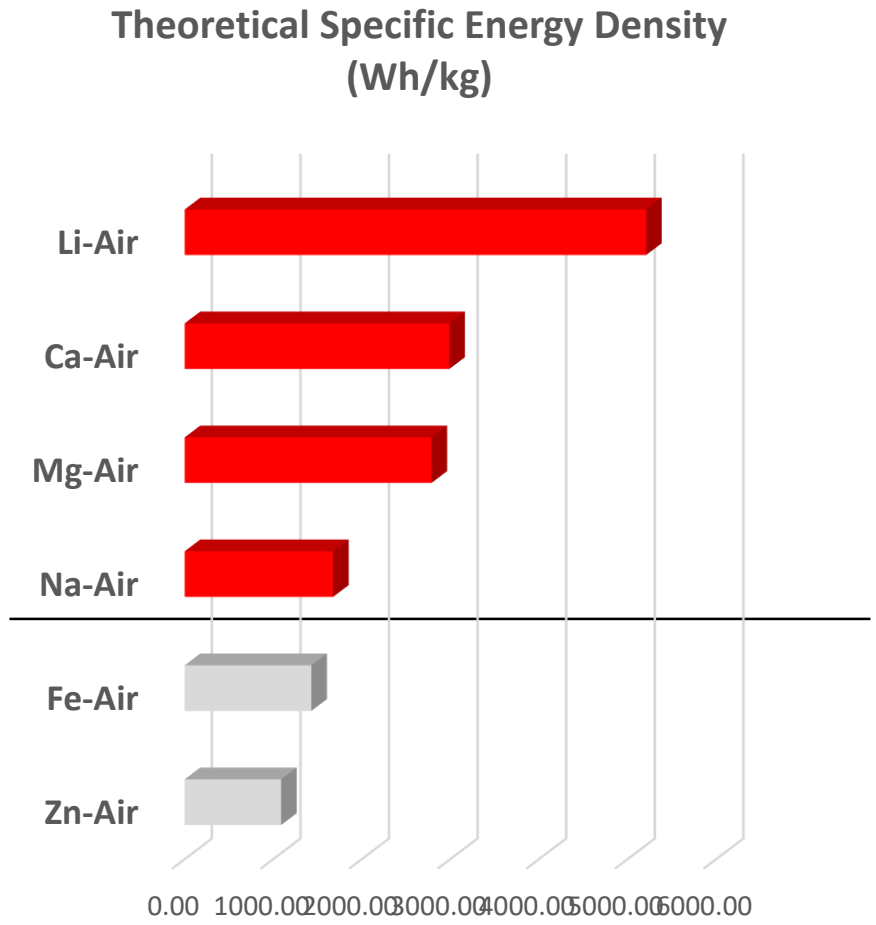
Pros:

- Highest potential for specific energy density and voltage

Cons:

- Metals react violently with air and/or moisture
- Cannot use aqueous electrolytes
- Need expensive, hazardous and potentially toxic fluorine-based electrolytes
- More complex, more challenging production needs
- Potentially difficult, hazardous and/or uneconomic to recycle

- Do we want to risk a another PFOS fiasco?



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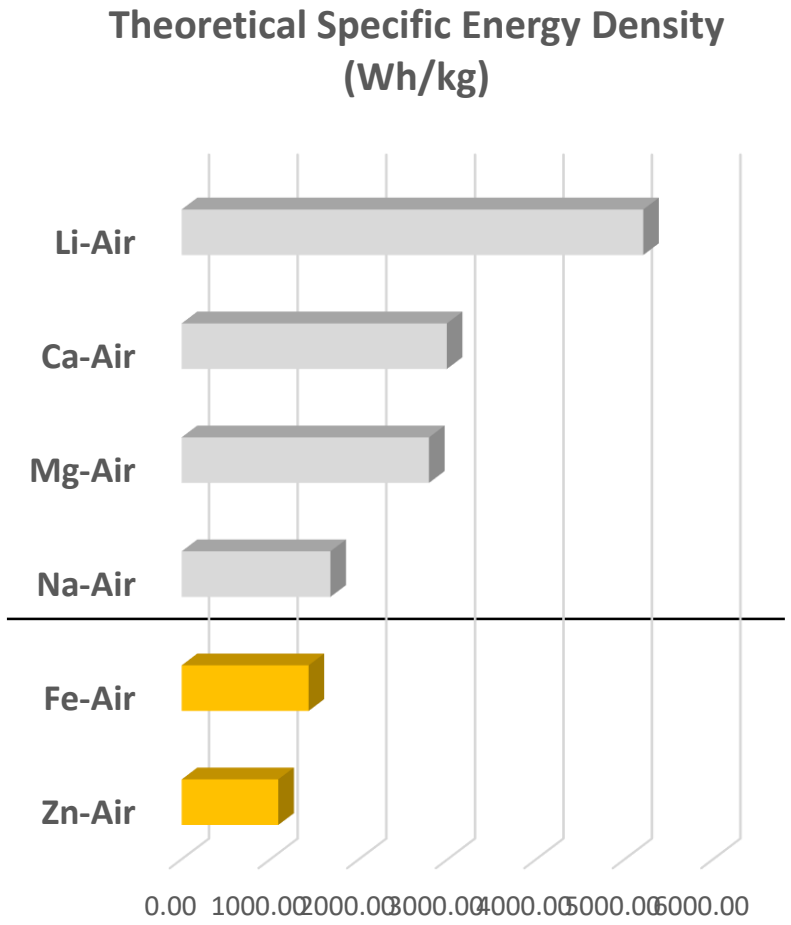
So why not Zinc or Iron?



Cons:

- Lower potential for energy density and voltage
- Development fatigue “We tried that but…”

Pros:

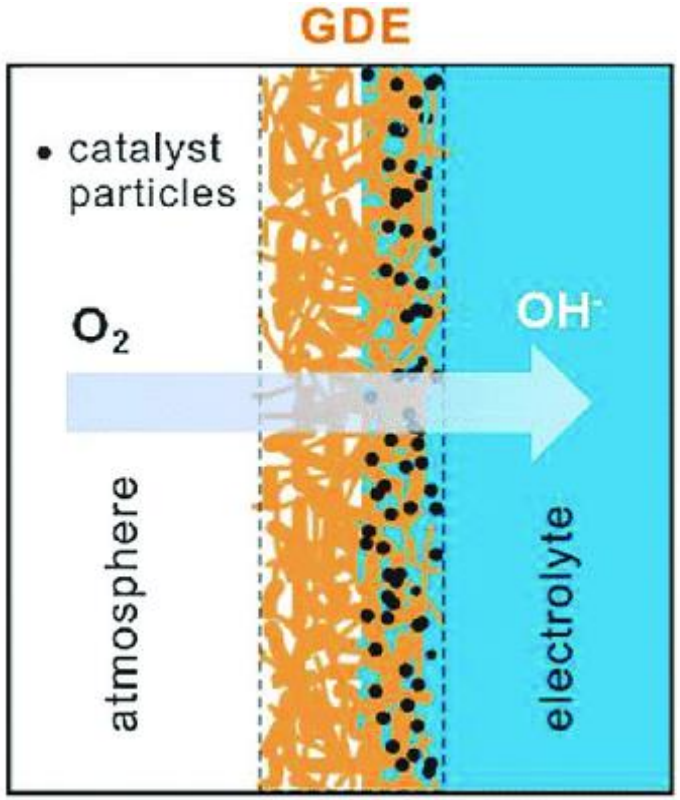
- Still potentially 4x Li-ion at system level
- These metals do not spontaneously combust
- Safe, non-toxic, aqueous electrolytes
- Potential for very low-cost product and production equipment
- Recycle friendly chemistry and packaging
- Likely to be very tolerant of state of charge (SOC)

We believe Zn-Air is worth another look

- Potential Benefits:
  - >400Wh/kg at the system level with no thermal management and minimal BMS
  - Very low cost <$70/kWh at the system level
  - Tolerant of p-SOC operation (partial state of charge)
  - Thermal runaway unlikely
  - No toxic or hazardous components - easily recycled
- Challenges
  - Development fatigue - lots and lots of failed attempts
- But we know what the challenges are
  - GDE failures and CO_2 adsorption
  - Poor kinetics (power delivery and charge rate) - see above

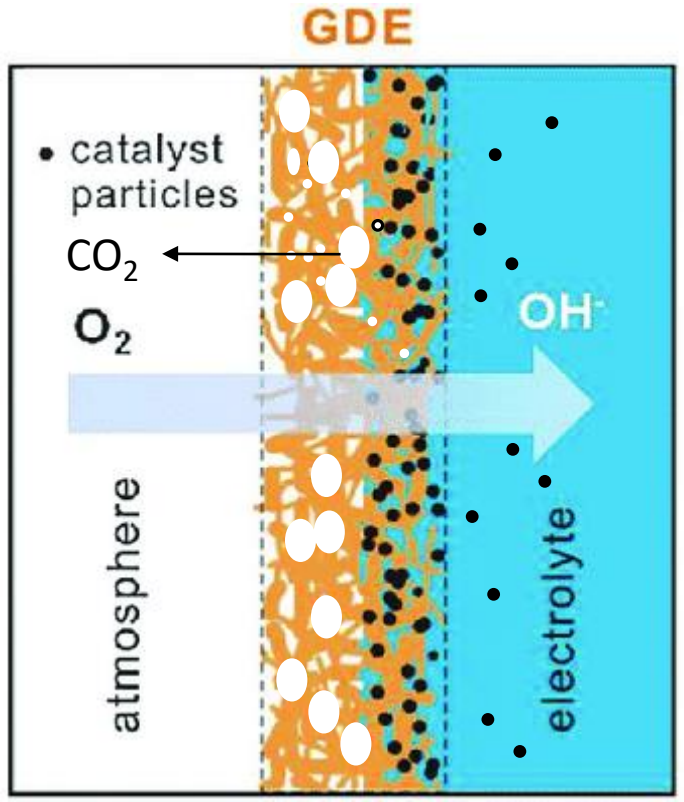
1st Challenge is the Gas Diffusion Electrode (GDE)

- GDEs need to support good reaction kinetics in a complex 3 phase (gas, liquid, solid) interface.
  - Good porosity for gas transport
  - High specific surface area for good kinetics
  - Low surface tension/hydrophilic for liquid wetting and transport
  - Fine, well distributed catalyst for good kinetics
  - Good electron conductor for efficiency
- Power delivery, charge rate and cycle life are largely determined by the GDE



MAB GDEs need to cycle and evolve O_2

- GDEs are the heart of a MAB – but these were largely copied directly from PEM fuel cells
- MAB operation is fundamentally different:
  - They cycle between charge and discharge
  - They evolve O_2 at the GDE during charge
  - O_2 evolution starts with $\underline{O}_1$ a highly reactive free radical which consumes any carbon catalyst support (even Graphene) making CO_2
  - Pt catalyst lost as carbon support erodes
- Carbon based GDE performance and cycle life has been poor and MAB developers were slow to recognize the issue.



2nd Challenge – alkaline (KOH) electrolytes

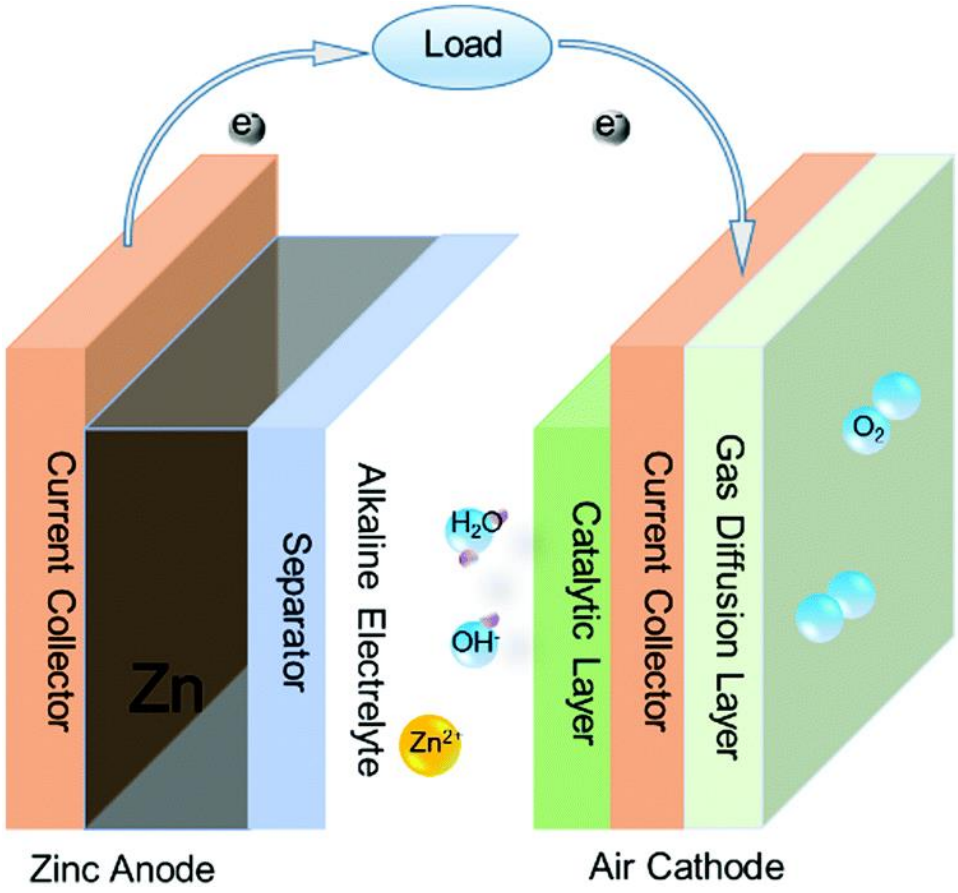
Zn MAB's used alkaline electrolytes, which readily absorb CO_2 from air. This precipitates and consumes the electrolyte as carbonate

A CO_2 inhibiting membrane/separator is required

- Limits transport kinetics
- Compromises power density
- Adds cost & complexity

Zinc forms dendrites when plated (charging) from alkaline solution at anything more than a minimal charge rate. This generates shorts and limits cycle life

- Also be reduced with a separator or "leverers"
- But this further limits transport kinetics and charging rate



Priorities for success:

1. High cycle life GDE:
   - Stable non-corroding catalyst support to support oxygen evolution on charge
   - Excellent electron conductor
   - Excellent kinetics - high specific surface area
2. Alternative electrolyte
   - CO_2 rejecting, membrane free operation
   - Dendrite limiting
   - Non-toxic
   - Excellent kinetics
   - High metal concentration

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Ti sub-oxide based high cycle life GDE

Magneli Phase Ti-sub oxides (Ebonex^{tm})

Titanium sub-oxides of the general formula Ti_nO_{2n-1} where n = 4-7

- i.e. Ti_4O_7, Ti_5O_9, Ti_6O_{11} , Ti_7O_{13}

Characteristic graphite-like crystalline structure (Magneli Phase) with established and characteristic X-ray diffraction spectra

- Not simply doped Titania or casual mixtures of TiOx

Produced from TiO_2 which is an abundant and widely available commercial commodity

Combines high levels of electron conductivity with exceptional catalyst enhancement, corrosion resistance and stability

Compound	x in TiO_x	Structure	X-ray density
TiO_2	2	Rutile	4.25
		Anatase	3.89
$Ti_{10}O_{19}$	1.9		
Ti_9O_{17}	1.89	Triclinic	3.75
Ti_8O_{15}	1.875	Triclinic	3.84
Ti_7O_{13}	1.857	Triclinic	3.9
Ti_6O_{11}	1.833	Triclinic	4.0
Ti_5O_9	1.8	Triclinic	4.31
Ti_4O_7	1.75	Triclinic	4.32
γTi_3O_5	1.67	Monoclinic	4.35
		Monoclinic	4.24
		Monoclinic	4.11
Ti_2O_3	1.5	Tetragonal	4.585
TiO	1.0	Hexagonal	5.69
		Cubic	5.82
		Monoclinic	5.89
Ti_2O	0.5	Hexagonal	5.0
Ti	0	Hexagonal	4.5

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“Magneli Phase” crystal structure

Ebonex’s structure is based on but distinguishable from rutile TiO_2

- Crystals are built up of TiO_2 octahedra blocks which share edges and corners to form a shear plane
- In $Ti_nO_{(2n-1)}$, every n^{th} layer has an oxygen deficiency, which leads to shear planes in the crystal structure.
- These shear planes occur at n spacing in layers of inert TiO_2 octahedra and provide pathways for electron transport – delivering true metallic conductivity

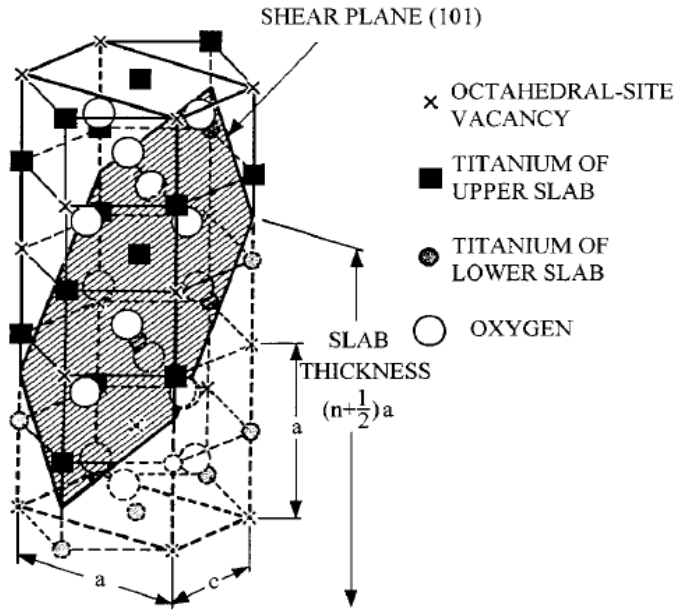

Fig. 2. Unit cell projection of the shear plane in the Magnéli phase Ti_4O_7. c, a and (1 0 1) refer to axes of rutile slabs [6].

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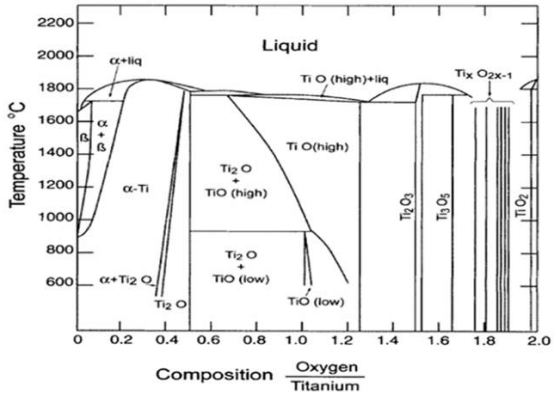
Ebonex^{tm} contains the preferred Magneli Phases (Ti_4 Ti_5 and Ti_6)

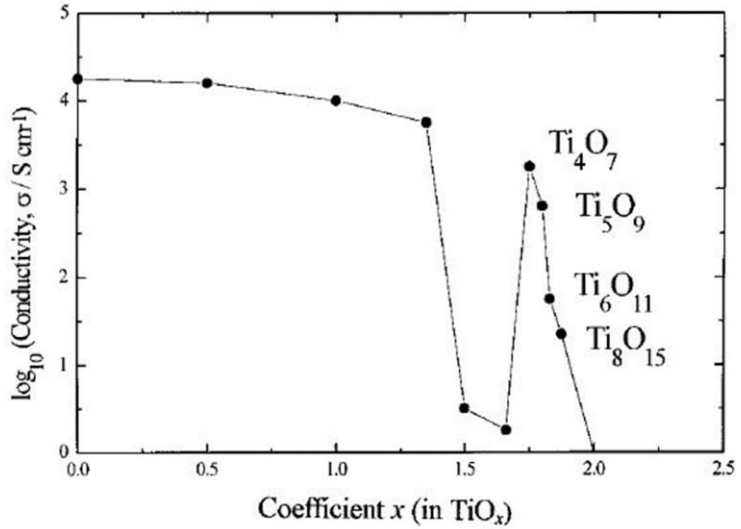
True electron conductor up to 4 times higher conductivity than graphite

Exceptional corrosion resistance in aggressive acidic and basic solution

- Exceptionally robust in HF, BF_4, PF_6, HCl, KOH and other highly oxidizing environments
- Exceptionally stable under electrically polarized conditions

Provides the basis for very high-performance anodes and cathodes





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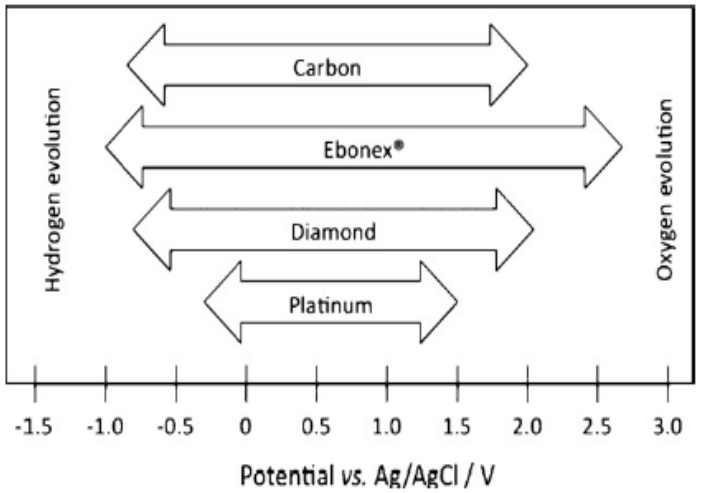
Delivers key advantages in electrochemistry….

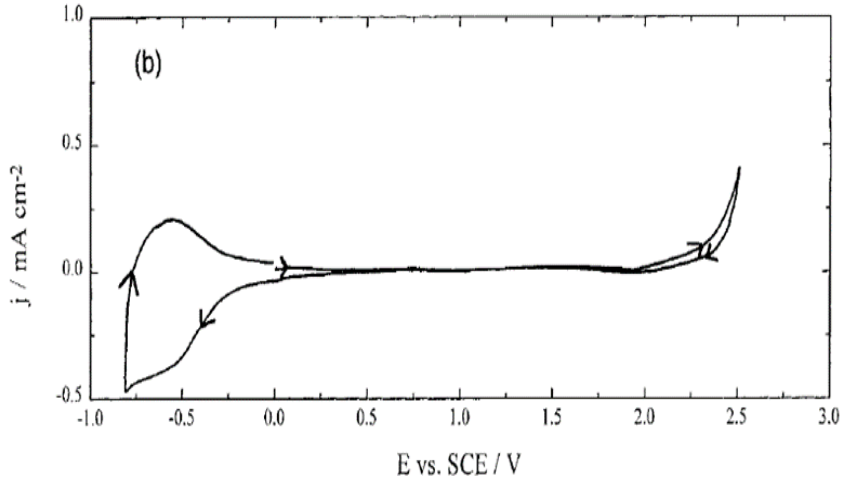
Wide over-potential window that suppresses O_2 and H_2 evolution in water

- Important benefit for batteries, reducing electrolyte decomposition and drying

Exceptional catalyst retention and catalyst enhancement

- Longer life, less catalyst required, broader range of catalysts





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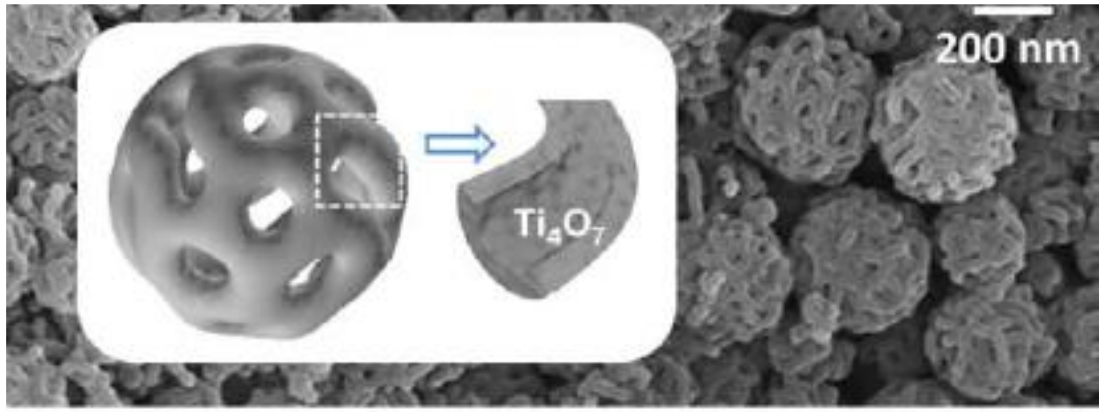
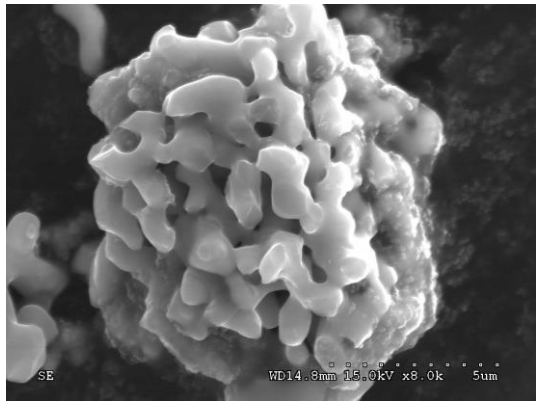
……and many complementary properties



Credit: Helmholtz Zentrum, Berlin



QuanVerge microporous Ebonex

Very hydrophilic – Promotes wetting, electrolyte transport and catalytic activity

Very broad range of morphology, porosity and specific surface areas

Non-toxic – equivalent to TiO_2

High microwave absorption

Lubricious – similar to graphite but with higher wear resistance

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Strong published support for this approach

1. Li X. et. al. “Magneli phase Ti4O7 electrode for oxygen reduction and its implication for zinc-air batteries”. 2010 Institute for Fuel Cell Innovation, National Research Council of Canada. Vancouver
2. Ponovic P. et al. “Co-Magneli phases electrocatalysts for hydrogen and oxygen evolution” 2010. International Journal of Hydrogen Energy Center for Fuel Cell Research University of Delaware
3. Palanichamy K. et. al. “Magneli phase TinO(2n-1) as corrosion resistant PEM fuel cell catalyst support” 2012 Journal of Solid State Electrochemistrty
4. Kundu D. “A highly active nanostructured metallic oxide cathode for aprotic LiO2 batteries” 2014 Energy and Science, RSC Publications
5. Borisov G R, et. al. “A novel non-carbon gas diffusion layer for PEM water electrolysis anodes” 2015 Bulgarian Academy of Sciences
6. “New Ti4O7 microporous electrode for Li Sulfur” 2017. Helmholtz Zentrum, Berlin, Humboldt University, Potsdam University
7. Mei S., et. al. “Porous Ti4O7 Particles with Interconnected-Pores Structure as High-Efficiency Polysulfide Mediator for Lithium-Sulfur Batteries” 2017 Advanced Functional Materials doi: 10.1002/adfm.201701176

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Methanesulfonic Acid based, CO_2 rejecting electrolyte

Methanesulfonic Acid (MSA)

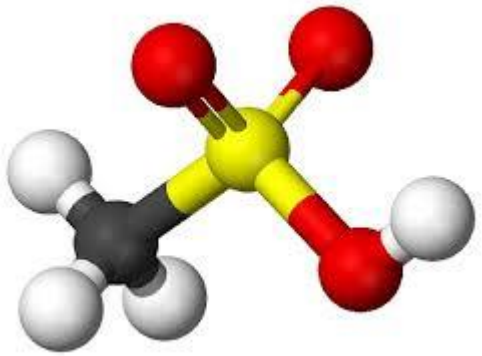
Properties:

- Formula: CH_3SO_3H BP: 167°C Density: 1.48 g/cm^3

EPA "Green Circle" classification

- Preferred alternative to H_2SO_4 and HCl as a metal plating acid
- Used to plate lead/tin in electronics manufacturing
- Used to extract zinc from Jarosite smelter waste

Established commercially in electronics, plating and re-cycling



Researched and tested in zinc, lead and vanadium flow-battery systems

Established advantages

- High solubility for Zn, Sn, Pb and other metals
- Low solubility for aluminum and stainless steel
- Rejects CO_2 adsorption
- Excellent reaction kinetics supported >5,000A/m2 on discharge and charge
- Zn does not form dendrites in MSA even at >5,000A/m2

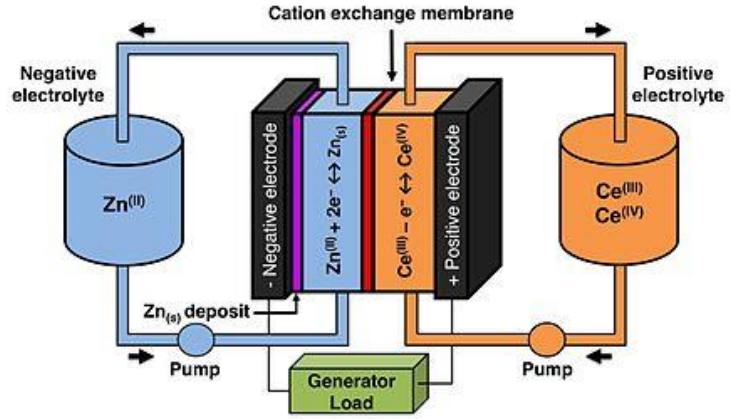


Diagram of the Divided Zinc-Cerium Flow Battery

Demonstrated > 10 years and thousands of cycles in Zn/Ce and other flow batteries

Summary – A different approach to Zn-Air

Conventional

- Carbon based GDE
- Alkaline electrolyte

Alternative

- Novel non-corroding GDE
- Methane Sulfonic Acid (MSA) electrolyte

Limitations & Failure Modes

- Carbon GDE gradually consumed by evolved O_2 on charging. Needs additional catalyst (Pt)
- Alkaline electrolyte absorbs CO_2 and fails
- Membrane limits CO_2 but adds cost and compromises power density
- Zn can form dendrites on charge, which short the battery

Advantages

- Non-carbon GDE extends cycle life and reduces catalyst loading. Opens options for non PMG catalysts
- CO_2 rejected by acidic electrolyte CO_2 membrane eliminated, improving cost and kinetics
- Organic acid inhibits Zn dendrites

Targets: >400Wh/kg system level >$70/kWh system level