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National Academies of Sciences • Engineering • Medicine
Powering the US Army of the Future: A Study
12 June 2020

Next-generation rechargeable batteries enabled by 3D zinc anodes

Team Zinc

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NRL's "Advanced Electrochemical Materials" Section: Addressing Navy & Marine Corps Power & Energy Needs through Focused R&D

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NRL 6171's motivations & themes for power source development:

- Scalable energy-storage:
  micropower → personal power → grid-scale
- Battery chemistries inherently safer than Li-ion → *target aqueous systems*
- Low-cost, domestically sourced components; manufacture-friendly fabrication processes
- Variable form factors for ready integration into established architectures
  → *opportunities for "structural" energy storage*
- Hybrid configurations that integrate various energy storage/conversion components
  → *energy-dense battery + high-power capacitor*

Navy/Marine Corps applications that we target:

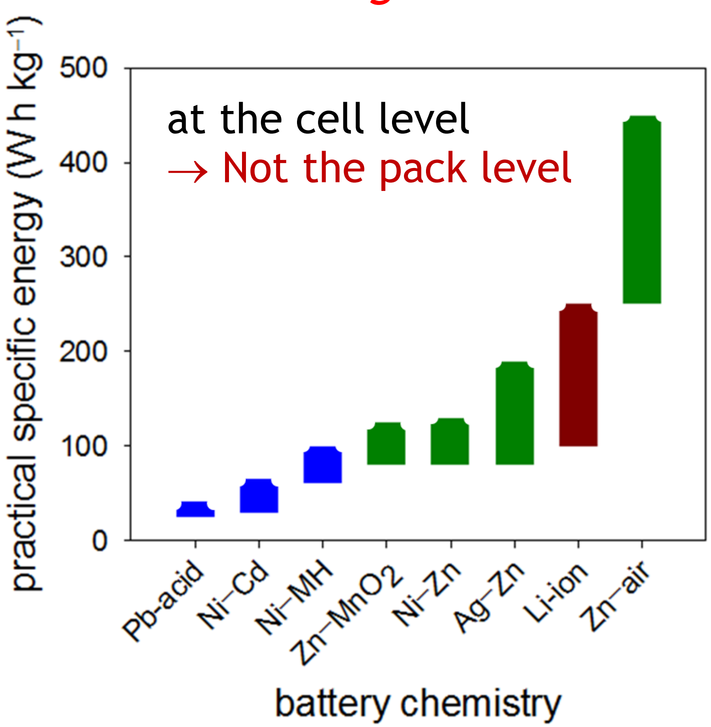
- Portable electronics
- Communications
- Wearable power
- Autonomous sensors
- UUV & UAV
- Hybrid vehicles
- Wireless recharging
- Directed-energy weapons
- Space-based platforms

Looking towards the next energy- & power-dense (& safe) battery

Zn-based batteries

- ✓ High practical specific energy
- ✓ High specific power
- ✓ Safe, aqueous electrolyte
- ✓ *Globally available* materials
- ⊗ Limited rechargeability
- ⊗ Subpar material utilization

Once Zinc is made rechargeable → Rechargeable Zn–air, Ag–Zn, Ni–Zn, MnO_2–Zn & Zn-ion batteries

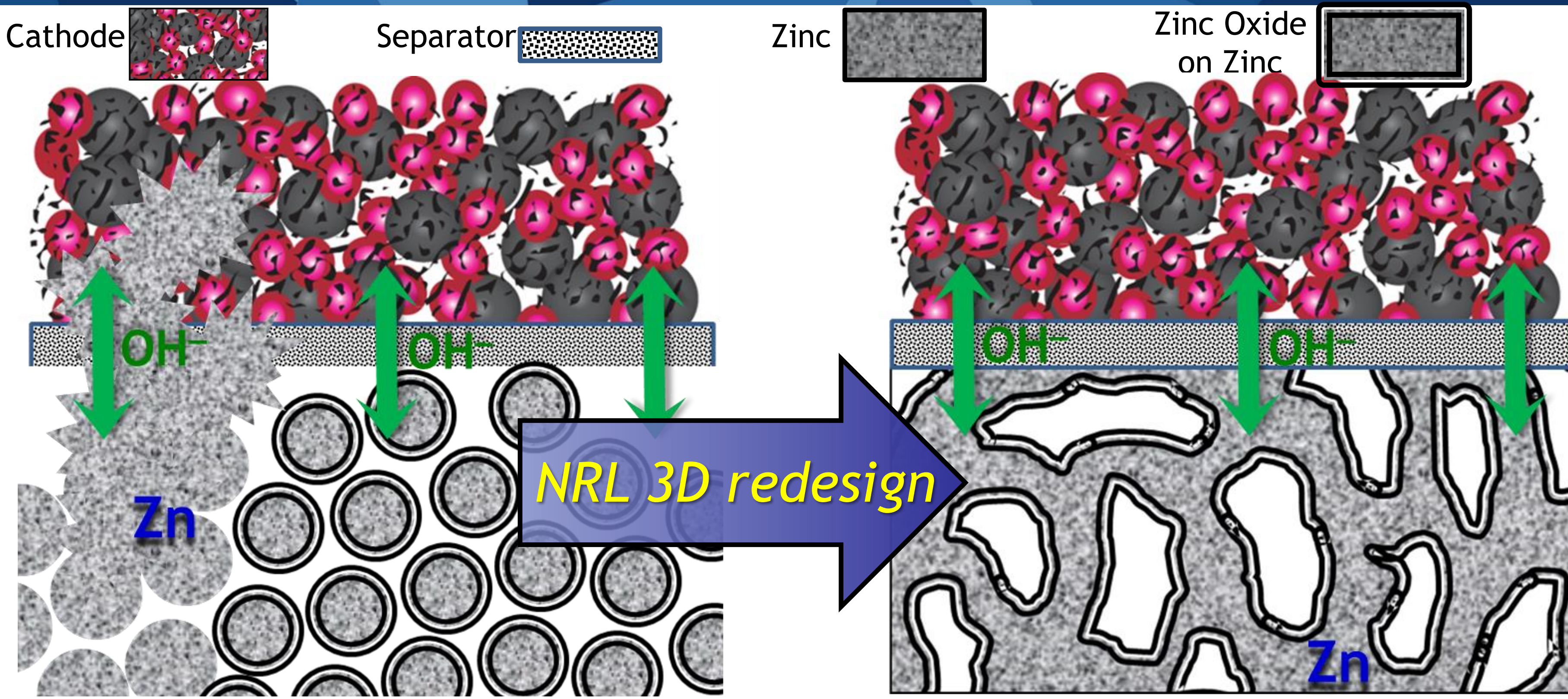


What will be the impact?

- ❑ Replace Pb-acid, Ni–Cd & Ni–MH batteries with higher energy density, rechargeable, Zn–X batteries
- ❑ Provide alternative to Li-ion batteries in niche applications or extreme environments or where safety is high priority

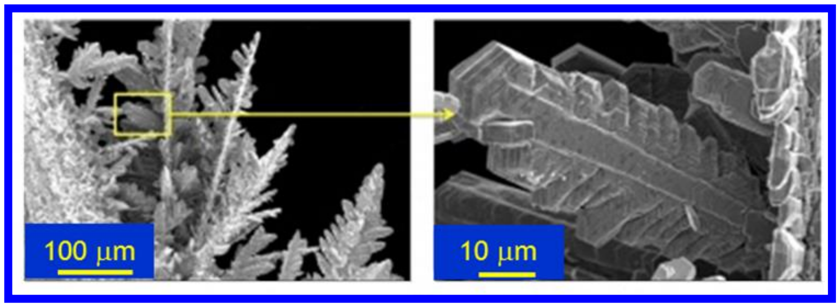
→ *Disruptive technology for the military & consumer battery market*

NRL Breakthrough:
3D redesign of the Zn anode



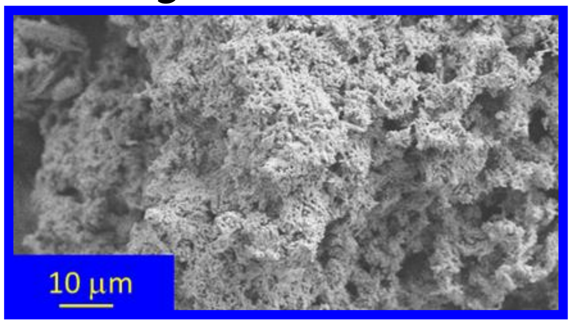
Traditional powder-composite Zn anode

Next-gen 3D Zn



Current density required to Initiate dendrites: ~ 10 mA cm^{-2}

Oxley, Fleishmann, NSWC Quarterly Report (1966)



NRL Breakthrough
3D redesign of the Zn anode

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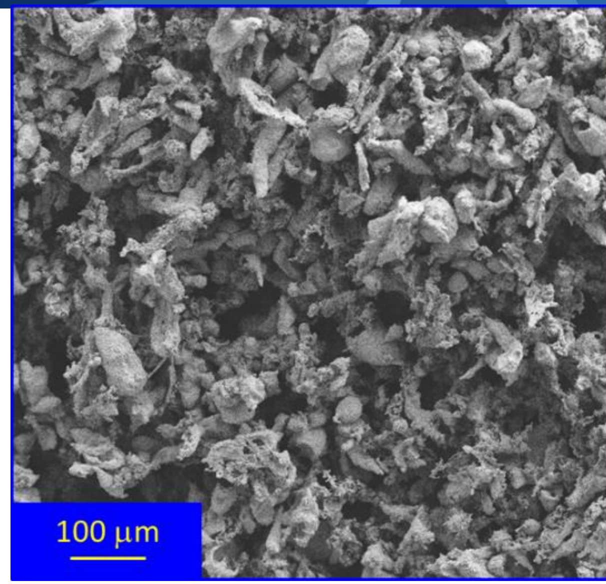
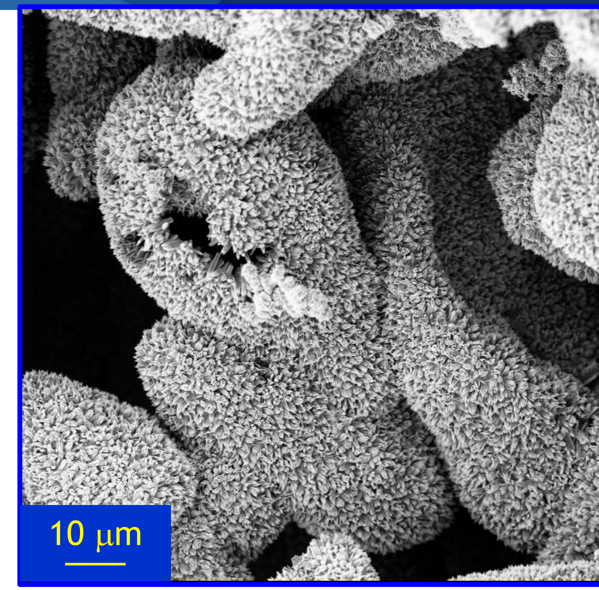




✓ *Scalable, monolithic form factor*
- → tailor size to desired cell dimensions
- → mechanically robust

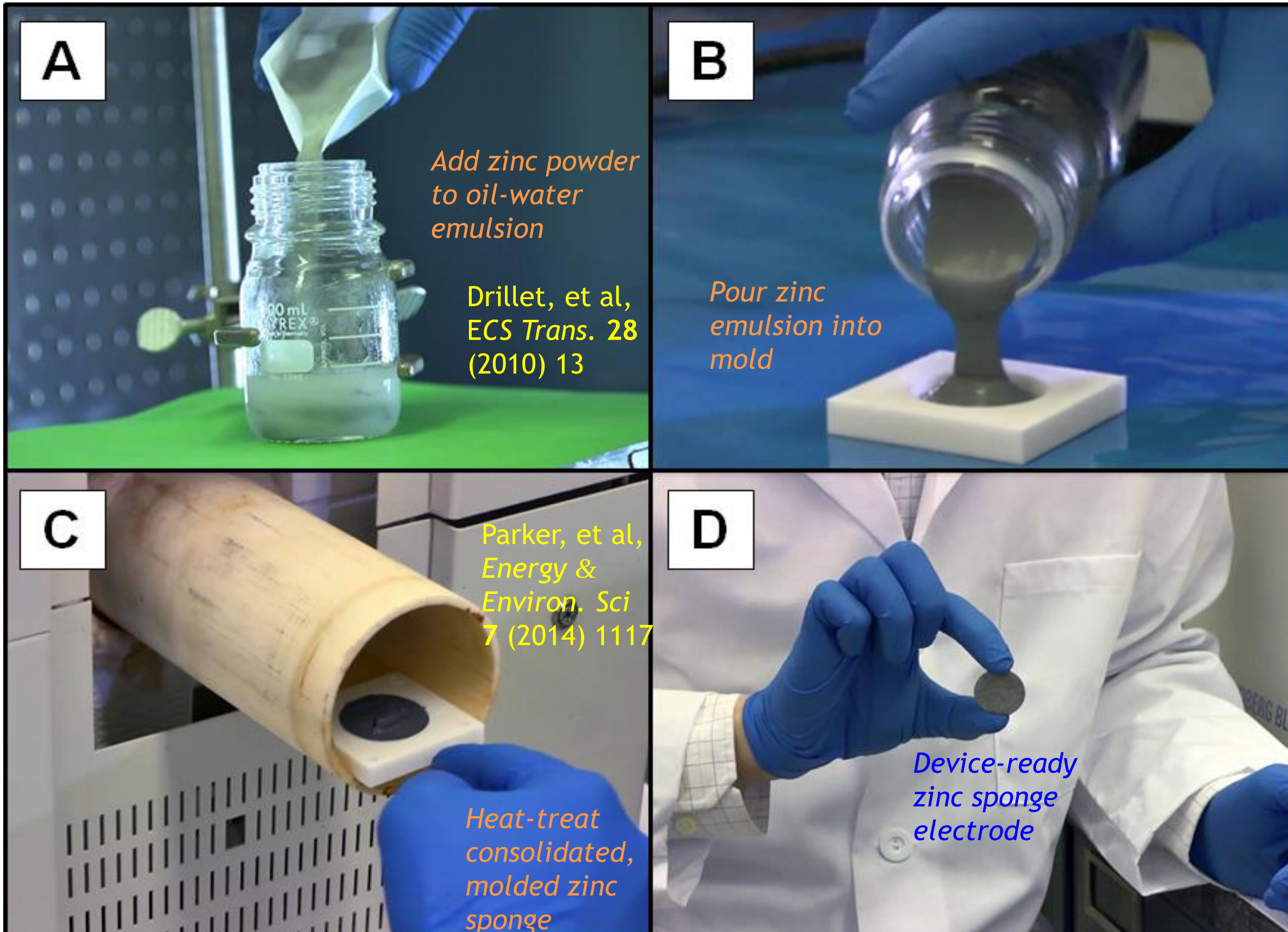
✓ *Fully metallic, highly conductive pathways in 3D*
- → improve current distribution
- → suppress dendrite formation

✓ *Confined volume elements*
- → ensure more uniform ZnO precipitation inside & out on discharge
  - → ZnO@Zn core–shell

"ZINC ELECTRODES FOR BATTERIES." **U.S. Patents #9,802,254,10,008,711** + **Applications** (Nov-2012 primacy date): **#2014-0147757** (29-May-2013), **Continuations-in-Part** (3 Aug-2017): Rolison, Parker, Long

Fabrication of 3D Zn (“sponge”) anode

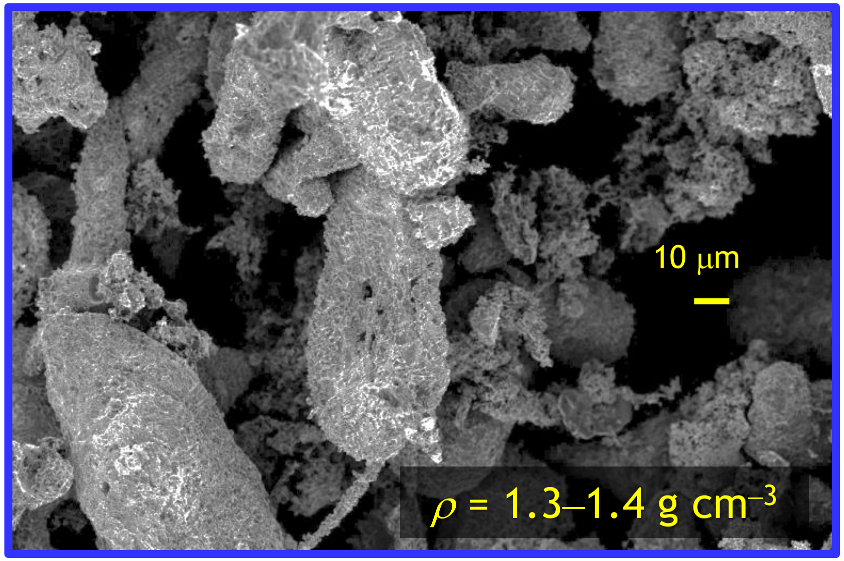
https://www.youtube.com/watch?v=YnRp49d4FMA

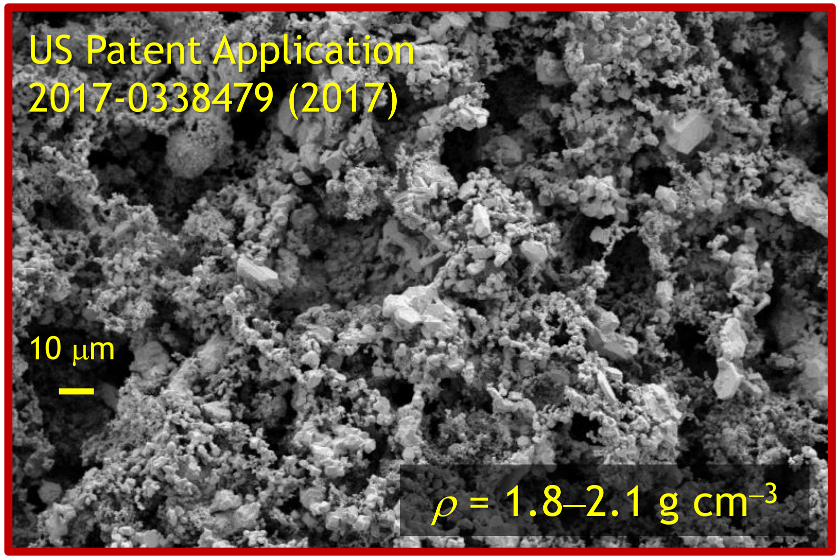


Increasing density of Zn sponge: Gen-1 (Zn_{20}) to Gen-2 (Zn_{30})

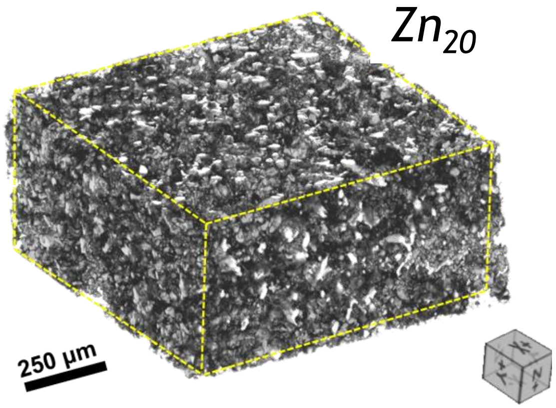
Gen-1 (Zn_{20})
→ 20% volume fill of Zn

Gen-2 (Zn_{30})
→ Denser, more mechanically robust



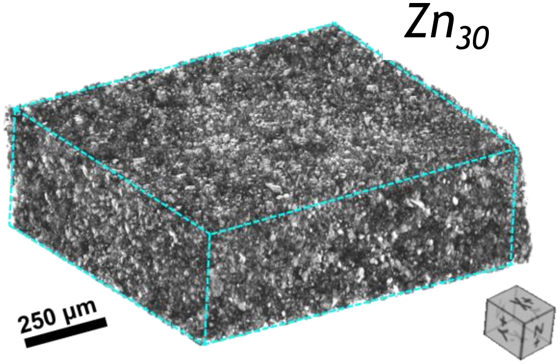


Zn_{20}



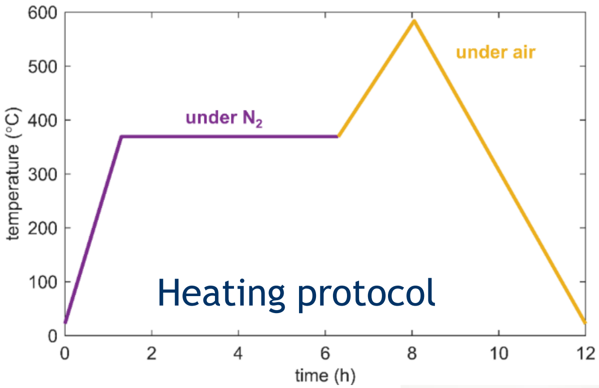
X-ray tomography verifies 3D interconnectivity of monolithic Zn sponges

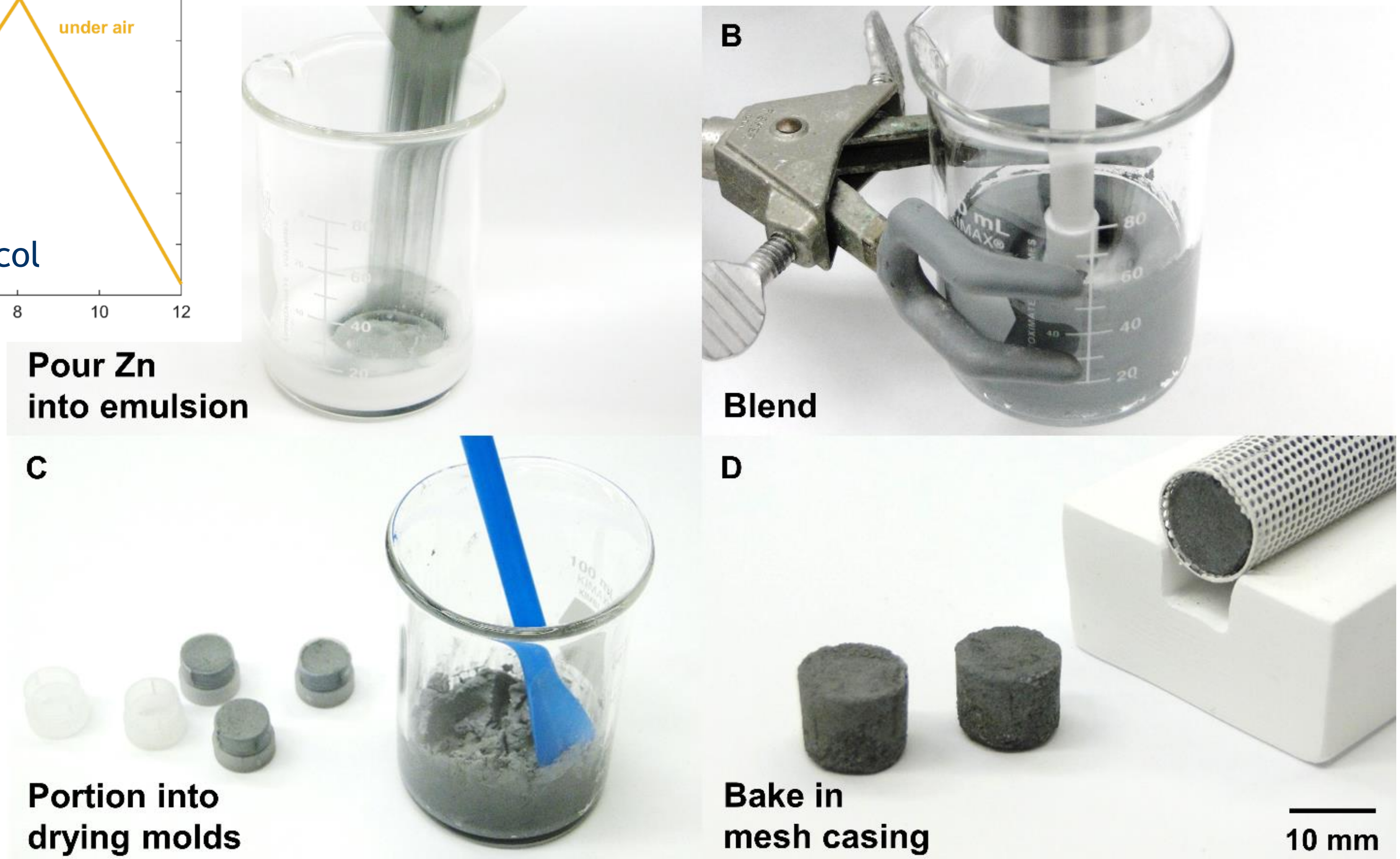
Zn_{30}



Ko, Geltmacher, Hopkins, Rolison, Long, Parker, *ACS Adv. Energy Mater.* **2** (2019) 212

… and with manufacturability in mind





No electroreduction required before cell assembly

Hopkins, Sassin, Chervin, DeSario, Parker, Long, Rolison, "Low-cost green synthesis of zinc sponge for rechargeable, sustainable batteries," *Sustainable Energy & Fuels* (2020)

The Path Forward for Next-Gen Zinc Batteries

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Present: TRL 4

Primary Zn–X with **enhanced energy density**

- **Micro/nano UAVs**
- Communications
- Recharge of Li-ion

Enhanced rechargeability for Ni–Zn & Ag–Zn in conventional electrolytes

- UUVs
- Power systems for HE weapons
- **Drop-in for current Li-ion**

Zn-ion **Batt-caps**

- Communications
- **Renewables**
- **Hybrids**

Rechargeable Zn–air

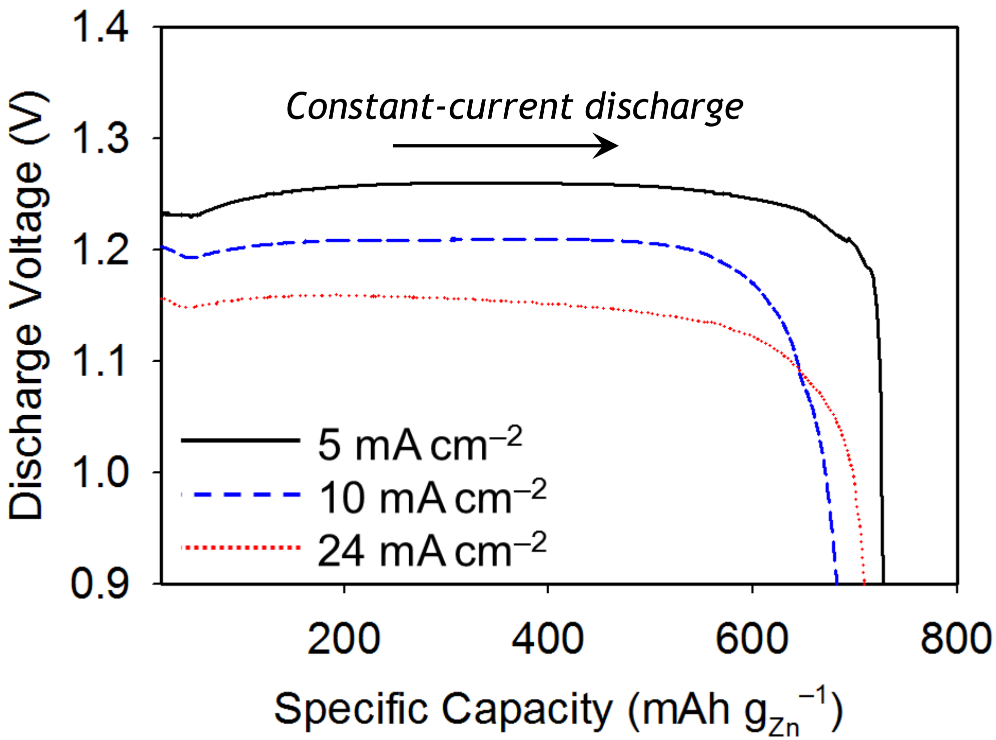
- Electric vehicles
- **Toughbooks™**
- **GPS**

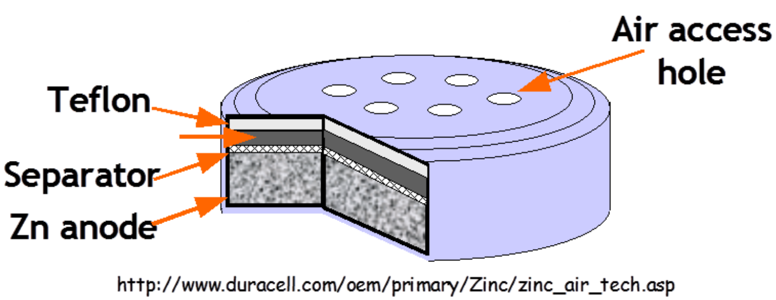
Solid-state 3D Ag–Zn, Ni–Zn, Zn–MnO_2

- **Structural batteries**
- Space applications
- UUVs/UAVs

2022

Evaluation in prototype primary Zn-air cells

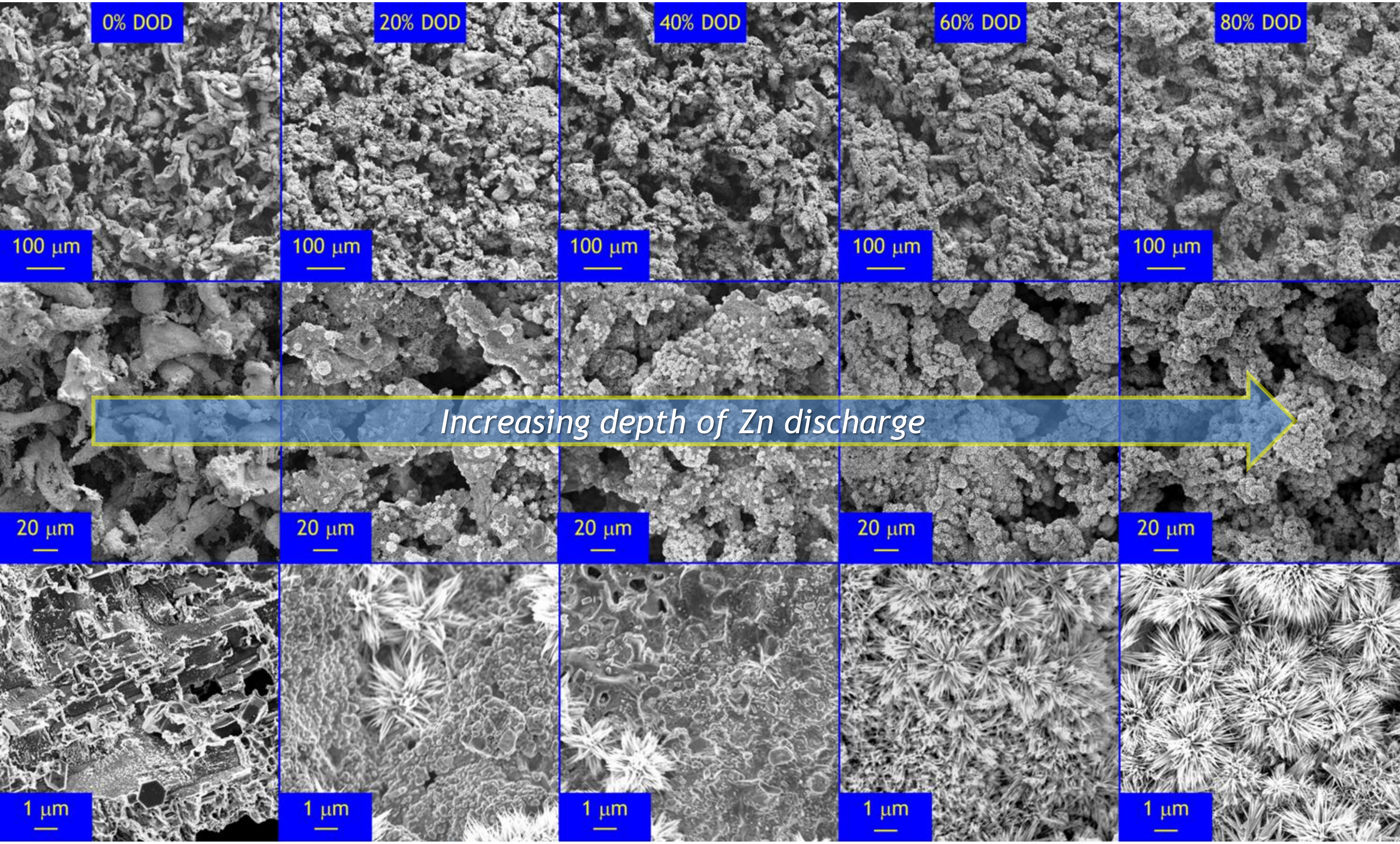




- ✓ NRL's 3D Zn sponge increases battery lifetime by 50% relative to commercial batteries
- ✓ Allows for plug-&-play into existing Zn-based battery technologies
  - → Ag–Zn
  - → Ni–Zn
  - → Zn–air

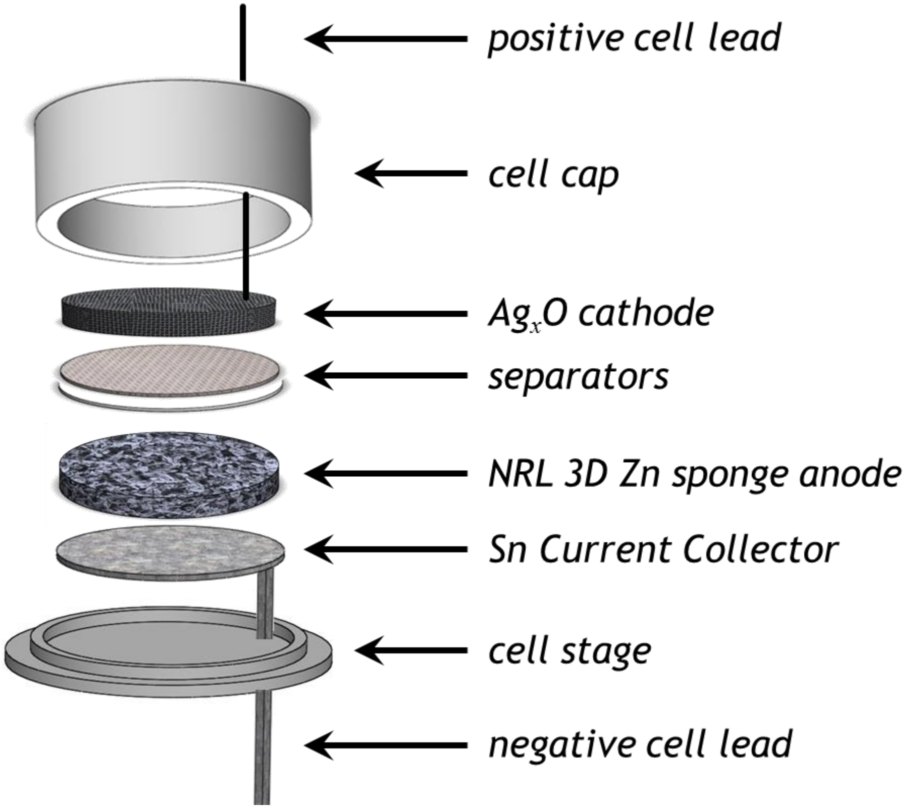
	Percentage utilization of Zn
Commercial Zn-Air (Zn bed)*	60
NRL Zn–Air (3D Zn sponge)	95

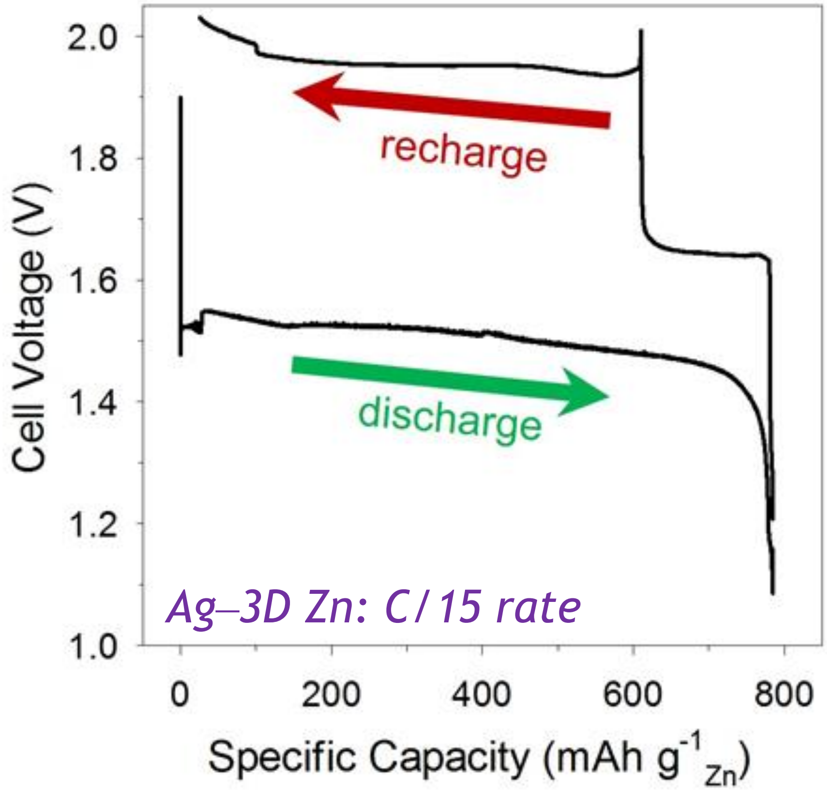
Maintaining 3D Zn structure to deep discharge



Parker, Nelson, Wattendorf Chervin, Long, Rolison, *ACS Appl. Mater. Interfaces* **6** (2014) 19471

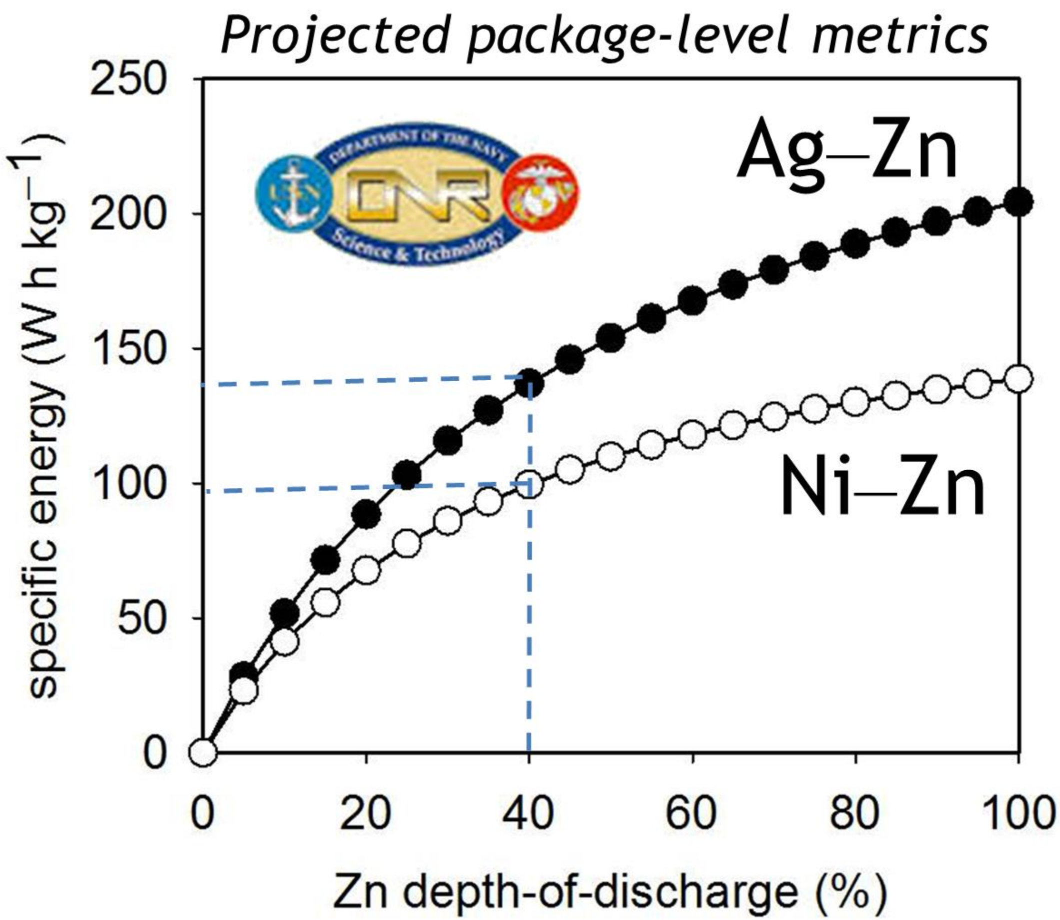
Accessing unprecedented levels of discharge (and recharge) with 3D Zn anodes





- ✓ 95% of theoretical Zn specific capacity (820 mA h g^{-1}_{Zn})
- ✓ 97% recovery of exhaustive discharge
- → Only 40–60% DOD_{Zn} achieved with commercial Zn–based batteries

High DOD_{Zn} cycling → Achieve Li-ion–competitive specific energy

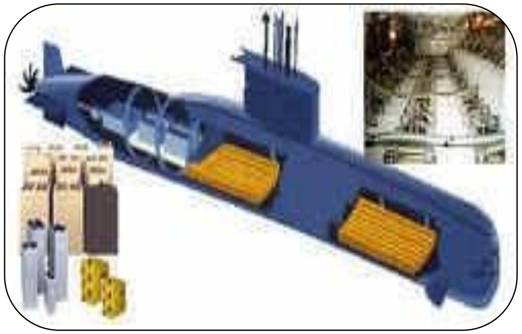


"Depth-of-discharge" metrics for commercial batteries typically refer to "nominal" capacity:

- → Commercial rechargeable Ni–Zn cells typically tap ~20% theoretical DOD_{Zn} (up to 66 W h kg^{-1})
- → NRL 3D Zn supports ≥40% theoretical DOD_{Zn} with extended cycling

Pushing DoD_{Zn} beyond 60%? Not necessary!

USN applications for Ni–3D Zn & Ag–3D Zn batteries



Submarines
Ni–3D Zn: energy density + lifetime
Ag–3D Zn: ✓ ✓ + power

SEAL Delivery Vehicles
Ni–3D Zn: safety + cost
Ag–3D Zn: safety + power

Replace Pb-acid batteries

Opportunities for next-generation Ni–3D Zn & Ag–3D Zn batteries

Replace Li-ion batteries

Ship Backup-Power
Ni–3D Zn: reliability + lifetime
Ag–3D Zn: ✓ ✓ + power

Unmanned Vehicles
Ni–3D Zn: cost
Ag–3D Zn: power

Ni–3D Zn batteries →
High performance in three fields of use

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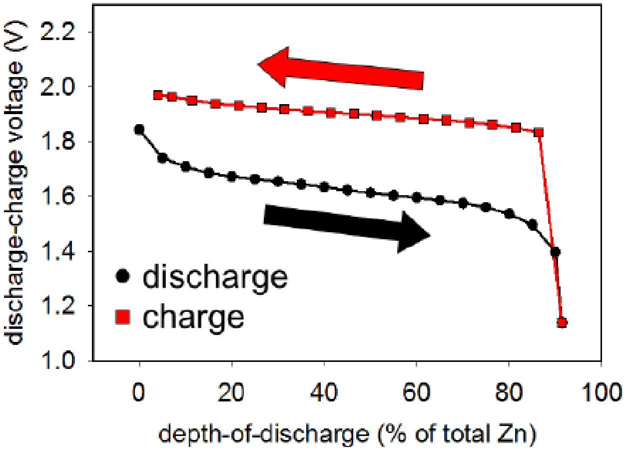
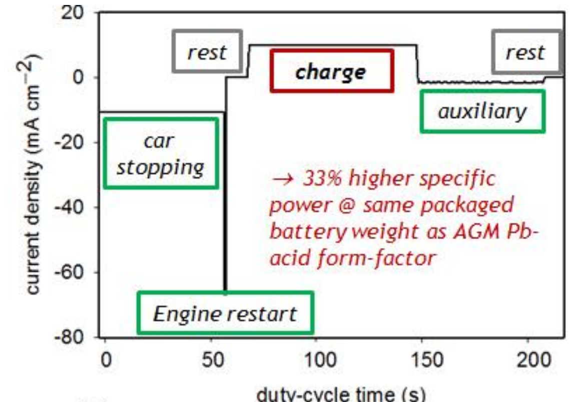
Single discharge to deep utilization

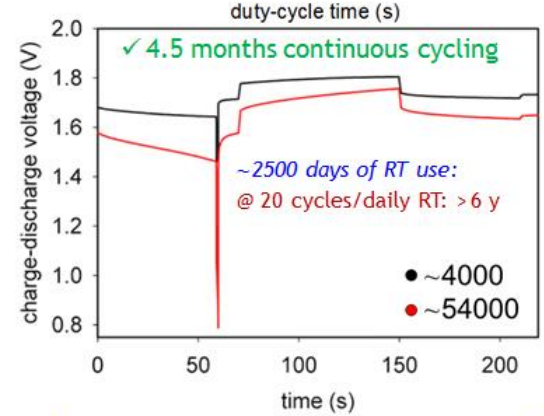


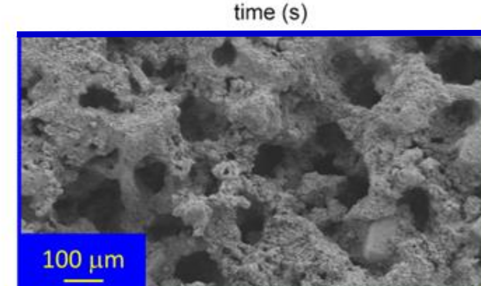
"Rechargeable nickel–3D zinc batteries: An energy-dense, safer alternative to lithium-ion."
Parker, Chervin, Pala, Machler, Burz, Long, Rolison
Science **356** (2017) 415

Achieved >90% DOD with 95% capacity recovery on charge

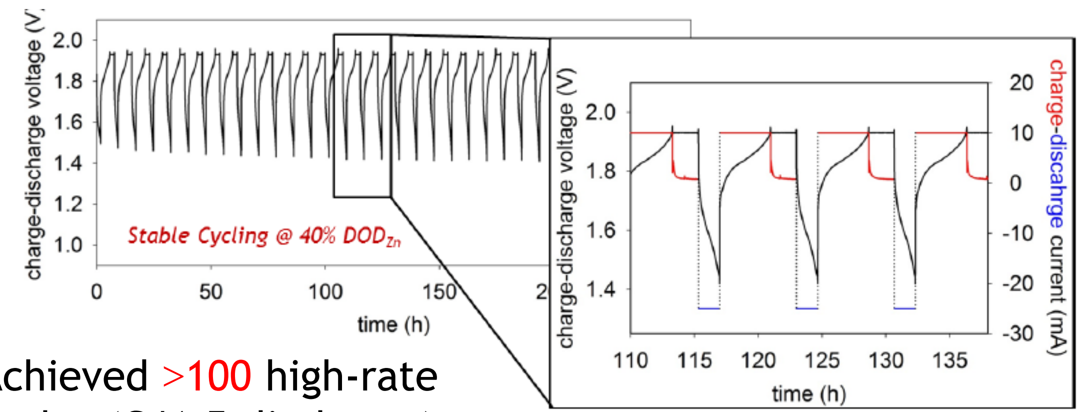
High-power duty cycles relevant to start–stop EVs







Rechargeability at Li-ion competitive specific energy



Achieved >100 high-rate cycles (C/1.5 discharge)

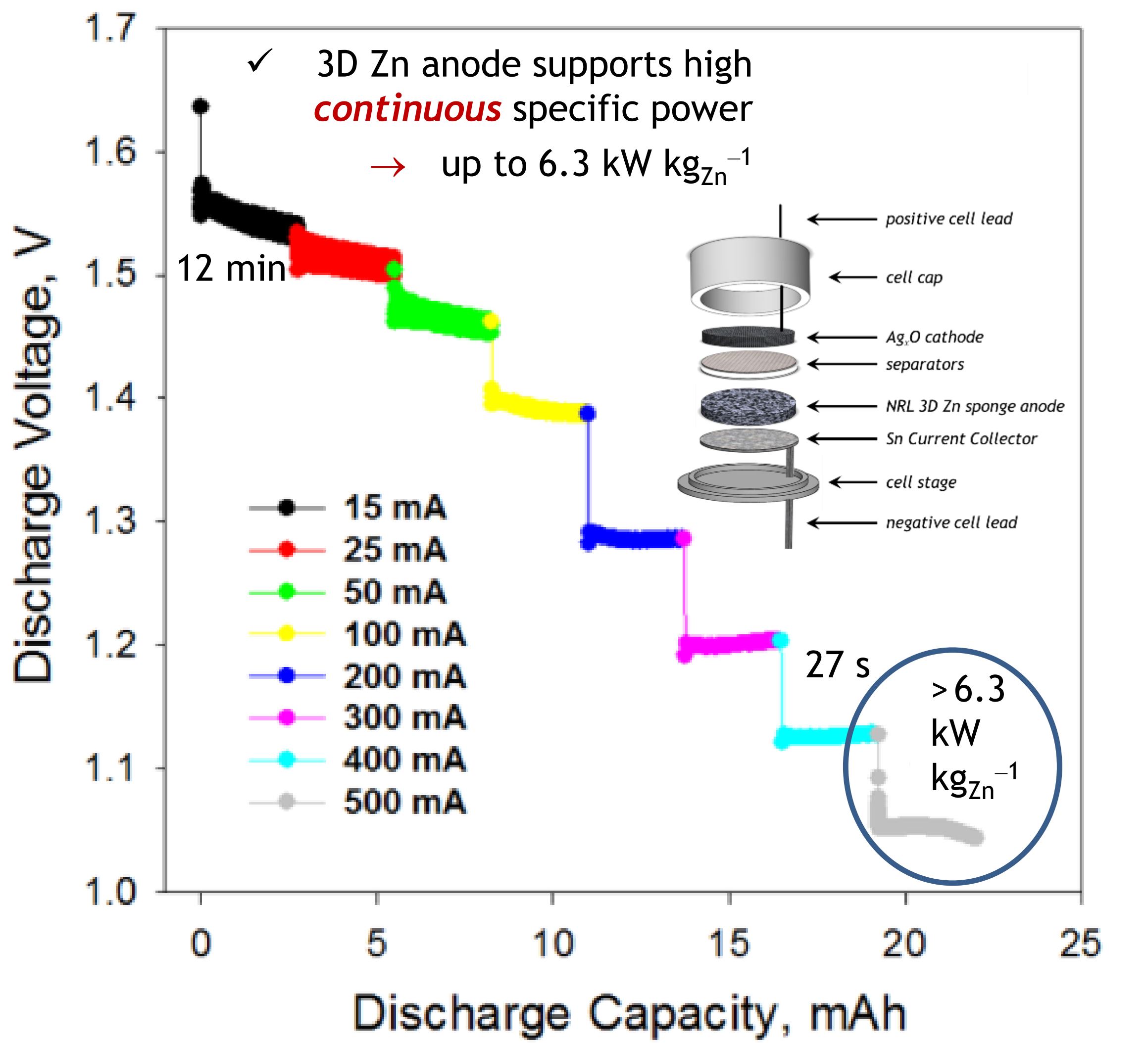
328 mA h $g^{-1}{}_{Zn}$ cycling

Zn sponge anode delivers performance in Ni–3D Zn cells to power EVs

Parker, Chervin, Pala, Machler, Burz, Long, Rolison, *Science* **356** (2017) 415

	E-bike		Start–stop / Microhybrid		Battery Electric Vehicle	
	SLA [1]	Ni–3D Zn	AGM [2]	Ni–3D Zn	Li-ion [3]	Ni–3D Zn
Energy Capacity (W h)	540	540	1720	1720	24000	24000
Weight (kg)	12.2	5.9	45.0	21.7	339	220
Effective [4] Specific Energy (W h kg^{-1})	44.3	91.8	38.2	79.2	71	109
Effective Energy Density (W h L^{-1})	140	225	126	164	96	216
Range (miles; years for start–stop)	10–18	10–18	1–2 y	4–5 y (est.)	84	90

Extreme power of Ag–3D Zn_{30} cells



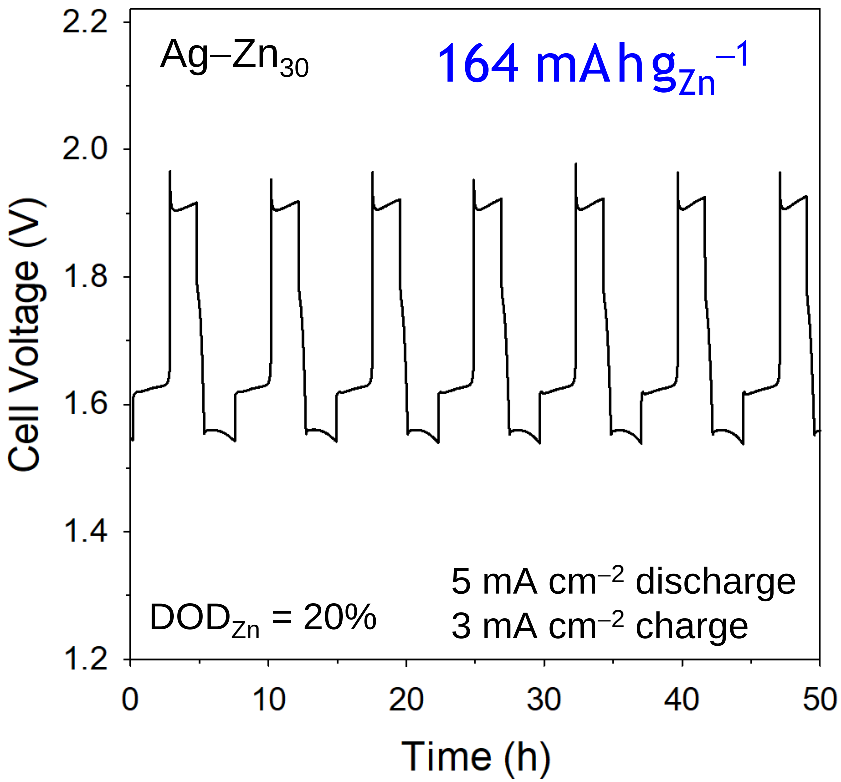
- Denser Zn sponges enable routine use of thinner anodes
- Thinner electrodes confer higher power

Power performance:

- ✓ Peak rate of 500 mA cm^{-2} (~17C rate)
- ✓ Peak power of 6,300 W kg_{Zn}^{-1}
- ✓ 1,200 W kg^{-1} in fully packaged Ag–3D Zn cell

Rolison, Parker, Ko, Long, US Patent Application 2018-0130998

Excellent cycling performance of Ag–3D Zn_{30} cells



- 100 cycles for Zn_{30} sponges *vs.* <50 cycles for Zn_{20}
  - even with using unoptimized Ag cathode + unoptimized separator system)
- 100% coulombic efficiency
- *still* no dendrites …

More uniformly reactive Zn → more uniformly reactive Ag

Ko, Geltmacher, Hopkins, Rolison, Long, Parker
ACS Adv. Energy Mater. ***2*** (2019) 212

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Rechargeable Zn–air:
The Holy Grail of zinc batteries

❑ Integrate multiple functions to achieve next-gen rechargeable Zn–air battery:

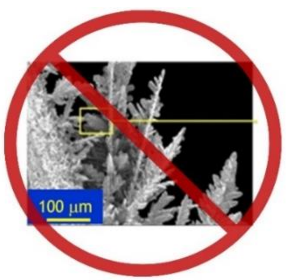
(1) ***"Fuel cell"*** → O_2 reduction (ORR)

(2) ***"Electrolyzer"*** → O_2 evolution (OER)

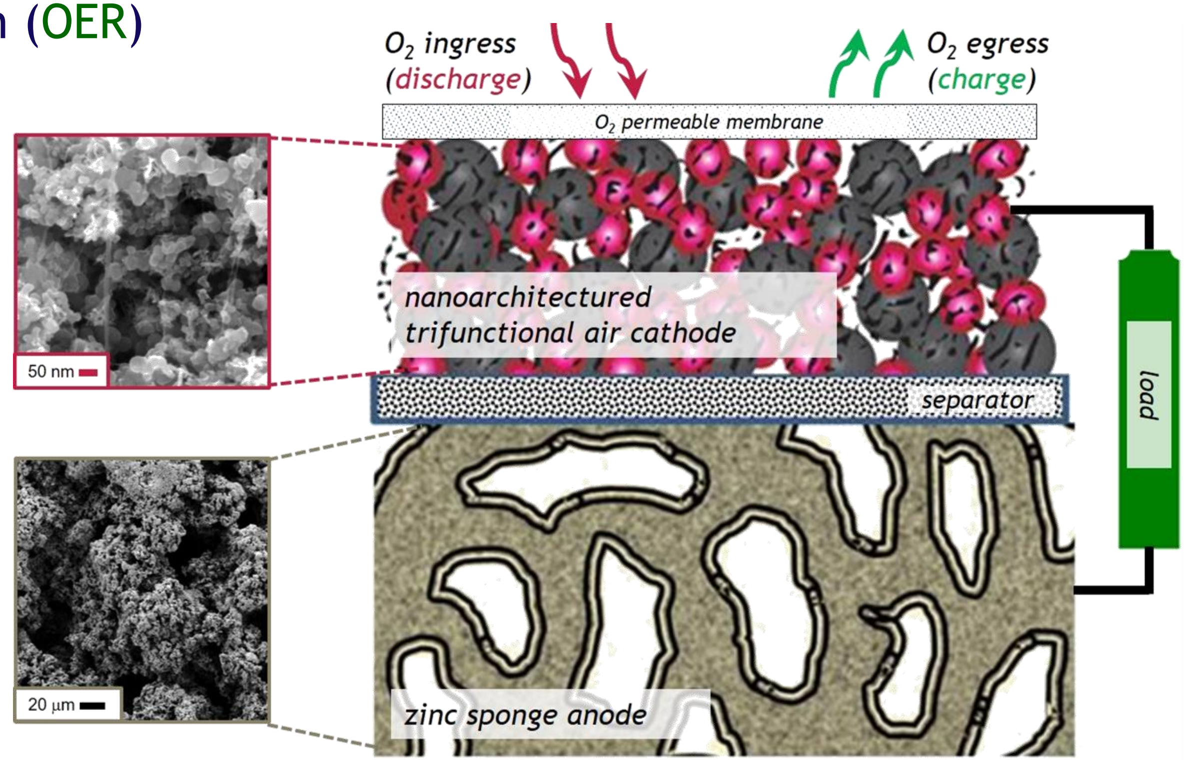
(3) ***"Electrochemical capacitor"***
→ Pulse power

"Trifunctional" air cathodes

(4) ***"Battery"*** → Reversible Zn



No Dendrites!

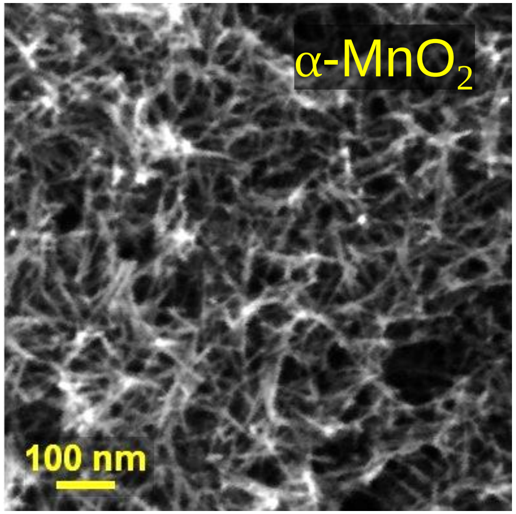


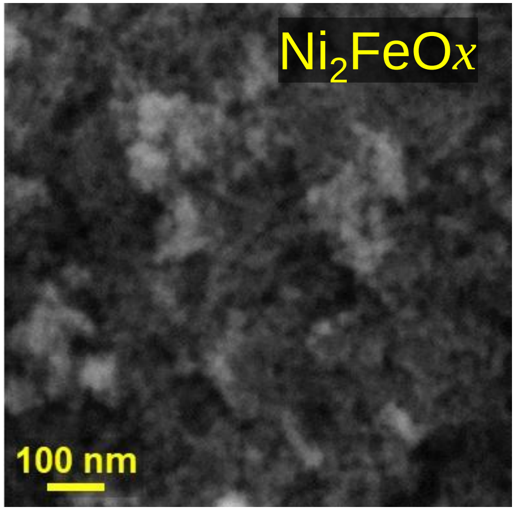
Overall reaction: $2Zn + O_2 \leftrightarrow 2ZnO$

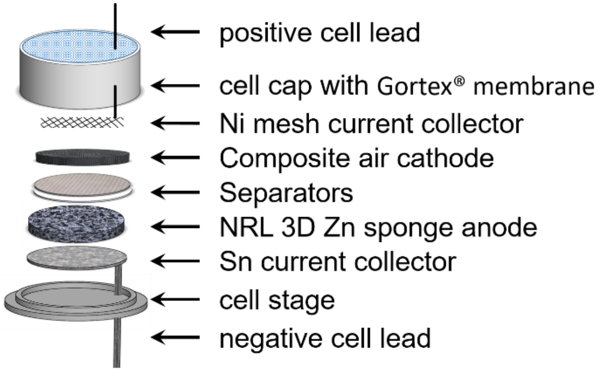
✓ Target specific energy of 300 Wh kg^{-1} with >500 cycles

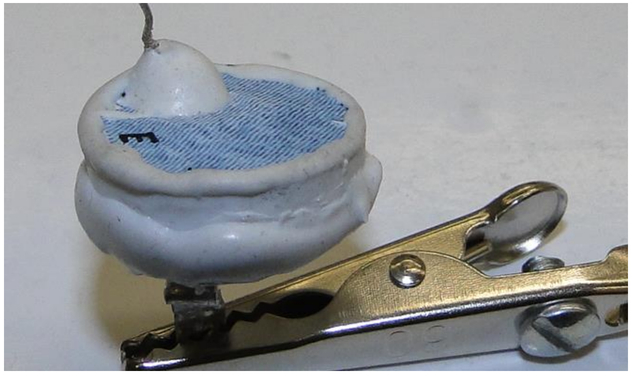
Rechargeable Zn–air:
3D Zn + Nanoarchitectured e-catalysts

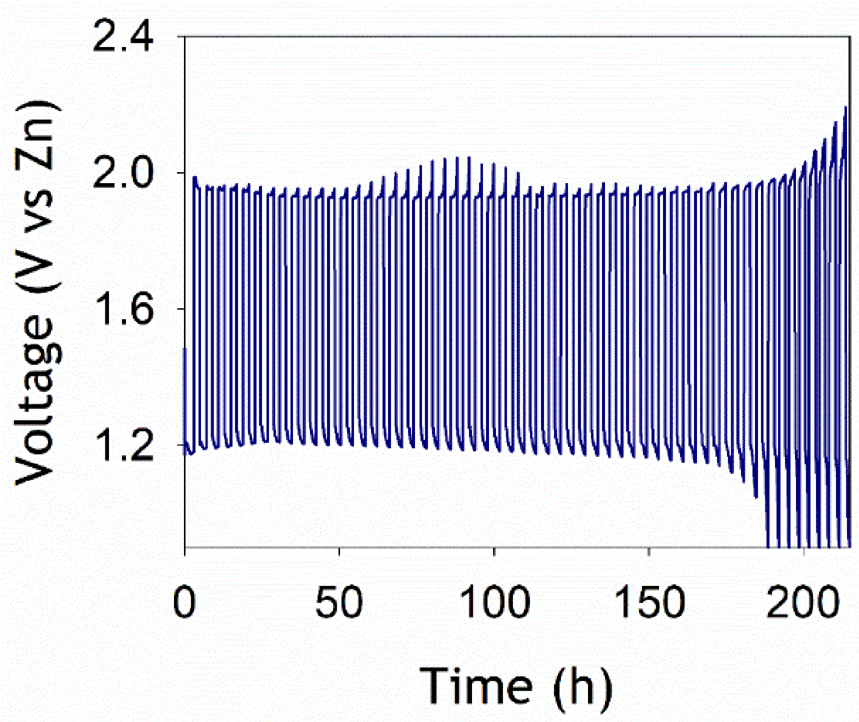
Air cathode comprising two aerogel-type electrocatalysts











Promising initial cycling, but additional optimization of air cathode needed to reach cycle-life goals

Chervin, Hopkins, Hoffmaster, Skeele, Ko, Parker, Long, Rolison, *J. Power Sources (submitted)*

Revisiting Zn–MnO_2 chemistry: Rechargeable "Zn-ion" batteries

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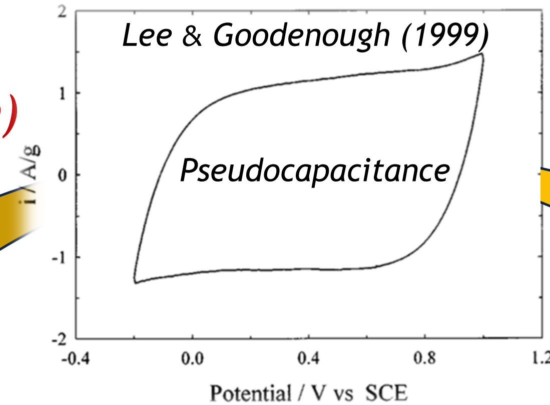
- ❑ *Asymmetric ECs (e.g., MnO_2/carbon)*



Toupin, Brousse Belanger, Chem. Mater. (2004)

- *Up to 1 e⁻ per Mn for thin-film MnO_2 @ Pt*

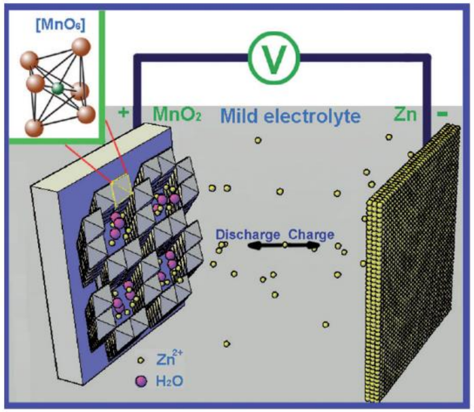
- ○ *Mild-pH electrolyte*
- ○ *Cation-compensated redox*
- ○ *Highly reversible*
- ○ *Moderate capacity*
- ○ *Fast response*

- ❑ *Primary alkaline Zn/MnO_2*

- ○ *Strong alkaline electrolyte*
- ○ *H^+-based redox @ MnO_2*
- ○ *Irreversible (mostly)*

? *Rechargeable "zinc-ion"*

- ○ *Mild-pH Zn^{2+} electrolyte*
- ○ *H^+ or Zn^{2+} redox?*
- ○ *Reversible (mostly)*
- ○ *High capacity*



Xu *et al. Angew. Chem. Int. Ed.* **2012**

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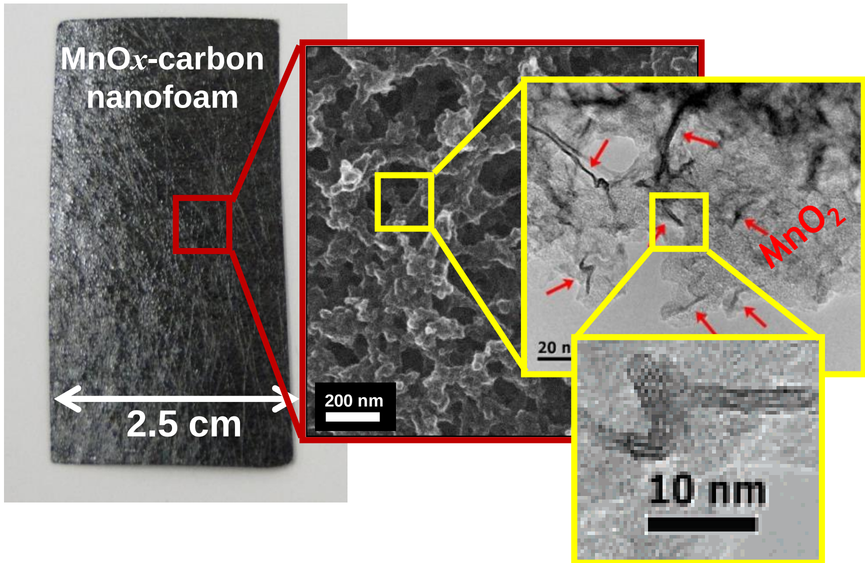
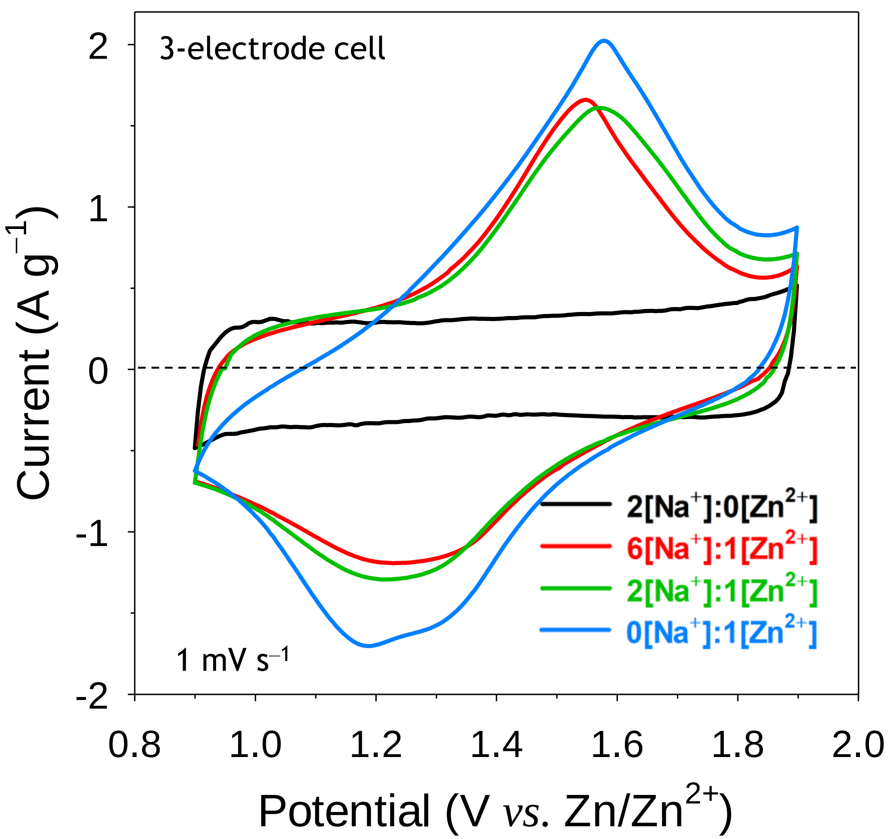
Rechargeable Zn–air: The Holy Grail of zinc batteries



- Partially exchange $ZnSO_4$ for Na_2SO_4 in aqueous electrolyte to tap MnO*x* pseudocapacitance mechanisms

Molar concentration of electrolyte	Electrolyte notation (atom:atom ratio)
1 M $ZnSO_4$	0[Na^+]:1[Zn^+]
0.5 M Na_2SO_4 + 0.5 M $ZnSO_4$	2[Na^+]:1[Zn^+]
0.75 M Na_2SO_4 + 0.25 M $ZnSO_4$	6[Na^+]:1[Zn^+]
1 M Na_2SO_4	2[Na^+]:0[Zn^+]



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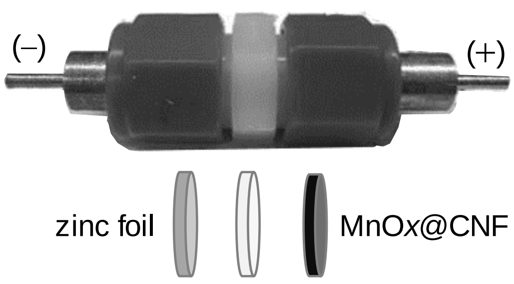
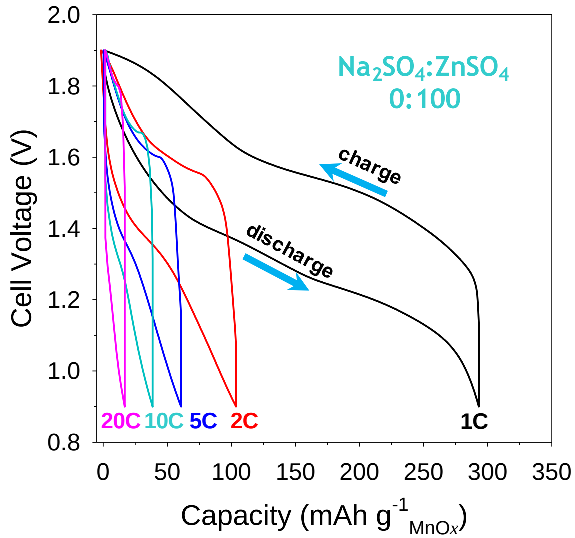
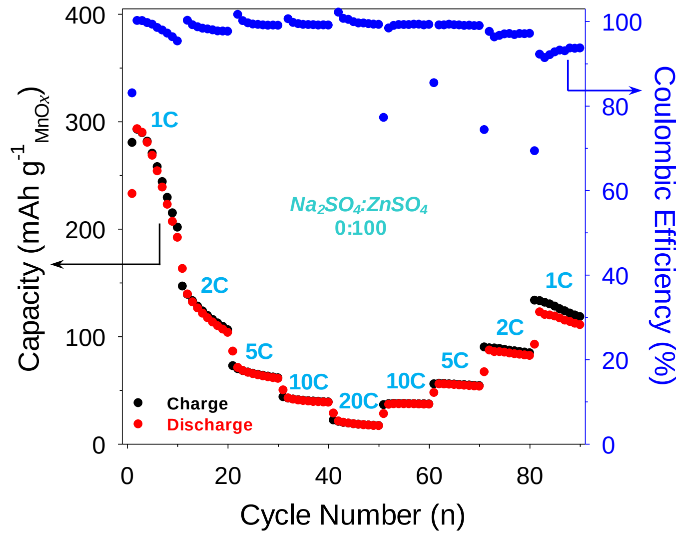
Rechargeable Zn-ion + power!
(power requires a cathode architecture)

PFA Swagelok Cell

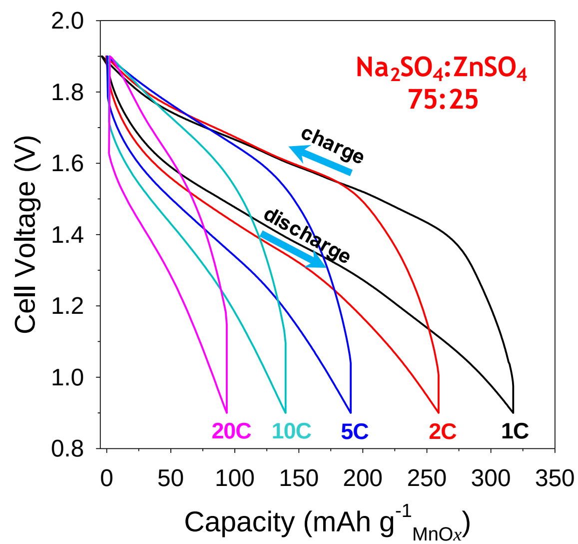


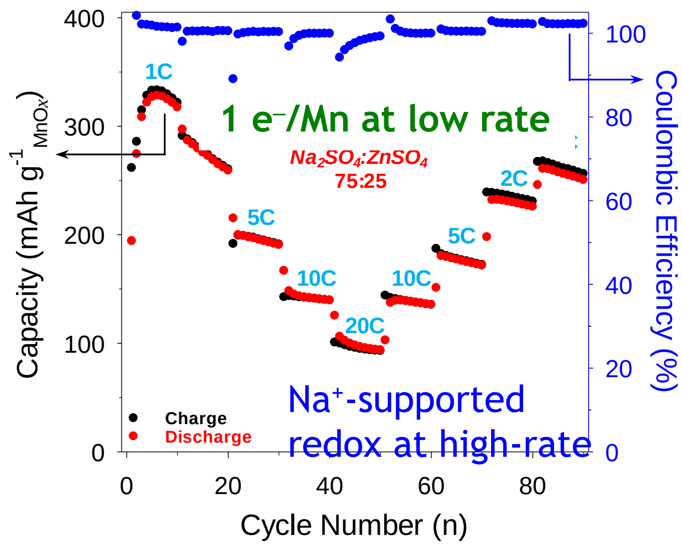




Mixed Zn^{2+}/Na^{+} electrolyte yields:

- ✓ Greater capacity retention with increasing rate
- ✓ Greater recovery in capacity upon return to slow rates





The Path Forward for Next-Gen Zinc Batteries