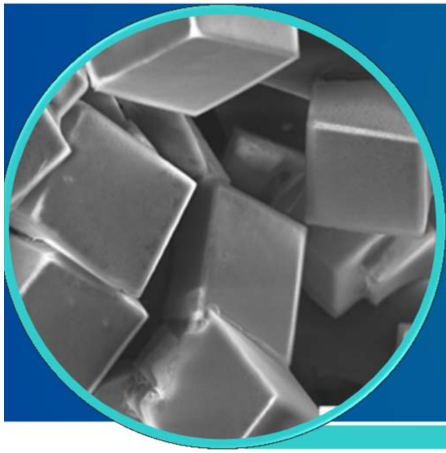
NAATBatt Workshop on Zinc Battery Technology: Mechanisms for Increasing Cycle Life in Zinc Batteries



Development of Zinc Ion Batteries for Advanced Electrochemical Energy Storage

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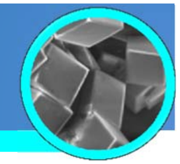
Electrochemical energy storage: challenge of the century?



Exploit renewable energy resources

Power the world: big computing, small devices

Electric vehicles, drones

Different energy needs

Different materials

Different cost point

MWh

Wh – MW

kWh

Non-aqueous Li-ion batteries not necessary

olar is dropping around the world

What are the options for electrochemical energy storage?

- **low cost**
- **reliable, safe**
- **dispatchable**
- **high power**

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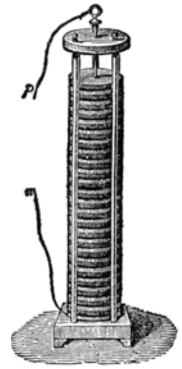
Aqueous Zn- batteries: Zn metal “ideal” anode for H_2O

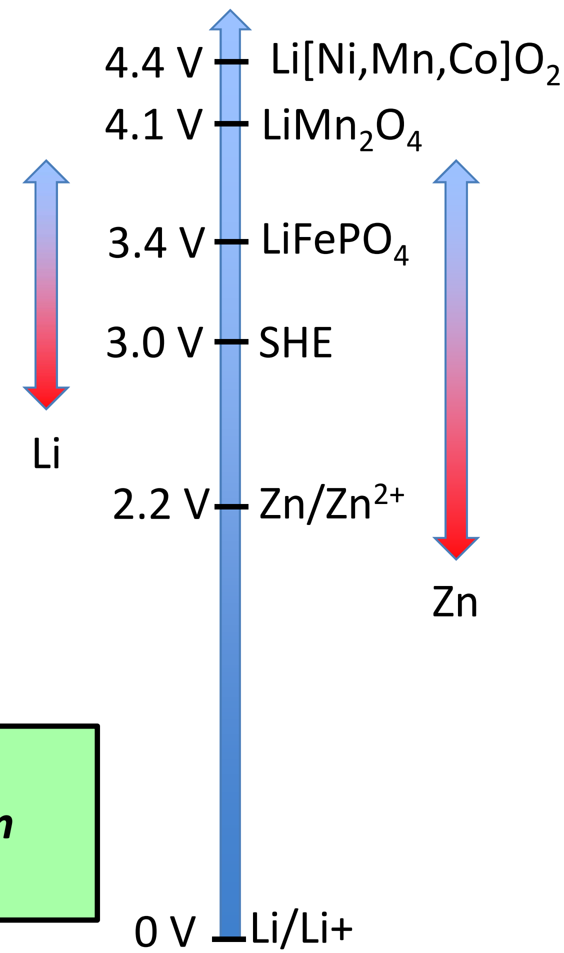
Why Zn metal ?

Early inception:
Volta Pile 1800



- stable in water: high corrosion resistance
- high abundance, production; non toxic
- suitable redox potential (-0.76 V vs. SHE)
- high volumetric energy density (d: 7.14 g cm^{-3})
- small exchange current for hydrogen evolution
- **large kinetic voltage window ~2.4 V due to overpotential**
- Zn anode - low-cost, safe, easy to manufacture and recycle

Safe and environmentally benign alternatives BUT
must prevent dendritic formation/surface passivation that limits cycle life of alkaline cells!



Highly reversible Zn stripping and plating at pH < 7

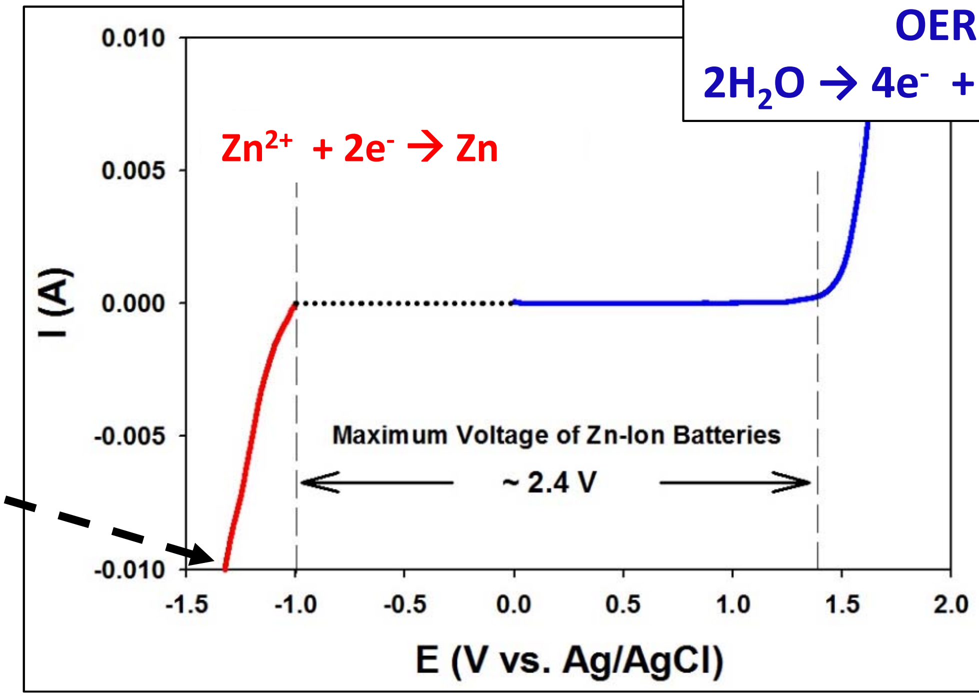
Overpotential for hydrogen evolution is strongly dependant on the type of electrode used

HER

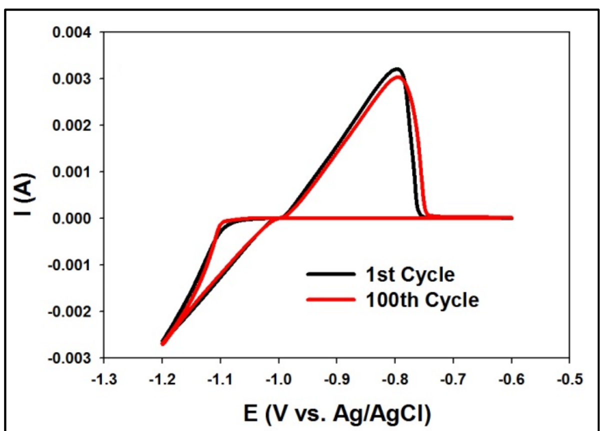
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

OER

$2H_2O \rightarrow 4e^- + 4H+ O_2$



Electrolyte: 1M $ZnSO_4$-H_2O



- **$Zn^{2+} + 2e^- \leftrightarrow Zn$ with ~100 % coulombic efficiency (Q_{ox}/Q_{red})**
- **Rechargeable aqueous Zn-ion batteries: ~2.4 V window**
- **No dendritic growth at pH < 7**

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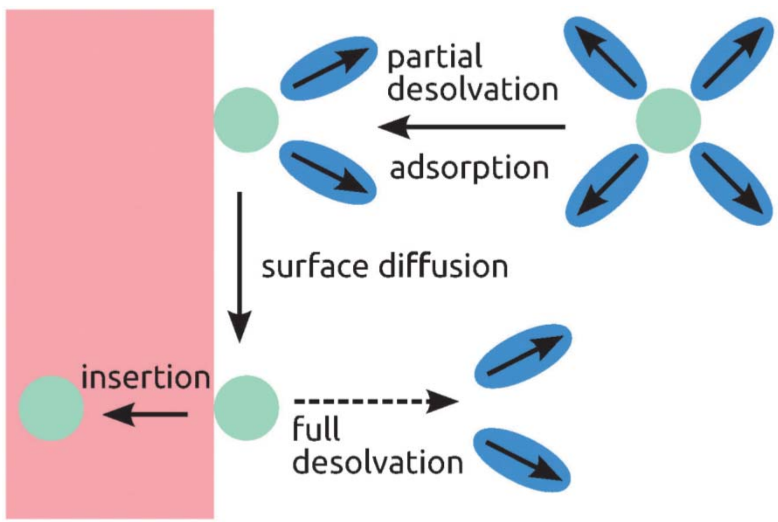
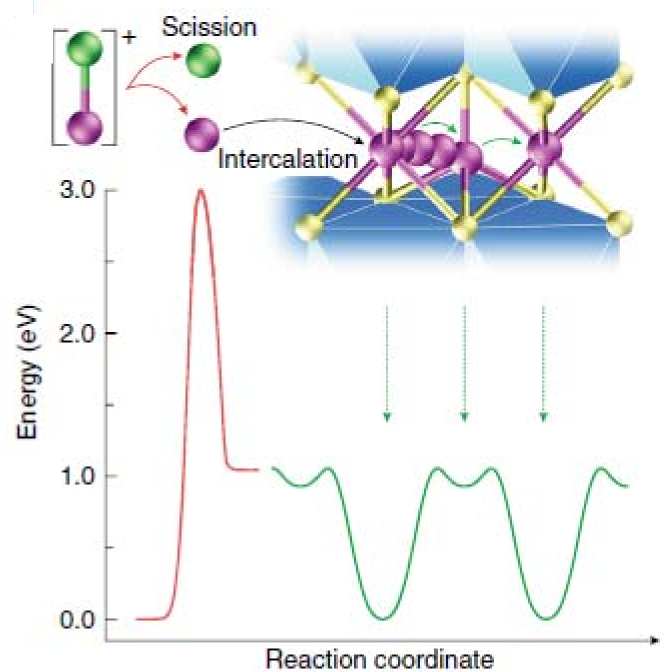
How about Zn^{2+} intercalation? Kinetic limitations

Increased electrostatic interaction compared to monovalent ions leads to:

1. **Large desolvation penalty** at the electrolyte-electrode interface
2. **Relatively high barrier for diffusion** through host lattice

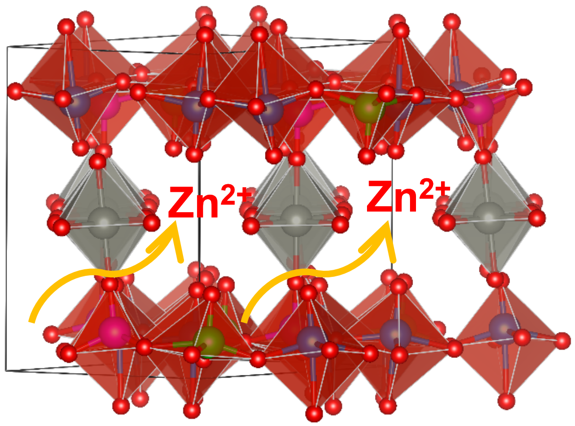


J. Lück and A. Latz, *Phys. Chem. Chem. Phys.*, 2016, **18**, 17799.



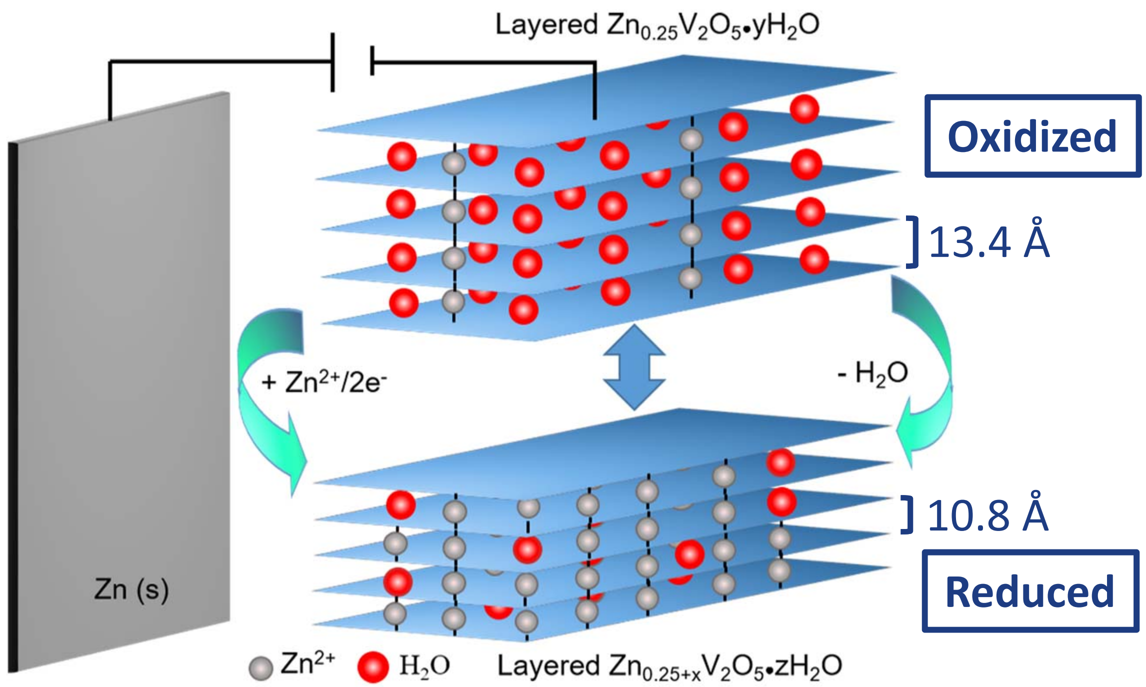
Y. Yao *et al.*, *Nat. Commun.*, 2017, **8**, 339.

A hydrated layered oxide cathode



$Zn_{0.25}V_2O_5$

- **300 mAh/g** capacity
- **450 Wh/L** energy density
- > 80% capacity retention for **1,000 cycles at full DOD**



D. Kundu, L. F. Nazar *et al*, *Nature Energy*, 2016, **1**, 16119.

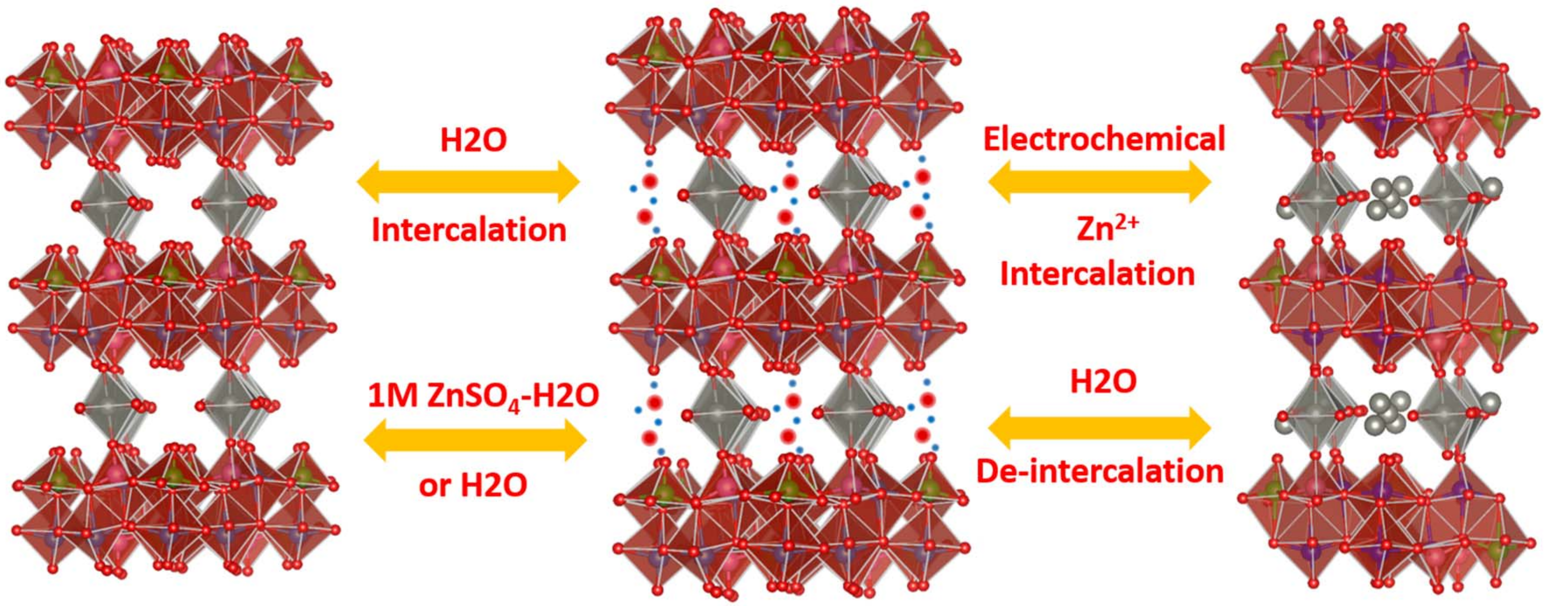
1. Intercalating ion does not require full de-solvation from solvent shell
2. Solvent co-intercalation enhances mobility by screening divalent charge in lattice
3. Ion pillars stabilize the layered structure and prevent degradation on cycling

$Ca_{0.25}V_2O_5$: C. Xia, H. Alshareef et al., *Angew Chemie*, 2018;
$Na_{0.25}V_2O_5$, $K_{0.25}V_2O_5$, D. Chao et al, *Adv. Mater* 2018; $Mg_{0.25}V_2O_5$...

Layered host: Water assisted facile Zn^{2+} intercalation

$$Zn_{0.25}V_2O_5 + 1.1\ Zn^{2+} + 2.2e^- \leftrightarrow Zn_{1.35}V_2O_5$$

Specific energy: 175 Wh/kg
(positive + negative electrodes)



Pristine host Structure	Expanded host structure in electrolyte	Zn^{2+} intercalated host

Stable operation: no gas evolution or dendrites

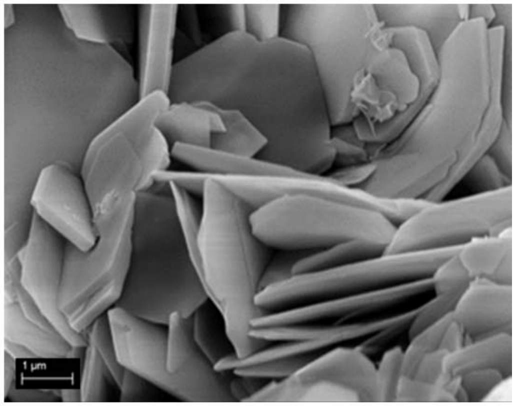
Operando Mass Spectrometry

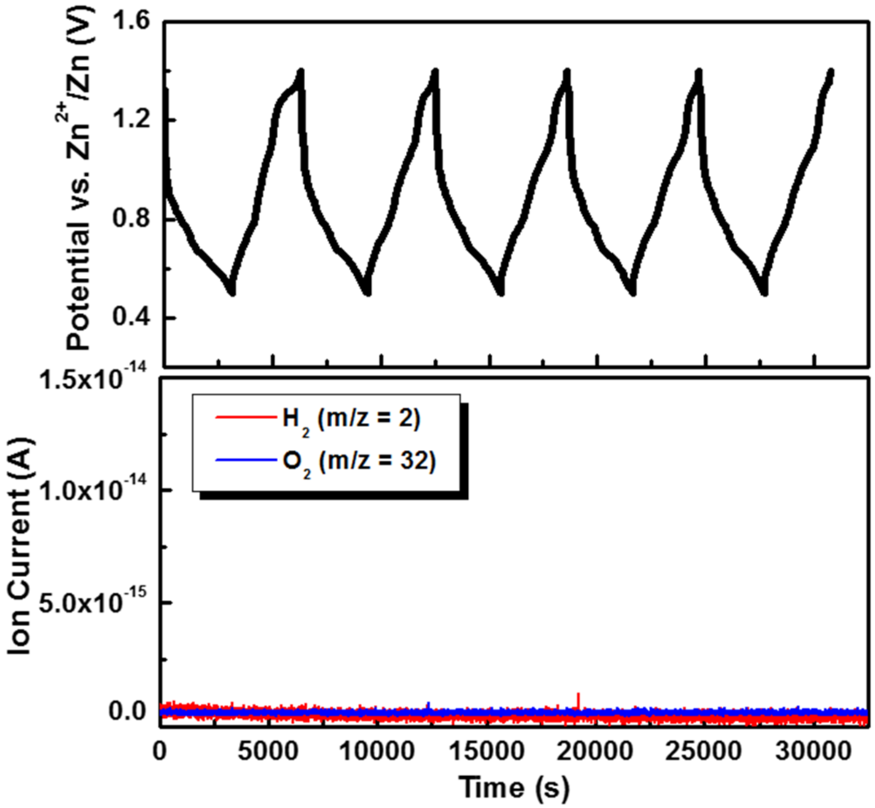
↓

No gas evolution detected

↓

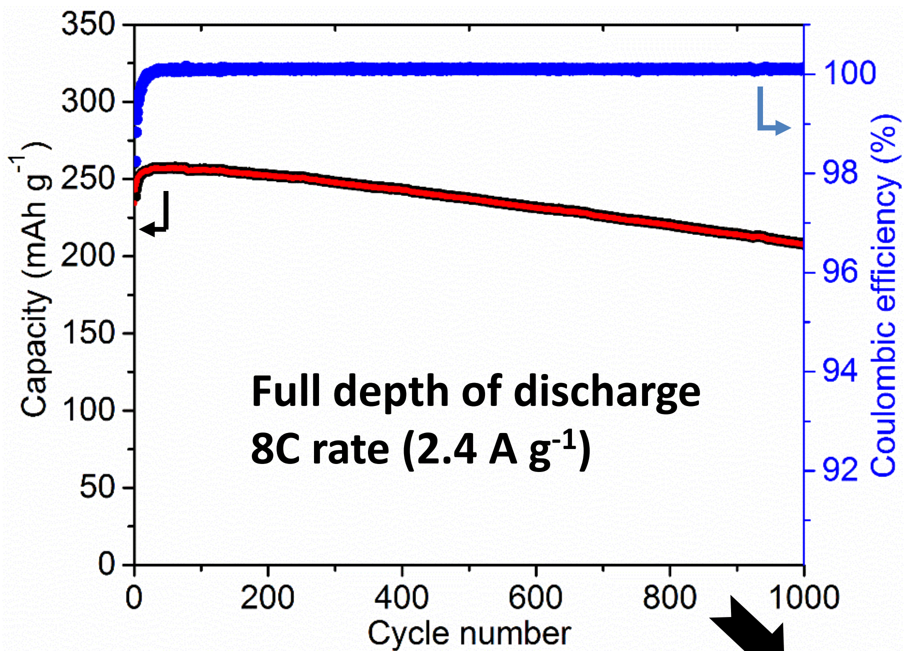
No Zn dendrite formation

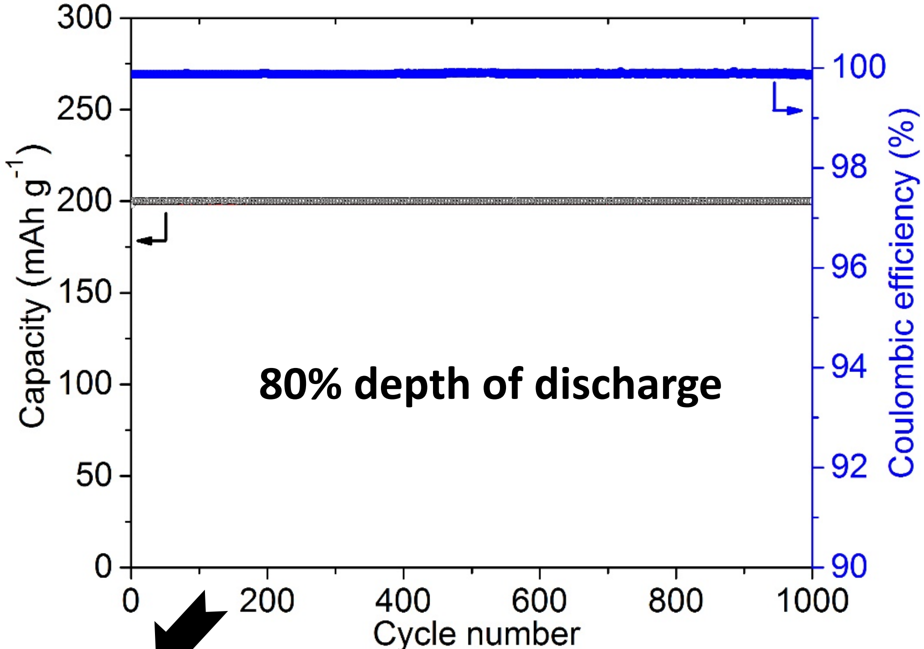




SEM of the stripped Zn electrode after cycling a Zn//1 M $ZnSO_4$//zinc symmetrical cell, current density 10 mA cm^{-2}

Reversible & sustainable Zn^{2+} storage





- **Highly reversible Zn intercalation & stable cycling**
- **1000 cycles: ≥ 80 % capacity retention (full DOD)**
- **1000 cycles: ~100 % capacity retention (80% DOD)**
- **Energy density (cathode + anode + sep): 450 Wh/L**
- **Coulombic efficiency: 99.7%**

raw materials cost
<< $60/kWh
non-battery grade V_2O_5

D. Kundu, L.F. Nazar *et al.*, *Nature Energy* (2016)

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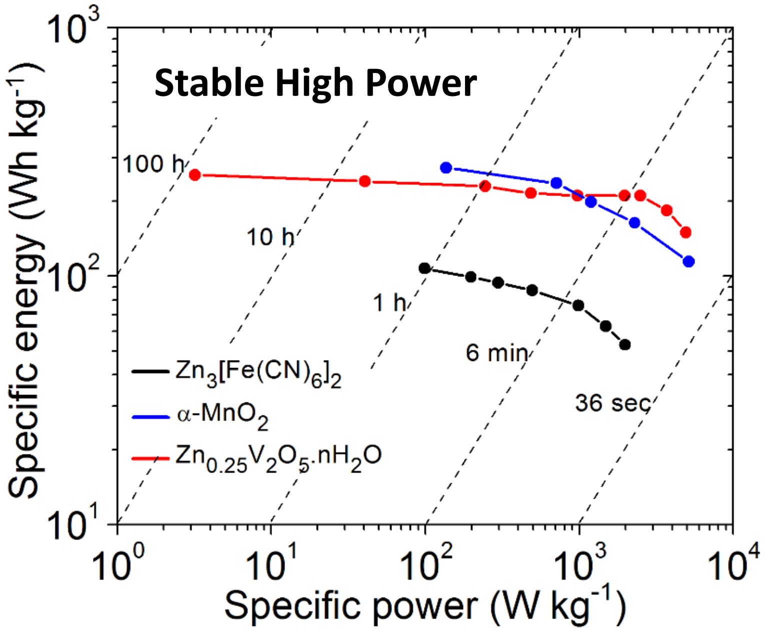
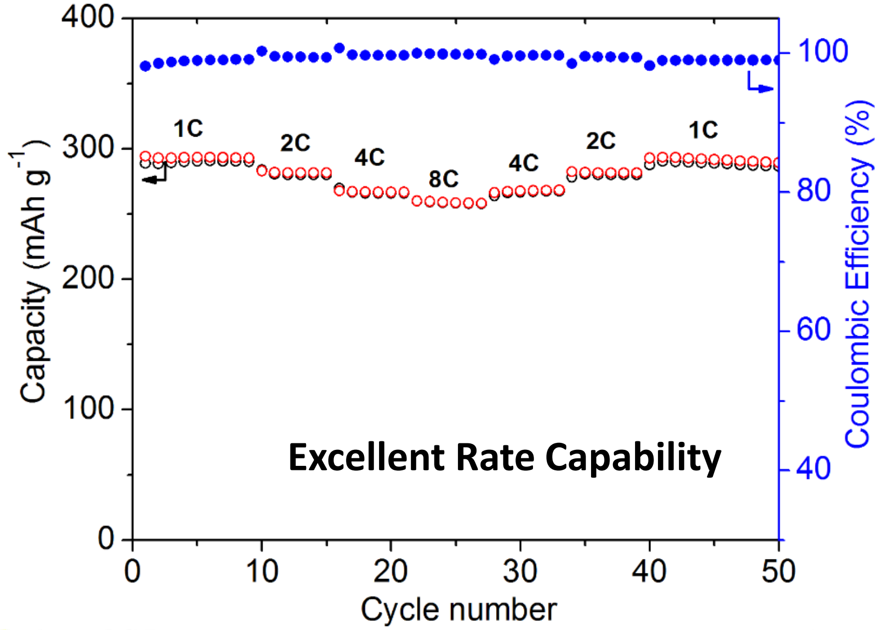
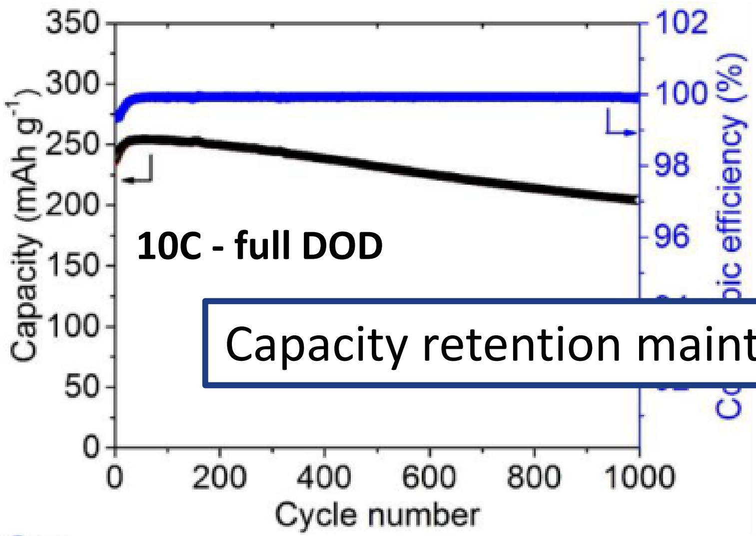
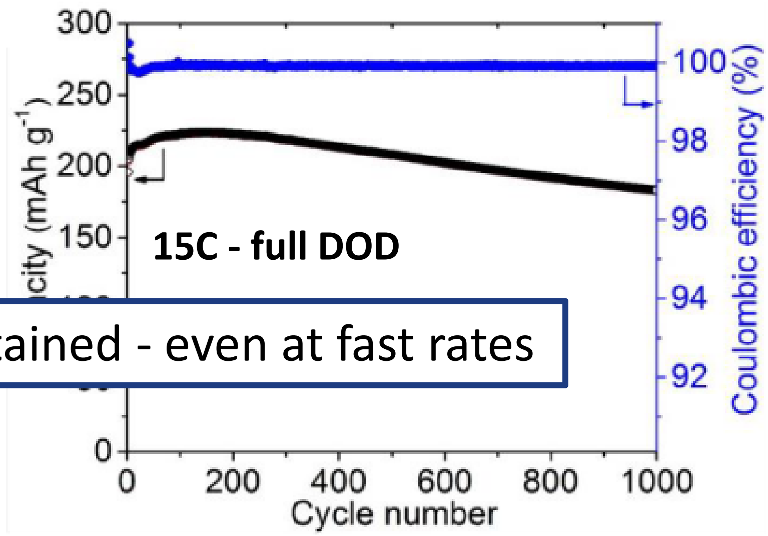
High rate performance



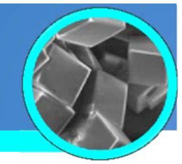






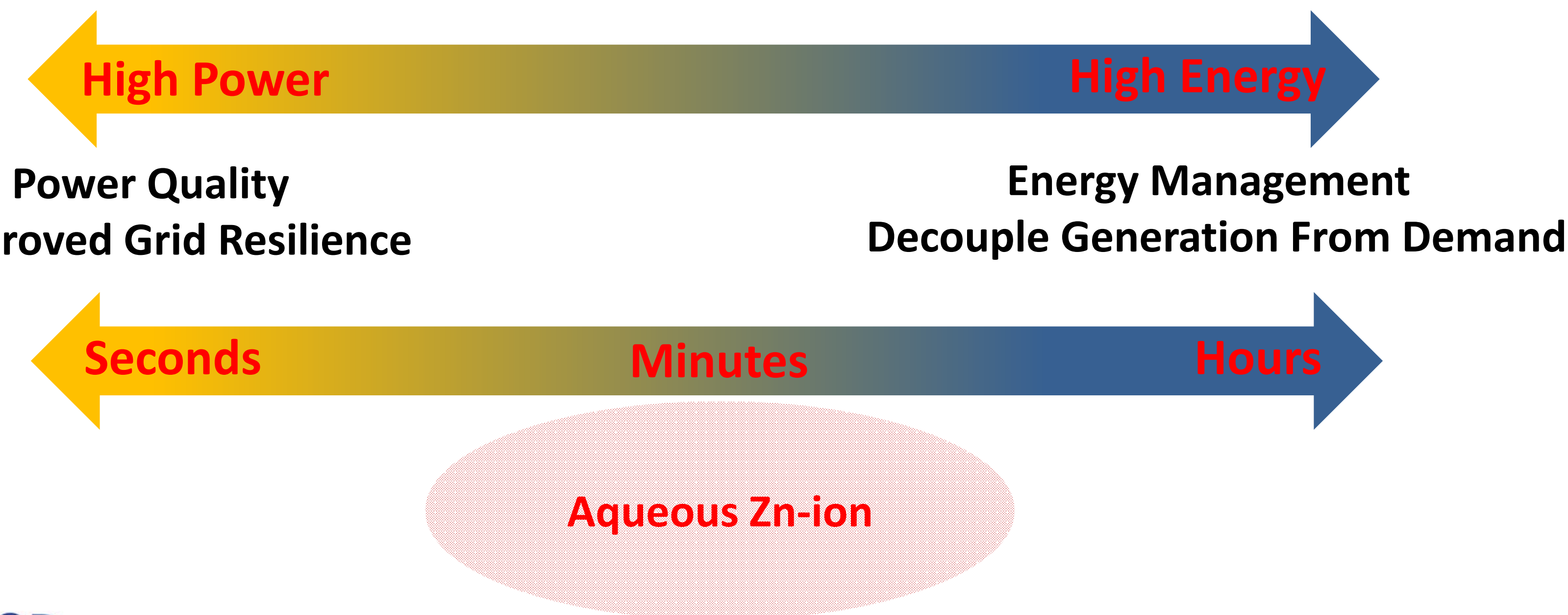
Capacity retention maintained - even at fast rates

Significance & Impact



Benefits of zinc ion batteries with pillared vanadium oxide electrodes:

- Good volumetric energy density of 400 Wh/L (½ Li-ion @ cell level but stackable)
- Excellent rate performance and cyclability
- Scalable & green (only water) synthesis and electrode processing
- Inexpensive raw materials (highly abundant Zn, non-battery grade V, cost-effective (in air) and easy cell fabrication)
- Low cost and safe aqueous electrolyte (salt + H_2O)



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