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New Aqueous Zn Chemistries

Kang Xu

Electrochemistry Branch, SEDD
U. S. Army Research Laboratory

Chunsheng Wang

Department of Chemical and Biomolecular Engineering, University of Maryland

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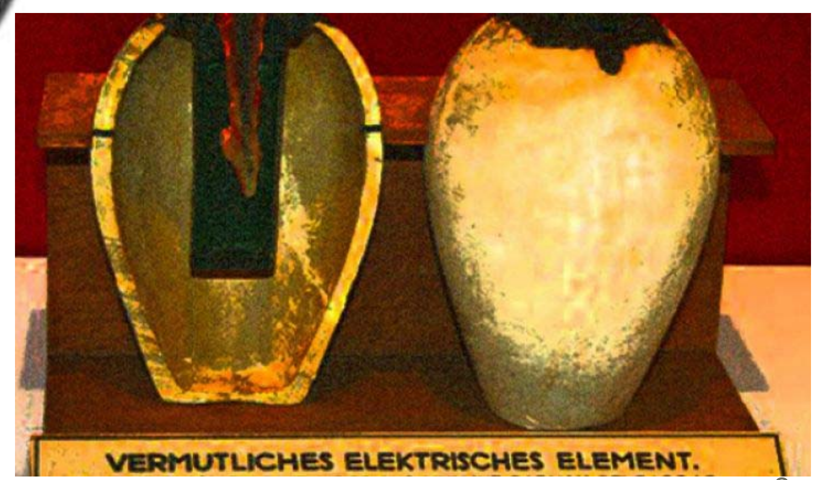
THE GLORIOUS PAST OF ZINC

- The earliest battery was not based on Cu/Fe chemistry
  - So-called “*Babylon Battery*”
- But instead on Zn chemistry
- Alessandro Volta (1799)



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ZINC BEGETS LITHIUM

SECTION III. *Lithium.*

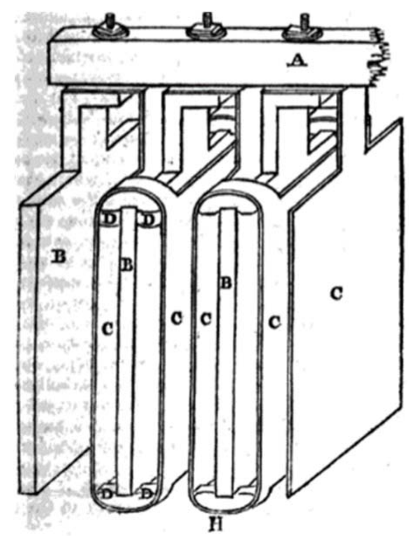
607. IN the analysis of a mineral, called *petalite*, M. Arfwedson discovered about three *per cent.* of an alcaline substance, which was at first supposed to be soda; but, finding that it required for its neutralization a much larger quantity of acid than soda, he was led to doubt its identity with that alcali, and the further prosecution of his inquiries fully demonstrated that it possessed peculiar properties. The mineral called *tri-*

608. When lithia is submitted to the action of the Voltaic pile, it is decomposed with the same phænomena as potassa and soda; a brilliant white and highly combustible metallic substance is separated, which may be called *lithium*, the term *lithia* being applied to its oxide.

The properties of this metal have not hitherto been investigated, in consequence of the difficulty of procuring any quantity of its oxide.

Brande (1821)
Manual of Chemistry

Thomas Brande



ZINC: PROS AND CONS

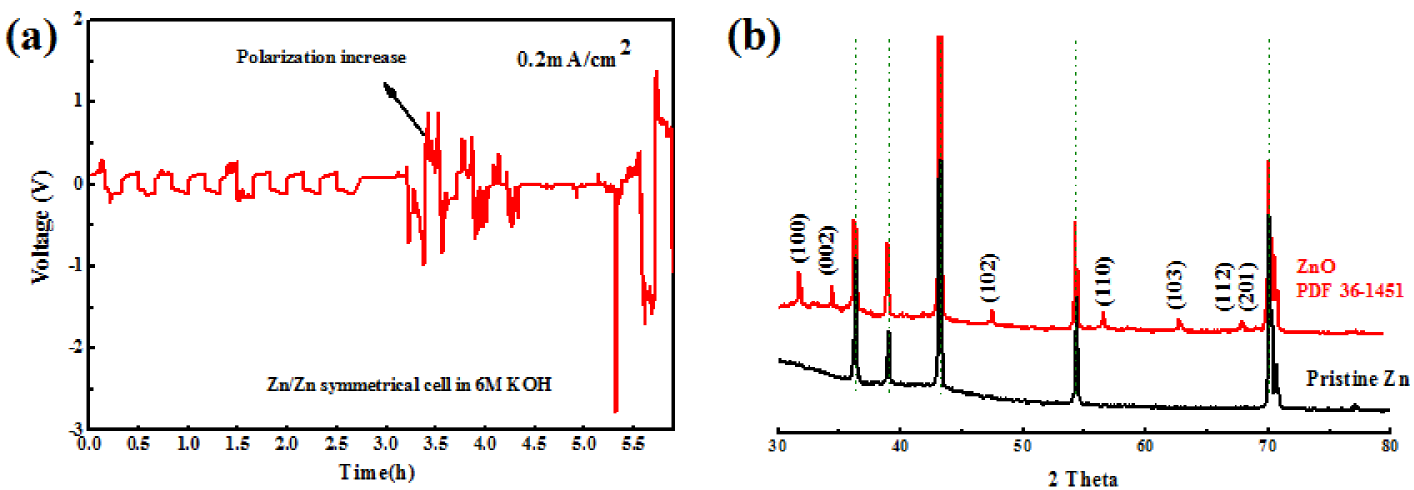
Advantages

- Abundance in earth crust
  - Low cost
- Workable in aqueous
  - Safety, low toxicity
- High capacity (820 mAh/g)
- Low V (-0.762 V)
  - Potentially high Energy

Challenges

- Irreversibility
  - Low CE
- Consumption of both Zn and water
- Dendrite

- Alkaline condition promotes dendrite
- Inactive ZnO forms eventually



OVERVIEW

Zn anode reversibility

- Altering Zn-solvation sheath

Zn^{2+} Intercalation Mechanism

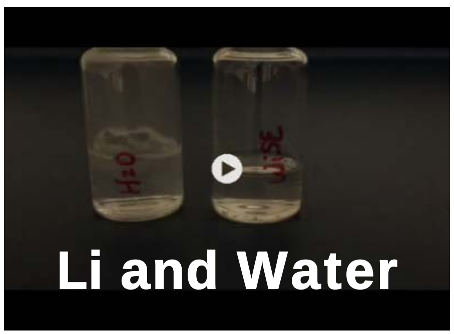
- Role of H_2O molecule

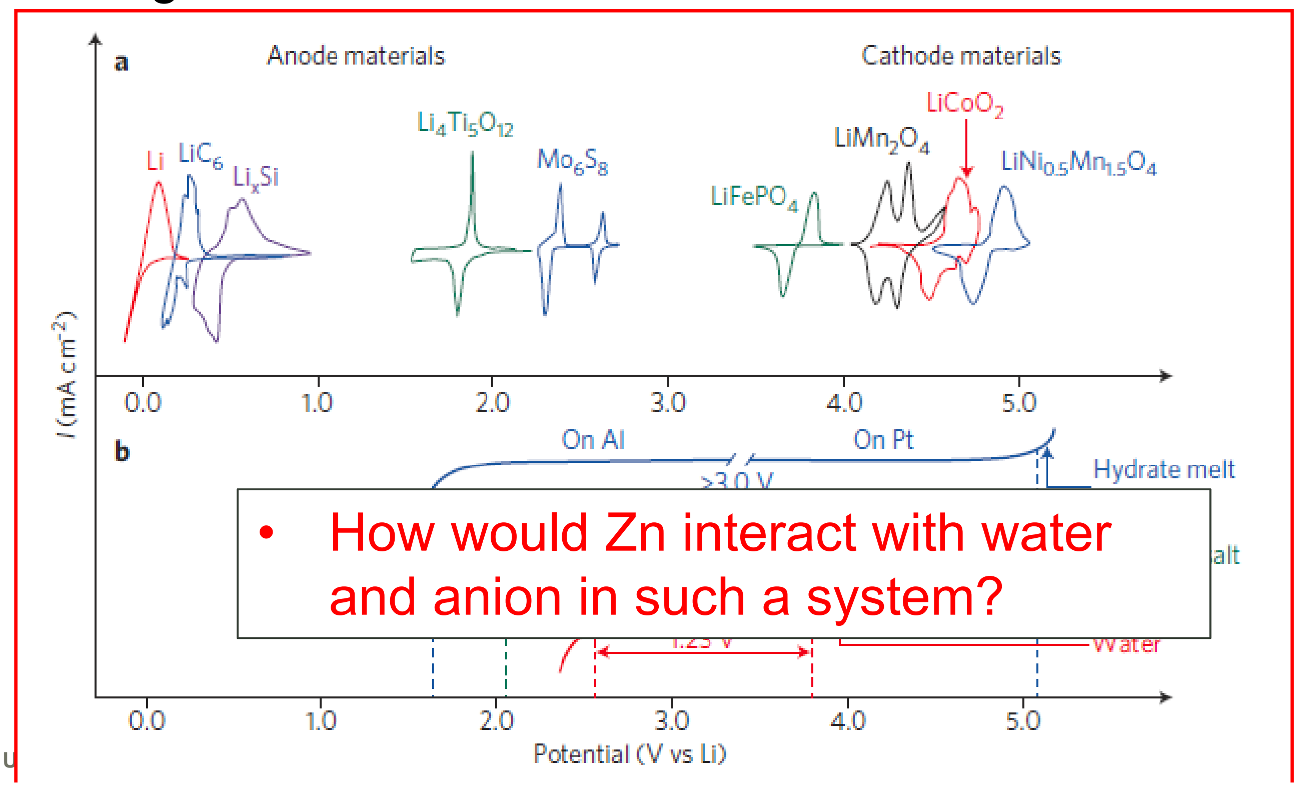
Zn^{2+} Intercalation Chemistry

- New cathode intercalation hosts

HIGH V AQUEOUS ELECTROLYTES

- Initially developed for Mg
  - Basic concept: drastically alter solvation sheath of cation
    - So that interphase changed
- Demonstrated for Li-ion chemistries
  - Stable vs. ambient
- Can support open cell configuration

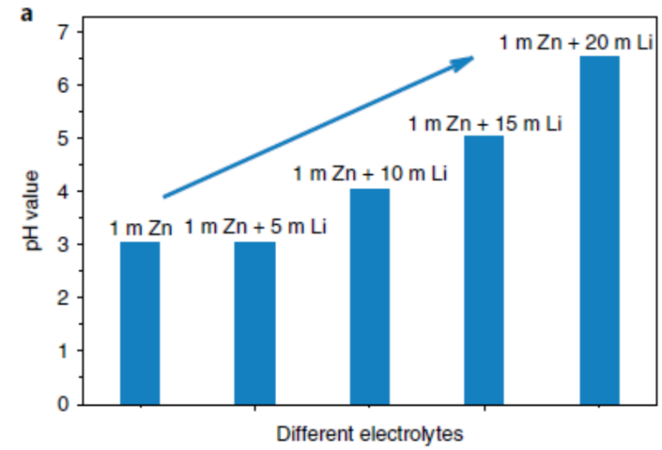


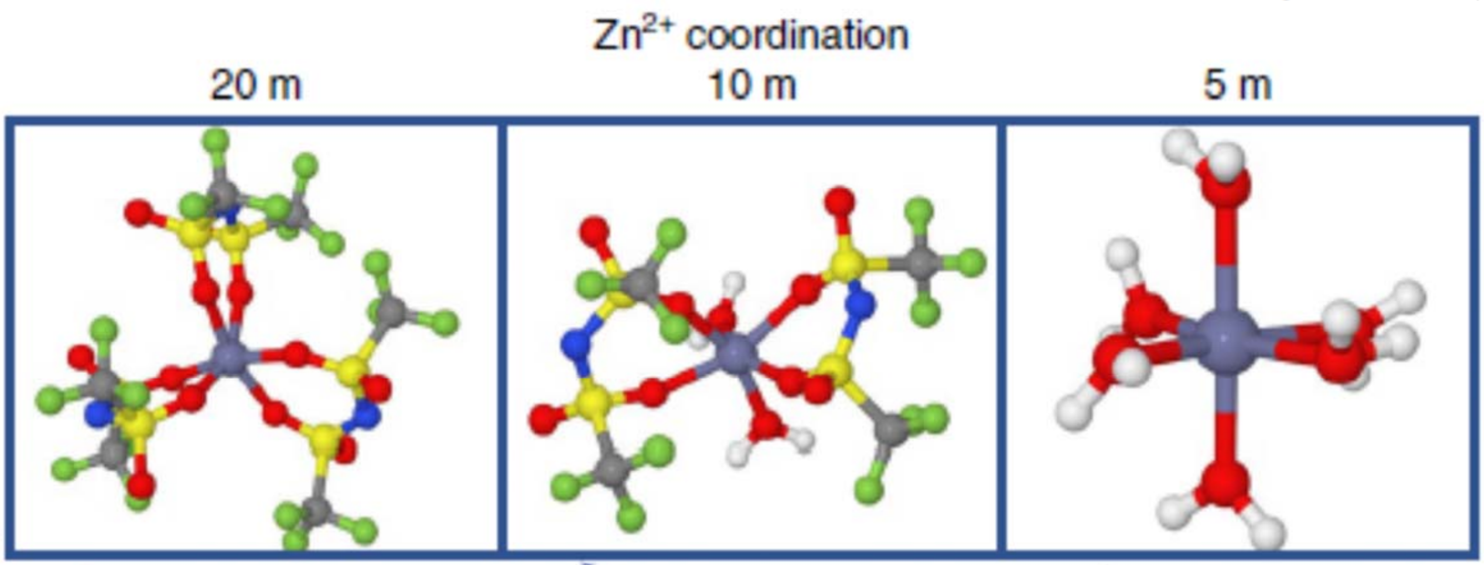


- How would Zn interact with water and anion in such a system?

ZINC SOLVATION SHEATH RESTRUCTURED

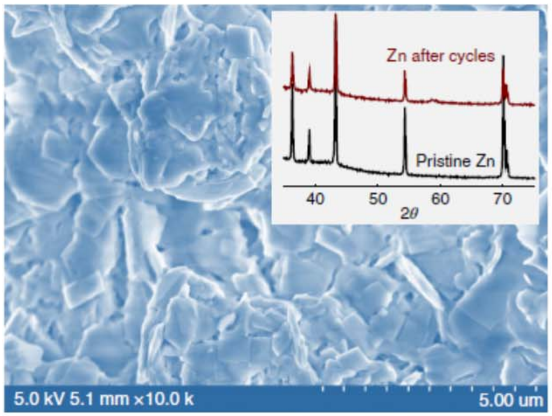
- High Li salt concentration (21 m LiTFSI) compete for H_2O solvation
  - Zn-solvation sheath dominated by anions
    - Formation of $Zn(OH)_6$ (and hence ZnO) prevented
- TFSI is a super-acid anion
  - Hence $Zn(TFSI)_2$ is nearly neutral
    - Dendrites prevented
- H_2O activity significantly reduced
  - Water stability limits expanded

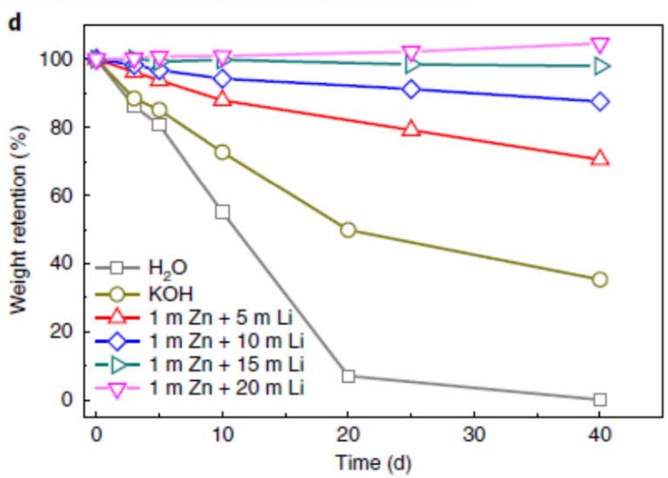


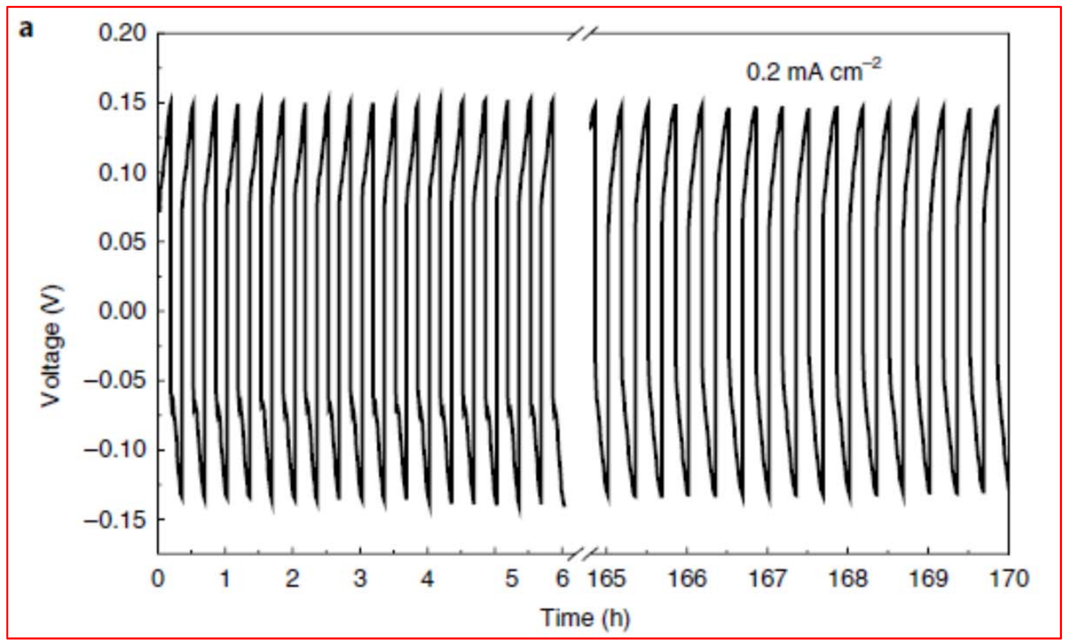


BENEFITS FROM THE NEW SOLVATION STRUCTURE

- A different deposition mechanism
  - High CE 99.8~99.9%; ZnO-free
  - Non-dendritic deposition
- Non-evaporating electrolyte: open-cell configuration possible







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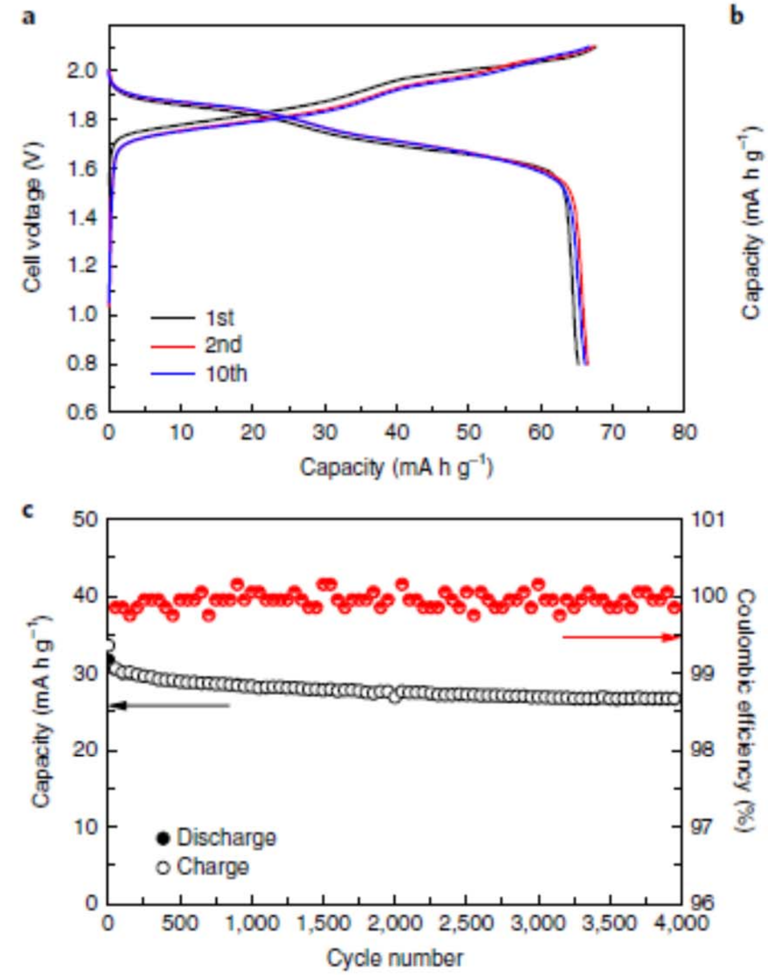
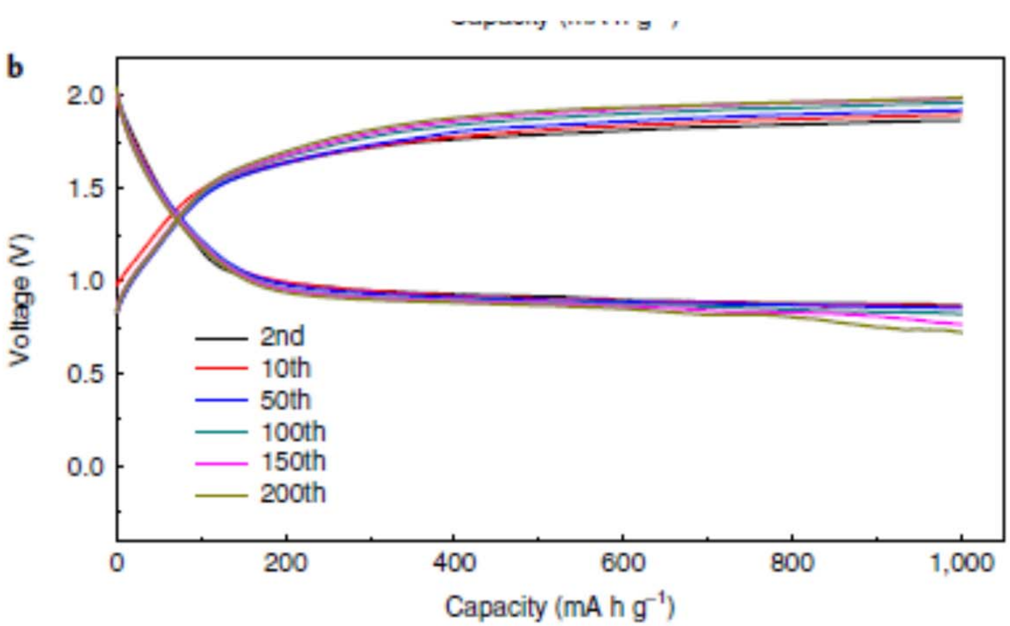
DEMO ON VARIOUS CHEMISTRIES

- A Hybrid Chemistry
  - Zn at anode; Li at cathode (LMO)
- Zn/O_2 Chemistry
  - No catalyst was used at cathode





Wang et al, *Nature Materials*. 2018

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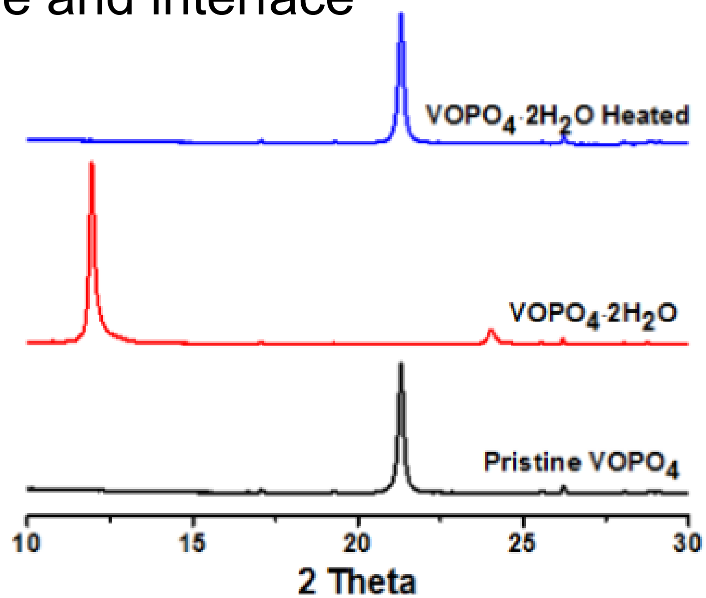
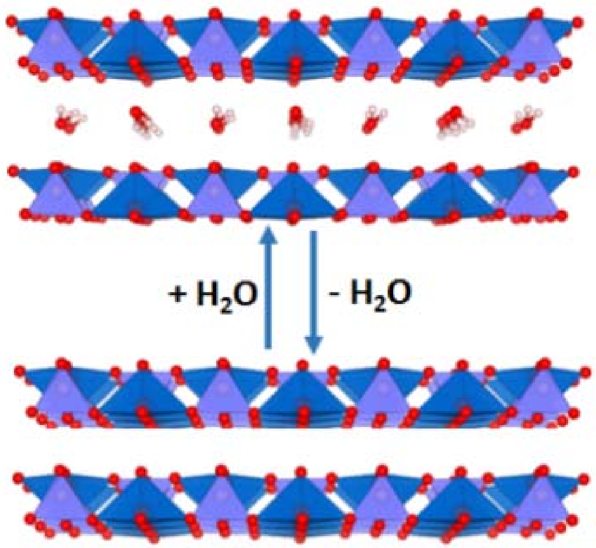
ZINC INTERCALATION MECHANISM

- Multi-valent cation experience much steeper desolvation barrier at electrolyte/electrode interface
- $VOPO_4$ selected as intercalation template
  - Zn^{2+}-intercalation kinetics studied as function of H_2O presence
  - H_2O at interface assists Zn^{2+}-transport across interfaces
  - H_2O in lattice dictates potential
  - H_2O equilibrium between bulk electrolyte, bulk electrode and interface





Wang et al, *Angew. Chem.* 2018

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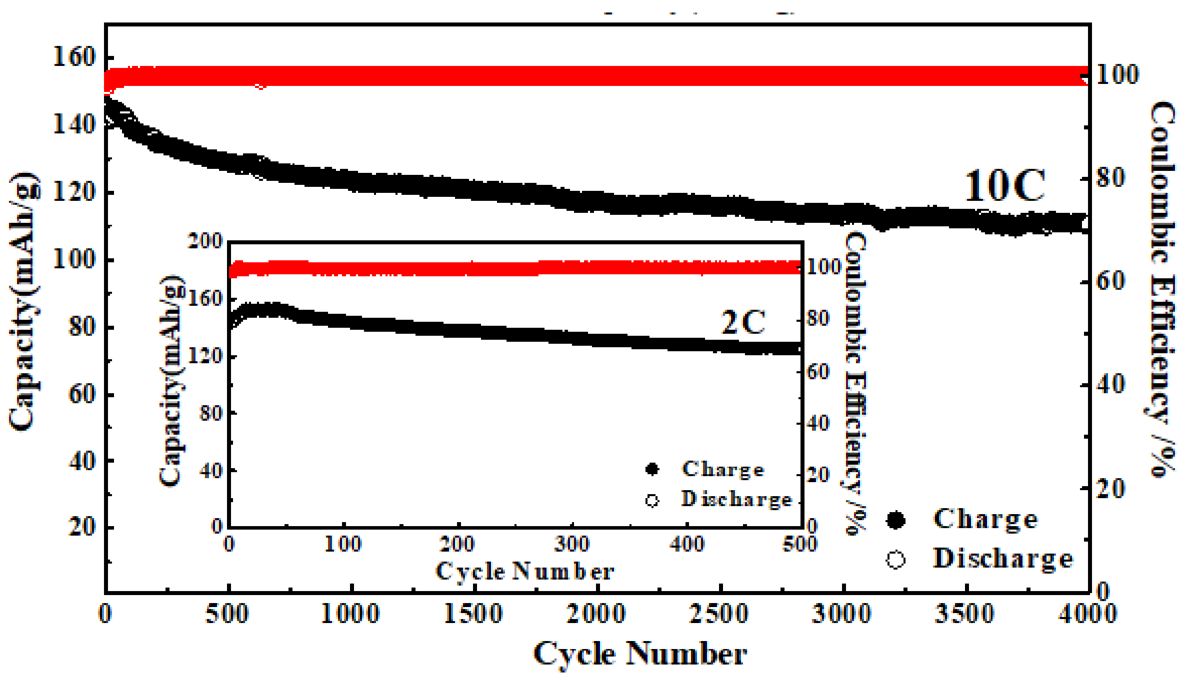
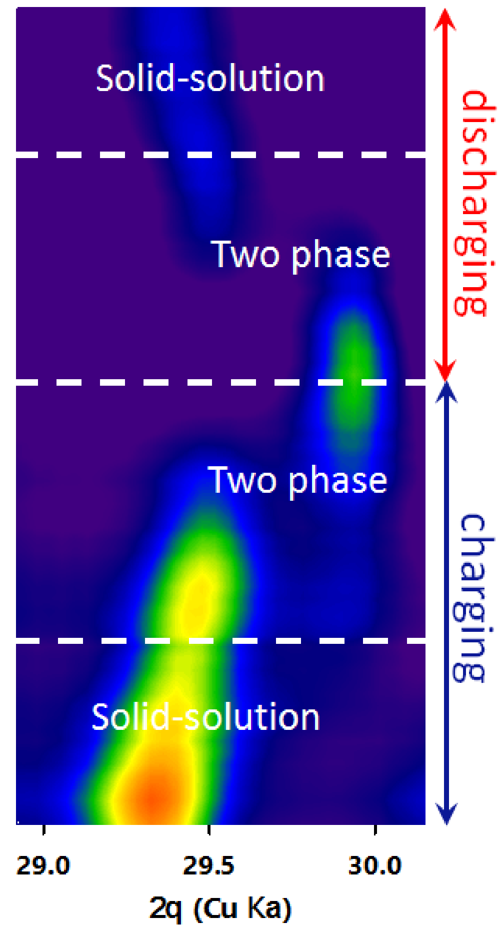
NEW INTERCALATION HOST FOR ZINC ION

- A ultra-fast/reversible Zn^{2+}-intercalation host was synthesized
- High power density (8000 W/Kg)
- Comparable energy density to LIB (218 Wh/Kg)
  - 150 Wh/Kg at cell level
- Stable cycling (4000 cycles)
- Mechanism still under investigation





Wang et al, under review

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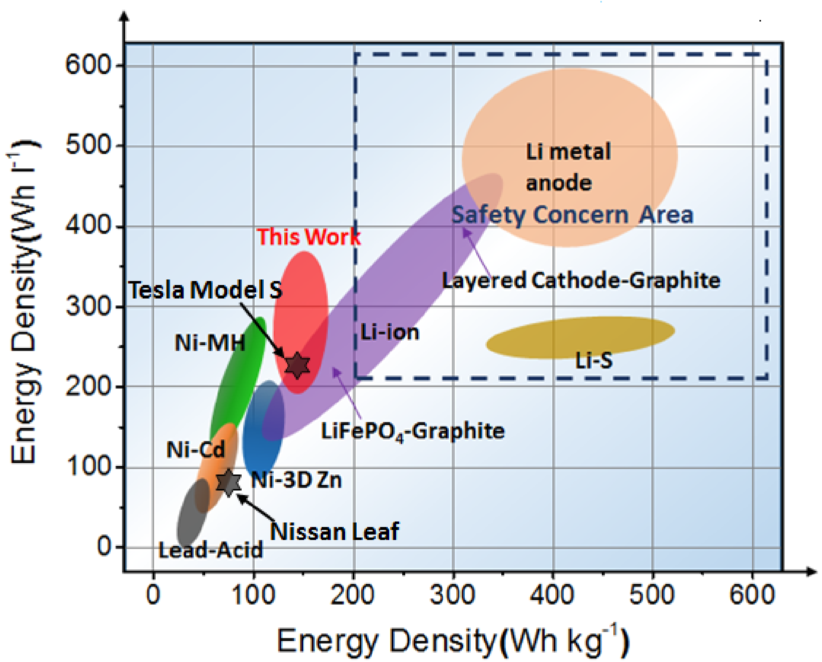
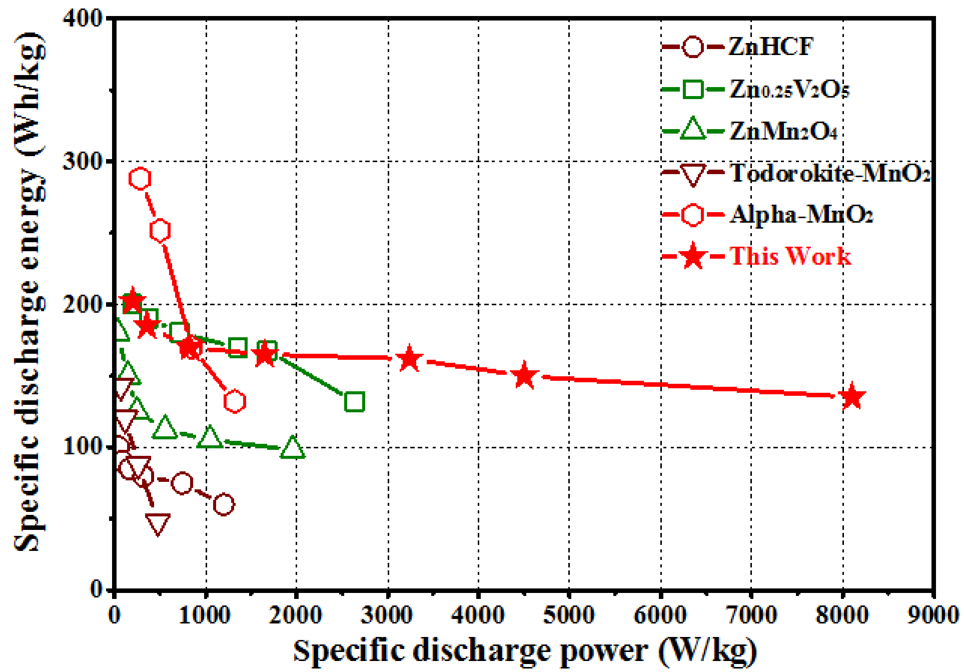
A COMPETITIVE CHEMISTRY WITH LIB

- The new chemistry provides an alternative to LIB
  - With comparable energy, much higher power and safety






Conclusion
A new horizon of “uncharted water”

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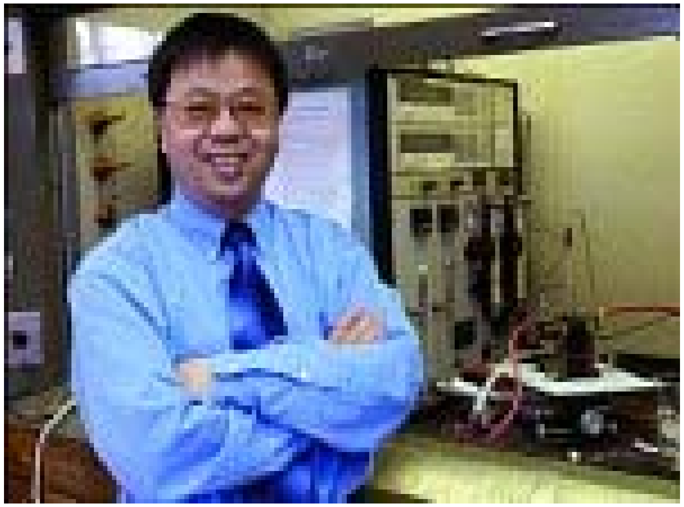

Chunsheng Wang
(UMD)

conrad.k.xu.civ@mail.mil
kang_xu@hotmail.com