Future Energy System Conference
April 10, 2019, Troy, NY

High Energy Aqueous Li-ion Batteries

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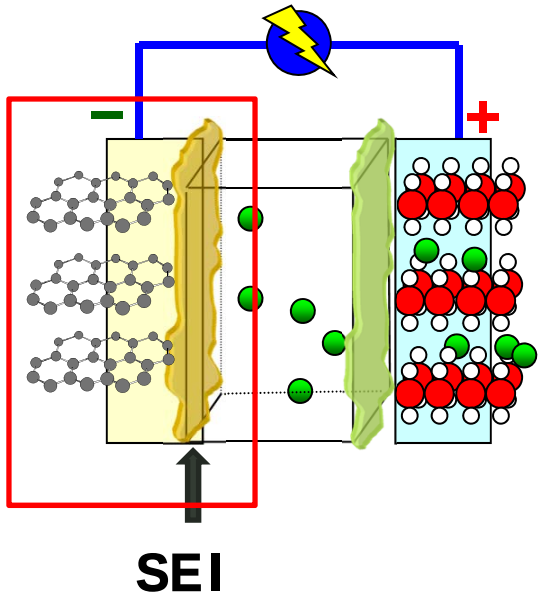
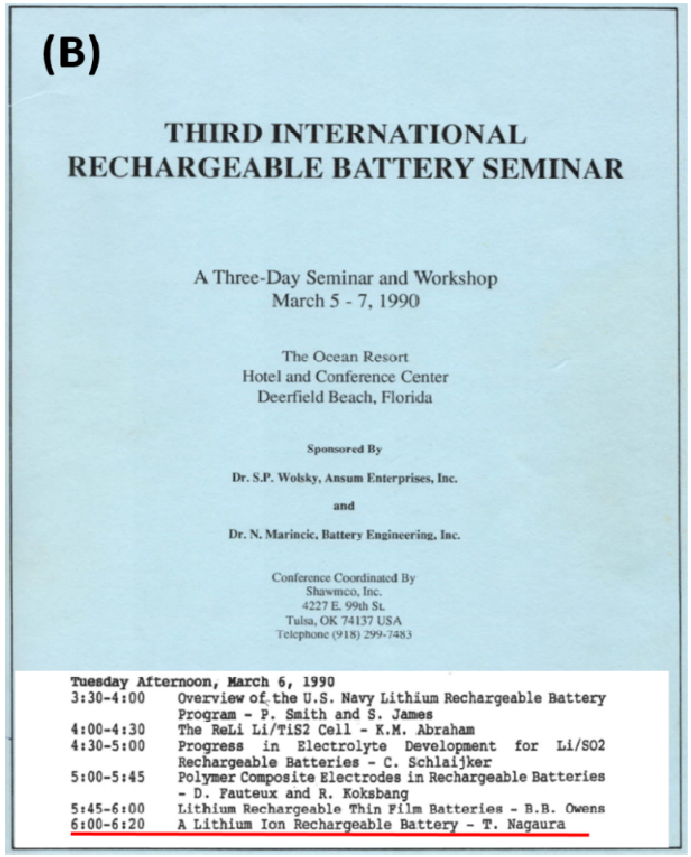
CCDC U. S. Army Research Laboratory

The first ever black hole photo

(taken for Galaxy M87, 55 Mln-Lys away)
9:00 AM, April 10, 2019

Li-ion Battery: 1990





(B)

THIRD INTERNATIONAL
RECHARGEABLE BATTERY SEMINAR

A Three-Day Seminar and Workshop
March 5 - 7, 1990

The Ocean Resort
Hotel and Conference Center
Deerfield Beach, Florida

Sponsored By

Dr. S.P. Wolsky, Ansum Enterprises, Inc.

and

Dr. N. Marincic, Battery Engineering, Inc.

Conference Coordinated By
Shawmco, Inc.
4227 E. 99th St.
Tulsa, OK 74137 USA
Telephone (918) 299-7483

Tuesday Afternoon, March 6, 1990

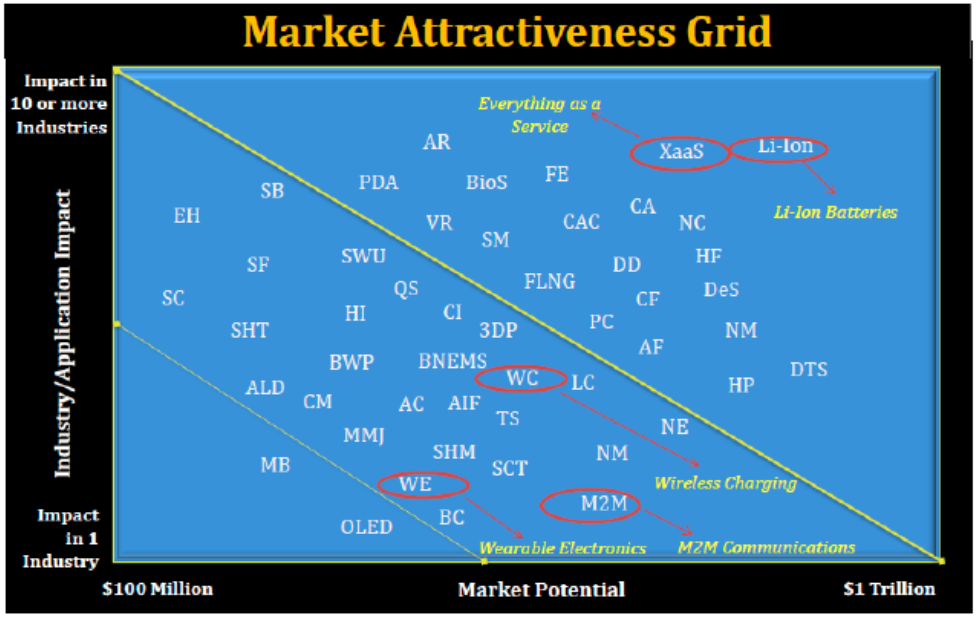
3:30-4:00	Overview of the U.S. Navy Lithium Rechargeable Battery Program - P. Smith and S. James
4:00-4:30	The ReLi Li/TiS2 Cell - K.M. Abraham
4:30-5:00	Progress in Electrolyte Development for Li/SO2 Rechargeable Batteries - C. Schlaijker
5:00-5:45	Polymer Composite Electrodes in Rechargeable Batteries - D. Fauteux and R. Koksbang
5:45-6:00	Lithium Rechargeable Thin Film Batteries - B.B. Owens
6:00-6:20	A Lithium Ion Rechargeable Battery - T. Nagaura

Thermodynamic non-equilibria

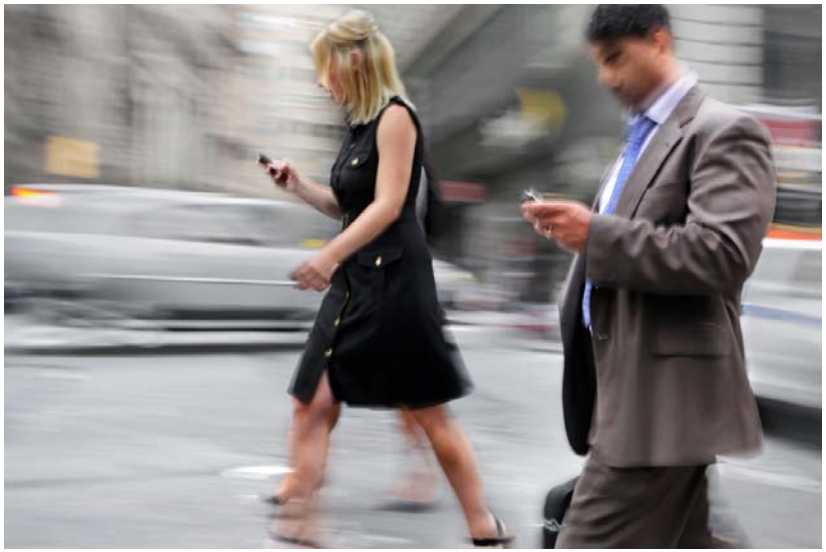
- **Reversibility enabled by kinetic protection from interphases**
  - SEI on anode
- **Interphase universally exists in any advanced electrochemical systems**

The success of LIB

"Among the top 50 disruptive technologies, LIB is predicted to be of the highest volume and impact…"

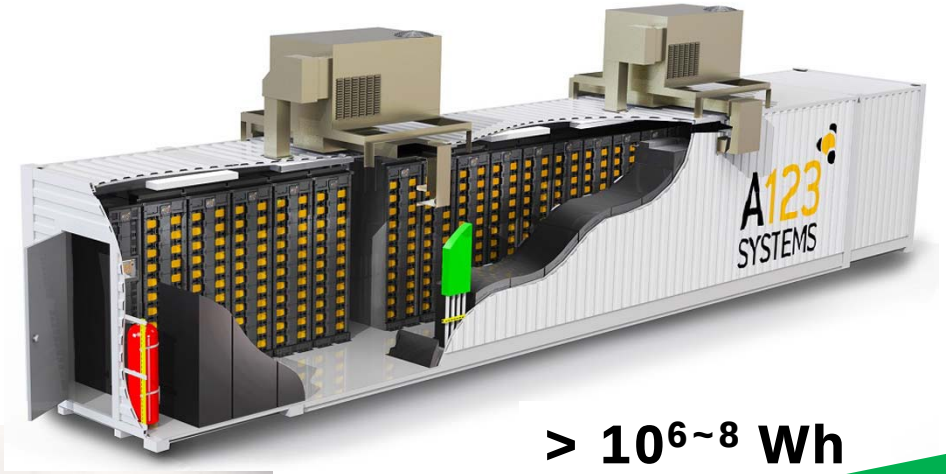


Source: Forrester & Sullivan, 2014



It changed our life!

The expansion of LIB



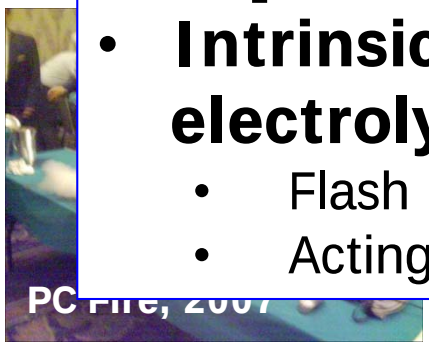
$> 10^{6\sim8}$ Wh

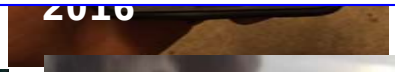
$10^{3\sim4}$ Wh

10^{2} Wh

The primary challenge of LIB

Safety: Primary challenges of SOA LIB





Non-aqueous electrolytes held responsible …

- **Intrinsic Flammability: non-aqueous electrolytes**
  - Flash points of most carbonates are below 0 ºC
  - Acting as fuel when thermal run-away

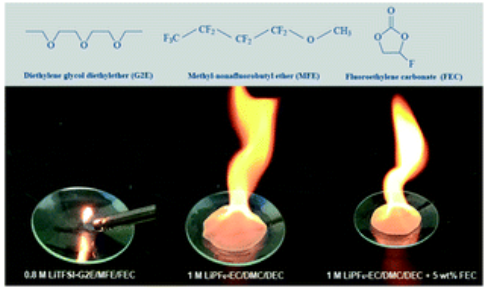
The Safety Measures

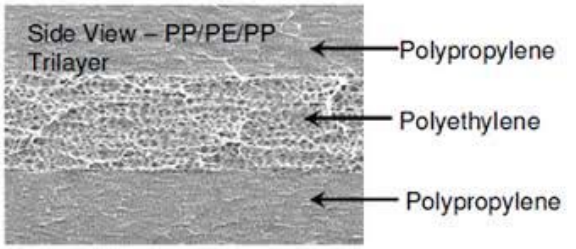
On system level

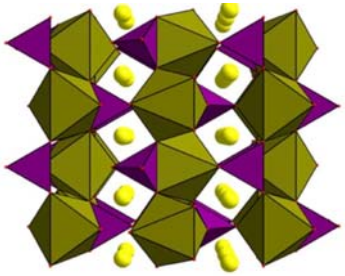
- **Battery management system (BMS)**
- **Phase change medium**
  - Cost, dead-weight

On materials level

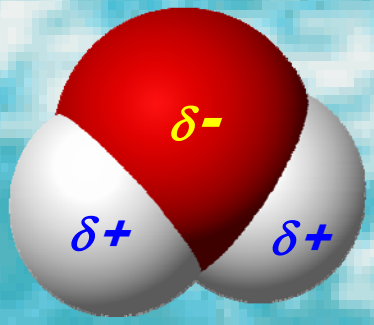
- **Non-flammable electrolytes**
  - Compromise in energy and power densities
  - May not work in thermal runaway
  - Separator still reacts with cathodes
- **Separator**
  - Cost, effectiveness
- **Safe cathode**
  - Metal phosphate of olivine structure
  - Compromise in energy & power densities



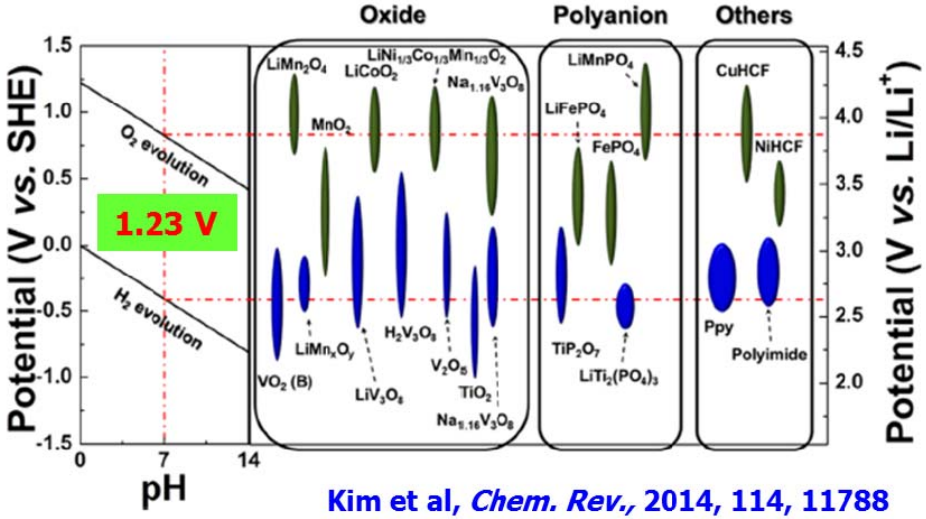




Can we use water?



- **Highly polar: ε 78 at RT**
  - One of the strongest solvents known
- **Non-flammable and green**



Kim et al, *Chem. Rev.*, 2014, 114, 11788

Replacing carbonate esters with water

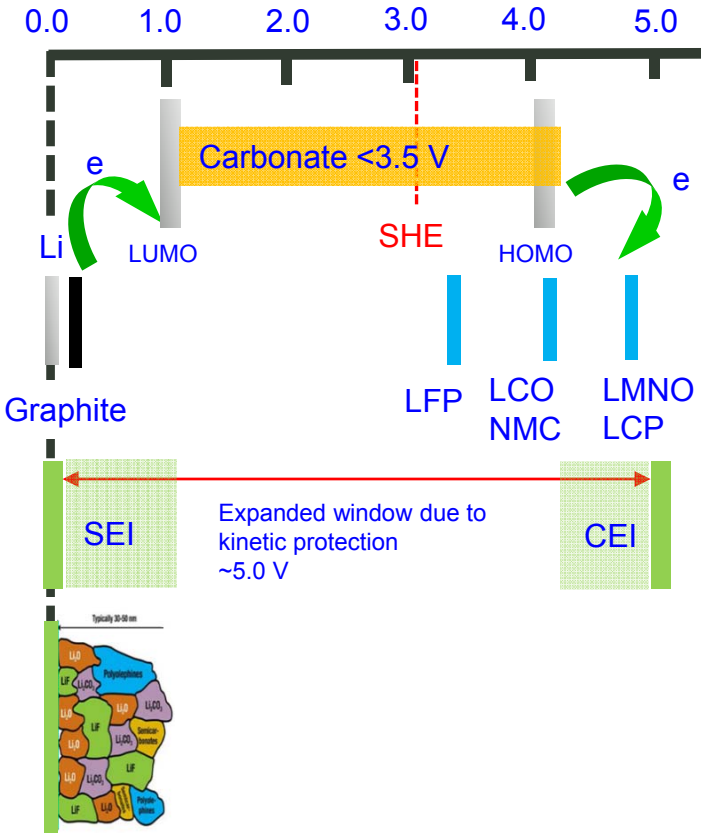
- The most universal on the planet and a very excellent solvent
- Resolving flammability and environmental concerns

However, the electrochemical stability window of water <1.5 V

- 1.23 V thermodynamically stable

Scientific challenge: Expanding the electrochemical window

How LIB works at Non-equilibrium



Anode:

- Potential near 0 V vs Li
- *Almost nothing is stable*

Cathode:

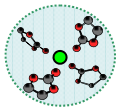
- Potential 3.5 ~ 4.2 V
- Within stable window of esters; on the edge of ether

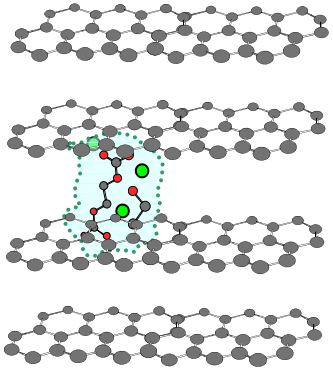
Can we form SEI in aqueous electrolytes?

How SEI was formed

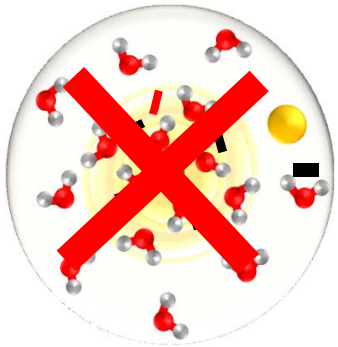
Li^+-Solvation a key factor

- Main chemical contribution comes from solvent molecules in primary sphere
- Solvent decomposition products constitutes SEI





<u>This clearly does not apply to WATER!</u>

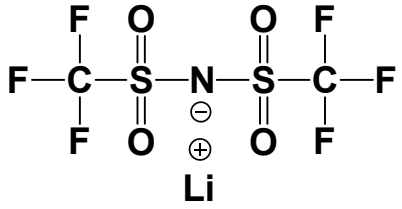


H_2, O_2, OH^-

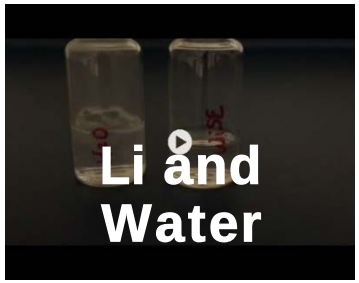
We need to change the solvation structure of Li^+ (or other M^+)

SEI in Water

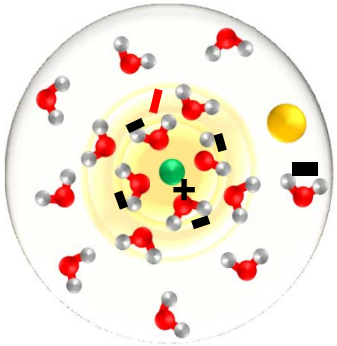
Super-concentration alters solvation structure



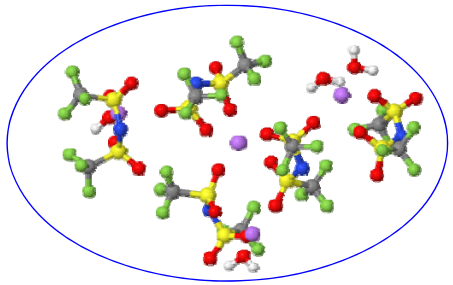
LiTFSI in H_2O



Water-in-Salt Electrolytes (WiSE)



Diluted (< 5 m)

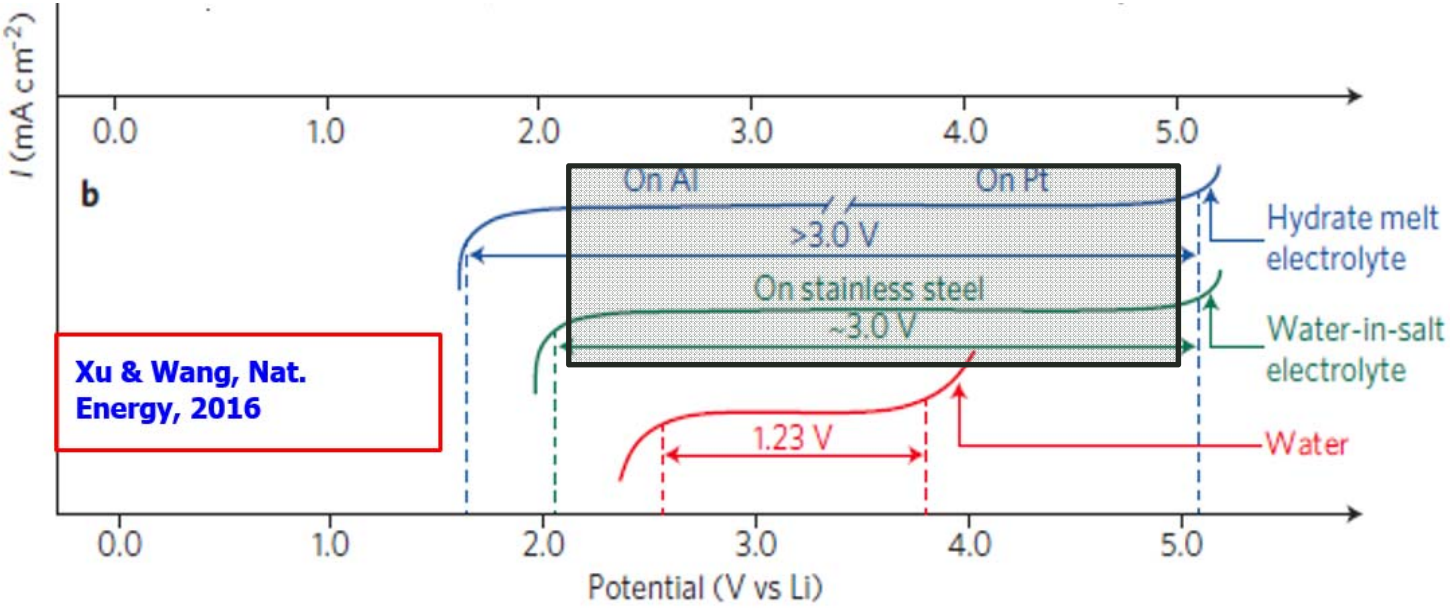


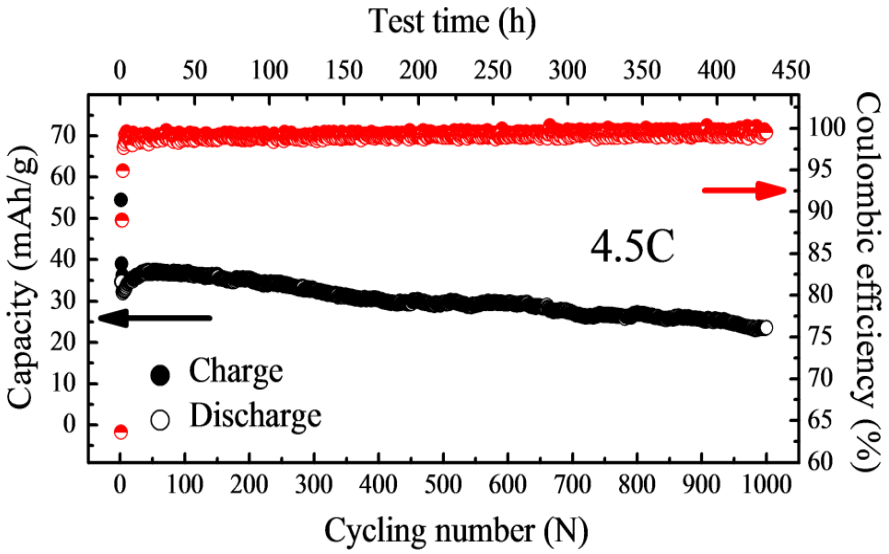
Super-concentrated (~ 20 m)

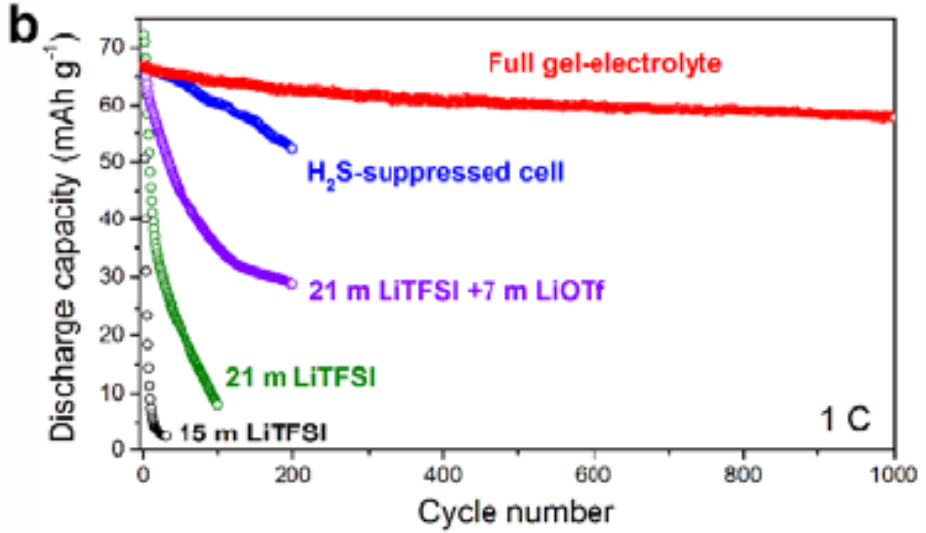
We rely on anion to form SEI in water

- Water is stabilized by strong ion-solvent interaction
- Ion-solvation sheath structure
- Insoluble products in water: LiF, Li_2O, Li_2CO_3
- Reduction potential of anion

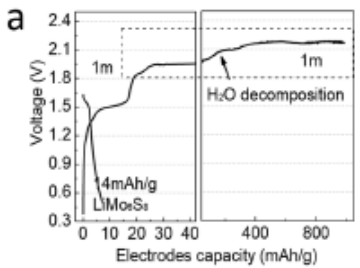
Expanded Echem Window

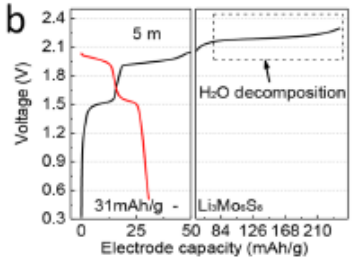


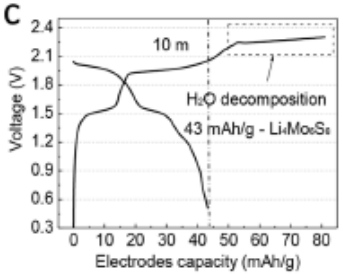


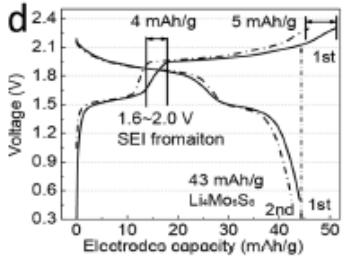


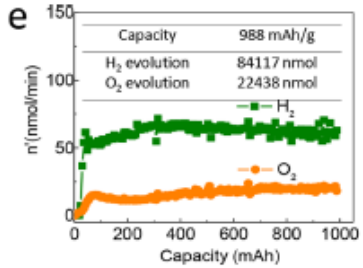
Aq. SEI Formation Mechanism

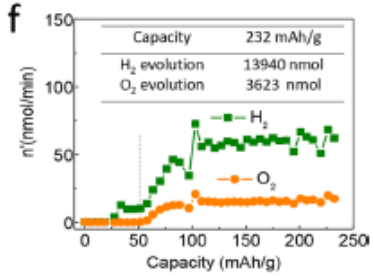


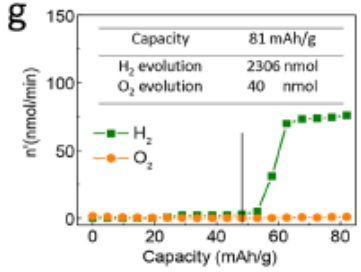


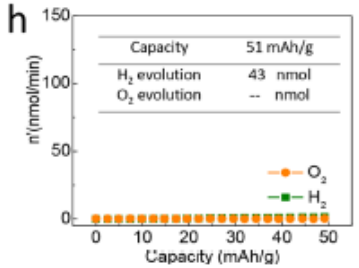


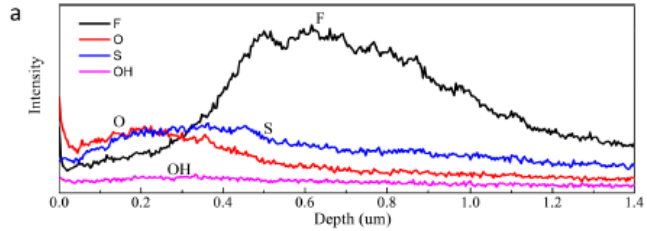


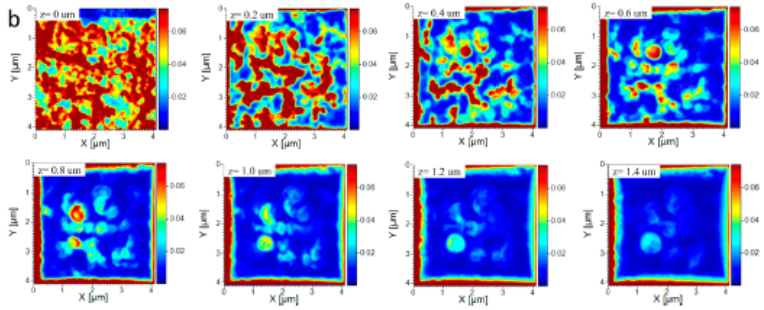


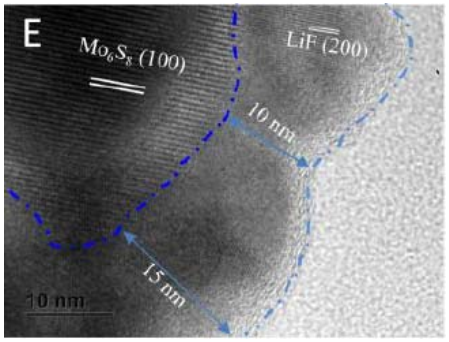


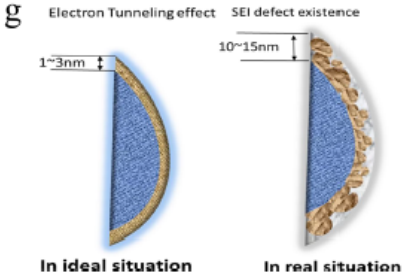












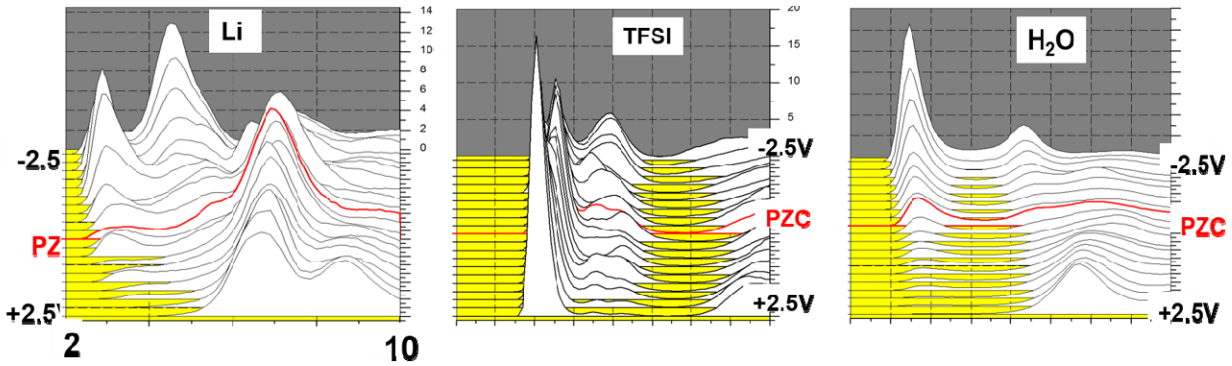
Suo et al, *JACS*, 2017

- **TFSI reduction; LiF nucleation**
- **Li_2CO_3 and Li_2O form**

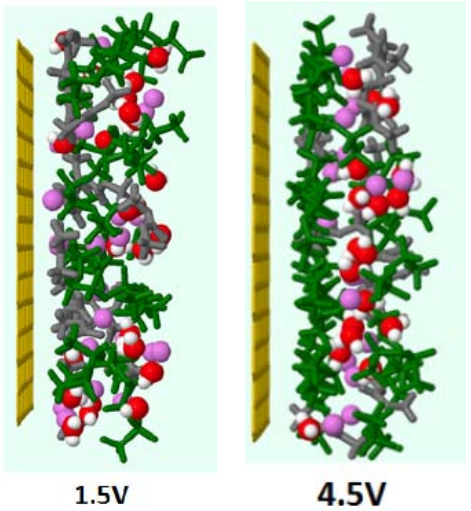
Hybrid Electrolytes

Hybrid Aqueous/Non-aqueous Electrolyte (HANE)

- Use a non-aqueous component to resolve the “Cathodic Challenge”
- Introducing a third component to disrupt the inner-Helmholtz layer structure



- The Non-aqueous components helps repels water via preferential adsorption till < 1.5 V
- The non-aqueous also provides the necessary SEI component



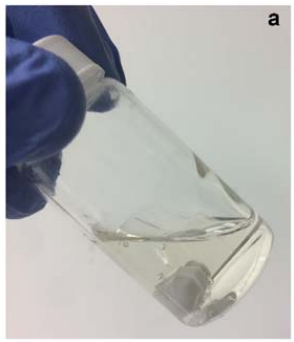
4.0 V Aqueous LIBs

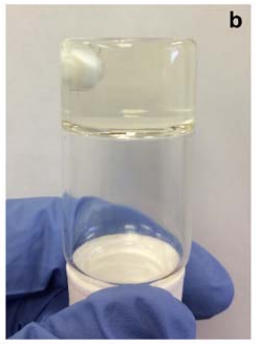
Pre-formation assembly at inner-Helmholtz layer

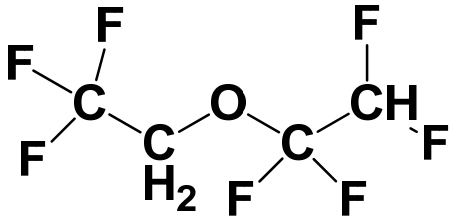
- Anion repelled, water preferred <1.5 V
- "Cheating" the cathodic challenge
- An artificial SEI-precursor had to be used

A >4.0 V window realized

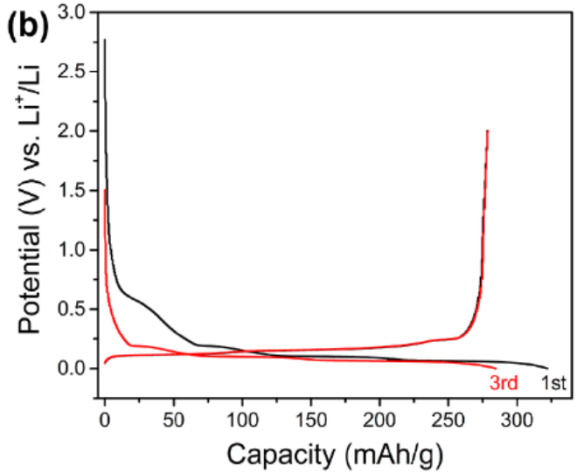
- LIB full cells in "Water-in-Bisalt" GPE can deliver an average output voltage of >4.0 V;
- ED 278~300 Wh/kg
- SEI formation at anode enables nearly 1st stage LiGIC (>300 mAh/g)
- Cycle-life still needs improvement

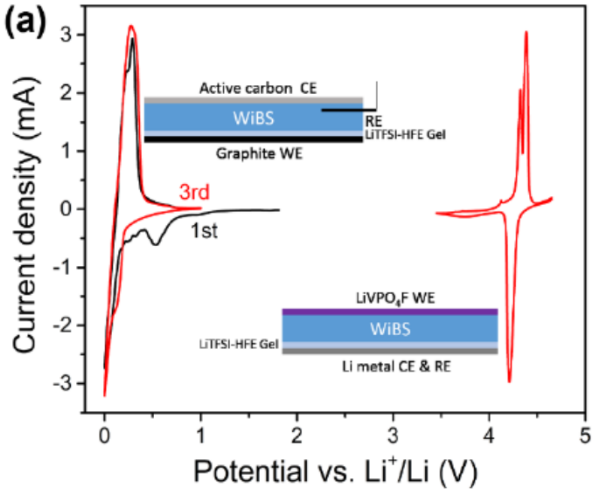






Yang et al, *Joule,* 2017





“Stabilized Water”

High tolerance against mechanical abuses

CONCLUSIONS

- Interphase holds the key to enabling extreme battery chemistries
- Aqueous chemistries will lead us in a new direction seeking new battery chemistries

Acknowledgement

DOE
BES, ARPA-E

Your attention!

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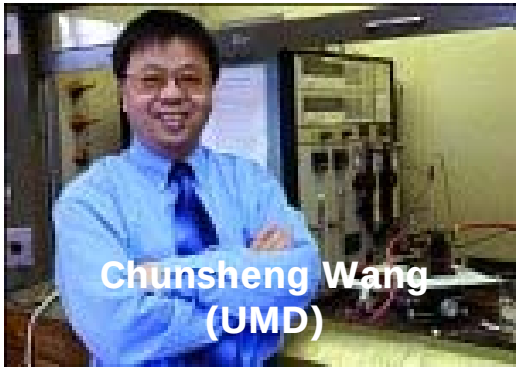
kang_xu@hotmail.com

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