Prospects and Challenges of Lithium-Sulfur Batteries

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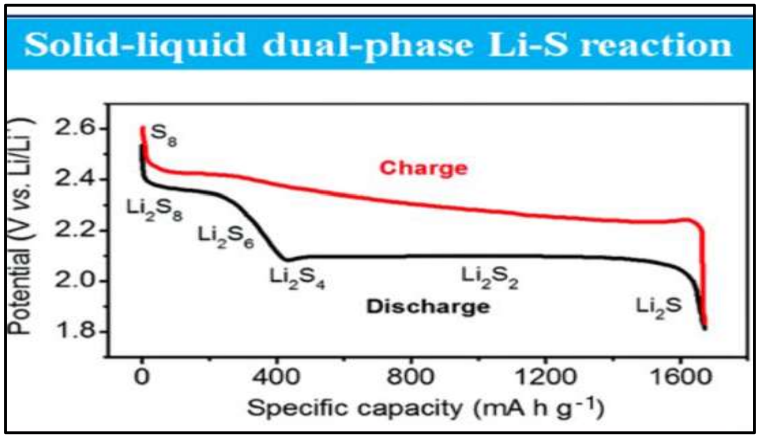
What makes Li-S attractive



Discharge

Anode: $16Li \rightarrow 16Li^+ + 16e^-$

Cathode: $S_8 + 4Li^+ + 4e^- \rightarrow 2Li_2S_4$ (Step I)

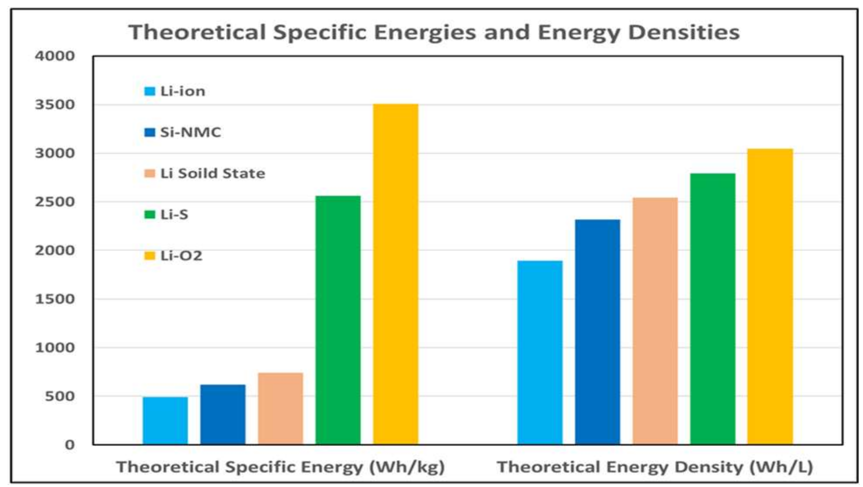
$2Li_2S_4 + 12Li^+ + 12e^- \rightarrow 8Li_2S$ (Step II)

Charge

Anode: $16Li^+ + 16e^- \rightarrow 16Li$

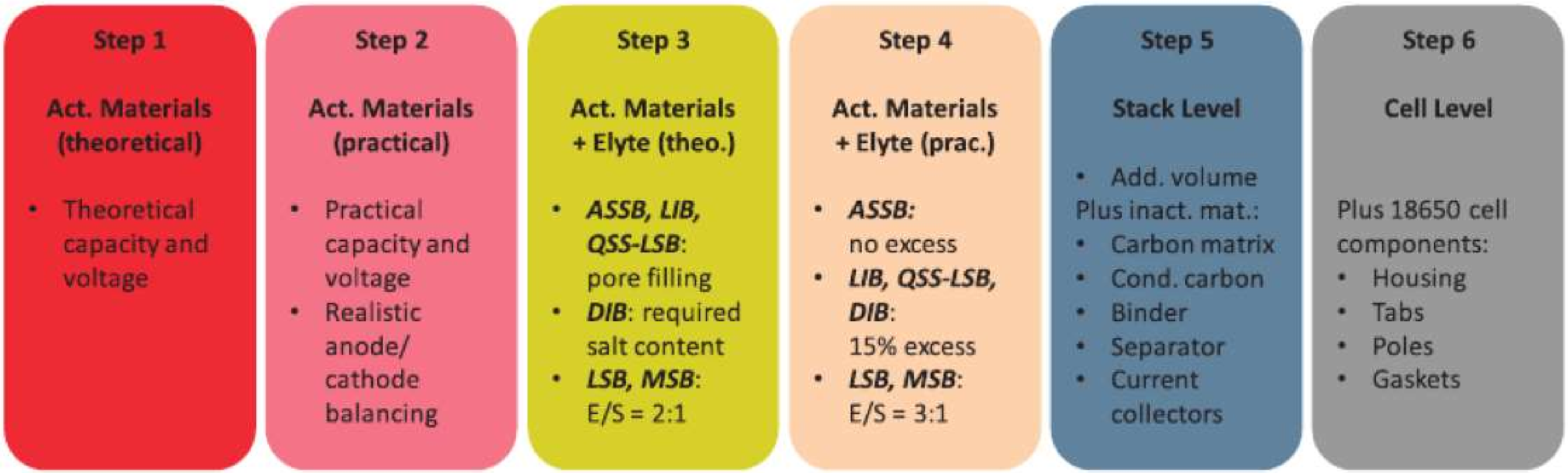
Cathode: $8Li_2S \rightarrow S_8 + 16Li^+ + 16e^-$

- Low equivalent weight (16g) resulting in high specific capacity of 1675 mAh/g (vs 200 mAh/g for Li-ion)
- High theoretical specific energy of 2567 Wh/kg
- Abundance of raw materials
  - Li-ion batteries have serious supply chain issues due to the fast-expanding EV market
- Environmentally compatible (no heavy metals)
- Low-cost (lowers the cost of the EV battery by ~50%)
- Safety



- Highest specific energy system (other than Li-air)

Theoretical versus Practical Energy

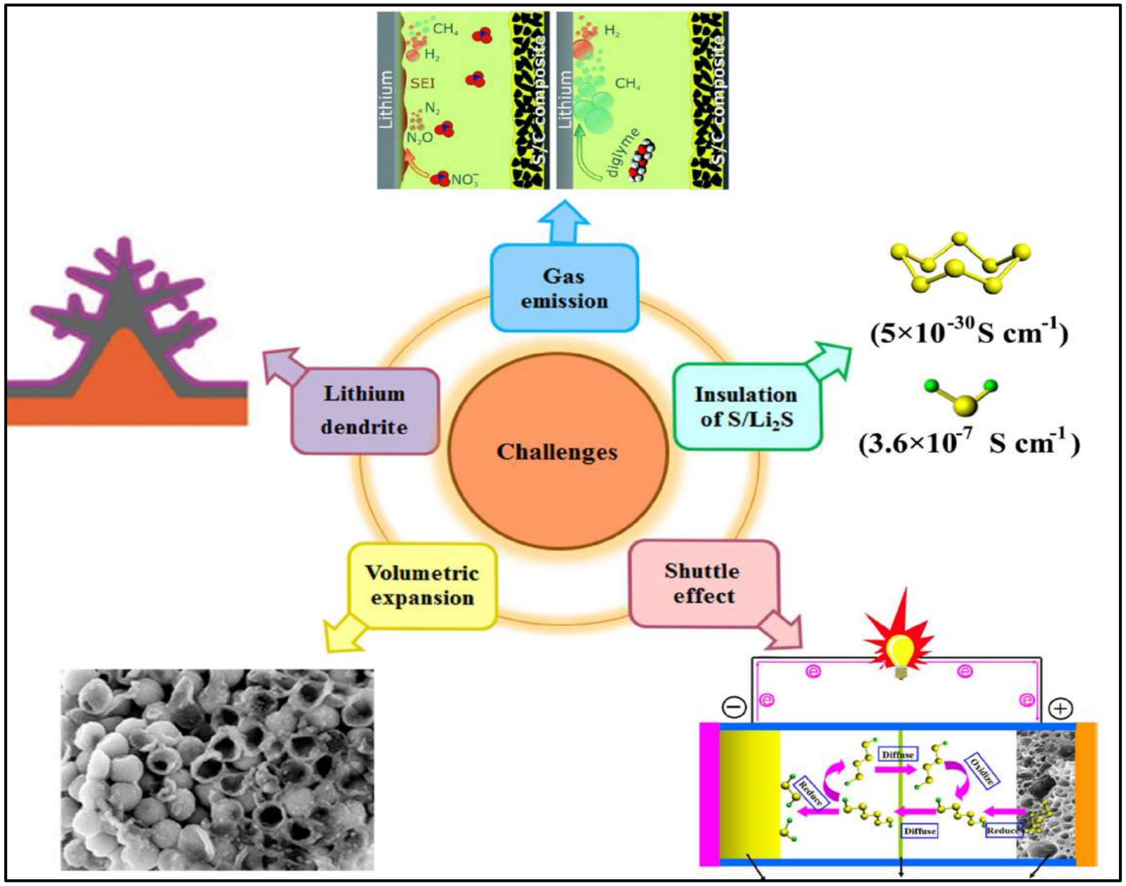


- Experimental specific energies and energy densities are typically 20-30% of theoretical

Martin Winter et al Adv Energy Materials 2019

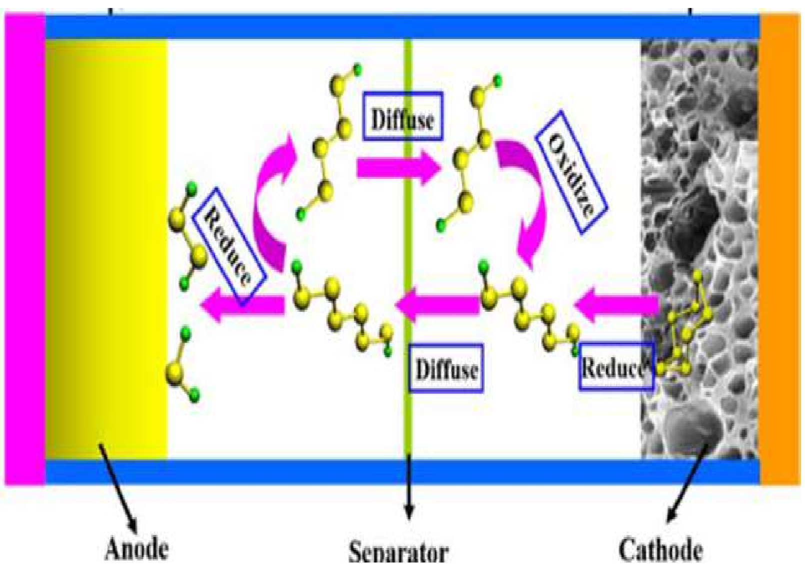
Challenges of Li-S Chemistry

- Problems with S
  - Insulating nature of S and Li_2S
  - Volumetric expansion
  - Polysulfide solubility resulting in a 'redox shuttle'
- Problems with the Li anode
  - Li dendrites
  - Poor cycling efficiency
  - Requires stable SEI
  - Li passivation (Dead Li) and the need to use excess Li
  - Morphological changes
  - Impedance growth from SEI and from the Li_2S deposition
  - Some of the problems common with other Li metal batteries



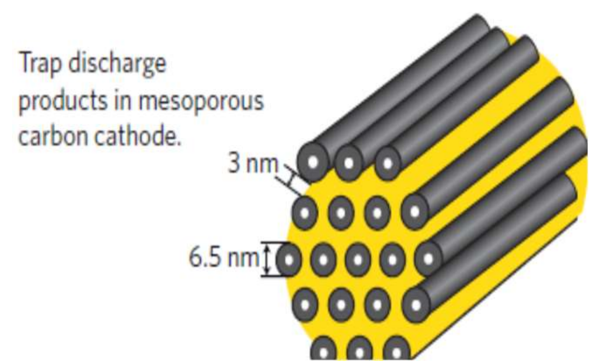
X. Yang, X. Li, K. Adair, H. Zhang and X. Sun, Electrochemical Energy Reviews (2018) 1:239–293

Polysulfide shuttle- the Serious Bottleneck

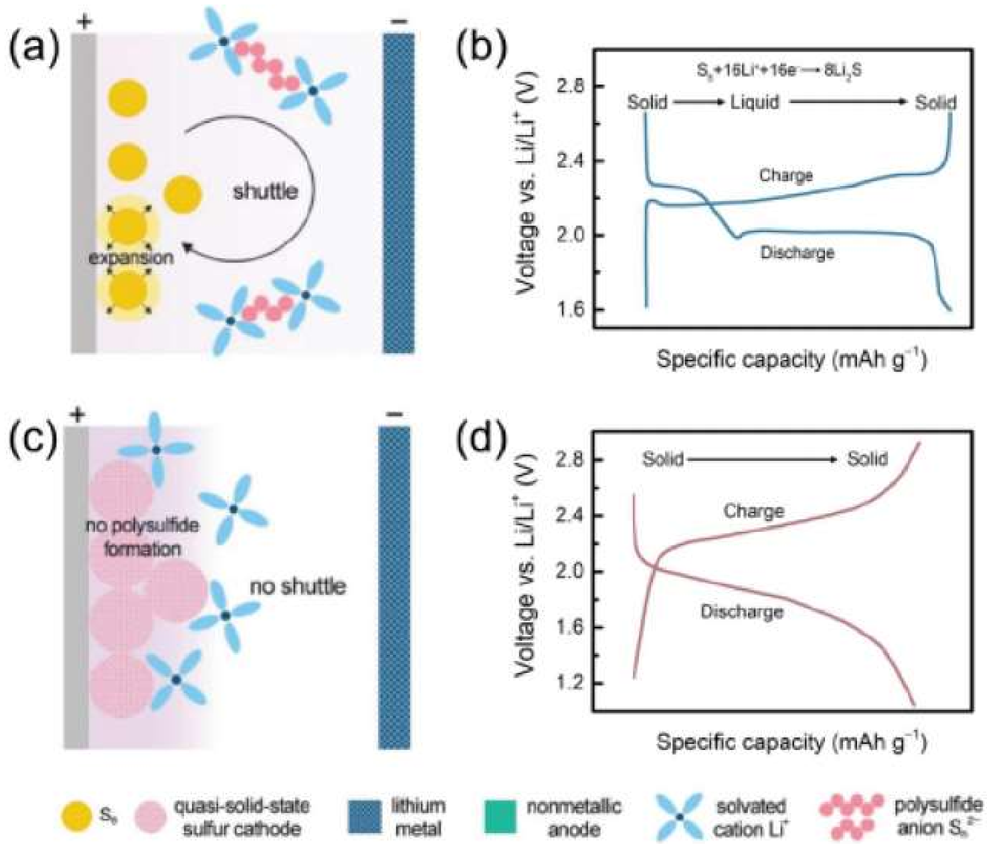


- Polysulfide shuttles affects coulombic efficiency
- PS causes capacity loss during cycling and
- PS is also responsible for (high) self discharge
- Polysulfides cause corrosion of Li anode

- Cathodes with porous host structures to trap sulfur and its reduction products (Carbon and porous metals)
- Electrolytes (more crucial than Li-ion)
  - High donor electrolytes
    - Ether based systems similar to Li-O2 battery
    - Carbonates not compatible
  - Ionic Liquids
  - Solid electrolytes
- Polysulfide blocking layers
  - Carbon, V_2O_5, $LiCoO_2$
- PS blocking separators (Nafion, inorganic-coatings)
- Use of Li_2S as cathode (enables use of Si anode)



Should the polysulfides be in the electrolyte or not?



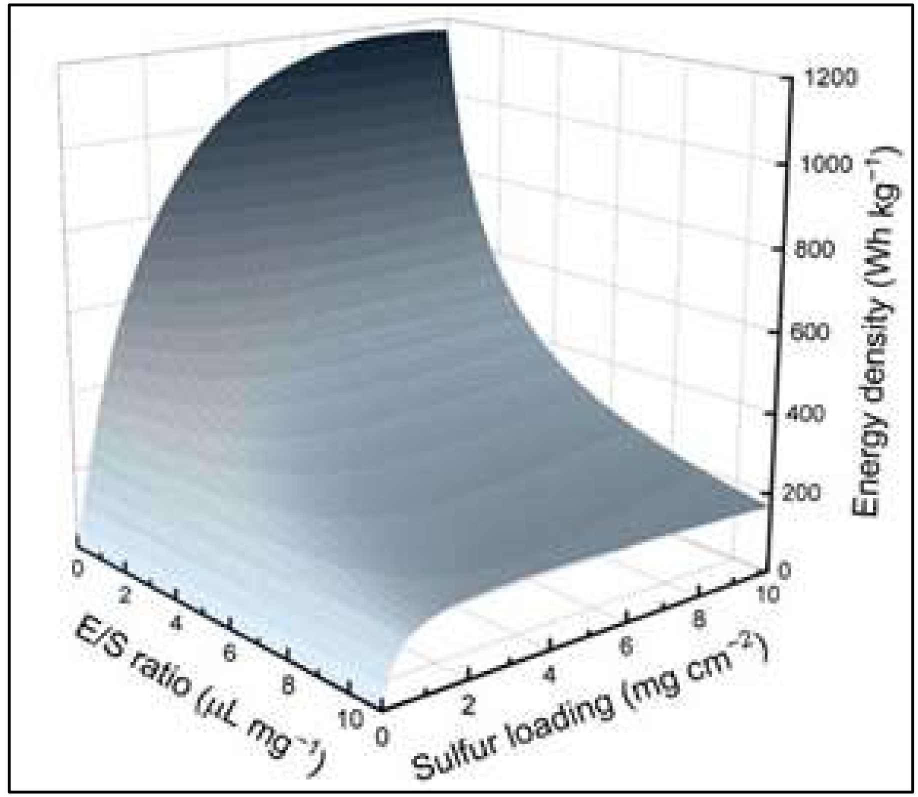
- Solid-liquid-solid reactions
  - Sulfur (with carbon)
  - Liquid organic electrolytes, typically ethers (with good solubility for polysulfide
  - Disadvantage: Polysulfide shuttle
- Solid-solid reactions
  - Sulfurized polymers (SPAN)
  - Concentrated electrolytes (Solvents in salt)
  - Ionic liquids
  - Solid electrolytes
  - Disadvantage: Poor kinetics

- Li–S batteries based on a) the dissolution–precipitation mechanism and c) the solid–solid multiphasic conversion. The typical charge/discharge voltage profiles for b) the solid–liquid Li–S reaction and d) the solid-phase Li–S reaction

Meng Zhao, Bo-Quan Li, Hong-Jie Peng, Hong Yuan, Jun-Yu Wei, and Jia-Qi Huang, Angew. Chem. Int. Ed. 2020, 59, 12636–12652

Design Considerations for High Specific Energy Li-S Cells

- Most of the studies reported in literature deal with low loadings and/or high E/S
- High sulfur loadings (>5 mg of S/cm^2)
- High sulfur utilization
- High Area-specific capacity
  - >6 mAh/cm^2 (per side) vs 2.7 for Li-ion
- Lean-Electrolyte (Low E/S)
  - Requires higher amount of electrolyte (ml per Ah) compared to Li-ion
  - E/S <3



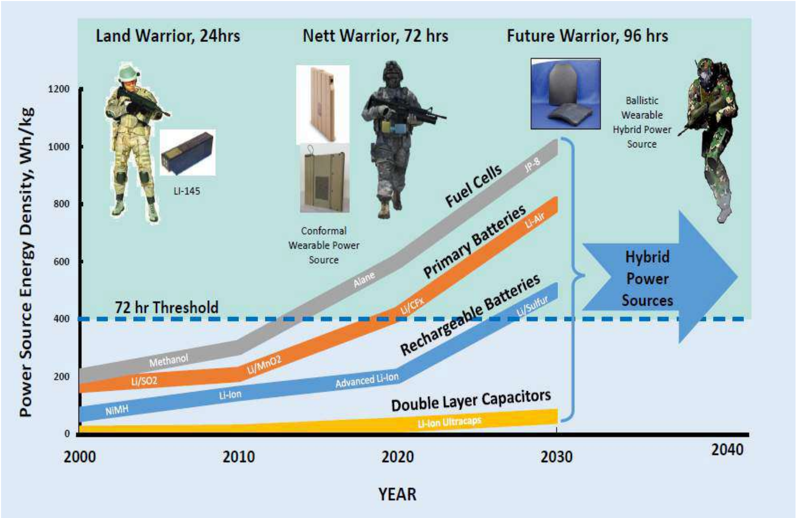
Calculated gravimetric energy densities of a Li–S pouch cell depending on areal sulfur loading and E/S ratio

- **Higher the sulfur loading, more will be the PS in the electrolyte**

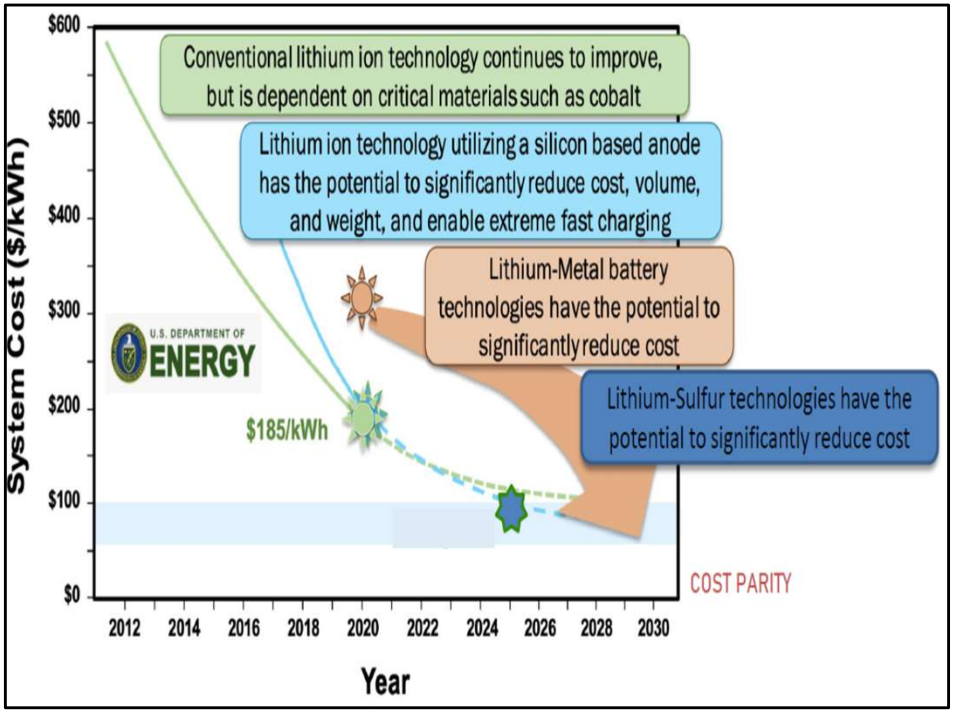
X. Yang, X. Li, K. Adair, H. Zhang and X. Sun, Electrochemical Energy Reviews (2018) 1:239–293

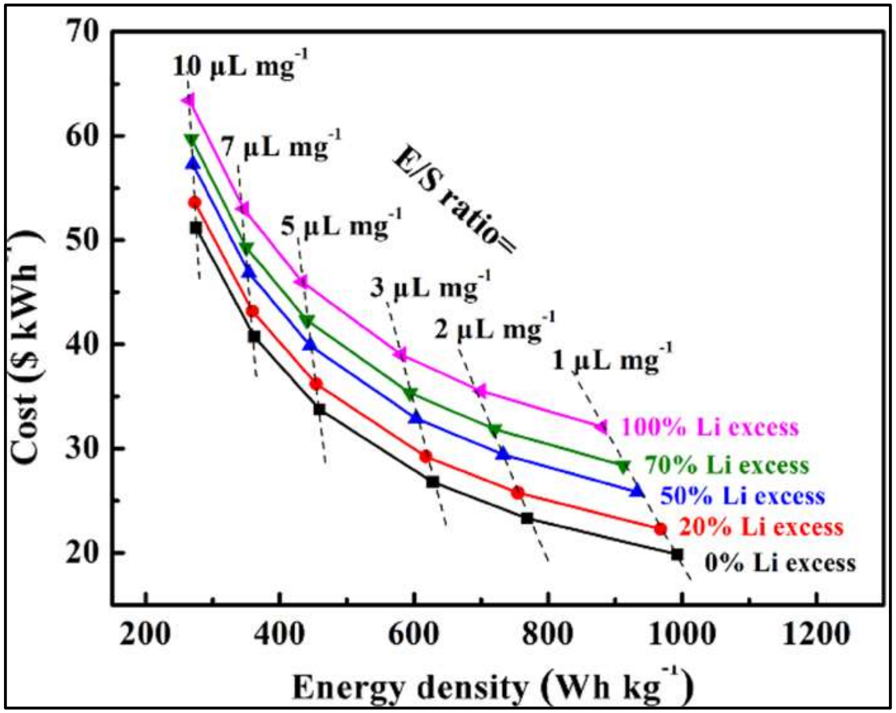
Applications for Li-S Batteries

- Electric Vehicles (High specific energy, energy density and low-cost)
  - Passenger and Heavy-duty
- Aviation (Electric Aircraft) (High specific energy, energy density and high power)
- Drones, UAVs (High specific energy, energy density and high power)
- Space (High specific energy, energy density and Wide operating temperature)
  - Planetary aerial vehicles (balloons and helicopters)
  - Planetary lander and rovers
  - Satellites and Planetary Orbiters
  - Extra Vehicular Activities
- Consumer applications (High specific energy, energy density and low cost)



Li-S Battery offers the Highest Wh/$



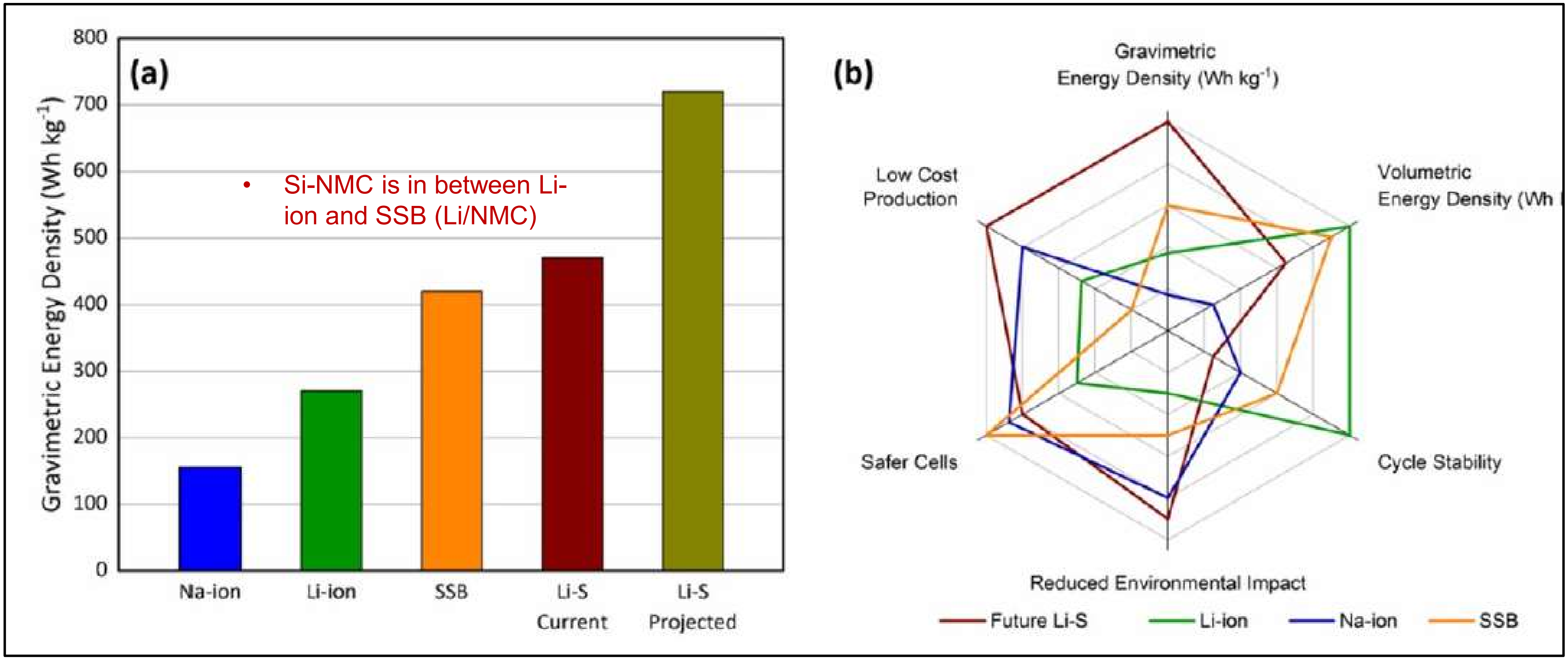


- Li-S is the leading technology to meet the cost targets for EV by virtue of its high specific energy

- Cost decreases as the specific energy increases

Low-cost and high energy Li-S batteries enable widespread use of EVs and 'Grid Storage'

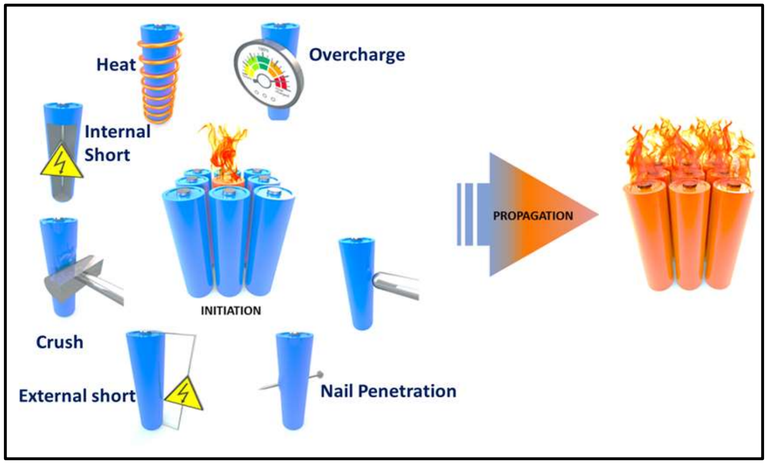
Comparison with Li-ion and other Beyond Li-ion technologies



- The only drawback is cycle life; Possibly solid electrolyte may be the solution, albeit with a marginal drop in specific energy

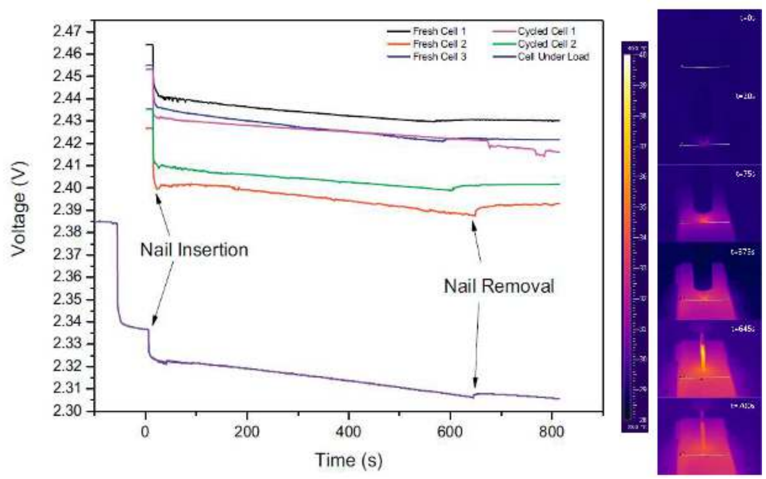
Safety of Li-S Cells

- Li-ion cells can experience thermal runaway during
  - Overheat
  - Overcharge
  - Nail penetration
  - Crush test
  - External short
  - Internal short
- Cells may experience sidewall rupture during failure
- Thermal runaway failure can propagate from cell to cell and to the entire battery



Nail Penetration on 16 Ah Li-S cells

- Li-S cells tolerant to nail penetration
  - Cells continued to provide current during and for a short period after penetration.
  - Mild temperature rise approximately 5–10°C,
  - No flames, smoke or charring were evident, unlike in Li-ion cells.



Why are Li-S cells expected to be safer

- During overcharge, there is no release of oxygen, which exacerbates the failure in Li-ion cells leading to thermal runaway.
- No failure from copper shorts during over discharge (thermodynamically no copper dissolution at 0V).
- Because of the low voltage tolerance, cells and batteries may be shipped/handled at low voltages (which is an issue with the Li-ion batteries.
- No thermal runaway on nail penetration because of the insulating polysulfides in the electrolyte, which may also provide protection during crush and bullet impact test.
- Because of the expected enhanced safety of Li-S cells, battery designs may be simplified to realize higher proportion of cell energies at the battery level (Li-ion batteries need thermal and electrical management and mechanical reinforcement lowering the battery level energies to 60-70% of the cell values.

I. Hunt, Y. Patel, M. Szczygielski, L. Kabacik, G. J. Offer, J. Energy Storage 2 (2015) 25–29

Summary

- Lithium-sulfur battery technology is rapidly evolving and showing promise to offer higher specific energy with lower cost compared to the widely used Li-ion batteries
  - Will be extremely beneficial and relevant to the electric vehicles (both passenger and heavy-duty). Even a partial replacement of Li-ion batteries will ease the burden on the supply chain issues of Li-ion batteries and offset the risk from over-dependence on Asian countries who have overwhelming control on resources and dominance on manufacturing.
  - High specific energy and moderate life Li-S batteries will be available in the near-future, but the applications requiring long-life will be a couple of years away.
  - Electrolyte is the key, need new electrolytes that can provide high efficiencies form cathode with high sulfur loadings in lean-conditions .
  - Solid-state Li-S batteries will be excellent candidates for long-life application, especially with several new solid electrolytes that have emerged in the last decade.