Interfacial Design for Cathode Materials in Lithium-Sulfur Batteries via an Integrated Computational Approach

Yuxiao Lin[a,b], Xinsheng Zhao[a], Yue Qi[b,c]

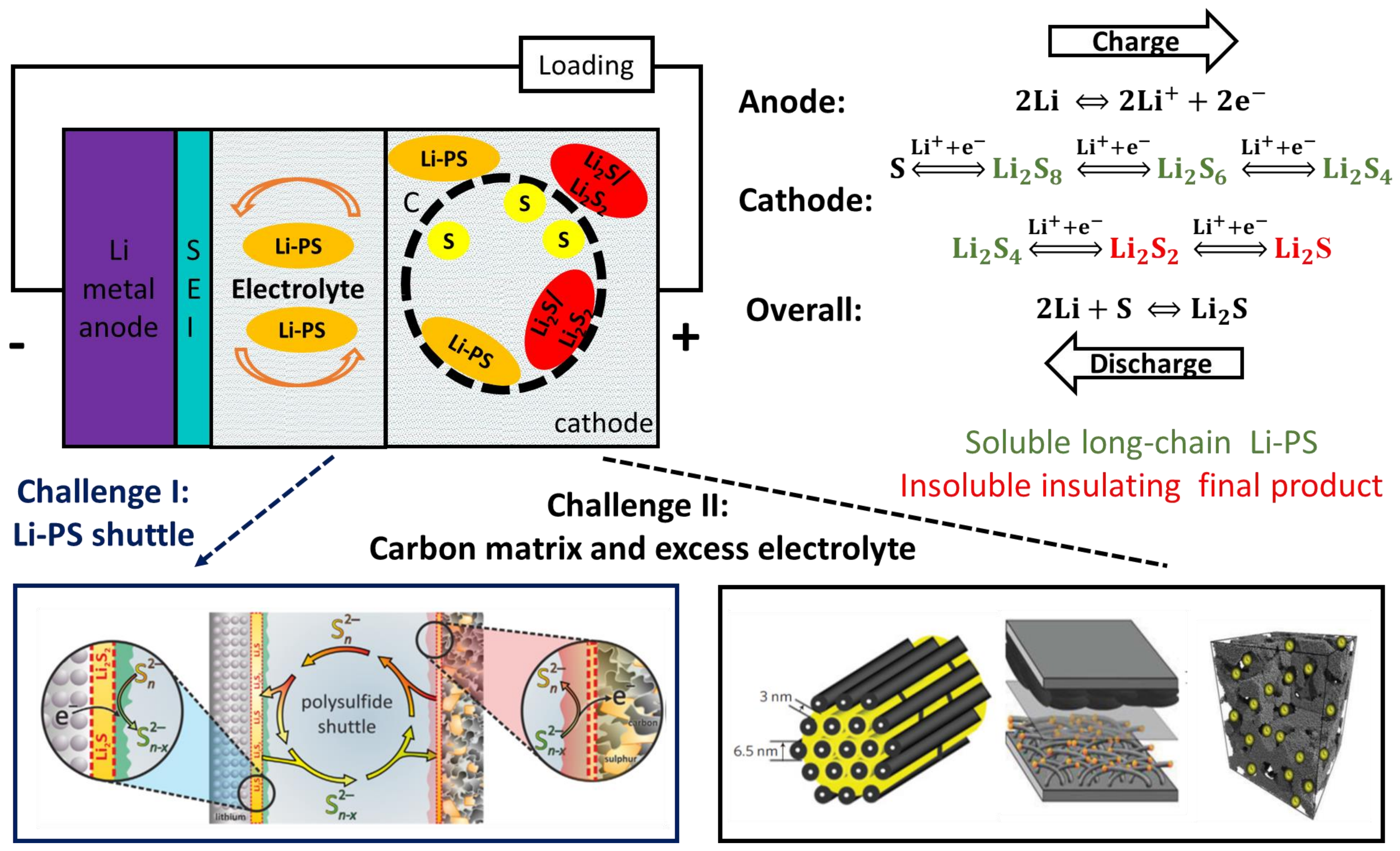
a. School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou, Jiangsu Province, China, 221116.

b. Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI, USA, 48824.

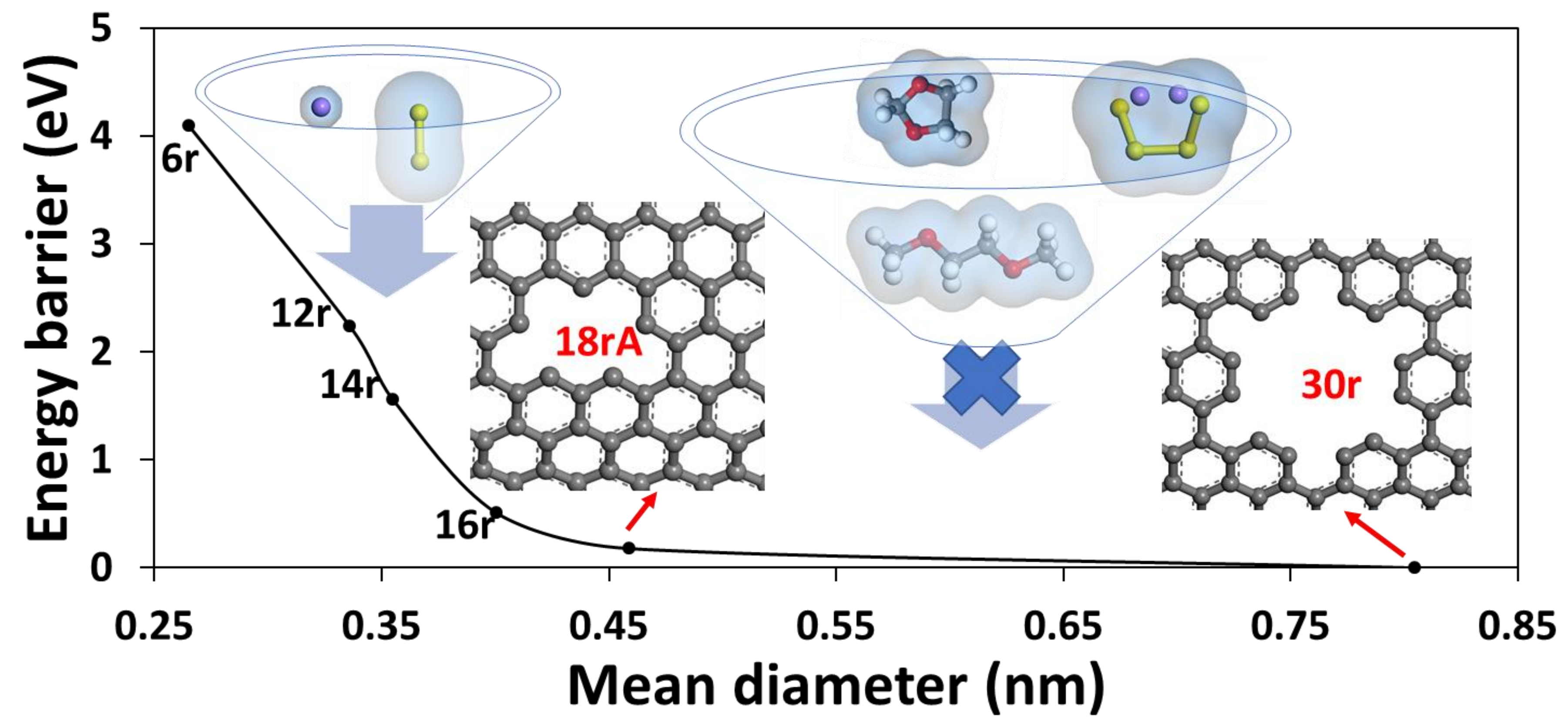
c. School of Engineering, Brown University, Providence, RI, USA, 02912.

Motivation: Challenges faced by Li-S batteries

- Due to its high theoretical energy density (2567 Wh/kg, 5 times higher than Li-ion battery), abundance of sulfur and low cost, Li-S battery has been widely considered as a potential alternative to Li-ion battery.
- Challenge I: Li-PS shuttle problem caused deposition of insulating Li_2S_2/Li_2 layer, leading to blocked Li diffusion pathway, loss of active S, and rapid capacity fading.
- Challenge II: Porous carbon matrix and excess electrolyte are required to improve the electronic conductivity of elemental S cathode and discharge product of Li_2S_2/Li_2, but lead to low cell-lell energy density.
- Pore and interface structures are directly connected to the cell-level performance, thus modeling these connections provided an integrated approach for the cathode design in Li-S batteries.



Optimizing micropore size and synthesis parameters for CNT-encapsulated-S cathode [2]



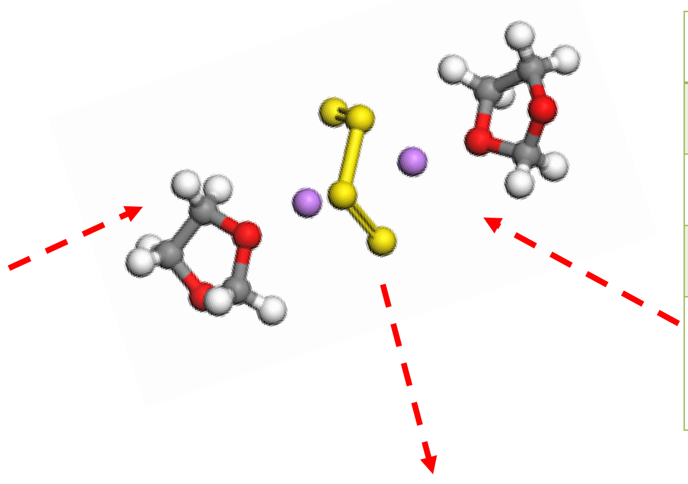
O:C	T (K)	Periodic length (nm)	10ps	50ps	100ps	200ps	500ps	1000ps
17%	800	2.46	12	12	12	12	11	11
17%	800	4.92	12	12	15	15	15	Vaporized at 670 ps
17%	800	7.38	14	14	14	14	Vaporized at 390 ps	
34%	800	2.46	11	11	11	Vaporized at 220ps		
34%	1000	2.46	10	14	12	Vaporized at 150ps		
34%	1000	4.92	17	18	Vaporized at 55 ps			
34%	1000	7.38	14	14	14	20	vaporized at 250 ps	
34%	1300	2.46	10	Vaporized at 50ps				

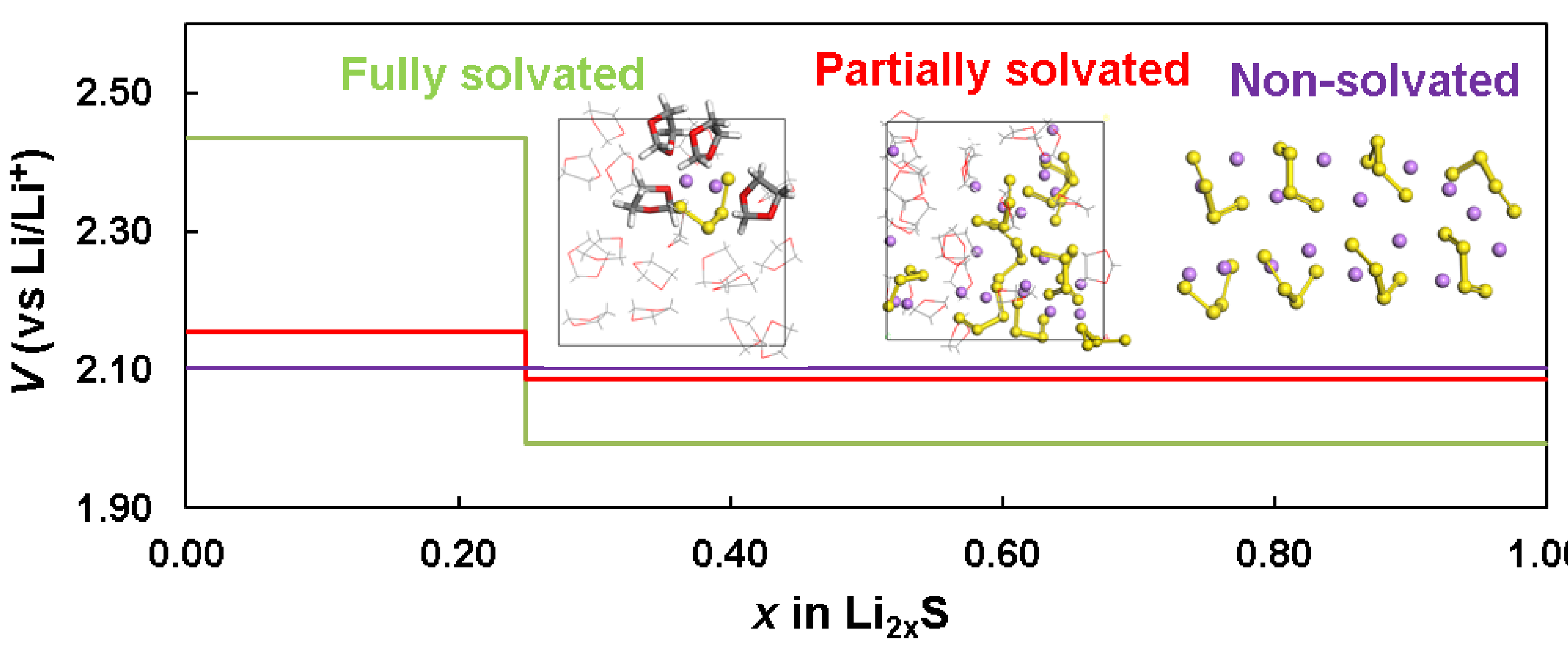
Too Small / Optimum / Vaporized

- Optimum open rings within the range of 16r to 30r are predicted to selectively allow transportation of Li and S while blocking both Li-PS and electrolyte.
- The optimum open-ring-size can be achieved by controlling oxidation parameters within a narrow window.

Partial solvation to mitigate Li-PS shuttle [1]

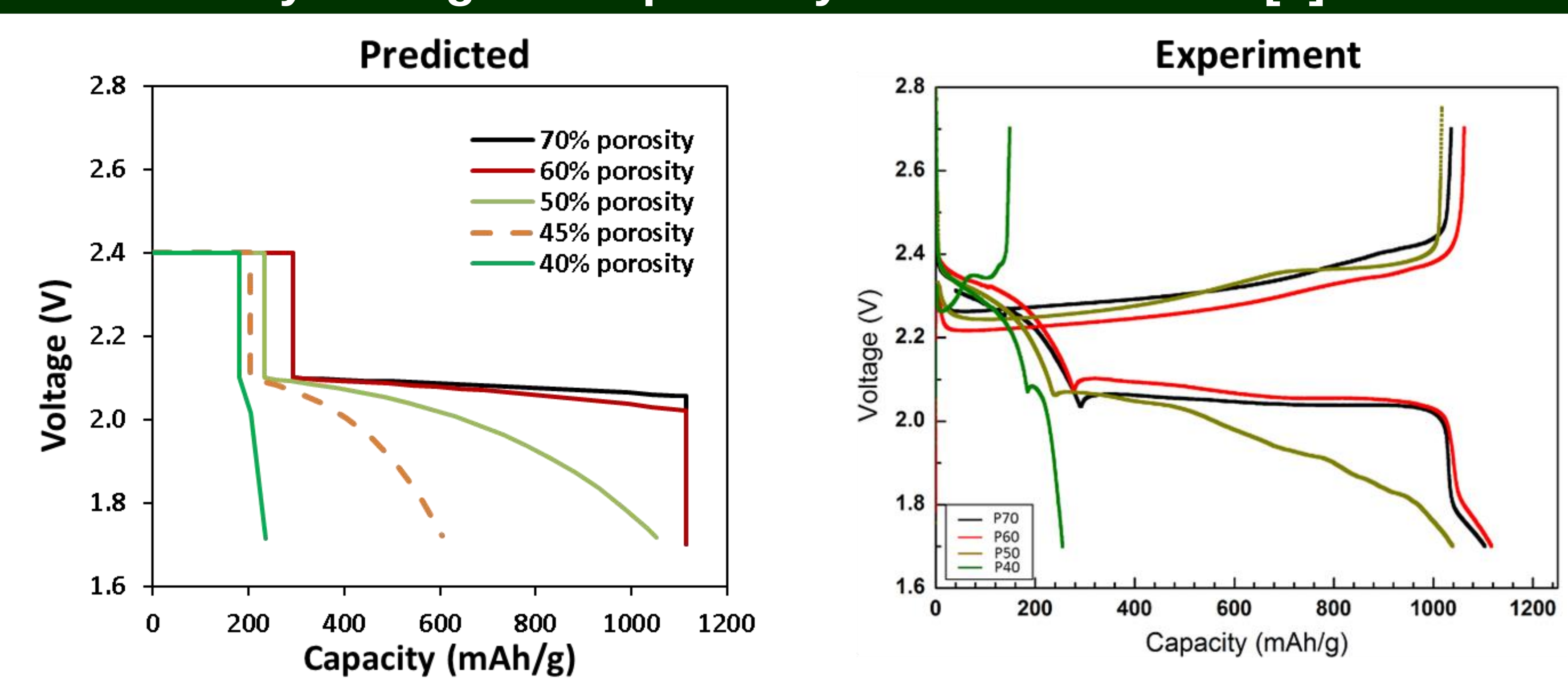
Liquid electrolyte	Solid electrolyte
Fully solvated	Non-solvated
Two-plateaued	One-plateaued
Fast Li ion transport	Slow Li transport
Capacity fading due to severe Li-PS shuttle	High capacity retention due to inhibited Li-PS

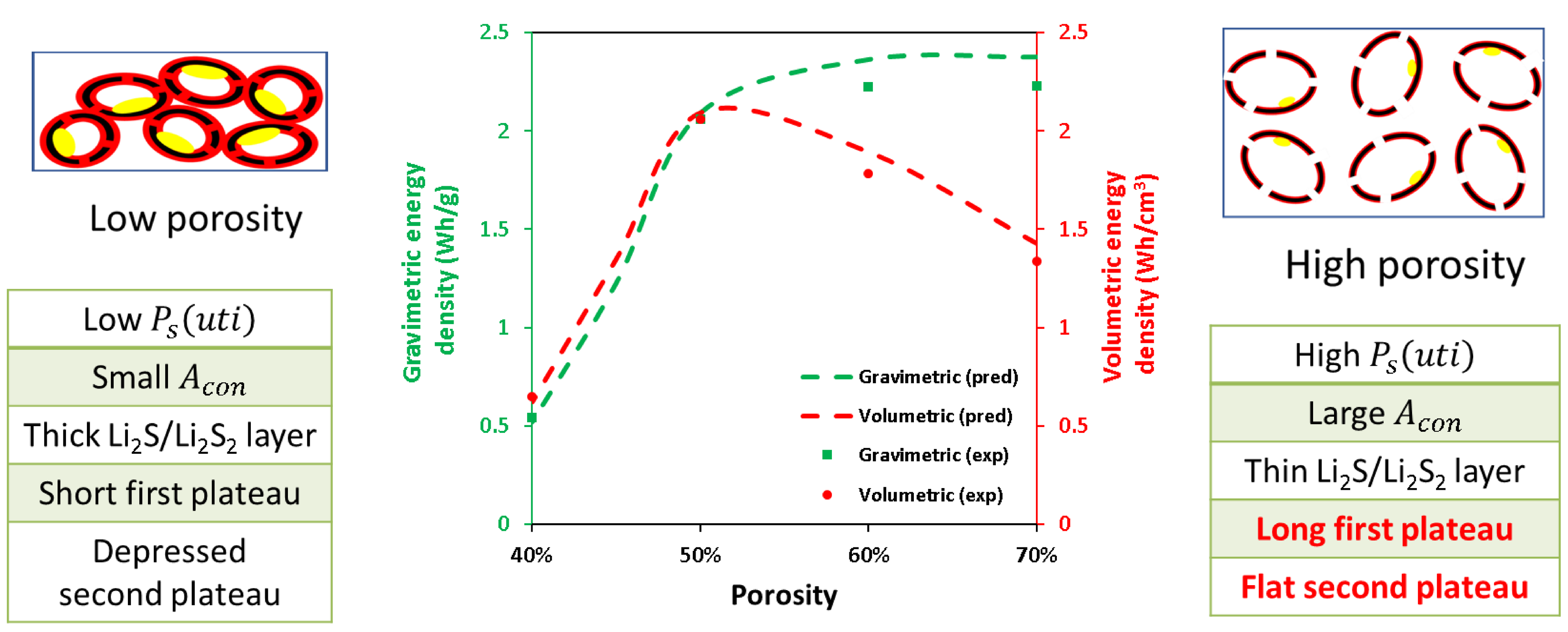




- Formation energy increases in the order of fully solvated Li-PS, partially solvated Li-PS and non-solvated Li-PS, leading the discharging curves gradually changes from two plateaud to one plateaued.
- Partial solvation can be created with a highly-concentrated solution or by varying pore size and volume in the carbon matrix to confine S and limit the number of solvents transported into the pores.

Optimizing cell-level energy density by tuning macroporosity in carbon matrix [3]





Low porosity	High porosity
Low $P_s(uti)$	High $P_s(uti)$
Small A_{con}	Large A_{con}
Thick Li_2S/Li_2S_2 layer	Thin Li_2S/Li_2S_2 layer
Short first plateau	Long first plateau
Depressed second plateau	Flat second plateau

- The saturation of Li-PS in electrolytes is the limiting factor for the 1st plateau, while the loss of the effective surface area due to the deposition of insulating Li_2S_2/Li_2S products is the limiting factor for the 2nd plateau.
- The cell reaches a maximum energy density at an electrode porosity of 52% without sacrificing sulfur utilization rate.

Conclusion

- Fully solvation energy stabilized the Li-PS and led to the two-plateaued OCV; while the energetic unfavorable non-dissolved Li-PS led to one-plateaued OCV.
- Proposed synergetic effect between nanopore size and electrolyte concentration to mitigate Li-PS shuttle through partially solvated Li-PS.
- Determined the optimum sub-nanopore size and its controlling method to solve Li-PS shuttle problem.
- Decrease in micrometer level porosity led to shortened first plateau due to saturation of Li-PS and depressed second plateau due to limited electronically-accessible surface area of the carbon matrix.

Related Publication

[1] **Y. X. Lin,** *et al. Nano Lett.* 22(2022) 1 441.

[2] **Y. X. Lin*,** J. Zheng*, *et al. Nano Energy.* 75(2020) 104915.

[3] N. Kang*, **Y. X. Lin*,** *et al. Nat. Commun.* 10(2019) 4597.

(Highlighted by *Nat. Energy* 4(2019) 908.)