Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2020

## Supporting information

For

## Inverse vulcanized conductive polymer for Li-S battery cathode

Guoping Gao<sup>1</sup>, Xiaotian Sun<sup>1,2</sup>, Lin-Wang Wang<sup>1\*</sup>

- 1. Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA. E-mail: <u>lwwang@lbl.gov</u>
  - 2. College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function- Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, P. R. China



Figure S1 The schematic of vulcanization S into 5-Decene via cycloaddition(a) and crosslinking(b); (c) the vulcanization S into 1-Decene via crosslinking.

Table S1 The vulcanization energy of 5-Decene via cycloaddition, 5-Decene via crosslinking, and 1-Decene via crosslinking.

τ	2	3	4	5	6	7	8
5-Decene-	0.38		-0.01		0.01		0.02
Cycloaddition							
5-Decene-		0.23	0.24	0.09	-0.10	0.03	0.01
Crosslinking							
1-Decene-			-0.30	-0.26	-0.30	-0.18	-0.39
Crosslinking							



Figure S2 The configures of vulcanization S into 5-Decene (a) and 1-Decene (b) via crosslinking. As we can see, the repulsive force between S and C from both sides of the S-C bond alters the 5-Decene into a 'V'. However, The repulsive force in 1-Decene is available on one side of the S-C bond. Therefore, the steric effects in vulcanization S into 1-Decene is small than that of 5-Denece.



Table S2 The Boltzmann distribution based on the vulcanization energy(chains during vulcanization at 185 °C.

τ	4	5	6	7	8	Total
Crosslinking	14.81%	3.31%	36.53%	29.36%	13.19%	97.20%
Cycloaddition	0.01%	0.17%	2.55%	0.07%	0.00%	2.80%

)of different S



Figure S3 The configuration of  $Li_{11}S_6$  on vulcanized polymer via condensation.



Figure S4 The band structures with group velocities of valence band maximum (VBM or HOMO) and the conduction band minimum (CBM or LUMO) of the polymer via condensation after vulcanization ( $S_6^*$ , a), to lithiation ( $Li_{10}S_6^*$ , b). The color in the

band structures indicates the weight of group velocities of VBM and CBM. The group velocity of vulcanization is about  $\sim$ 1.5×10<sup>-4</sup> m/s.



Figure S5 The final structure of initial product vulcanization of S via crosslinking (a) and final lithiation production with  $Li_{20}S_{12}$  on the poly (2-vinyl, 1, 4-phenylene sulfide) (b) within 1,2-dimethoxyethane(DME)/1,3-dioxolane(DOL) (mole ratio=1: 1) after ab initio molecular dynamics simulation in the NVT ensemble under 300 K with a time constant of 3000 fs.