Electronic Supplementary Information

Stable cycling of lithium sulfide cathodes through strong affinity with a bifunctional binder

Zhi Wei Seh, Qianfan Zhang, Weiyang Li, Guangyuan Zheng, Hongbin Yao, Yi Cui[*]

[*] Correspondence should be addressed to Y.C. (Email: yicui@stanford.edu)

Experimental Methods

***Ab initio* simulations.** *Ab initio* simulations were performed using the Vienna *Ab Initio* Simulation Package (VASP) in the framework of density functional theory (DFT).[1,2] The projector augmented-wave (PAW) pseudopotential[3] and the generalized gradient approximation (GGA) exchange-correlation function described by Perdew-Burke-Ernzerhof (PBE)[4] were adopted. To ensure convergence, 500 eV was chosen as the cut-off energy of the plane-wave basis. The vacuum between a polymer and its image exceeds 30 Å, while the distance between the Li–S·/Li_2S cluster and its image is no less than 15 Å along the periodic direction. These systems were large enough to avoid any artificial interaction caused by periodicity. The binding energy, E_b, was defined as the energy difference between the Li–S·/Li_2S–polymer adsorbed system (E_{tot}) and the summation of pure Li–S·/Li_2S cluster ($E_{LiS/Li2S}$) and pristine polymer ($E_{polymer}$): $E_b = (E_{LiS/Li2S} + E_{polymer}) - E_{tot}$. The three-dimensional visualization models were constructed using VESTA 3 software.[5]

Electrochemical measurements. Due to the sensitivity of Li_2S to moisture, all the electrode preparation and cell assembly procedures were carried out in an argon-filled glove box with moisture and oxygen levels below 0.5 ppm. Commercial Li_2S particles (99.9%, Alfa Aesar) were first ball-milled in a tightly-sealed vial for 4 h using a SPEX 8000D miller. Conductive carbon black (Super P) and polyvinylpyrrolidone (PVP; M_w ~ 1,300,000) were dried under vacuum prior to use. The ball-milled Li_2S particles were then ground with carbon black and PVP binder in a weight ratio of 60: 35: 5 using a mortar and pestle, followed by dispersion in *N*-methyl-2-pyrrolidinone (NMP) to form a slurry. After overnight stirring, the slurry was then drop-cast onto carbon fiber paper (AvCarb P50) and dried at 60°C to form the working electrode. 2032-type coin cells were assembled using lithium foil as the counter electrode and Celgard 2250 as the separator. The electrolyte used was a freshly-prepared solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1 M) in 1:1 v/v 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) containing $LiNO_3$ (1 wt%). Using a 96-channel battery tester (Arbin Instruments), the Li_2S cathodes were first activated at C/20 (1C = 1,166 mA g^{-1}) by charging to a high cutoff voltage of 3.8 V vs. Li^+/Li for complete delithiation followed by discharge to 1.8 V as described in previous work.[6] Galvanostatic cycling was then carried out at the specified C-rate from 1.8 to 2.6 V vs. Li^+/Li. The typical mass loading of Li_2S was ~ 2 mg cm^{-2} and specific capacity values were calculated based on the mass of Li_2S or the corresponding mass of S in the samples.

Electrolyte testing. For analysis of sulfur content in the electrolyte after cycling, a sulfur-free lithium salt of $LiClO_4$ (1 M) in 1:1 v/v DME/DOL solution with $LiNO_3$ (1 wt%) was used as the electrolyte. After 1, 5, 10 and 20 cycles at 0.2C, the cells were discharged to 1.8 V vs. Li^+/Li and the voltage was maintained for over 20 h, following which they were disassembled and the contents (cathode, anode and electrolyte-soaked separator) were washed with DOL solution. This polysulfide-containing solution was then oxidized with concentrated HNO_3 and diluted with deionized water for analysis of sulfur content using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Thermo Scientific ICAP 6300 Duo View Spectrometer).[7]

References:

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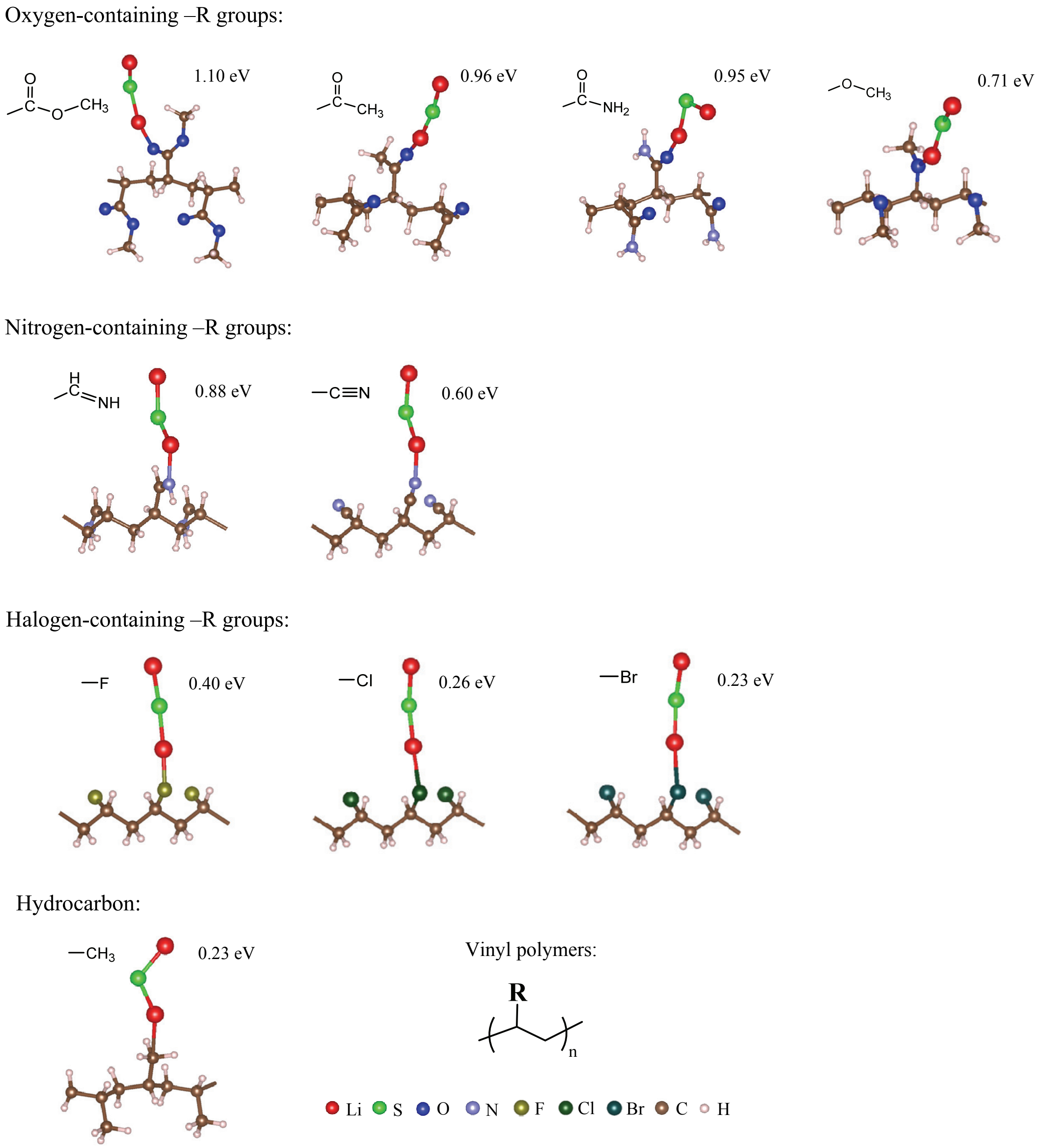

Fig. S1. *Ab initio* simulations showing the most stable configuration and calculated binding energy of Li_2S with various functional groups (R) based on the framework of vinyl polymers $–(CH_2–CHR)_n–$.

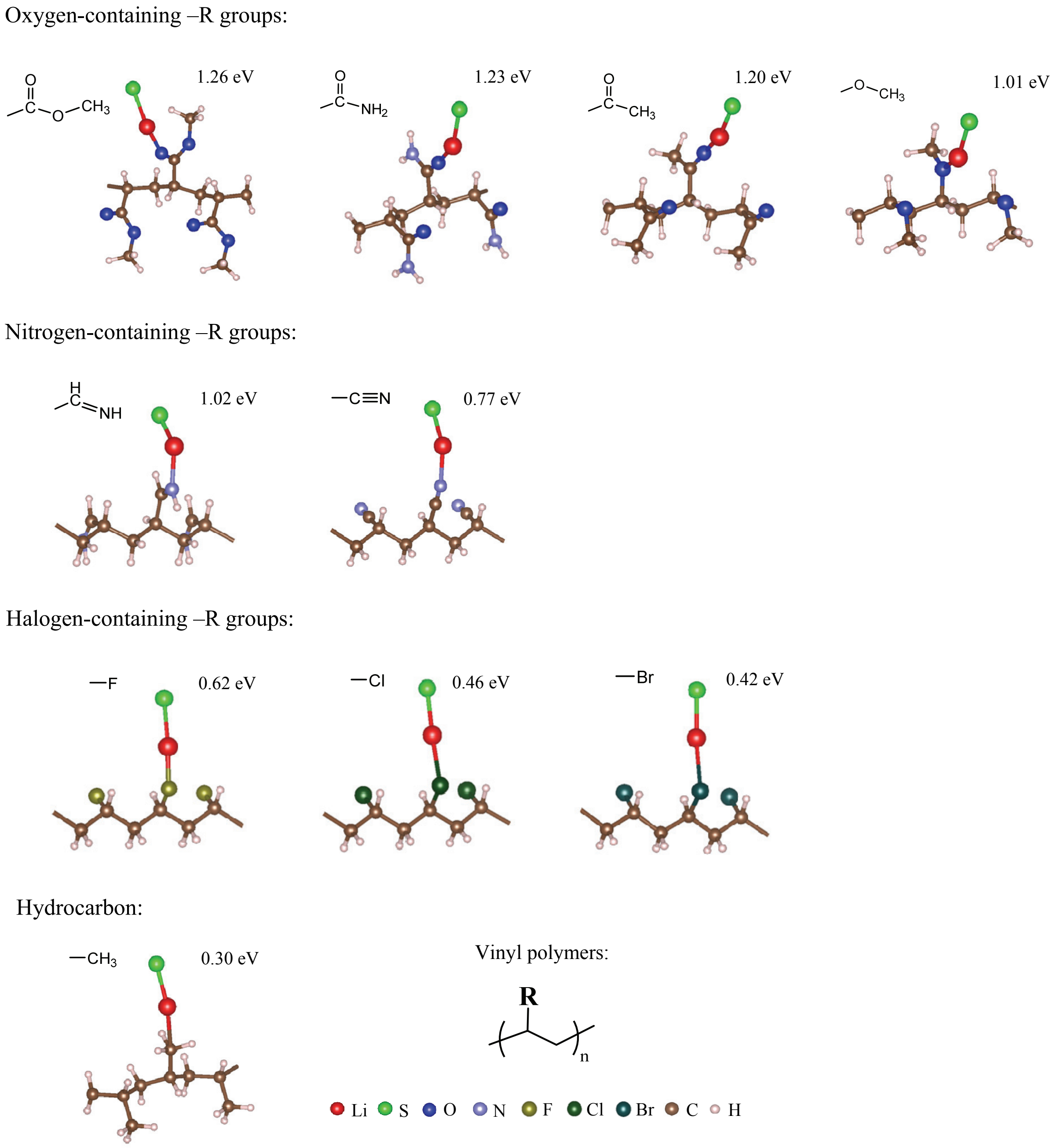

Fig. S2. *Ab initio* simulations showing the most stable configuration and calculated binding energy of Li–S· species with various functional groups (R) based on the framework of vinyl polymers –(CH_2–CHR)$_n$–.