Supplemental Information for:

A Novel Lithium-sulfur Battery Cathode from Butadiene Rubber-caged Sulfur-rich Polymeric Composites Bin Zhang,<sup>a</sup>Shuanjin Wang, <sup>a</sup> Min Xiao, <sup>a</sup>Dongmei Han, <sup>\*a</sup> Shuqin Song,<sup>a</sup> Guohua Chen<sup>b</sup> and Yuezhong Meng<sup>\*a</sup> <sup>a</sup>The Key Laboratory of Low-carbon Chemistry & Energy Conservation of GuangdongProvince/State Key Laboratory of Optoelectronic Materials and Technologies, SunYat-sen University, Guangzhou 510275, P. R. China. <sup>b</sup>Department of Chemical Engineering, Hong Kong University of Science & Technology, Hong Kong , P. R. China. \* Corresponding author. Fax: 86 20 84114113; Tel: 86 20 84114113 E-mail: mengyzh@mail.sysu.edu.cn (Yuezhong Meng) and

handongm@mail.sysu.edu.cn (Dongmei Han)

*Electrochemical Measurement:* The BR-SPC and BR-SPC-SP cathodes were prepared by a slurry coating procedure. The cathode slurry consisted of 70 wt % of BR-SPC composites, 20 wt % of carbon black (Super P) and 10 wt% of polyvinylidene fluoride (PVDF). N-methyl pyrrolidinone (NMP) was used as the solvent. The slurry was coated onto aluminum foil current collectors and then dried at 60 °C overnight. The electrodes were cut into disks of 10 mm in diameter. CR2025type coin cells were assembled in an argon-filled glove box, using an electrolyte of 1 M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) in a mixed solvent of 1,3dioxolane (DOL) and dimethoxymethane (DME) at a volume ratio of 1 : 1, including 0.1 M LiNiO<sub>3</sub> as an electrolyte additive. Lithium metal was used as the counter electrode and a microporous polyethylene membrane (Celgard 2400) was used as separator. Galvanostatic charge–discharge tests were performed at different current densities in the potential range of 1.5-2.8 V versus Li/Li+ using a CT2001A cell test instrument (LAND Electronic Co. Ltd., China). All specific capacity values were calculated on the basis of sulfur mass. Cyclic voltammetry (CV) measurements were performed using a Solartron S1287 electrochemical interface at a scan rate of 0.1 mV s<sup>-1</sup> in the potential range of 1.5 to 2.8 V versus Li/Li<sup>+</sup>. Electrochemical impedance spectroscopy (EIS) was measured in the 1 MHz to 0.1 Hz frequency range with the applied voltage of 5 mV on an electrochemical working station PCI4/300 (Gamry Instrument, Warminster, PA, USA). All the electrochemical tests were performed at room temperature.

Fig. S1 depicts the cyclic performance of BR-SPC and BR-SPC-SP composites at a rate of 0.5 C. It can be seen that BR-SPC-SP composite has fewer activation circulations and displays better cycling performance than BR-SPC composite. A reversible discharge capacity of 690 mAh g<sup>-1</sup> is achieved at the 4<sup>th</sup> cycle, and keeps 480mAh g<sup>-1</sup> after 100 cycles. Over 50 cycles, the capacity retention of 85 % (from 690 to 583 mAh g<sup>-1</sup>) at 0.5 C is obtained. The high initial specific capacity and short activation process of BR-S-SP composite at 0.5 C are believed resulting from the good electron conductivity of composite by the introduction of Super P, which can facilitate the electrochemical reaction of sulfur or sulfides. This result is in agreement with the result at 0.1 C. However, it is opposite to the result of 0.1 C that BR-SPC-SP composite exhibits higher reversible capacities than BR-SPC during most 100 cycles at 0.5 C. As mentioned above, the fast capacity loss of BR-SPC-SP at 0.1 C is supposed to result from the sulfur or sulfides on the surface and in the pores of Super P. However, the difference between sulfur species confined in and out cage structure becomes smaller at high C-rate. Therefore, BR-SPC-SP composites with higher conductivity show better cyclic performance than BR-SPC composites with lower conductivity. It can be concluded that electron conductivity is crucial for shortening the activation process and increasing the utilization of sulfur effectively. The addition of conductive Super P promotes the cyclic performance for BR based cathode materials at high rate.

EIS profiles of BR-SPC and BR-SPC-SP composites are depicted in Fig. S2 between 1MHz and 0.1 Hz. Comparing its EIS profiles before circulation, after 5 cycles and 10 cycles, as shown in Fig. S2 a, BR-SPC composites possess a similar ohmic resistance (Ro) of 6  $\Omega$  from the high frequency intercept on the real axis, which is related to the intrinsic resistance of the active materials, the ionic resistances of the electrolyte and the contact resistance of the interface between the current collectors and the electrodes.<sup>1</sup>The Nyquist plots of both before circulations and after 10 chargedischarge cycles are composited of two depressed semicircles, but only one depressed semicircle is found for the one after 5 charge-discharge cycles. The depressed semicircle in the high-frequency region corresponds to the total resistance of solid electrolyte interface (SEI) film formed on the electrodes' surface (Rs)<sup>2</sup>, and the depressed semicircle in the medium-frequency region corresponds to the charge transfer resistance (Rct). We can see that both Rs and Rct decrease remarkably after several circulations, indicating a smaller resistance on the electrodes and a better charge transporting for electrochemical reactions in the cells. It can explain well why there is an activation process in the cyclic performance. Rs and Rct of BR-SPC composite after 10 cycles are higher than those of after 5 cycles, suggesting the formation of an insulating layer of lithium sulfide (Li<sub>2</sub>S) after several circulations.<sup>3</sup>A sloping straight line is observed at low-frequency region of Nyquist plots, which corresponds to a semi-infinite Warburg diffusion process.<sup>4</sup>

BR-SPC-SP composite shows the same behavior in EIS profiles as BR-SPC composite, but possesses lower Ro, Rs and Rct than BR-SPC composite, demonstrating the facile transportation of electron and Li+ for electrochemical reactions.<sup>5</sup> It is believed that the addition of Super P boosts electron conductivity, accelerates the reaction kinetics and alleviates interface impedance in the BR based composites. As a result, BR-SPC-SP composite exhibits better cyclic performance than BR-SPC composite at high C-rate.

## Supplementary figures:



Fig. S1 Discharge cyclic performance of BR-SPC and BR-SPC-SP at a current rate of 0.5 C



Fig. S2 EIS profile of BR-SPC (a) and BR-SPC-SP (b) composites between 1MHz and 0.1 Hz

## References

- 1. N. A. Canas, K. Hirose, B. Pascucci, N. Wagner, K. A. Friedrich, R. Hiesgen. Electrochim. Acta. 2013, 97, 42-51.
- Z. F. Deng, Z. A. Zhang, Y. Q. Lai, J. Liu, J. Li, Y. X. Liu. J. Electrochem. Soc. 2013, 160, A553-A558.
- 3. J. Wang, J. Yang, J. Xie, N. Xu. Adv. Mater. 2002, 14, 963–965
- 4. B. Ding, L. F. Shen, G. Y. Xu, P. Nie, X. G. Zhang. Electrochim. Acta. 2013, 107, 78-84.
- 5. K. Jeddi, K. Sarikhani, N.T. Qazvini, P. Chen. J. Power Sources, 2014,245, 656-662.