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**Cover Feature:**

*Zeng et al.*

Conducting Polymers Crosslinked with Sulfur as Cathode Materials  
for High-Rate, Ultralong-Life Lithium–Sulfur Batteries

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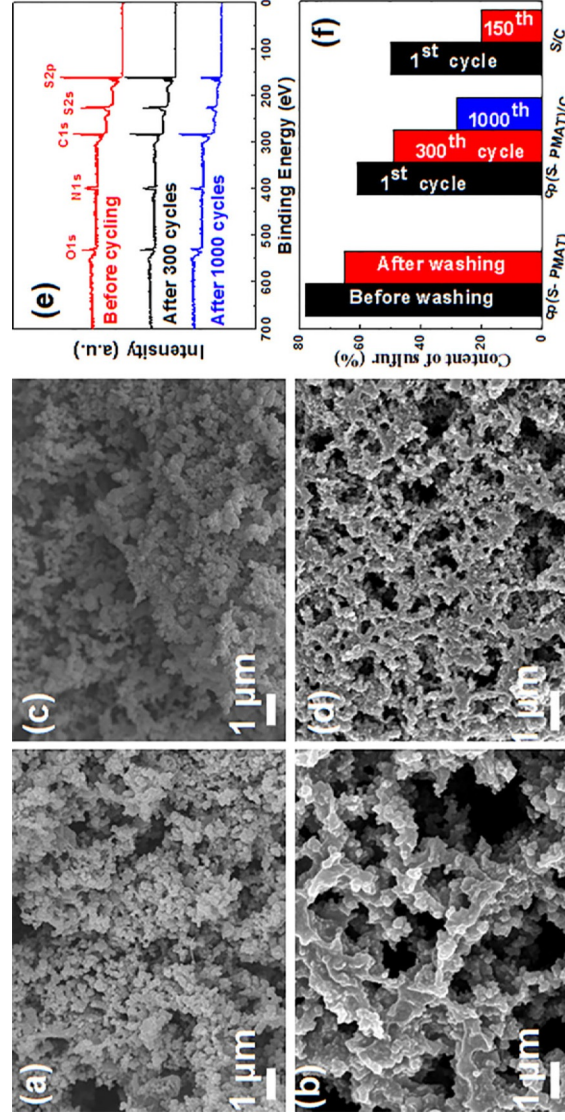












**Figure 6.** SEM images of the S/C electrode (a) before and (b) after 1000 discharge-charge cycles at 2 C and the cp(S-PMAT)/C electrode (c) before and (d) after 1000 discharge-charge cycles at 2 C. (e) XPS survey spectra of the cp(S-PMAT)/C electrode after different discharge-charge cycles at 2 C. (f) Sulfur contents of the samples after different treatments.

remained largely unchanged even after 1000 discharge-charge cycles at 2 C (Figure 6d), but the cavities were significantly smaller. This suggests that the cycling stability of sulfur in cp(S-PMAT)/C was enhanced dramatically compared with that of the S/C electrode owing to the covalent bonding with the thiol groups of PMAT.

The electrode sulfur content was also monitored quantitatively through XPS measurements. As shown in Figure S4b, the relative intensities of the S2s and S2p peaks for S/C decreased drastically owing to the dissolution of a large quantity of polysulfides into the electrolyte. The decline occurred at a much slower rate for cp(S-PMAT) (Figure 6e) from 61 wt% before cycling to 49 wt% after 300 cycles and 30 wt% after 1000 cycles (Figure 6f). Consistent results were obtained through EDS (Figure S12), FTIR spectroscopy, and Raman spectroscopy (Figure S13), through which a vibrational band was observed at  $\tilde{\nu} = 780 \text{ cm}^{-1}$  for the stretching vibration of the C–S bond,<sup>[17a,27]</sup> and another at  $\tilde{\nu} = 1000 \text{ cm}^{-1}$  was attributed to the S–S stretching vibration.<sup>[27]</sup> No apparent variations were observed with the cp(S-PMAT) electrode even after 1000 discharge-charge cycles at 2 C; therefore, cp(S-PMAT) was structurally robust. Taken together, these observations show clearly that the copolymerization of sulfur with PMAT to form covalent bonds between sulfur and the thiol groups of PMAT represents an effective strategy for the chemical confinement of active sulfur and leads to a dramatic enhancement of the rate performance and cycling stability of sulfur-containing cathodes in Li–S batteries.

## Conclusion

Organosulfur cathodes were synthesized by a facile and scalable strategy through the direct copolymerization of sulfur with preformed poly(*m*-aminothiophenol) (PMAT) through inverse

vulcanization. The thus-synthesized cp(S-PMAT) copolymer contained approximately 80 wt% of sulfur, which was cross-linked with the conducting polymer and exhibited a crystalline phase. Electrochemical measurements showed the excellent rate performance of the cp(S-PMAT) cathode, which has capacities of  $880 \text{ mAh g}^{-1}$  at 1 C,  $780 \text{ mAh g}^{-1}$  at 2 C, and  $600 \text{ mAh g}^{-1}$  at 5 C. Notably, the cp(S-PMAT) cathode retained a high capacity of  $495 \text{ mAh g}^{-1}$  after 1000 cycles with an unprecedented capacity retention rate of over 66.9% at a high charge-discharge current of 2 C, which corresponds to a rate diminishment of only 0.040% per cycle. This may be ascribed to the conductive and stable crosslinked network structure of the copolymer cathode, which not only exhibited effective pathways for electron and ion transports but also confined sulfur strongly through abundant chemical bonds with the PMAT backbone. These results indicate that copolymerization is a facile method for the effective chemical confinement of polysulfides to improve the performances of Li–S batteries.

## Experimental Section

### Synthesis of PMAT

In a typical reaction, *m*-aminothiophenol (3 g) was dispersed in a 1 M HCl aqueous solution under magnetic stirring in an Ar-filled round-bottomed flask. The temperature of the solution was maintained at 0 °C with an ice bath. A 1 M ammonium persulfate (APS) aqueous solution (30 mL) was added slowly into the above solution. The color of the mixture changed gradually from gray to light brown to dark brown and finally green, which signified the polymerization of *m*-aminothiophenol to PMAT. The reaction proceeded overnight in an ice bath. The solid product was collected, washed several times with deionized (DI) water, and dried at 30 °C in a vacuum oven to afford the PMAT product.



### Preparation of cp(S-PMAT)

The PMAT was mixed with sulfur at a PMAT/sulfur mass ratio of 1:6. The mixture was heated at 150 °C for 1 h in an argon atmosphere to impregnate the molten sulfur into the PMAT and then heated further at 170 °C for 8 h to initiate the ring-opening polymerization of sulfur with PMAT to form the highly crosslinked cp(S-PMAT) copolymer.

### Materials characterization

The SEM measurements were conducted with a Hitachi S-4800 field-emission scanning electron microscope (FESEM). The TEM measurements were conducted with a JEOL JEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV. The XRD profiles were obtained with a Bruker D8 instrument with CuK $\alpha$  radiation. The FTIR spectra were recorded with a Nicolet 6700 FTIR spectrometer in transmittance mode. The UV/Vis absorption spectroscopy measurements were performed with a UV-2600 spectrophotometer. The Raman spectra were acquired with a Lab RAM HR Evolution Raman spectrometer. The XPS measurements were performed with a Phi X-tool XPS instrument. The TGA was performed with a Mettler instrument under a N $_2$  atmosphere at a ramping rate of 10 °C min $^{-1}$ . For the electrical conductivity measurements, powder materials were compressed at a pressure of 40 MPa with a tablet-compression machine to form circular sheets with the same diameter. The electrical conductivities were measured with a Keithley 2636B source-meter by a two-probe method.

To ensure that the un-crosslinked sulfur was removed completely by CS $_2$  washing, the sulfur-rich composites dispersed in CS $_2$  were subjected to ultrasonic agitation in a water bath set at 25 °C for approximately 1 h and then dried for subsequent XRD, XPS, and EDS measurements.

### Coin-cell fabrication and battery tests

In brief, polyvinylidene fluoride (PVDF), which served as a binder, was dissolved in *N*-methyl-2-pyrrolidone (NMP) under vigorous magnetic stirring. The active material cp(S-PMAT) and conductive carbon black (Super P, Taiyuan Liyuan Li-ion Battery Technology Co., Ltd.) were added into the PVDF solution to form a homogeneous slurry at a cp(S-PMAT)/PVDF/conductive carbon black mass ratio of 80:10:10. Subsequently, the slurry was deposited on aluminum foil, which was used as a current collector, by the doctor-blade method and then dried at 45 °C for 24 h in a vacuum oven. The thus-prepared cathode foil was pressed and cut into circular sheets with a diameter of 12 mm. The mass loading of active sulfur was varied from 1.5 to 2.0 and 2.5 mg cm $^{-2}$  depending on the thickness of the coating layer. The CR2032-type coin cells were assembled in an Ar-filled glovebox with oxygen and moisture contents of less than 0.1 ppm. The cell comprised a cp(S-PMAT) positive electrode, a Celgard 2400 diaphragm separator, lithium foil as the reference/counter electrode, and a mixed solution of 1,3-dioxolane and 1,2-dimethoxyethane (1:1 v/v) containing 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.1 M LiNO $_3$  as the electrolyte. For comparison, coin cells with a mixture of PMAT and S as the cathode (S&PMAT) were prepared in a similar manner at the same loading of active sulfur. In addition, conventional sulfur cathodes were also prepared at a sulfur/conductive carbon black/PVDF mass ratio of 50:40:10 (also the same mass loading of active sulfur).

Galvanostatic discharge–charge measurements of the as-fabricated cells were performed by potential cycling between 1.5 and 3.0 V (vs. Li/Li $^{+}$ ) at different current rates with a button-cell testing system (LANHE CT2001A, 5 V, 20 mA). The cyclic voltammograms were recorded within the potential range 1.5 to 3.0 V at various scan rates. The EIS studies were performed in the charge state between frequencies of 100 kHz and 10 mHz at an alternating current (AC) amplitude of 5 mV.

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- [1] a) L. Borchart, M. Oschatz, S. Kaskel, *Chem. Eur. J.* **2016**, *22*, 7324–7351; b) M. A. Pope, I. A. Aksay, *Adv. Energy Mater.* **2015**, *5*, 1500124.  
 [2] H. Cheng, S. Wang, *J. Mater. Chem. A* **2014**, *2*, 13783–13794.  
 [3] a) V. Etacheri, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **2011**, *4*, 3243–3262; b) D. Zheng, X. Q. Yang, D. Qu, *ChemSusChem* **2016**, *9*, 2348–2350.  
 [4] D. Bresser, S. Passerini, B. Scrosati, *Chem. Commun.* **2013**, *49*, 10545–10562.  
 [5] L. Wang, D. Wang, F. Zhang, J. Jin, *Nano Lett.* **2013**, *13*, 4206–4211.  
 [6] Y. Xiang, J. Li, J. Lei, D. Liu, Z. Xie, D. Qu, K. Li, T. Deng, H. Tang, *ChemSusChem* **2016**, *9*, 3023–3039.  
 [7] J. Wang, J. Yang, C. Wan, K. Du, J. Xie, N. Xu, *Adv. Funct. Mater.* **2003**, *13*, 487–492.  
 [8] a) J. Zhou, X. Yu, X. Fan, X. Wang, H. Li, Y. Zhang, W. Li, J. Zheng, B. Wang, X. Li, *J. Mater. Chem. A* **2015**, *3*, 8272–8275; b) H. Yang, S. J. Bradley, A. Chan, G. I. Waterhouse, T. Nann, P. E. Kruger, S. G. Telfer, *J. Am. Chem. Soc.* **2016**, *138*, 11872–11881.  
 [9] a) G. Li, J. Sun, W. Hou, S. Jiang, Y. Huang, J. Geng, *Nat. Commun.* **2016**, *7*, 10601; b) J. Song, T. Xu, M. L. Gordin, P. Zhu, D. Lv, Y. B. Jiang, Y. Chen, Y. Duan, D. Wang, *Adv. Funct. Mater.* **2014**, *24*, 1243–1250; c) C. H. Chang, S. H. Chung, A. Manthiram, *Small* **2016**, *12*, 174–179; d) S. H. Chung, P. Han, R. Singhal, V. Kalra, A. Manthiram, *Adv. Energy Mater.* **2015**, *5*, 1500738; e) R. Singhal, S. H. Chung, A. Manthiram, V. Kalra, *J. Mater. Chem. A* **2015**, *3*, 4530–4538; f) R. Elazari, G. Salitra, A. Garsuch, A. Panchenko, D. Aurbach, *Adv. Mater.* **2011**, *23*, 5641–5644; g) M. Behzadriadi, O. Lavrova, T. Busani, *J. Mater. Chem. A* **2016**, *4*, 7830–7840; h) C. Tang, B. Q. Li, Q. Zhang, L. Zhu, H. F. Wang, J. L. Shi, F. Wei, *Adv. Funct. Mater.* **2016**, *26*, 577–585.  
 [10] S. H. Chung, C. H. Chang, A. Manthiram, *Energy Environ. Sci.* **2016**, *9*, 3188–3200.  
 [11] Z. W. Seh, W. Li, J. Cha, G. Zheng, Y. Yang, M. T. McDowell, P. C. Hsu, Y. Cui, *Nat. Commun.* **2013**, *4*, 1331.  
 [12] a) L. Qie, A. Manthiram, *Adv. Mater.* **2015**, *27*, 1694–1700; b) N. Osada, C. B. Bucur, H. Aso, J. Muldoon, *Energy Environ. Sci.* **2016**, *9*, 1668–1673.  
 [13] H. Wang, W. Zhang, H. Liu, Z. Guo, *Angew. Chem. Int. Ed.* **2016**, *55*, 3992–3996; *Angew. Chem.* **2016**, *128*, 4060–4064.  
 [14] R. Chen, T. Zhao, J. Lu, F. Wu, L. Li, J. Chen, G. Tan, Y. Ye, K. Amine, *Nano Lett.* **2013**, *13*, 4642–4649.  
 [15] Q. Zhang, X. B. Cheng, J. Q. Huang, H. J. Peng, F. Wei, *Carbon* **2015**, *81*, 850–852.  
 [16] Z. Li, J. Zhang, B. Guan, D. Wang, L. M. Liu, X. W. Lou, *Nat. Commun.* **2016**, *7*, 13065.  
 [17] a) S. N. Talapaneni, T. H. Hwang, S. H. Je, O. Buyukkakir, J. W. Choi, *Angew. Chem. Int. Ed.* **2016**, *55*, 3106–3111; *Angew. Chem.* **2016**, *128*, 3158–3163; b) W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Gu-

- alnick, J. Park, A. Somogyi, P. Theato, M. E. Mackay, Y. E. Sung, K. Char, J. Pyun, *Nat. Chem.* **2013**, *5*, 518–524; c) S. Diez, A. Hoeffling, P. Theato, W. Pauer, *Polymer* **2017**, *9*, 59–66; d) T. Tsuda, A. Takeda, *Chem. Commun.* **1996**, 1317–1318; e) Y. Ding, A. S. Hay, *J. Polym. Sci. Part A* **1997**, *35*, 2961–2968; f) H. Kim, J. Lee, H. Ahn, O. Kim, M. J. Park, *Nat. Commun.* **2015**, *6*, 7278; g) Y. Fu, A. Manthiram, *Chem. Mater.* **2012**, *24*, 3081–3087.
- [18] a) B. Oschmann, J. Park, C. Kim, K. Char, Y. E. Sung, R. Zentel, *Chem. Mater.* **2015**, *27*, 7011–7017; b) B. C. Yu, J. W. Jung, K. Park, J. B. Goodenough, *Energy Environ. Sci.* **2017**, *10*, 86–90; c) J. A. Chang, Q. Wu, X. Du, S. Chen, J. Shen, Q. Song, J. Xie, W. Wu, *Chem. Commun.* **2016**, 52, 4525–2528; d) S. Zeng, L. Li, D. Zhao, J. Liu, W. Niu, N. Wang, S. Chen, *J. Phys. Chem. C* **2017**, *121*, 2495–2503.
- [19] Y. Cui, Y. Fu, *ACS Appl. Mater. Interfaces* **2015**, *7*, 20369–20376.
- [20] a) N. Xu, T. Qian, X. Liu, J. Liu, Y. Chen, C. Yan, *Nano Lett.* **2017**, *17*, 538–543; b) B. Li, S. Li, J. Xu, S. Yang, *Energy Environ. Sci.* **2016**, *9*, 2025–2030.
- [21] B. Ding, Z. Chang, G. Xu, P. Nie, J. Wang, J. Pan, H. Dou, X. Zhang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 11165–11171.
- [22] a) C. Zu, A. Manthiram, *Adv. Energy Mater.* **2013**, *3*, 1008–1012; b) T. Ramanathan, F. T. Fisher, R. S. Ruoff, L. C. Brinson, *Chem. Mater.* **2005**, *17*, 1290–1295.
- [23] a) X. Peng, K. Huo, J. Fu, X. Zhang, B. Gao, P. K. Chu, *Chem. Commun.* **2013**, 49, 10172–10174; b) J. Chen, Z. Xia, H. Li, Q. Li, Y. Zhang, *Electrochim. Acta* **2015**, *166*, 174–182.
- [24] C. O. Baker, X. Huang, W. Neilson, R. B. Kaner, *Chem. Soc. Rev.* **2017**, *46*, 1510–1525.
- [25] Z. Wang, Y. Dong, H. Li, Z. Zhao, H. B. Wu, C. Hao, S. Liu, J. Qiu, X. W. Lou, *Nat. Commun.* **2014**, *5*, 5002.
- [26] a) M. R. Kaiser, X. Liang, H. K. Liu, S. X. Dou, J. Z. Wang, *Carbon* **2016**, *103*, 163–171; b) S. Li, T. Mou, G. Ren, J. Warzywoda, B. Wang, Z. Fan, *ACS Energy Lett.* **2016**, *1*, 481–489.
- [27] W. Li, M. Zhou, H. Li, K. Wang, S. Cheng, K. Jiang, *Energy Environ. Sci.* **2015**, *8*, 2916–2921.

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