DOI: 10.1002/ ((please add manuscript number))

Article type: Communications

Direct observation of the redistribution of sulfur and polysulfides in Li-S batteries during first cycle by *in situ* X-Ray fluorescence microscopy

Xiqian Yu^{a†}, Huilin Pan^{b†}, Yongning Zhou^a, Paul Northrup^a, Jie Xiao^b, Seongmin Bak^a, Mingzhao Liu^a, Kyung-Wan Nam^c, Deyang Qu^d, Jun Liu^{*b}, Tianpin Wu^e and Xiao-Qing Yang^{*a}

Dr. X. Q. Yu, Dr. Y. N. Zhou, Dr. P. Northrup, Dr. S. M. Bak, Dr. M. Z. Liu, Dr. X. -Q. Yang

Brookhaven National Laboratory, Upton, NY11973, USA

E-mail: xyang@bnl.gov

Dr. H. L. Pan, Dr. J. Xiao, Dr. J. Liu.

Joint Center for Energy Storage Research, Pacific Northwest National Laboratory, Richland, WA99352

E-mail: jun.liu@pnnl.gov

Prof. K. W. Nam

Department of Energy and Materials Engineering, Dongguk University-Seoul 26 Pil-dong, 3-ga, Jung-gu, Seoul, 100-715, Republic of Korea

Prof. D. Y. Qu

Department of Chemistry, University of Massachusetts at Boston, MA 02125-3393, USA

Dr. T. Wu

X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, USA

†Xiqian Yu and Huilin Pan contributed equally to this paper.

Keywords: Lithium-Sulfur batteries, energy storage, reaction mechanism, *in situ* technique, microspectroscopy

The demands on low cost and high energy density rechargeable batteries for both transportation and large-scale stationary energy storage are stimulating more and more research toward new battery systems.^[1-4] Since sulfur is an earth-abundant

material with low cost, research on the high energy density Li-S batteries (2600 Wh/Kg) are getting more and more attention.^[5-7] The reactions between sulfur and lithium during charge-discharge cycling are quite complicated, going through multiple electron transfer process associated with chemical and electrochemical equilibrium between long- and short-chain polysulfide Li_2S_x intermediates ($1 < x \leq 8$).^[8,9] It is reported that the long-chain polysulfides can be dissolved into electrolyte with aprotic organic solvents and migrated to the Li anode side. This so-called "shuttle effect" is believed to be the main reason for capacity loss and low columbic efficiency of the Li-S batteries.^[8,10] In the past few years, a great deal of efforts have been made on how to overcome the problem of polysulfide dissolution through new sulfur electrode construction and cell designs, as well as the modification of the electrolyte.^[11-17] Although it has been reported by several publications that some Li-S cells can sustain more than a thousand cycles based on the thin film electrode configurations, the long-term cycling stability is still one of the major barriers for the real application of Li-S batteries.^[18] More in-depth studies on the fundamental understanding of the sulfur reaction mechanism and interactions among the different polysulfide species, the electrolyte and the electrodes are still greatly needed. Various *in situ* techniques have been developed and applied to study the mechanism of the sulfur chemistry in Li-S batteries during electrochemical cycling, such as transmission X-ray microscopy (TXM),^[19,20] X-ray absorption spectroscopy (XAS),^[21-23] X-ray diffraction (XRD),^[23,24] UV-visible spectroscopy^[25] and electron paramagnetic resonance (EPR)^[26]. The applications of these characterization techniques have demonstrated

their power in probing the structure changes, morphology evolutions and coordination of sulfur and polysulfides with the electrolyte in Li-S cells, providing complementary information to each other thus enhancing the understanding in Li-S battery systems. In this communication, *in situ* X-ray fluorescence (XRF) microscopy was combined with X-ray absorption spectroscopy (XAS) to directly probe the morphology changes of Li-S batteries during first cycle. The morphology changes of the sulfur electrode and the redistribution of sulfur and polysulfides were monitored in real time through the XRF images, while the changes of the sulfur containing compounds were characterized through the XAS spectra simultaneously. In contrast to other studies using *ex situ* or single characterization technique as reported in the literatures, the *in situ* technique used in this work has the unique feature of probing the Li-S cell under operating conditions, as well as the combination of XRF imaging with spectroscopy data. By doing this, the morphology evolution and redistribution of specific sulfur particles during cycling can be tracked and identified at certain locations in a real time. In addition, this technique allows us to select the field of view (FOV) area from micron to centimetre size, providing the capability to study the Li-S reactions not just at the material level, but also at the electrode level. This is very important for both understanding Li-S chemistry and designing effective strategies for Li-S batteries.

Figure 1a shows the *in situ* cell configuration. A sulfur-carbon composite electrode for the XRF microscopy study was prepared by depositing micron-sized sulfur flakes on carbon paper (as the current collector), in order to fit with the spatial resolution of the instrument ($\sim 7\mu\text{m}$). The optical image of the electrode disk ($\phi=8\text{mm}$) is shown in

Figure 1b, in which some large micron-sized S flakes are visible as bright dots. The XRD pattern of the S flake/Carbon paper electrode is also presented in Figure 1b with the diffraction peaks associated with crystalline sulfur (JCPDS No. 08-0247). The inset in Figure 1b exhibits the XRF image of the S flake/Carbon paper electrode collected in the window region of the *in situ* cell. X-ray fluorescence (XRF) imaging is a technique based on the emission of characteristic fluorescent X-ray photons from a material that has been excited by incident X-ray. The emitted photon energy is uniquely related to certain element. The detected characteristic X-ray photon intensity is proportional to the weight concentration of the element, providing a capability of concentration distribution imaging for certain element in a quantitative way.^[27] In this work, the XRF microscopy experiments were performed by setting the X-ray energy at 2500eV, higher than inner-shell excitation energy of the sulfur atom for all sulfur species (Sulfur, polysulfides, Li_2S etc), the intensity of XRF signal is mainly related to the concentration of sulfur element only. XRF images were collected in a continuous scan mode. The data acquisition time for each data point was millisecond and it took several minutes to obtain a full image. The fluorescence signal level from the sulfur element (for the pristine sample, it represents the crystalline sulfur) is reflected by the color scale as shown in Figure 1b. The darker color indicates the stronger fluorescence signal from the sulfur element at that spot, equivalent to the higher weight concentration of the sulfur element. It can be seen from the image that the S particles, having a size distribution ranging from several microns to hundreds of microns, are embedded within the carbon matrix. This observation is in good

agreement with the optical and SEM result (Figure S2a). In order to avoid the artefacts which might be introduced by the X-ray radiation damage, pre-experimental test was also carried out to compare the *ex situ* XRF images of electrode before and after long time X-ray radiation (without simultaneous electrochemical cycling). As shown in Figure S1, illumination of the selected X-ray intensity for a period of 30 minutes didn't cause significant changes in term of morphology and the chemical nature of the S particles.

To study the morphology changes of the sulfur electrode during electrochemical cycling, an *in situ* Li-S cell was discharged/charged at a C/5 rate (332 mA g^{-1}) in the voltage range of 1.8V-3V, and the variation in particle morphology was monitored. The *in situ* cell delivers the first discharge capacity of 950 mAh g^{-1} but a lower charge capacity of 754 mAh g^{-1} , probably due to the specially designed sulfur electrode (loose structure of the carbon paper and low content of the sulfur) as well as the LiNO_3 additive used that can prevent the "shuttle effect". Figure 2 shows the XRF images collected at different depth of discharge (DOD) and state of charge (SOC) as labelled on the charge-discharge curve. The images were taken from an actual large area of $3\text{mm} \times 3\text{mm}$ covering the whole cell window (with lower resolution of $100\mu\text{m} \times 100\mu\text{m}$), giving the overall morphology changes of the electrode during electrochemical cycling. The most significant morphological changes occur from image a to image b, corresponding to the first plateau in discharge where crystallized sulphur with crown structure is reduced to the long-chain polysulfides.^[9] During this plateau, most of the visible micron-sized large particles disappear with simultaneously

increased background signal covering the whole imaging area, showing the spreading concentration of sulfur. This indicates that the cleavage of the crystallized sulphur rings takes place immediately at the beginning of the discharge process and simultaneously causes some active material loss in the electrode through the fast dissolution of polysulfides into electrolyte.^[28] At the end of the discharge (state c), essentially all the original S particles in the examined area disappear. At the same time the formation of new faceted large particles at different locations other than the original ones can be observed, which are believed to be insoluble polysulfide crystals, including Li_2S_2 and/or Li_2S , which will be further discussed later in this paper. During re-charge process, the overall morphology doesn't show significant changes. These results indicate that the major morphology changes take place at the first discharge process, which is associated with the dissolution of polysulfides. SEM measurements were also performed and the SEM observations are in good agreement with the XRF results as shown in Figure S2. In order to detect more detailed morphology changes of the sulfur active material, another set of images were collected simultaneously on a smaller area of $500\mu\text{m} \times 300\mu\text{m}$ with higher spot resolution of $7\mu\text{m} \times 7\mu\text{m}$. The results are displayed on Figure 3. The dissolution of the original S particles (from state a to state b) and the nucleation growth of the insoluble short-chain polysulfides (from state b to state c) can be clearly visualized during discharge process. During charge process from state c to state d, the dark color of the insoluble polysulfide particles turns into lighter color, indicating their possible conversion to the soluble long-chain polysulfides that dissolve into the electrolyte or spread again among carbon matrix.

From state d to state e, the appearance of some new dark spots at different locations than those in state d indicates the possible re-formation of sulfur particles. Such possibility can be confirmed by taking the *ex situ* XRF images and XAS data after recharging the sample to 3V as shown in supporting information Figure S3, in which the XAS results show clearly that the newly formed large particles are having the similar features with the crystal sulfur instead of Li_2S . It can be deduced from Figure 2 and Figure 3, that the S compounds are continuously redistributed during the electrochemical cycling, in a good agreement with what have been proposed in our previous published report.^[29] In addition, the re-deposition of the insoluble polysulfides at the end of the discharge takes place at different locations from where the original sulfur particles disappear. This is different from the results previously reported by Nelson *et al.* where they observed that the re-deposition of the insoluble polysulfides preferentially took place on the original particles.^[19] Our new results suggest that such nucleation and re-deposition process may be affected by the different charge-discharge conditions, such as current densities and cut-off voltages. The electrode configuration also matters. In fact, in some other areas on the same electrode, some discharged particles especially having relatively large particle size were dissolved again during the entire re-charge process (shown in Figure S4). It will be further discussed later that such areas become inactive in subsequent cycling, due to the deposition of the insoluble polysulfides.

Since the XRF images can only provide morphology images of sulfur without chemical information of the sulfur compounds, XANES spectra were collected at

certain spots after each XRF image was captured at various charge-discharge states. A micron-sized X-ray beam ($\sim 7\mu\text{m} \times 7\mu\text{m}$) was used to probe the evolution of the chemical state changes of the sulfur. Since the XAS spectra measured in the energy range around sulfur K-edge (2472eV) can be significantly altered by self-absorption (SA) effect, dilute samples with a low concentration of the absorbing element or thin film samples with thickness less than absorption length are normally required.^[22] Unfortunately, as mentioned above that the XRF microscopy measurements require micron-sized S flake electrode, which is thicker than the absorption length. Therefore, the self-absorption (SA) effect of the XANES measurements in this study is inevitable, resulting in a reduction of the absorption peaks and may cause some distortion of the XANES features. Therefore the quantitative analysis such as linear combination fitting was not performed.^[30] However, the general features, such as the relative positions and intensities of the absorption peaks are still meaningful to identify the reaction products by comparing with the reference spectra of the standard materials. The spectra of S and Li_2S standards are plotted in dash lines as shown in Figure 4. It can be seen in Figure 4a that the XANES spectrum collected on the pristine S particle shows a distorted absorption peak in comparison with spectrum collected on a dilute S sample (10wt%), due to the self-absorption effect. This self-absorption becomes less significant when discharge process is initiated and S particles begin to dissolve and redistribute in the cell, as evidenced by the increase of the peak intensity for state b. At the same time, a shoulder peak at the lower energy side appears, indicating the formation of the polysulfides.^[31] Upon further discharging

to state b1 and state c, the spectra reveal similar features to that of the Li_2S standard, indicating that Li_2S is one of the major components in the final discharge product. During re-charge process, the spectra change in a reverse manner as during discharge process. The spectrum collected at the 3V state (state e) shows that part of the long-chain polysulfides are not fully converted back to crystallized S at the end of the charge. Overall, the evolution of the spectra reveals the Li-S reaction mechanism, which is in a good agreement with the morphology changes observed through XRF images during discharge and charge. In order to see the particle size effects, additional XANES spectra were collected at the same sets of charge-discharge states but on a much larger size particle, which are shown in Figure 4b. For this larger particle, unlike in Figure 4a for small particle, the XANES results show that the Li_2S formed during discharge process didn't convert back to S during the recharge process, indicating the reaction kinetics might be strongly size dependent. In addition, the insoluble short-chain polysulfides and Li_2S re-deposited on the large particles may limit the complete penetration of the electrolyte into the interior particle and break the electronic contact with carbon conducting agent in the host matrix, making this particle "inactive" in the subsequent cycling. This type of inactivation is one important contributor for the rapid capacity fading of the Li-S batteries during cycling.^[8]

Since the *in situ* XRF experiment revealed the dissolution and re-deposition of the polysulfides leading to redistribution of the sulfur, the sulfur redistribution on the Li anode side was also studied. The *ex situ* XRF and XANES experiments were

performed on lithium foil anode. A sulfur/Ketjen black composite electrode with higher sulfur loading was used for the anode study in order to enhance the signal-to-noise ratio, which would not be good enough if dilute concentration of S were used in cathode. Figure 5a exhibits the S XRF images collected on sulfur/Ketjen black composite electrode, fresh lithium foil and lithium foil anode harvested from the Li-S cell after one cycle respectively. It is clearly seen that some of the sulfur species were deposited on the lithium anode, resulting in the low columbic efficiency as well as the poor cycle life of the Li-S cell.^[10] The XRF images of the lithium foils harvested from the Li-S cell discharged at 2.1V, 1.7V and charged to 3V are presented in Figure 5b (Full view images are shown in Figure S5), along with XANES spectra (Figure 5c) to identify the sulfur compounds on the lithium foils. Long-chain polysulfides can be found on the lithium foil anode from the discharged 2.1V cell while insoluble short-chain polysulfides or Li_2S can be identified on lithium foil anodes from both fully discharged (1.7V) and charged (3V) cells. These polysulfide species were either migrated from the cathode and then deposited on the lithium foil anodes, or chemically reacted with the lithium foil causing anode corrosion.^[32] These polysulfide deposition and anode corrosion are key factors of severe capacity fading of the Li-S batteries during cycling. It is worthwhile to point out that despite the sulfur was better encapsulated in sulfur/Ketjen black composite electrode than that in S flake/carbon paper electrode, the experiment results indicate that the dissolution and redistribution of the sulfur might still be unavoidable once discharge is initiated. In fact, sulfur active material is redistributed over the whole inside of Li-S cell upon cycling through

the electrolyte as shown in Figure 5d. These results tell us that in order to solve the capacity fading problem caused by sulfur redistribution in Li-S batteries, modification on the sulfur cathode side is not enough. Anode protection is equally important either through the interface modification or using alternative anode materials.^[33] The development of new “non-corrosive” electrolytes is also needed.^[34-37]

In summary, *in situ* XRF microscopy combined with XAS measurements were utilized to track the morphology and chemical state changes of the sulfur electrode in real time throughout the entire first electrochemical cycle. The results of these studies are schematically illustrated in Figure 5d. The dissolution and redistribution of the S was directly observed. The long-chain polysulfides were generated as soon as the discharge was initiated. Some of the dissolved polysulfide species were either deposited and/or reacted with lithium metal, resulting in low columbic efficiency and poor cycle life of the Li-S batteries. In addition, the results obtained through this work demonstrated that it is quite difficult to prevent the dissolution of the polysulfides only by the capsulation of S and other treatments of sulfur electrodes. Therefore, integrated approaches such as selection and development of new electrolytes, additives and other controlled charge-discharge protocols are quite important for the long-term cycling stability of the cells. These results will provide new fundamental insight and valuable guidance for the research and development of the Li-S system. Finally, the novel *in situ* XRF microscopy and combined XAS technique developed and applied in this study can be used as a powerful tool to investigate the Li-S systems in real time under operando conditions. It can also be applied to other energy

storage systems benefitted from its elemental selectivity and appropriate spatial resolution nature.

Experimental section:

Material synthesis and Electrochemical cells: S flake/carbon paper electrode was prepared by slurring the micro-sized sulfur flakes, carbon nanotube, and polyvinylidene fluoride (PVDF) with a weight ratio of 90:5:5 in *n*-methyl pyrrolidone (NMP) solvent, then coating the mixture onto carbon paper. For sulfur/Ketjen black electrode, the sulfur/Ketjen black composite was grounded at a weight ratio of 80:20 and then heat at 155 °C for 12h. The obtained composite was further mixed with super P and polytetrafluoroethylene (PTFE) homogeneously (weight ratio of 90:5:5). The final S/C electrodes with sulfur concentration of 19.6 wt% were obtained. *In situ* experiments were carried out using a CR2032 coin cell with a ϕ 3mm hole window covered with polyethylene film (Type: 3517) to allow X-ray beam to pass through. The detailed cell configuration was reported in our previous work.^[38] Coin cell was assembled with S flake/carbon paper or Sulfur/Ketjen black composite electrode as working electrode, lithium foil as counter electrode, Celgard film as separator in an Ar-filled glove box. The electrolyte was 1 M LiClO₄ and 1.5 wt % LiNO₃ dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 in volume).

X-ray fluorescence microscopy and X-ray absorption spectroscopy: X-ray fluorescence microscopy and Sulfur K-edge XAS experiments were carried out at beamline X15B of the National Synchrotron Light Source (NSLS) at Brookhaven

National Laboratory. X-ray fluorescence microscopy measurements were performed in a continuous scan mode with different step size for large-size and small-size image scanning respectively. Compound X-ray focusing was achieved using a toroidal first-stage mirror collecting 4 mrad of radiation from the Synchrotron bend-magnet source and focusing it to a secondary source aperture; this aperture was then re-focused to micron size by a pair of mirrors in the Kirkpatrick-Baez geometry. The X-ray energy was set at 2500eV, which is above the absorption edge of the sulfur. The *in situ* XAS experiments were performed in fluorescence mode using a Si (111) double-crystal; Energy resolution was optimized and higher-order harmonics were eliminated by using a vertically-collimating mirror between the source and monochromator. X-ray Absorption Near Edge Structure (XANES) data was analyzed by ATHENA software package.^[39]

Acknowledgement:

This work at BNL was supported by the U.S. Department of Energy, the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies under Contract Number DE-SC0012704. The research performed by the scientists at the Pacific Northwest National Laboratory (PNNL) was supported as part of the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES). Dr. Kyung-Wan Nam is supported by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning grant funded by

the Korea government Ministry of Trade, Industry & Energy (Project no. 20142020103090). SEM characterization was performed at the Center for Functional Nanomaterials (BNL), which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704. The authors acknowledge technical supports by the scientists at beamline X15B, X14A of NSLS (BNL) and 9-BM-B of APS (ANL), supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

Additional information:

Supporting Information is available from the Wiley Online Library or from the author.

Competing financial interests:

The authors declare no competing financial interests.

References

- [1] B. Dunn, H. Kamath, J. M. Tarascon, *Science* **2011**, 334, 928.
- [2] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater* **2012**, 11, 19.
- [3] J. Liu, J. G. Zhang, Z. Yang, J. P. Lemmon, C. Imhoff, G. L. Graff, L. Li, J. Hu, C. Wang, J. Xiao, G. Xia, V. V. Viswanathan, S. Baskaran, V. Sprenkle, X. Li, Y. Shao, B. Schwenzer, *Adv. Funct. Mater.* **2013**, 23, 929.
- [4] H. Pan, Y. S. Hu, L. Chen, *Energy Environ. Sci.* **2013**, 6, 2338.
- [5] X. Ji, K. T. Lee, L. F. Nazar, *Nat. Mater.* **2009**, 8, 500.
- [6] A. Manthiram, Y. Fu, Y. S. Su, *Acc. Chem. Res.* **2012**, 46, 1125.
- [7] A. Manthiram, Y. Fu, S. H. Chung, C. Zu, Y. S. Su, *Chem. Rev.* **2014**, 114, 11751.
- [8] S. E. Cheon, S. S. Choi, J. S. Han, Y. S. Choi, B. H. Jung, H. S. Lim, *J. Electrochem. Soc.* **2004**, 151, A2067.
- [9] S. S. Zhang, *J. Power Sources* **2013**, 231, 153.
- [10] Y. V. Mikhaylik, J. R. Akridge, *J. Electrochem. Soc.* **2004**, 151, A1969.
- [11] X. Ji, L. F. Nazar, *J. Mater. Chem.* **2010**, 20, 9821.
- [12] Y. S. Su, A. Manthiram, *Nat. Commun.* **2012**, 3, 1166.
- [13] H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li, A. Jackson, Y. Cui, H. Dai, *Nano Lett.* **2011**, 11, 2644.
- [14] L. Suo, Y. S. Hu, H. Li, M. Armand, L. Chen, *Nat. Commun.* **2013**, 4, 1481.

- [15] S. Xin, L. Gu, N. H. Zhao, Y. X. Yin, L. J. Zhou, Y. G. Guo, L. J. Wan, *J. Am. Chem. Soc.* **2012**, 134, 18510.
- [16] Y. X. Yin, S. Xin, Y. G. Guo, L. J. Wan, *Angew. Chem. Int. Ed.* **2013**, 52, 13186.
- [17] E. S. Shin, K. Kim, S. H. Oh, W. I. Cho, *Chem. Commun.* **2013**, 49, 2004.
- [18] Z. Wei Seh, W. Li, J. J. Cha, G. Zheng, Y. Yang, M. T. McDowell, P. C. Hsu, Y. Cui, *Nat. Commun.* **2013**, 4, 1331.
- [19] J. Nelson, S. Misra, Y. Yang, A. Jackson, Y. Liu, H. Wang, H. Dai, J. C. Andrews, Y. Cui, M. F. Toney, *J. Am. Chem. Soc.* **2012**, 134, 6337.
- [20] C. N. Lin, W. C. Chen, Y. F. Song, C. C. Wang, L. D. Tsai, N. L. Wu, *J. Power Sources* **2014**, 263, 98.
- [21] M. Cuisinier, P. E. Cabelguen, S. Evers, G. He, M. Kolbeck, A. Garsuch, T. Bolin, M. Balasubramanian, L. F. Nazar, *J. Phys. Chem. Lett.* **2013**, 4, 3227.
- [22] M. U. M. Patel, I. Arcon, G. Aquilanti, L. Stievano, G. Mali, R. Dominko, *ChemPhysChem* **2014**, 15, 894.
- [23] M. A. Lowe, J. Gao, H. Abruna, *RSC Adv.* **2014**, 4, 18347.
- [24] S. Walus, C. Barchasz, J. F. Colin, J. F. Martin, E. Elkaim, J. C. Lepretre, F. Alloin, *Chem. Commun.* **2013**, 49, 7899.
- [25] M. U. M. Patel, R. Dominko, *ChemSusChem* **2014**, 7, 2167.
- [26] Q. Wang, J. Zheng, E. Walter, H. Pan, D. Lv, P. Zuo, H. Chen, B. Y. Liaw, X. Yu, X. Q. Yang, J. G. Zhang, J. Liu, J. Xiao, *J. Electrochem. Soc.* **2015**, 162, A474.
- [27] A. Vertes, S. Nagy, Z. Klencsar, R. G. Lovas, F. Rosch, *Handbook of Nuclear Chemistry*, Springer, 2011.
- [28] Y. S. Su, Y. Z. Fu, B. Guo, S. Dai, A. Manthiram, *Chem. Eur. J.* **2013**, 19, 8621.
- [29] J. Zheng, M. Gu, C. Wang, P. Zuo, P. K. Koech, J. G. Zhang, J. Liu, J. Xiao, *J. Electrochem. Soc.* **2013**, 160, A1992.
- [30] X. Yu, Q. Wang, Y. Zhou, H. Li, X. Q. Yang, K. W. Nam, S. N. Ehrlich, S. Khalid, Y. S. Meng, *Chem. Commun.* **2012**, 48, 11537.
- [31] T. A. Pascal, K. H. Wujcik, J. Velasco-Velez, C. Wu, A. A. Teran, M. Kapilashrami, J. Cabana, J. Guo, M. Salmeron, N. Balsara, D. Prendergast, *J. Phys. Chem. Lett.* **2014**, 5, 1547.
- [32] D. Lv, Y. Shao, T. Lozano, W. D. Bennett, G. L. Graff, B. Polzin, J. Zhang, M. H. Engelhard, N. T. Saenz, W. A. Henderson, P. Bhattacharya, J. Liu, J. Xiao, *Adv. Energy Mater.* **2015**, 5, 1400993.
- [33] C. Huang, J. Xiao, Y. Shao, J. Zheng, W. D. Bennett, D. Lu, L. V. Saraf, M. Engelhard, L. Ji, J. Zhang, X. Li, G. L. Graff, J. Liu, *Nat. Commun.* **2014**, 5, 3015.
- [34] J. Hassoun, B. Scrosati, *Angew. Chem. Int. Ed.* **2010**, 49, 2371.
- [35] J. Brückner, S. Thieme, F. Böttger-Hiller, I. Bauer, H. T. Grossmann, P. Strubel, H. Althues, S. Spange, S. Kaskel, *Adv. Funct. Mater.* **2014**, 24, 1284.
- [36] J. S. Kim, T. H. Hwang, B. G. Kim, J. Min, J. W. Choi, *Adv. Funct. Mater.* **2014**, 24, 5359.
- [37] H. Kim, F. Wu, J. T. Lee, N. Nitta, H.-T. Lin, M. Oschatz, W. I. Cho, S. Kaskel, O. Borodin, G. Yushin, *Adv. Energy Mater.* **2014**, DOI: 10.1002/aenm.201401792.
- [38] X. Yu, Y. C. Lyu, L. Gu, H. M. Wu, S. M. Bak, Y. N. Zhou, K. Amine, S. N. Ehrlich, H. Li, K. W. Nam, X. Q. Yang, *Adv. Energy Mater.* **2014**, 4, 1300950.
- [39] B. Ravel, M. Newville, *J. Synchrotron Radiat.* **2005**, 12, 537.

Figures and Tables:

Figure 1. (a) Schematic of the *in situ* cell configuration. The design was adapted from a CR2032 coin cell, with a $\phi 3\text{mm}$ hole covered with polyethylene film (Type: 3517) to allow X-ray beam to pass through. Sulfur flakes were mixed with carbon nanotubes and PVDF to reach an overall sulfur content of $\sim 20\text{wt\%}$ of the whole electrode, and the slurry was casted on a carbon paper. The widely used LiTFSI salt in electrolyte was replaced by LiClO_4 to avoid the interference from the sulfur content in the salt; (b) The XRD pattern, optical and XRF image of the S flake/carbon paper electrode. The entire *in situ* experiment setup was positioned in a well-sealed chamber filled with helium gas to eliminate the X-ray absorption and scattering by the air.

Figure 2. *In situ* 2D-XRF images collected on the entire *in situ* cell window region.

Each image was obtained during *in situ* cell discharged/charged at certain DOD/SOC as labeled on the charge-discharge curve. The color at each pixel in the image reflects the concentration of the sulfur element, the darker the color, the higher the concentration of sulfur element.

Figure 3 *In situ* 2D-XRF images collected on the selected area as marked with red rectangle shown in the left-up figure in Figure 2. Each image was obtained during *in situ* cell discharged/charged at certain DOD/SOC as labeled on the charge-discharge curve as shown in Figure 2.

Figure 4. XAS spectra collected on selected areas (marked by red arrows) during *in situ* cell discharged/charged at each DOD/SOC as labeled on the charge-discharge curve shown in Figure 2.

Figure 5. (a) XRF images collected on Sulfur/Ketjen black electrode, fresh Li foil and Li foil harvest from the Li|Sulfur/Ketjen black cell after 1 cycle; (b) XRF images collected on Lithium anode electrodes harvested from the Li|Sulfur/Ketjen black cells at discharged 2.1V, discharged 1.7V and re-charged 3V states; (c) XAS spectra collected at the selected area as marked by red arrows shown on the images; (d) Schematic to illustrate sulfur dissolution and re-distribution after initial cycle.

The table of contents:

A novel *in situ* X-ray fluorescence microscopy combined with X-ray absorption spectroscopy technique is reported to investigate the Li-S batteries during electrochemical cycling. The evolution of morphology changes of the electrode is monitored in real time through the XRF images while the changes of the sulfur chemical state are characterized through the XAS spectra simultaneously.

ToC figure:

Supporting Information

Direct observation of the redistribution of sulfur and polysulfides in Li-S batteries during first cycle by *in situ* X-Ray fluorescence microscopy

Xiqian Yu^{a†}, Huilin Pan^{b†}, Yongning Zhou^a, Paul Northrup^a, Jie Xiao^b, Seongmin Bak^a, Mingzhao Liu^a, Kyung-Wan Nam^c, Deyang Qu^d, Jun Liu^{*b}, Tianpin Wu^e and Xiao-Qing Yang^{*a}

Dr. X. Q. Yu, Dr. Y. N. Zhou, Dr. P. Northrup, Dr. S. M. Bak, Dr. M. Z. Liu, Dr. X. -Q. Yang

Brookhaven National Laboratory, Upton, NY11973, USA

E-mail: xyang@bnl.gov

Dr. H. L. Pan, Dr. J. Xiao, Dr. J. Liu.

Joint Center for Energy Storage Research, Pacific Northwest National Laboratory, Richland, WA99352

E-mail: jun.liu@pnnl.gov

Prof. K. W. Nam

Department of Energy and Materials Engineering, Dongguk University-Seoul
26 Pil-dong, 3-ga, Jung-gu, Seoul, 100-715, Republic of Korea

Prof. D. Y. Qu

Department of Chemistry, University of Massachusetts at Boston, MA 02125-3393, USA

Dr. T. Wu

X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, USA

[†]Xiqian Yu and Huilin Pan contributed equally to this paper.

Keywords: Lithium-Sulfur batteries, energy storage, reaction mechanism, *in situ* technique, microspectroscopy

Figure S1 A test of the X-rays beam damage. The image shown on (a) left was collected on a fresh sample (X-ray Energy: 2500eV; X-ray spot/pixel size: $7\mu\text{m} \times 7\mu\text{m}$; Scanning step size: $7\mu\text{m}$). A micro-sized sulfur particle can be clearly seen. The image shown on the (b) right was collected after a continuous X-ray beam exposure for 30 minutes (X-ray size during exposure: $300\mu\text{m} \times 300\mu\text{m}$). (c) Sulfur K-edge XANES spectra were also collected on the position as marked by red arrow before and after X-ray beam exposure. Almost identical morphology and spectra features indicate X-ray damage during data collection can be neglected.

Figure S2 SEM images of the sulfur flake/carbon paper electrode at pristine (a, d, g), fully discharged 1.7V (b, e, h) and fully charged 3V (c, f, i) states with different magnification.

Figure S3 XRF images collected on S flake/Carbon paper electrode *ex situ* prepared at 3V charged state. The XRF images on both side [(a) face to the lithium electrode and (c) the back side] of the S flake/Carbon paper electrode were collected. Detailed views are shown in (b) and (d) respectively. (e) XAS spectra collected at the selected areas marked by arrows.

Figure S4 *In situ* 2D-XRF images collected on entire cell window region (scanning area size: 4mm*3.5mm; X-ray spot size: 7μm*7μm). Each image was obtained during *in situ* cell discharged/charged at certain DOD/SOC as labeled on the charge-discharge curve.

Figure S5 XRF images (Full view) on lithium electrodes harvested from the Li|sulfur/Ketjen black cells at (a) discharged 2.1V, (b) discharged 1.7V and (c) charged 3V states.