# Supplemental Information

# Fingerprinting lithium-sulfur battery reaction products by X-ray absorption spectroscopy

*Kevin H. Wujcik[ab], Juan Velasco-Velez[c], Cheng Hao Wu[cd], Tod Pascal[c], Alexander A. Teran[ab], Matthew A. Marcus[e], Jordi Cabana[bf], Jinghua Guo[e], David Prendergast[c], Miquel Salmeron[c], Nitash P. Balsara[ab]**

a Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, USA

b Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

c Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

d Department of Chemistry, University of California, Berkeley, California 94720, USA

e Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

f Department of Chemistry, University of Illinois at Chicago, 845 W. Taylor St., Chicago, Illinois 60607, United States

## Effect of air-exposure on X-ray absorption spectra

To elucidate the effect that air-exposure had on obtained X-ray spectra, XAS was performed on an unexposed sample of $x_{mix}$ = 8 dissolved in SEO. After this initial measurement, the sample was removed from the measurement chamber and allowed to sit in air at room temperature for one hour before another XAS measurement was performed. The resulting spectra can be seen in Figure S1 below. The peaks that occur at 2479.4 and 2480.8 eV are common in oxidized sulfur species,[1] and are direct evidence of the effect that air exposure may have on obtained X-ray spectra. The increase in intensity of these two peaks is also accompanied by a decrease in pre-edge peak intensity, possibly due to the reaction of anionic sulfur species with oxygen or water.

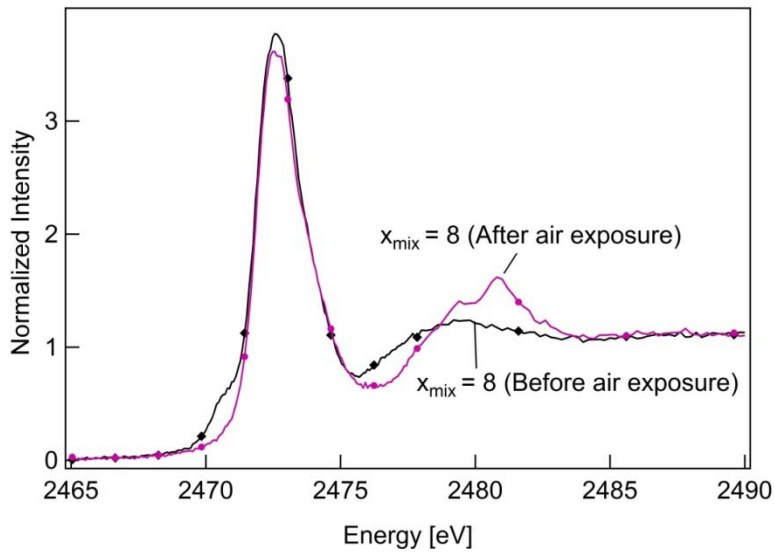


**Figure S1.** X-ray spectra of $x_{mix}$= 8 in SEO samples before and after air exposure

## Equations for the calculation of $x_{mix}$ error

1. Calculation of $x_{mix}$

$$x_{mix} = \frac{\left(\frac{moles\ S/_{mole\ S_8} \cdot mass\ of\ S_8}{molar\ mass\ S_8}\right) + \left(\frac{moles\ S/_{mole\ Li_2S} \cdot mass\ of\ Li_2S}{molar\ mass\ Li_2S}\right)}{\left(\frac{moles\ Li_2/_{mole\ Li_2S} \cdot mass\ of\ Li_2S}{molar\ mass\ Li_2S}\right)}$$

2. Overall calculation of $x_{mix}$ error

$$\Delta x_{mix} = \frac{\partial x_{mix}}{\partial mass\ S_8} \cdot \Delta mass\ of\ S_8 + \frac{\partial x_{mix}}{\partial mass\ Li_2S} \cdot \Delta mass\ of\ Li_2S$$

3. Calculation of error with respect to mass of $S_8$

$$\frac{\partial x_{mix}}{\partial mass\ S_8} = \frac{\left(\frac{moles\ S / mole\ S_8}{molar\ mass\ S_8}\right)}{\left(\frac{moles\ Li_2 / mole\ Li_2S \cdot mass\ Li_2S}{molar\ mass\ Li_2S}\right)}$$

4. Calculation of error with respect to mass of $Li_2S$

$$\frac{\partial x_{mix}}{\partial mass\ Li_2S} = \frac{\left(-\frac{moles\ S / mole\ S_8 \cdot mass\ S_8}{molar\ mass\ S_8}\right)}{\left(\frac{moles\ Li_2 / mole\ Li_2S \cdot (mass\ Li_2S)^2}{molar\ mass\ Li_2S}\right)}$$

**<u>Sample calculations for $x_{mix}$ error</u>**

| **Data for sample: $x_{av}$ = 2, PEO** | | |
|---|---|---|
| Mass of $Li_2S$ added | 0.0177 | g |
| Mass of $S_8$ added | 0.0122 | g |
| Moles S per mole $S_8$ | 8 | |
| Moles $Li_2$ per mole $Li_2S$ | 1 | |
| Molar mass $S_8$ | 256.0 | g/mol |
| Molar mass $Li_2S$ | 45.8 | g/mol |
| Δ mass of $S_8$ | ±0.0001 | g |
| Δ mass of $Li_2S$ | ±0.0001 | g |

1. Calculation of $x_{mix}$

$$x_{mix} = \frac{\left(\frac{8 \cdot 0.0122g}{256g/mol}\right) + \left(\frac{1 \cdot 0.0177g}{45.8g/mol}\right)}{\left(\frac{1 \cdot 0.0177g}{45.8g/mol}\right)} = 1.987$$

2. Calculation of error with respect to mass of $S_8$

$$\frac{\partial x_{mix}}{\partial mass\ S_8} = \frac{\left(\frac{8}{256g/mol}\right)}{\left(\frac{1 \cdot 0.0177g}{45.8g/mol}\right)} = 80.8g^{-1}$$

3. Calculation of error with respect to mass of $Li_2S$

$$\frac{\partial x_{mix}}{\partial mass\ Li_2S} = \frac{\left(-\frac{8 \cdot 0.0122g}{256g/mol}\right)}{\left(\frac{1 \cdot (0.0177g)^2}{45.8g/mol}\right)} = -55.7g^{-1}$$

4. Overall calculation of $x_{mix}$ error

$$\Delta x_{mix} = 80.8g^{-1} \cdot 0.0001g + -55.7g^{-1} \cdot 0.0001g = \pm 0.0025$$

**<u>Equations for the calculation of sulfur concentration error</u>**

1. Calculation of sulfur concentration

$$Sulfur\ concentration\ \left(\frac{g\ S}{g\ polymer}\right) = \frac{(mass\ Li_2S)(wt\%\ S\ in\ Li_2S) + mass\ S_8}{mass\ polymer}$$

2. Overall calculation of sulfur concentration error

$$\Delta\ sulfur\ conc. = \frac{\partial sulfur\ conc.}{\partial mass\ S_8} \cdot \Delta mass\ of\ S_8 + \frac{\partial sulfur\ conc.}{\partial mass\ Li_2S} \cdot \Delta mass\ of\ Li_2S + \frac{\partial sulfur\ conc.}{\partial mass\ polymer} \cdot \Delta mass\ polymer$$

3. Calculation of error with respect to mass of $S_8$

$$\frac{\partial sulfur\ conc.}{\partial mass\ S_8} = \frac{1}{mass\ polymer}$$

4. Calculation of error with respect to mass of $Li_2S$

$$\frac{\partial sulfur\ conc.}{\partial mass\ Li_2S} = \frac{(wt\%\ S\ in\ Li_2S)}{mass\ polymer}$$

5. Calculation of error with respect to mass of polymer

$$\frac{\partial sulfur\ conc.}{\partial mass\ polymer} = -\frac{(mass\ Li_2S)(wt\%\ S\ in\ Li_2S) + mass\ S_8}{(mass\ polymer)^2}$$

**<u>Sample calculations for sulfur concentration error</u>**

| **Data for sample: $x_{av}$ = 2, PEO** |
|---|

| | | |
|---|---|---|
| Mass of $Li_2S$ added | 0.0177 | g |
| Mass of $S_8$ added | 0.0122 | g |
| Mass of polymer added | 0.0543 | g |
| wt% S in $Li_2S$ | 0.699 | - |
| Δ mass of $S_8$ | ±0.0001 | g |
| Δ mass of $Li_2S$ | ±0.0001 | g |
| Δ mass of polymer | ±0.0001 | g |

1. Calculation of sulfur concentration

$$Sulfur\ concentration\ \left(\frac{g\ S}{g\ polymer}\right) = \frac{(0.0177g)(0.699) + 0.0122g}{0.0543g} = 0.452\frac{g\ S}{g\ polymer}$$

2. Calculation of error with respect to mass of $S_8$

$$\frac{\partial sulfur\ conc.}{\partial mass\ S_8} = \frac{1}{0.0543g} = 18.4g^{-1}$$

3. Calculation of error with respect to mass of $Li_2S$

$$\frac{\partial sulfur\ conc.}{\partial mass\ Li_2S} = \frac{0.699}{0.0543g} = 12.8g^{-1}$$

4. Calculation of error with respect to mass of polymer

$$\frac{\partial sulfur\ conc.}{\partial mass\ polymer} = -\frac{(0.0177g)(.699) + 0.0122g}{(0.0543g)^2} = -8.3g^{-1}$$

5. Calculation of sulfur concentration error

$$\Delta\ sulfur\ conc. = 18.4g^{-1} \cdot 0.0001g + 12.8g^{-1} \cdot 0.0001g - 8.3g^{-1} \cdot 0.0001g$$
$$= \pm 0.0022\frac{g\ S}{g\ polymer}$$

## References


(1) Jalilehvand, F. *Chemical Society Reviews* **2006**, *35*, 1256.