

Sulfur spillover on carbon and its effect on metal-sulfur solid-state batteries

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HZB Helmholtz
Zentrum Berlin



12th Workshop Li-S Batteries, Nov 17-18 2025, Dresden

Elemental sulfur possesses a rich allotropy and polymorphism (+30 sulfur forms)

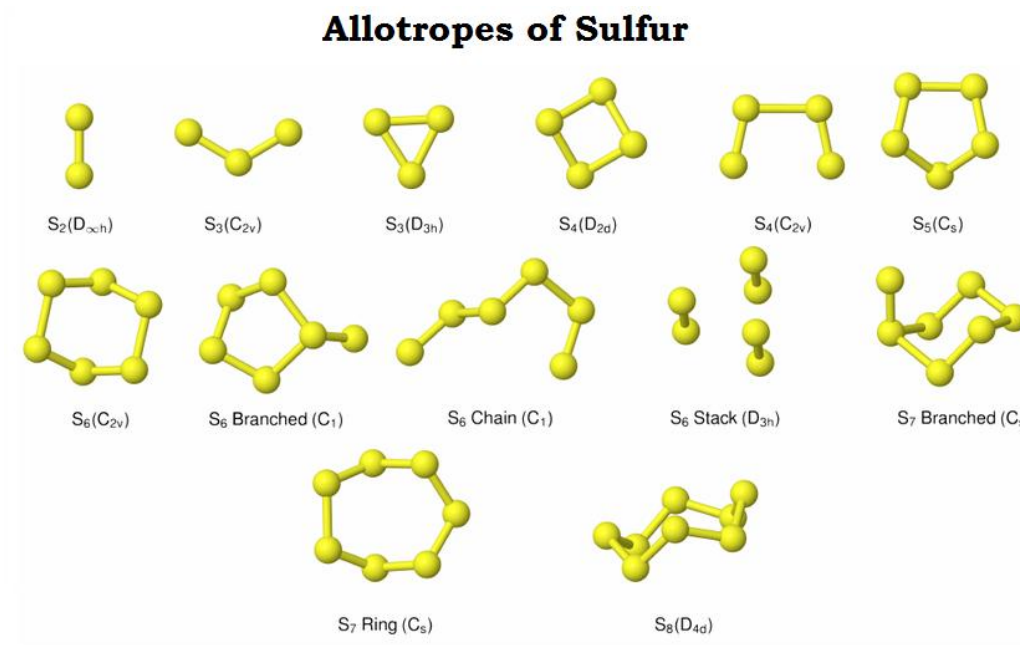
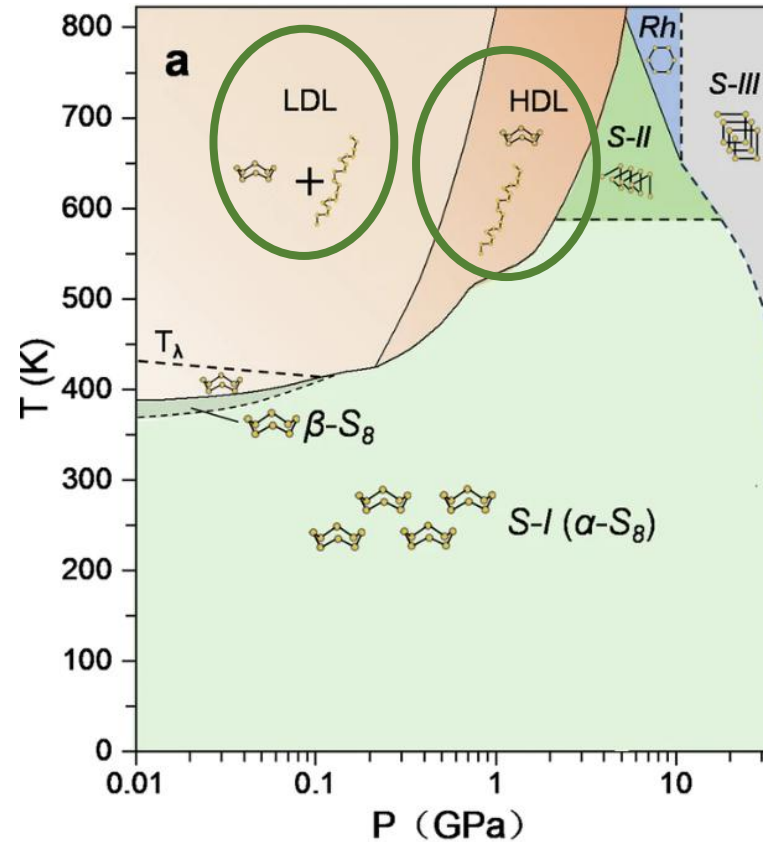


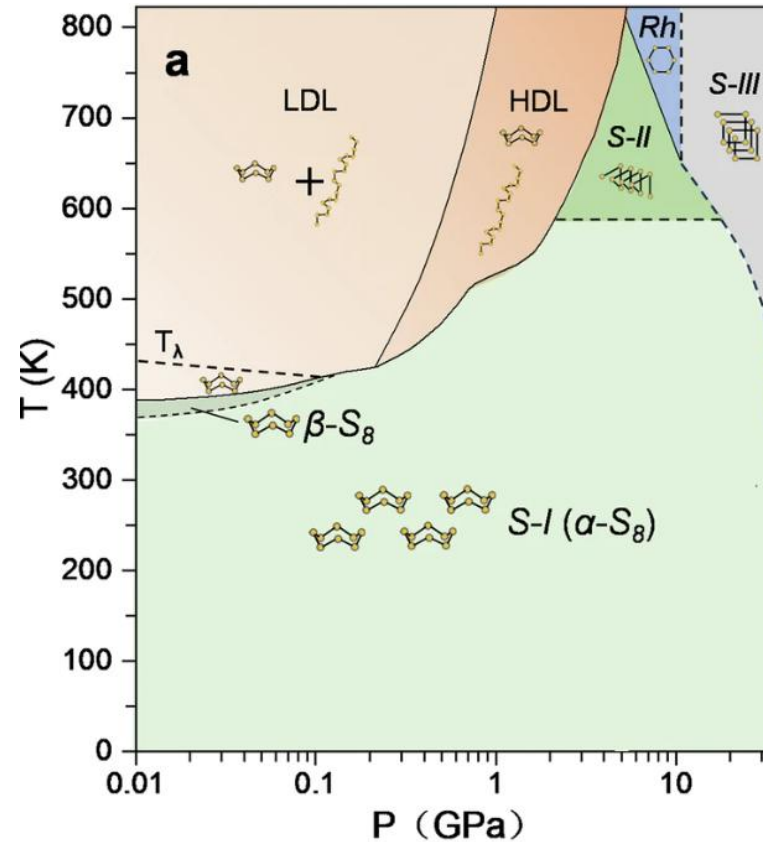
Image from: The Tri-Octave Movements of Allotropic Elements

Sulfur has two liquid states: LDL and HDL. They consist of ring and chain molecules



K. Shi *et al.*, "Sulfur chains glass formed by fast compression," *Nature Communications*, vol. 16, no. 1, Dec. 2025, doi: 10.1038/s41467-024-55028-w.

Pressure and temperature are essential to changing the state of sulfur

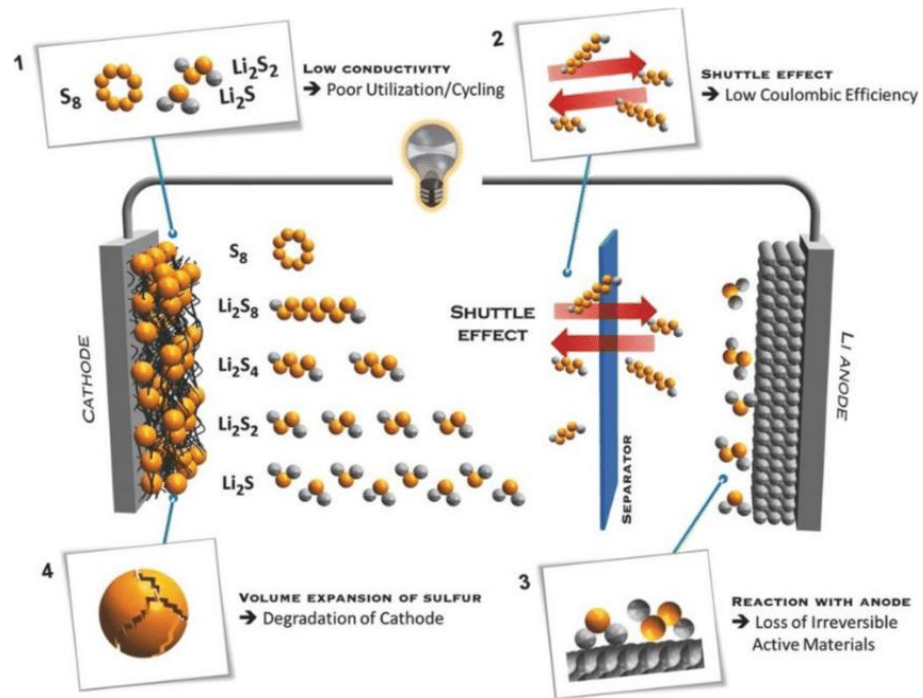


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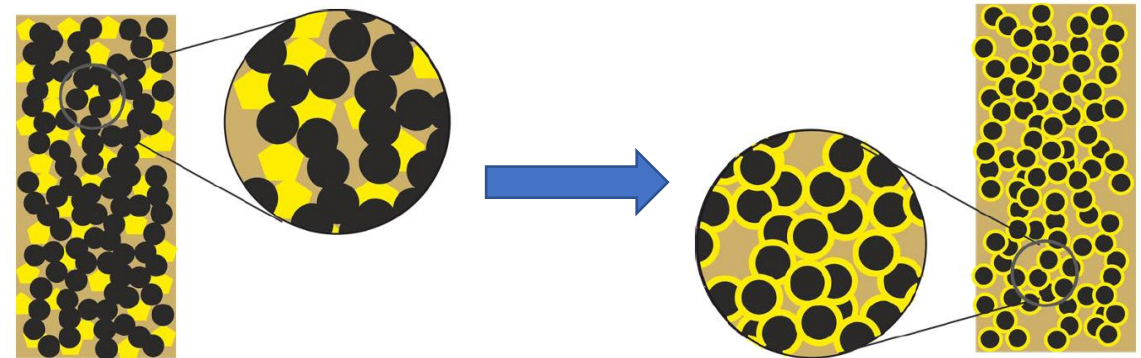
How does this link to batteries?

In a Li-S battery...

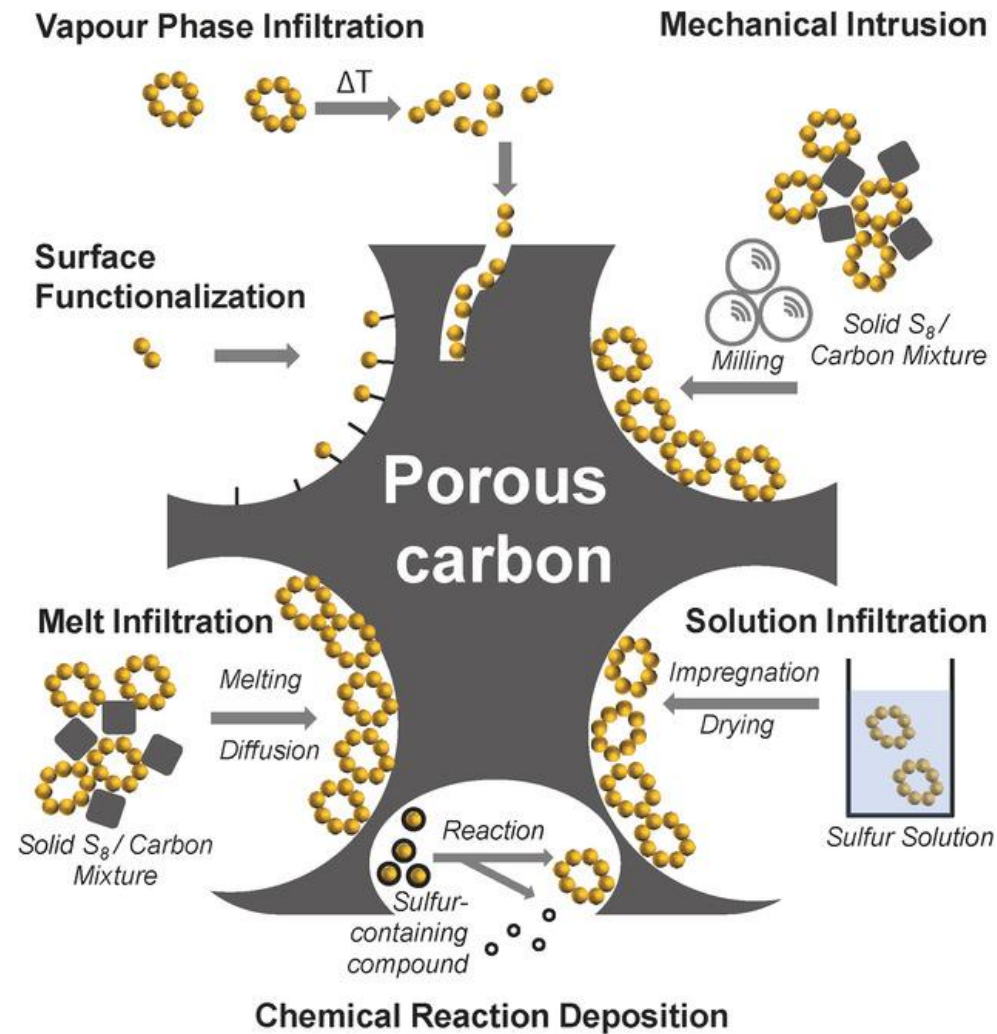
Several challenges to solve



Preparation of sulfur-carbon composites



How are sulfur-carbon composites prepared?

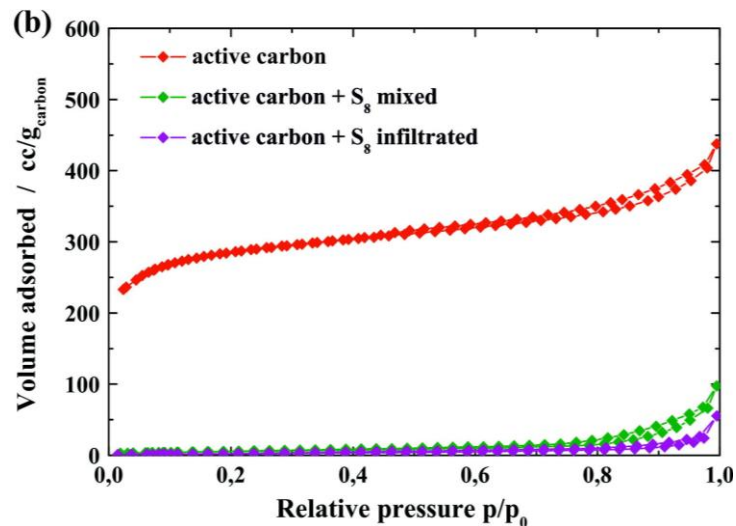


BACKGROUND

Story behind the spillover process

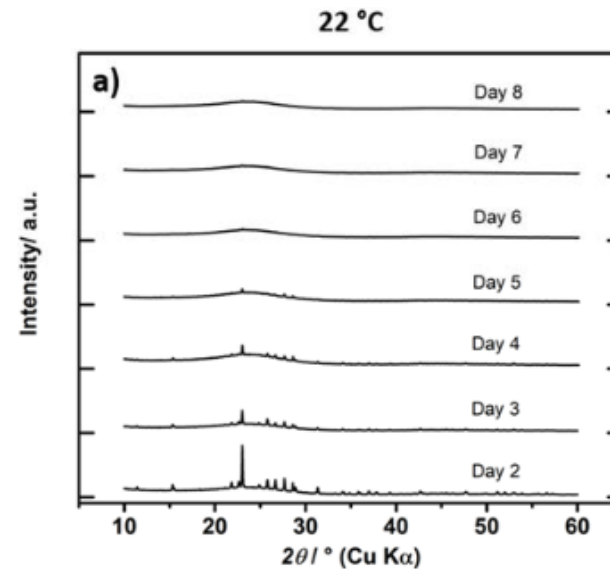
Pitfalls in the characterization of sulfur/carbon nanocomposite materials for lithium–sulfur batteries

Christine Raiß, Klaus Peppler, Jürgen Janek, Philipp Adelhelm*
Carbon **2014**, 79, 245–255.
<https://doi.org/10.1016/j.carbon.2014.07.065>



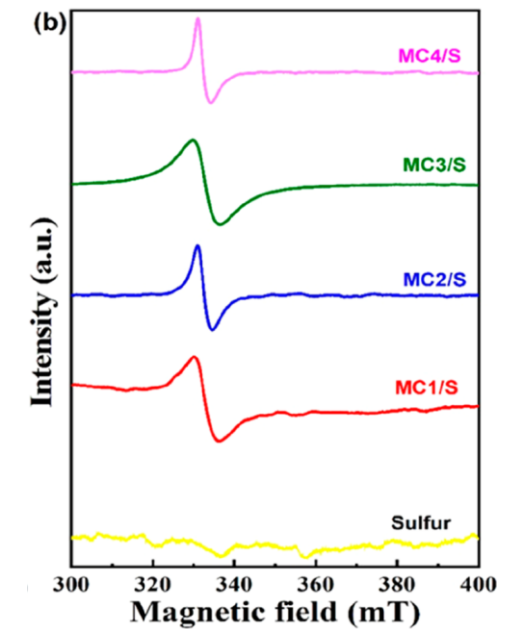
Sulfur Spillover on Carbon Materials and Possible Impacts on Metal–Sulfur Batteries

Lukas Medenbach, Ines Escher, Nicolas Köwitsch, Marc Armbrüster, Linda Zedler, Benjamin Dietzek, and Philipp Adelhelm*
Angewandte Chemie International Edition **2018**, 57 (41), 13666–13670.
<https://doi.org/10.1002/anie.201807295>



Probing the “Universal” Amorphization of Crystalline Sulfur in its Mixture with Ultrahigh Surface Area Porous Carbon

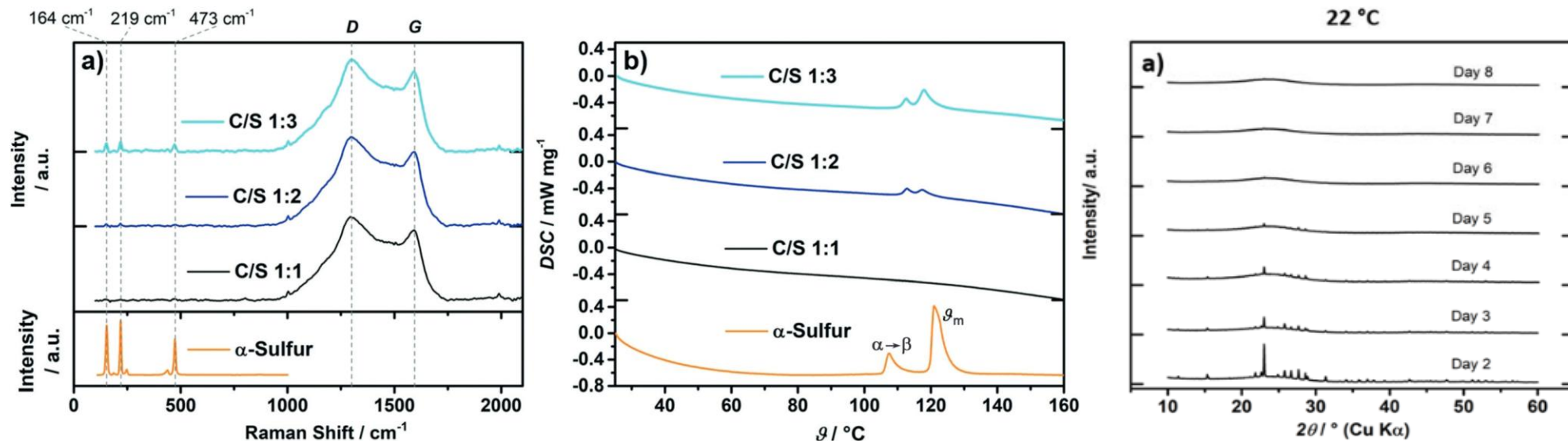
Neeraj Pal and Aninda Jiban Bhattacharyya*
J. Phys. Chem. C **2023**, 127 (12), 5713–5719.
<https://doi.org/10.1021/acs.jpcc.3c00276>



BACKGROUND

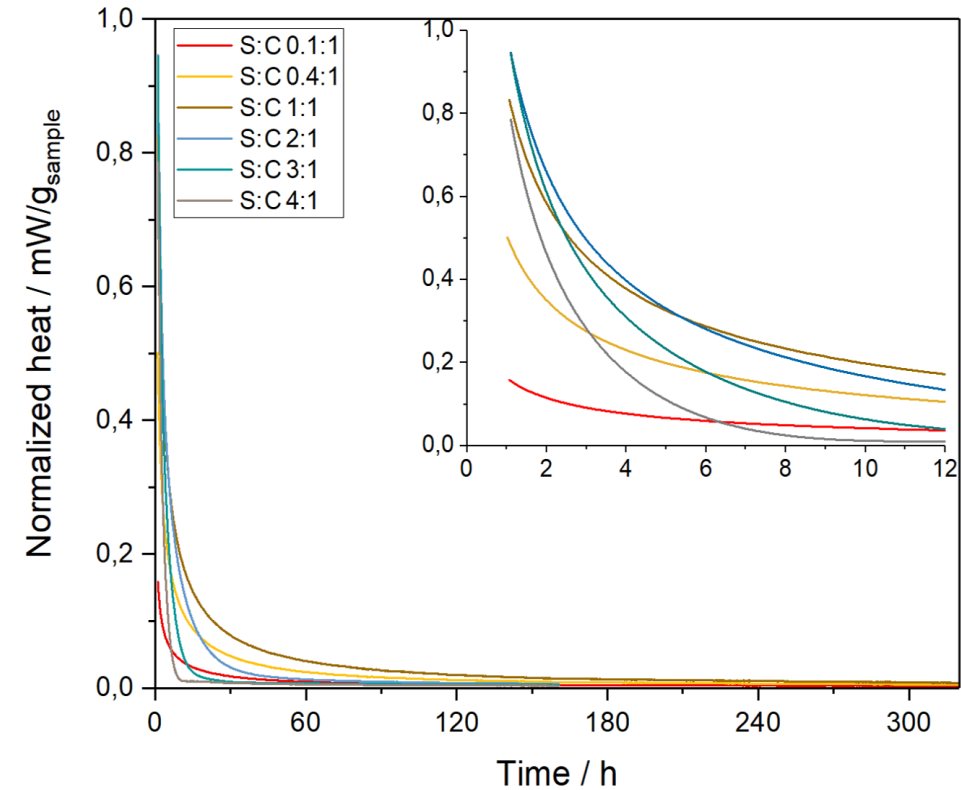
Sulfur spillover process

- Extremely fast process, in which sulfur fills carbon pores at RT
- The chemical state of sulfur after spillover is unclear
- Raman, DSC or XRD cannot provide much information → peaks disappear



THERMODYNAMICS

Heat of the reaction

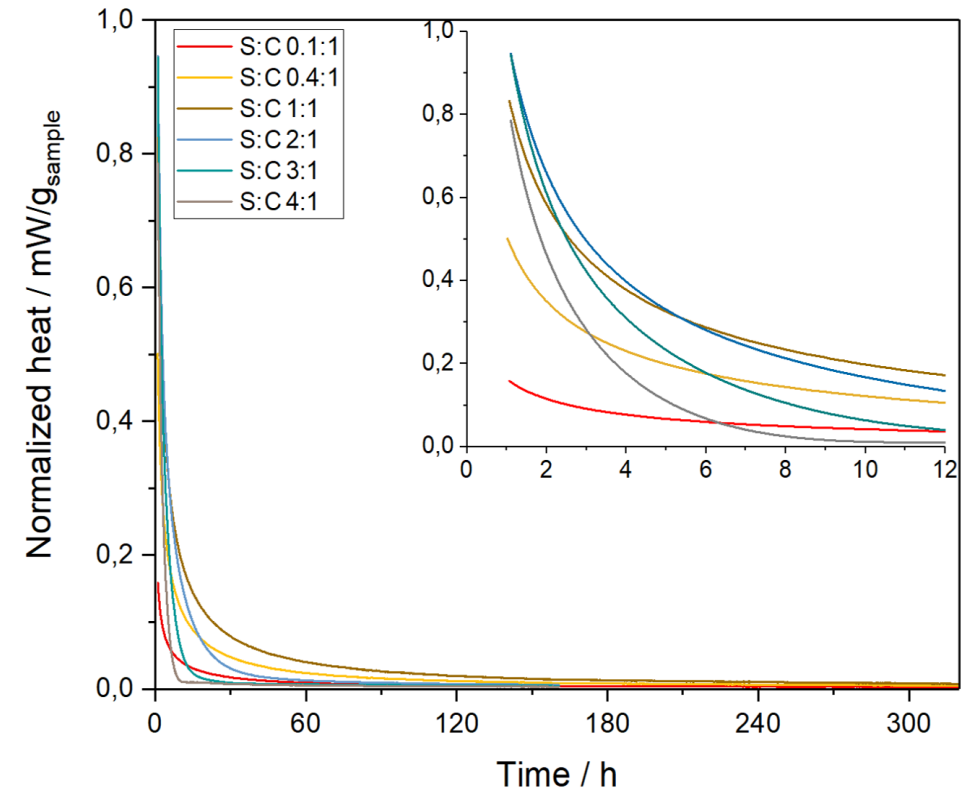
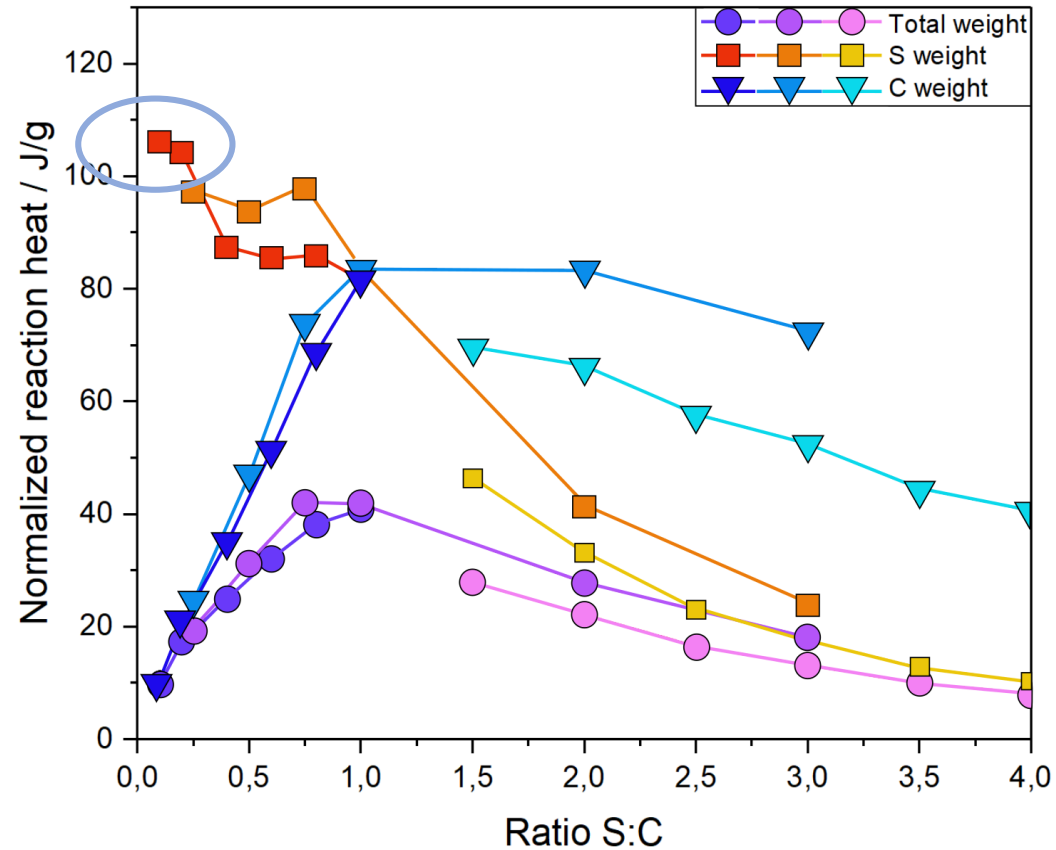


Piccolo, F. et al. Unraveling the Spontaneous Adsorption of Sulfur onto Activated Carbon: Mechanism and Thermodynamic of the Sulfur Spillover. **In Preparation**



THERMODYNAMICS

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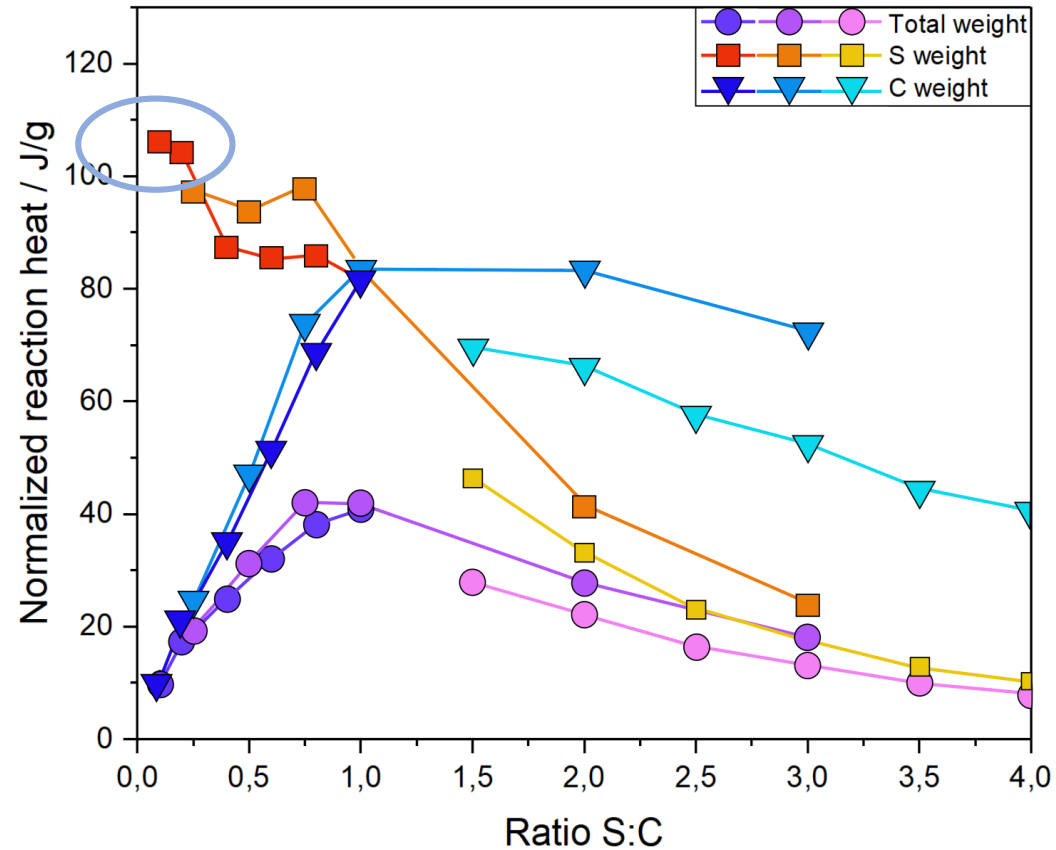


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THERMODYNAMICS

Heat of the reaction



$$\Delta H \approx -28.2 \text{ kJ/mol}_{\text{S}_8}$$

S-S dissociation energy in an S_8 ring = $138 \text{ kJ/mol}_{\text{S}_8}$

Bonding energy S_8 -graphene $\approx 60 \text{ kJ/mol}_{\text{S}_8}$

Wasalathilake, K. C. et al. Interaction between Functionalized Graphene and Sulfur Compounds in a Lithium–Sulfur Battery – a Density Functional Theory Investigation. *RSC Adv.* **2018**, 8 (5), 2271–2279. <https://doi.org/10.1039/C7RA11628D>.

Steudel, R. Properties of Sulfur-Sulfur Bonds. *Angewandte Chemie International Edition in English* **1975**, 14 (10), 655–664. <https://doi.org/10.1002/anie.197506551>.

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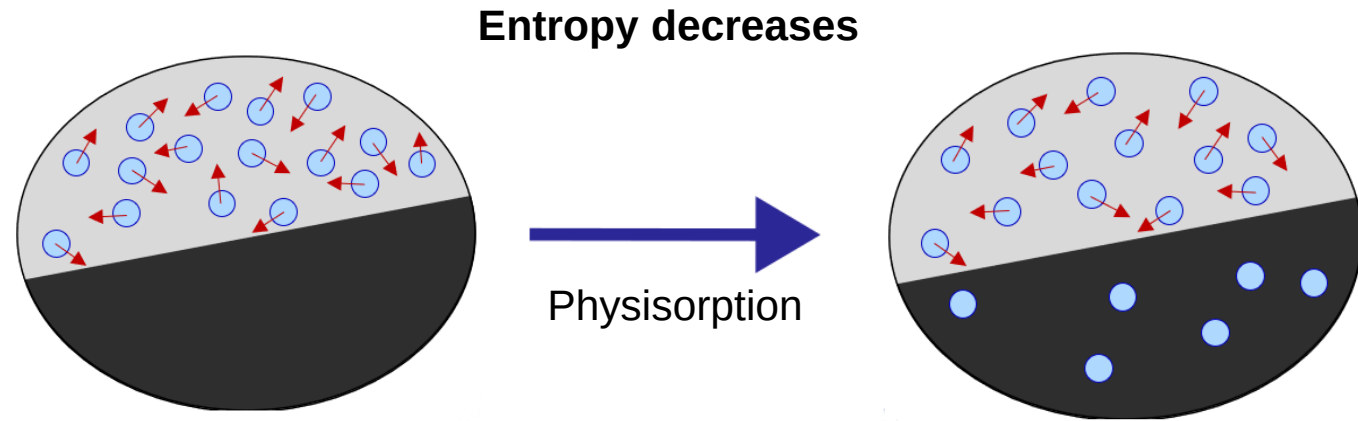


THERMODYNAMICS

$$\Delta_{\text{sp}} G = \Delta H - T\Delta S$$

$$\Delta H = -28.2 \text{ kJ/mol}_{\text{S}_8}$$

$$\Delta S = ?$$



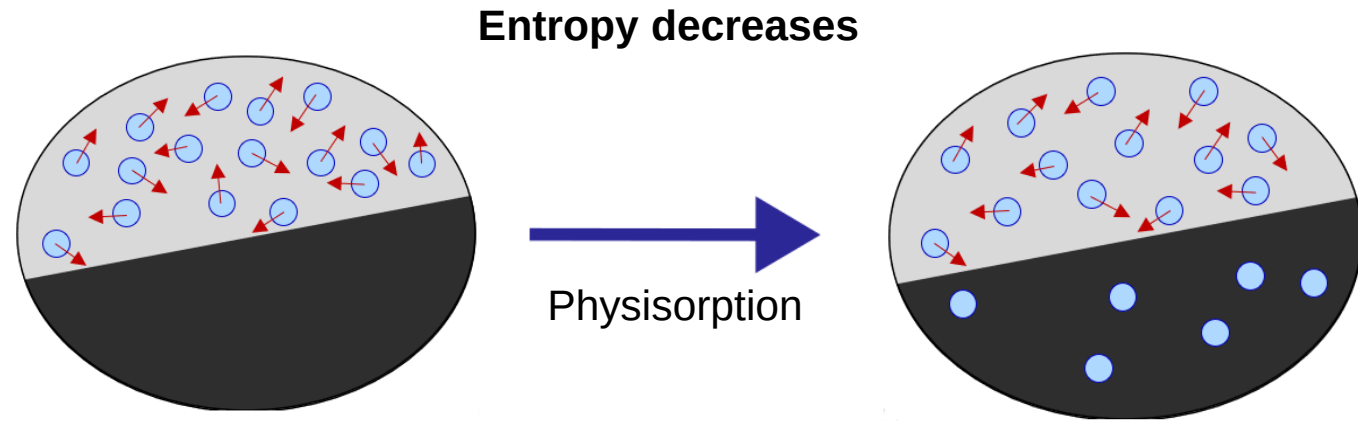
THERMODYNAMICS

$$\Delta_{\text{sp}} G = \Delta H - T\Delta S$$

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$$S_{\text{ads}}^{\circ} = 0.7 S_{\text{gas}}^{\circ} - 3.3R$$



Campbell, C. T.; Sellers, J. R. V. The Entropies of Adsorbed Molecules. *J. Am. Chem. Soc.* **2012**, *134* (43), 18109–18115. <https://doi.org/10.1021/ja3080117>

Hill, T. L. Statistical Mechanics of Multimolecular Adsorption II. Localized and Mobile Adsorption and Absorption. *The Journal of Chemical Physics* **1946**, *14* (7), 441–453. <https://doi.org/10.1063/1.1724166>

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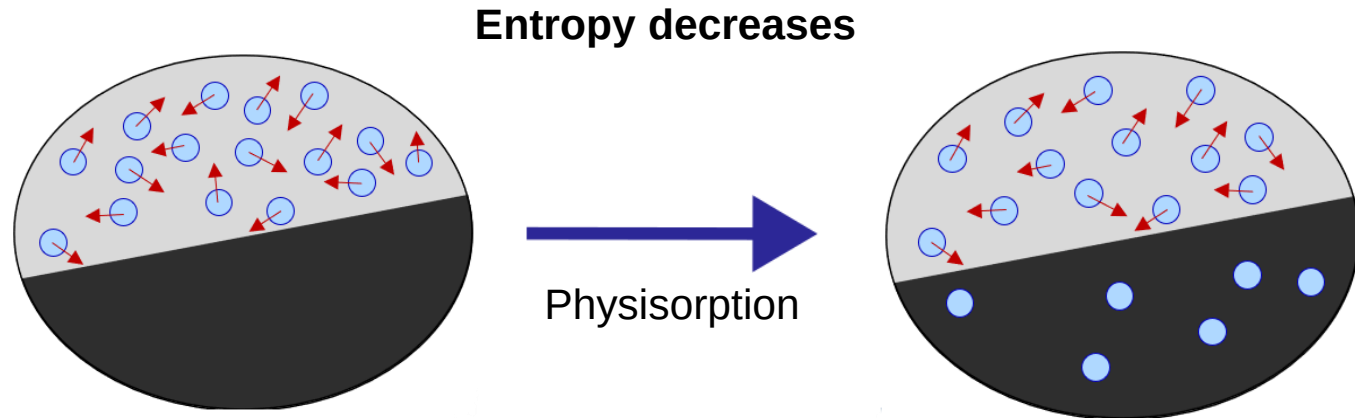


THERMODYNAMICS

$$\Delta S = ?$$

$$S_{\text{ads}}^{\circ} = 0.7 S_{\text{gas}}^{\circ} - 3.3R$$

$$S_{\text{S8 gas}}^{\circ} (298.15\text{K}, 1 \text{ bar}) = 430.31 \text{ J/(K mol}_{\text{S8}})$$



Assessment, U. E. N. C. for E. *NIST-JANAF thermochemical tables, monograph 9*. https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/1487617 (accessed 2024-03-11)

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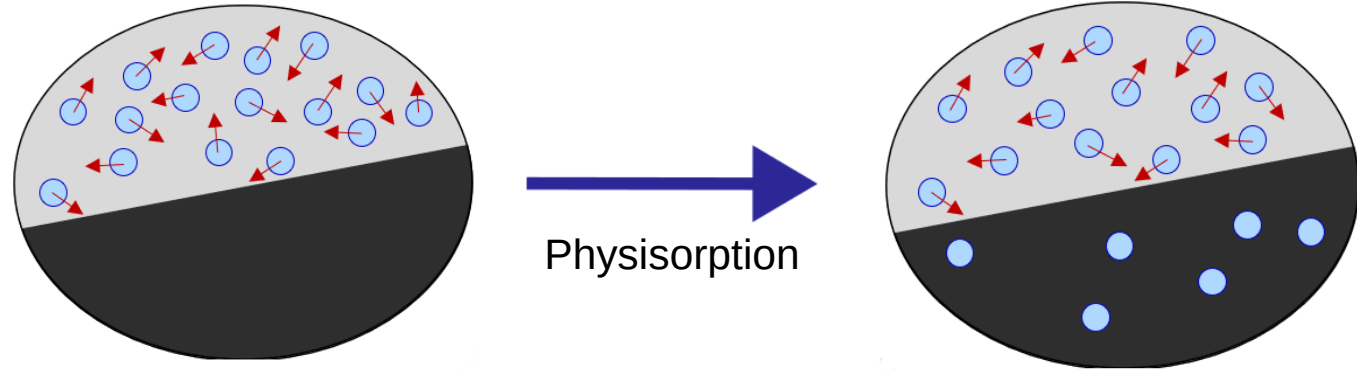
$$S_{\text{S8}}^{\circ} \text{ gas (298.15K, 1 bar)} = 430.31 \text{ J/(K mol}_{\text{S8}})$$

$$S_{\text{S8}}^{\circ} \text{ ads (298.15K, 1 bar)} = 273.78 \text{ J/(K mol}_{\text{S8}})$$

$$S_{\text{S8}}^{\circ} \text{ rhombic (298.15K, 1 bar)} = 32.06 \text{ J/(K mol}_{\text{S8}})$$

$$\Delta S = S_{\text{S8}}^{\circ} \text{ ads} - S_{\text{S8}}^{\circ} \text{ rhombic}$$

Entropy decreases



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THERMODYNAMICS

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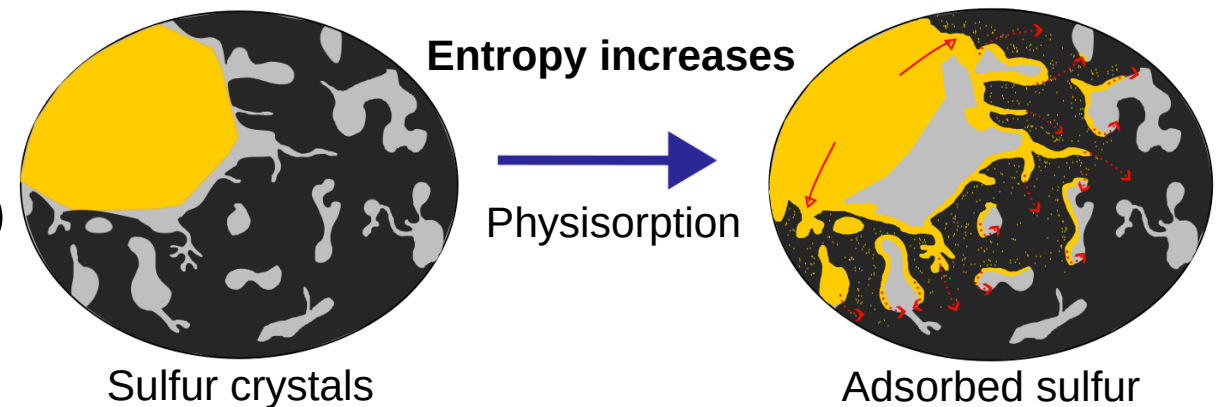
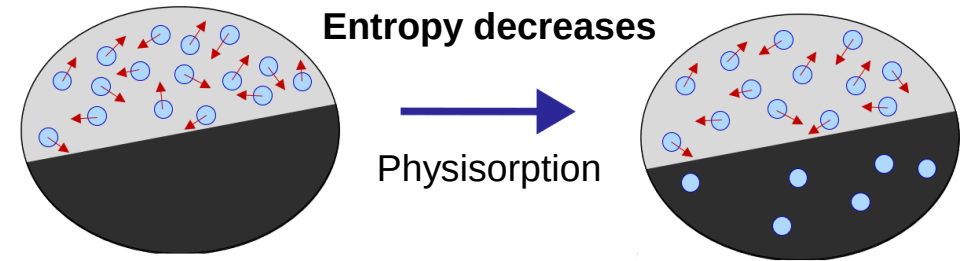
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$$\Delta S = 241.72 \text{ J/(K mol}_{\text{S8}})$$



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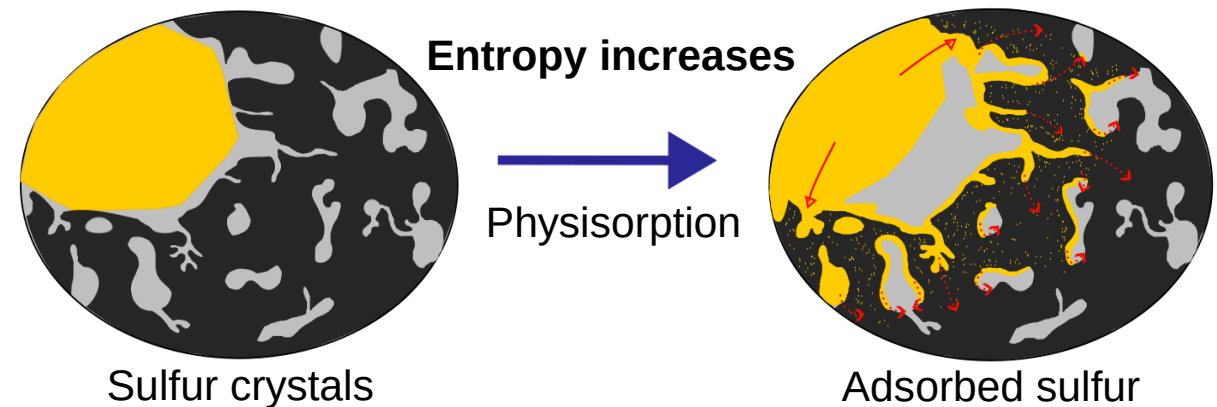
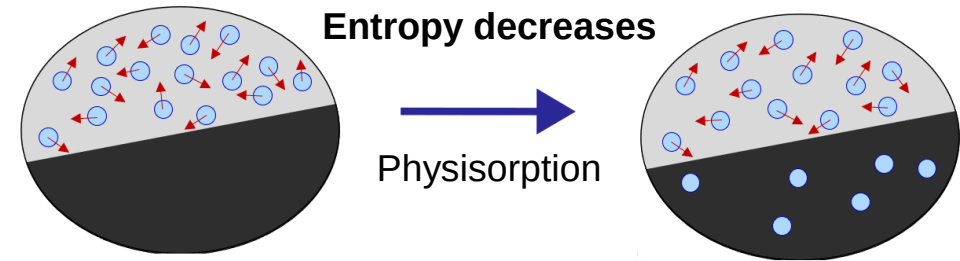
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$$\Delta H = -28.2 \text{ kJ/mol}_{\text{S}_8}$$

$$\Delta S = 241.72 \text{ J/(K mol}_{\text{S}_8})$$

$$\Delta_{\text{sp}}G = -100.23 \text{ kJ/mol}_{\text{S}_8}$$



Assessment, U. E. N. C. for E. *NIST-JANAF thermochemical tables, monograph 9*. https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/1487617 (accessed 2024-03-11)

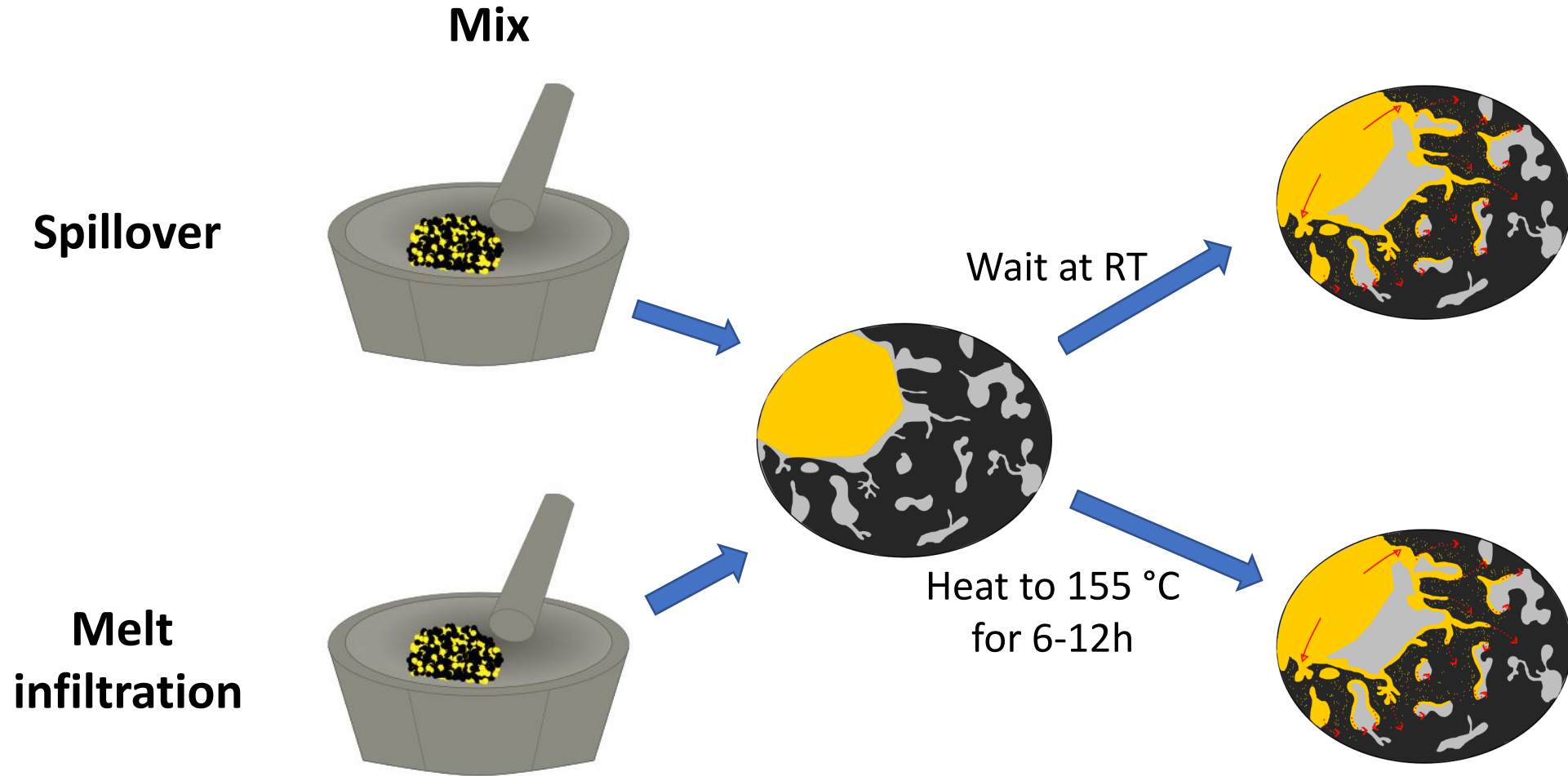
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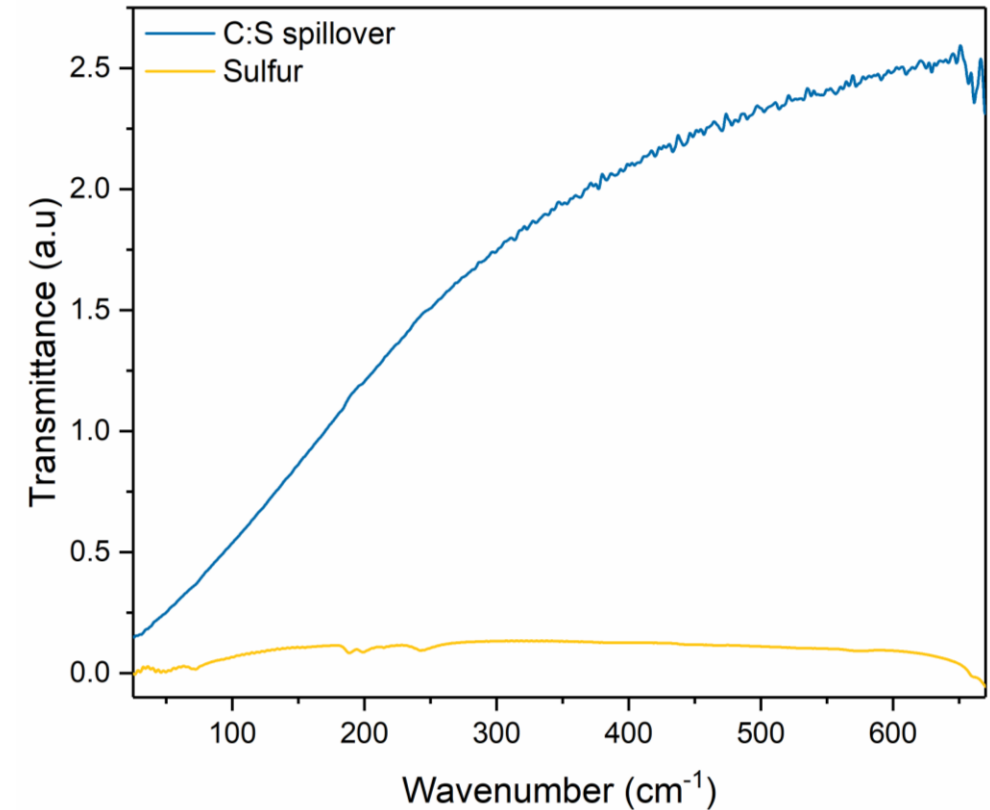
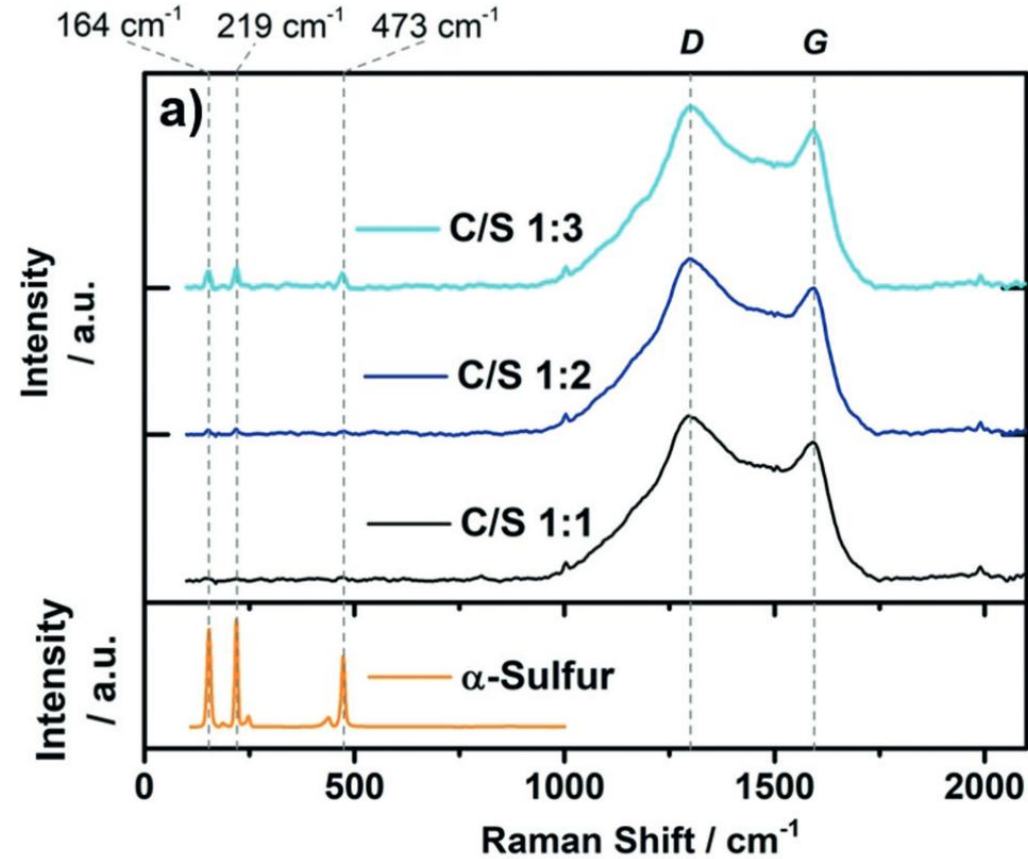
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BENCHMARKING SULFUR SPILLOVER



CHEMICAL STATE OF SULFUR



L. Medenbach et al., Sulfur spillover on carbon materials and possible impacts on metal-sulfur batteries; *Angew. Chemie. Int. Ed.*, **2018** doi:10.1002/anie.201807295

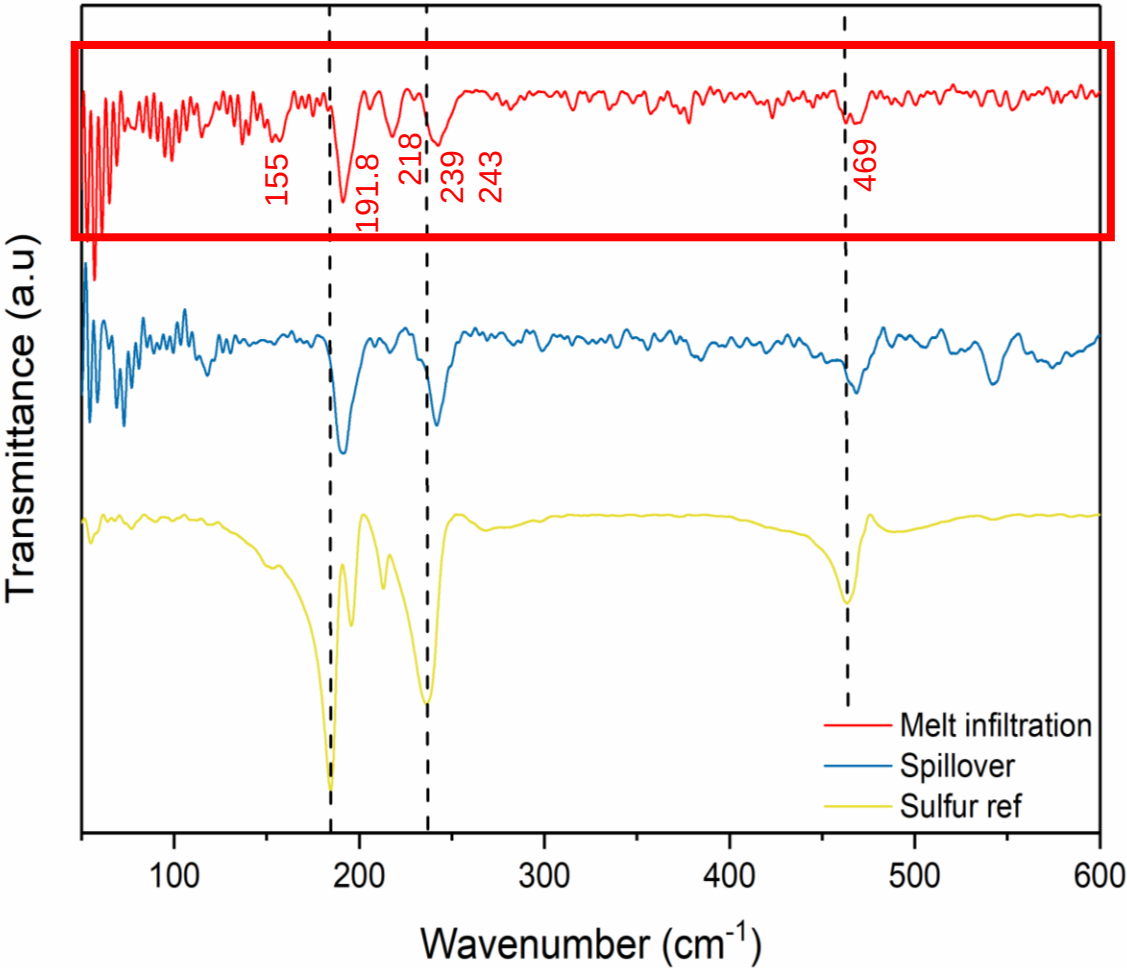
Healy Corominas, R. et al. Revisiting sulfur-carbon composite preparation and its effect on Li-S solid-state batteries. *In Preparation*

CHEMICAL STATE OF SULFUR

TABLE I
Infrared and Raman spectra of sulfur*

Infrared							
Mode and species	Solution		Crystal		Raman, crystal, ref. 5§	Melt infiltration	Spillover
	Ref. 3	This work	Refs. 3, 4†	This work‡			
$\nu_9(e_2)$	—	—	—	78	$\left\{ \begin{array}{l} 77 \\ 79 \\ 85 \\ 91 \end{array} \right.$	-	-
$\nu_8(e_2)$	—	—	154	149	$\left\{ \begin{array}{l} 149 \\ 152 \\ 156 \\ 159 \end{array} \right.$	155	-
$\nu_6(e_1)$	191	192	$\left. \begin{array}{l} 186 \\ 197 \end{array} \right\}$	$\left. \begin{array}{l} 182 \\ 187 \\ 198 \end{array} \right\}$	$\left\{ \begin{array}{l} 182 \\ 187 \\ 197 \end{array} \right.$	191.8	191.5
$\nu_2(a_1)$	—	—	214	214	$\left\{ \begin{array}{l} 214 \\ 218 \end{array} \right.$	218	-
$\nu_4(b_2)$	243	242	239	$\left. \begin{array}{l} 240 \\ 243 \end{array} \right\}$	236	239, 243	242
$\nu_{10}(e_3)$	—	—	435	442	441	-	-
$\nu_5(e_1)$	471	470.5	465	$\left. \begin{array}{l} 470 \\ 472.5 \\ 476.5 \end{array} \right\}$	—	469	468
*Frequencies of maximum absorption or intensity in cm^{-1} .						-	542
†Temperature = 300 °K.						-	542
‡Temperature = 95 °K.						-	542
§Temperature = 100 °K, only those peaks close to i.r. frequencies are recorded here						-	542
Overlaps with strong ν_1 peaks at 470 and 477 cm^{-1} .						-	573

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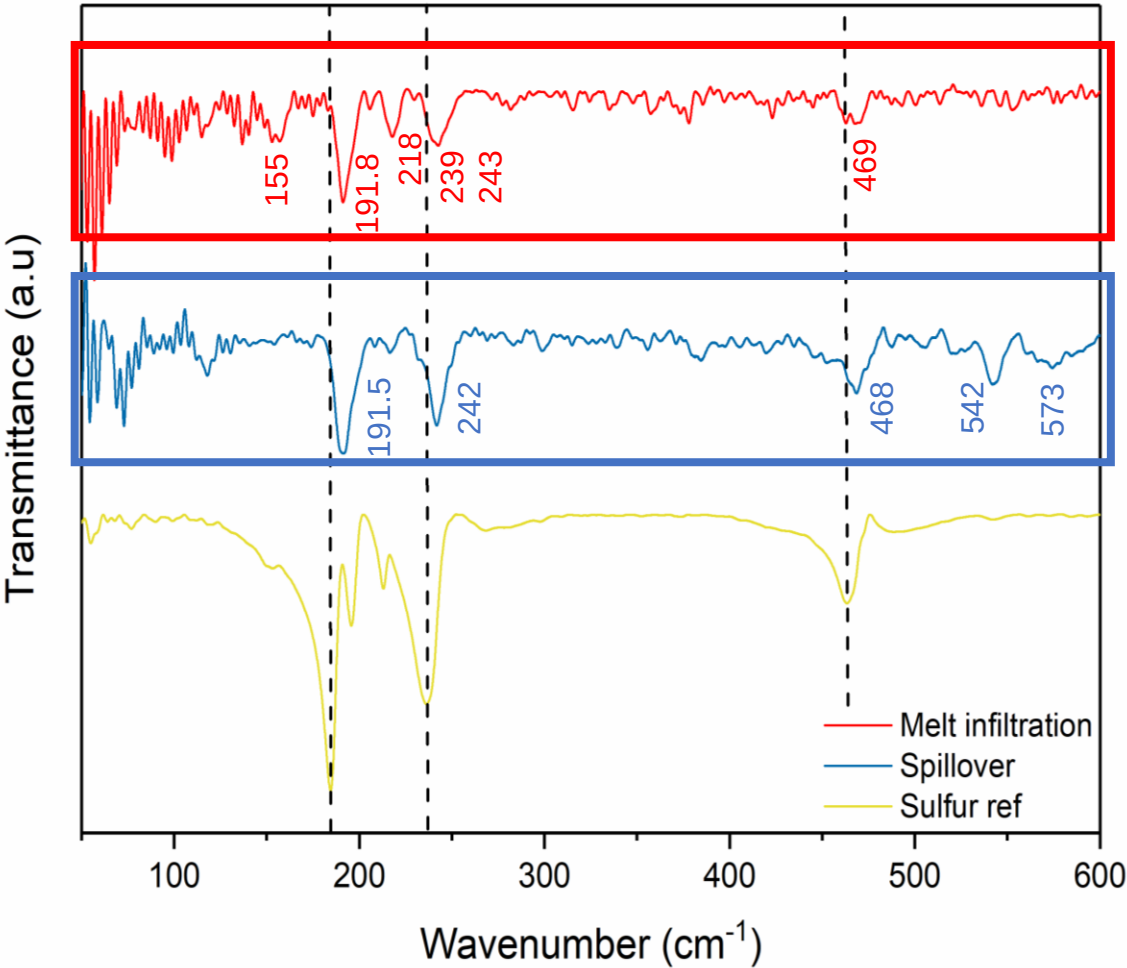
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Anderson, A. & Wong, L. Y. *Crystal Field Splitting in the Far Infrared Spectrum of Rhombic Sulfur*. *Canadian Journal of Chemistry* vol. 47 (1969); **10.1139/v69-445**

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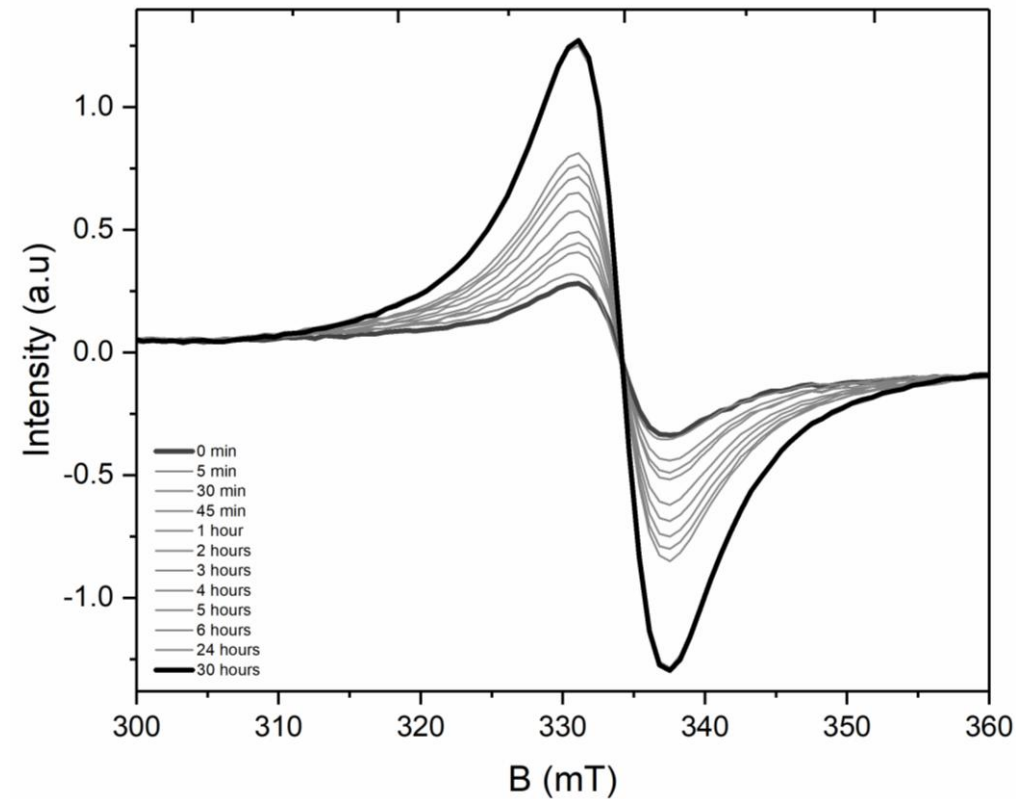
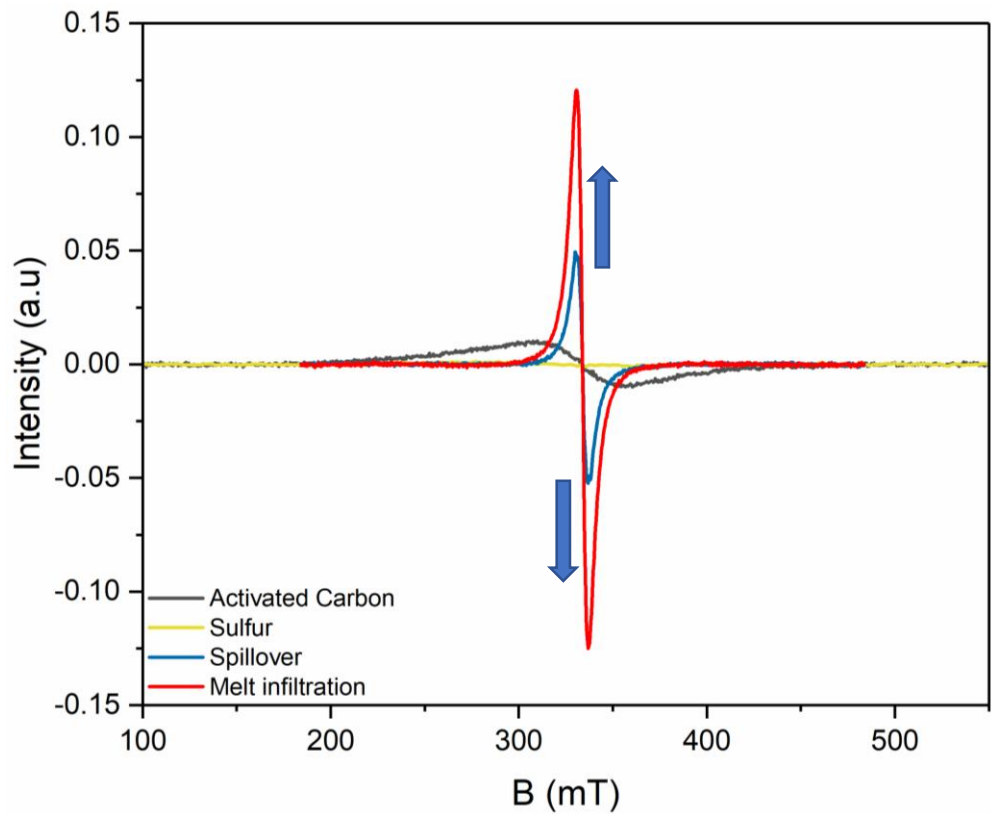
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	Solution	Crystal			
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$\nu_{10}(e_3)$	—	—	435	442	—
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				—	
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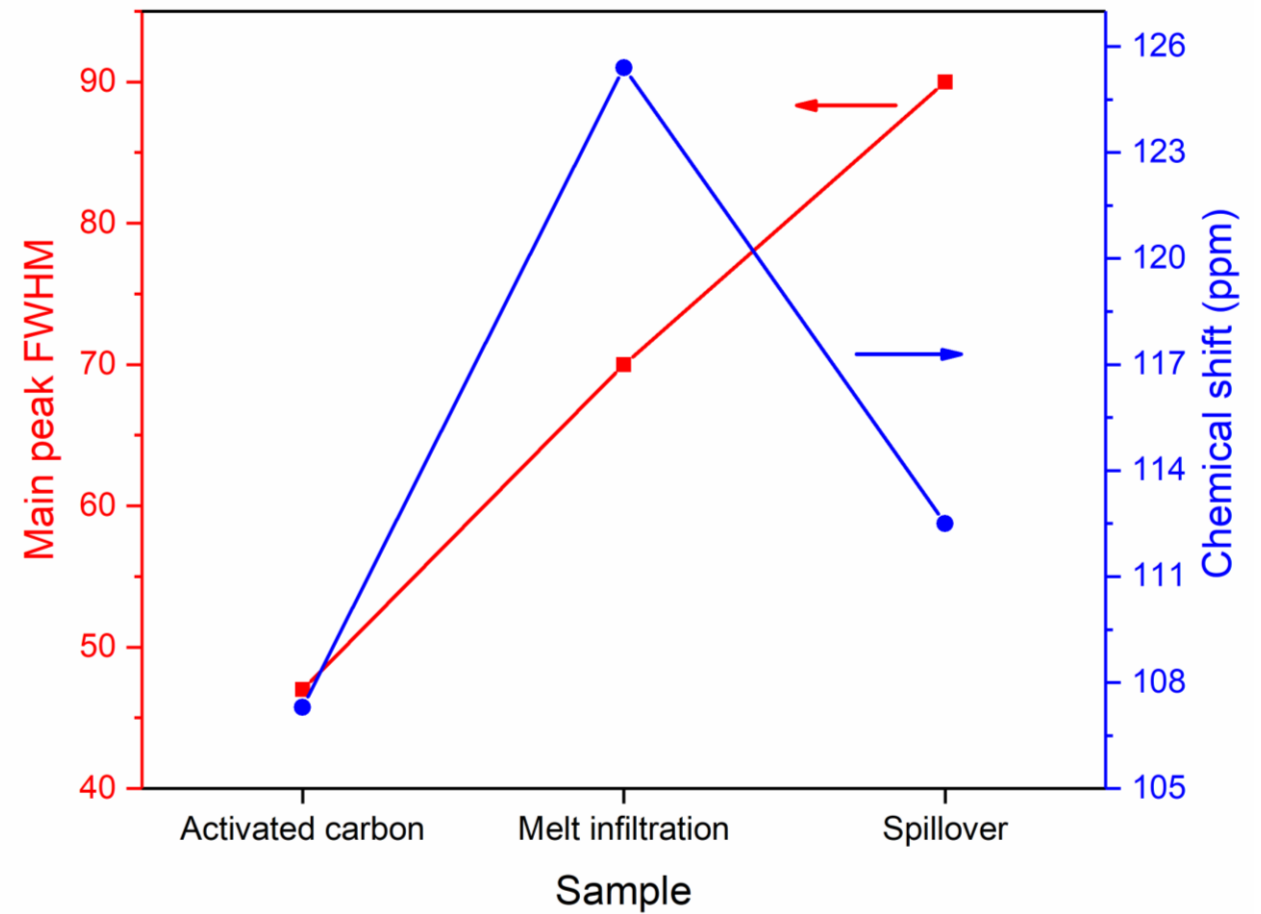
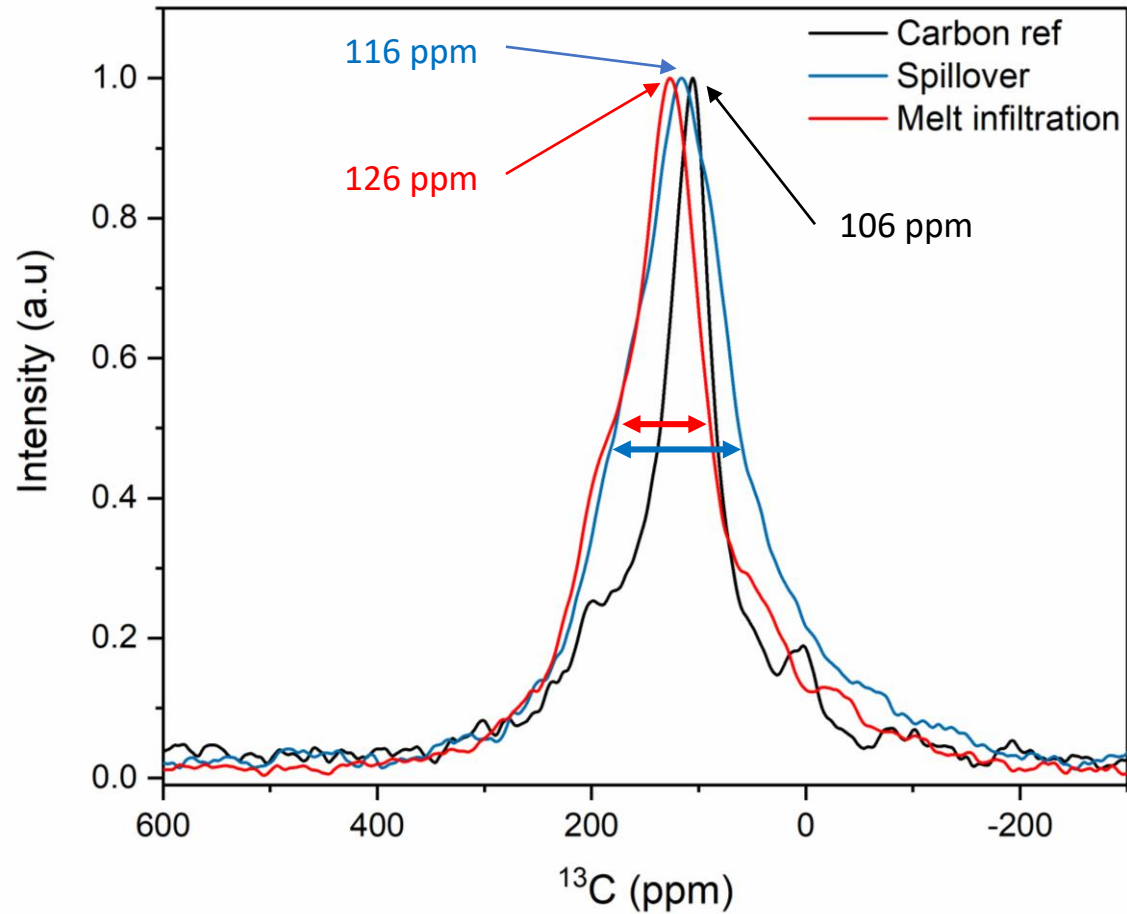
DIFFERENCE IN RADICAL FORMATION



Sample	Weight (mg)	Num spins	Spins / mg
C:S spillover	11.74	6.45E+16	5.50E+15
C:S melt infiltration	10.25	1.56E+17	1.52E+16

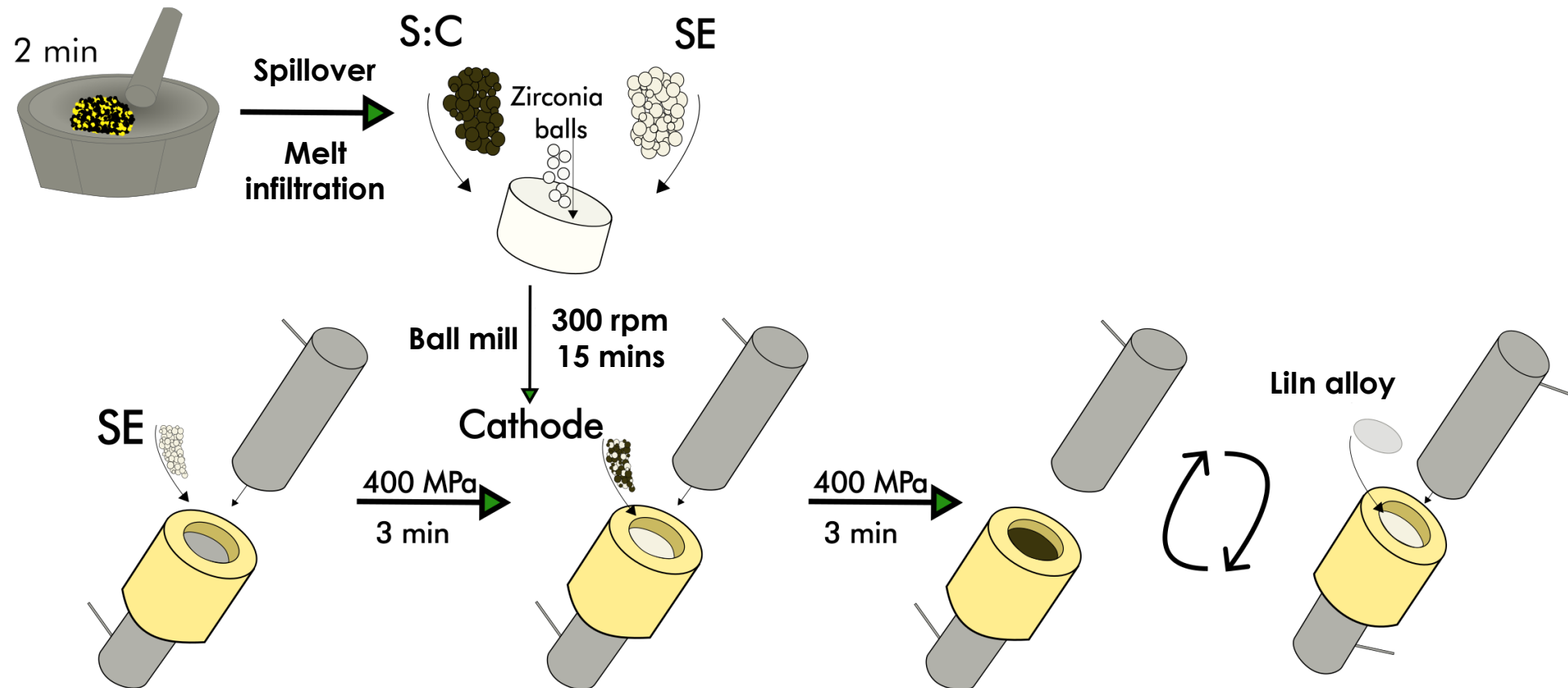
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CHANGES ON CARBON ENVIRONMENT

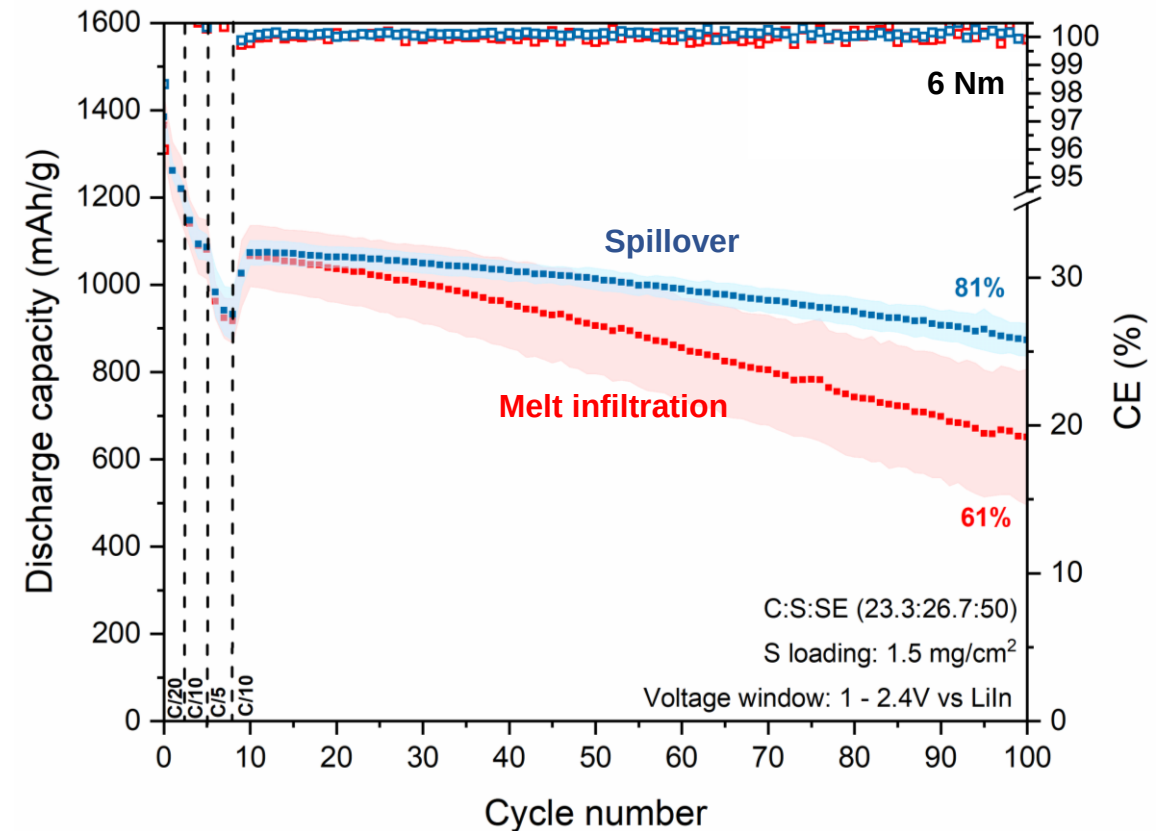
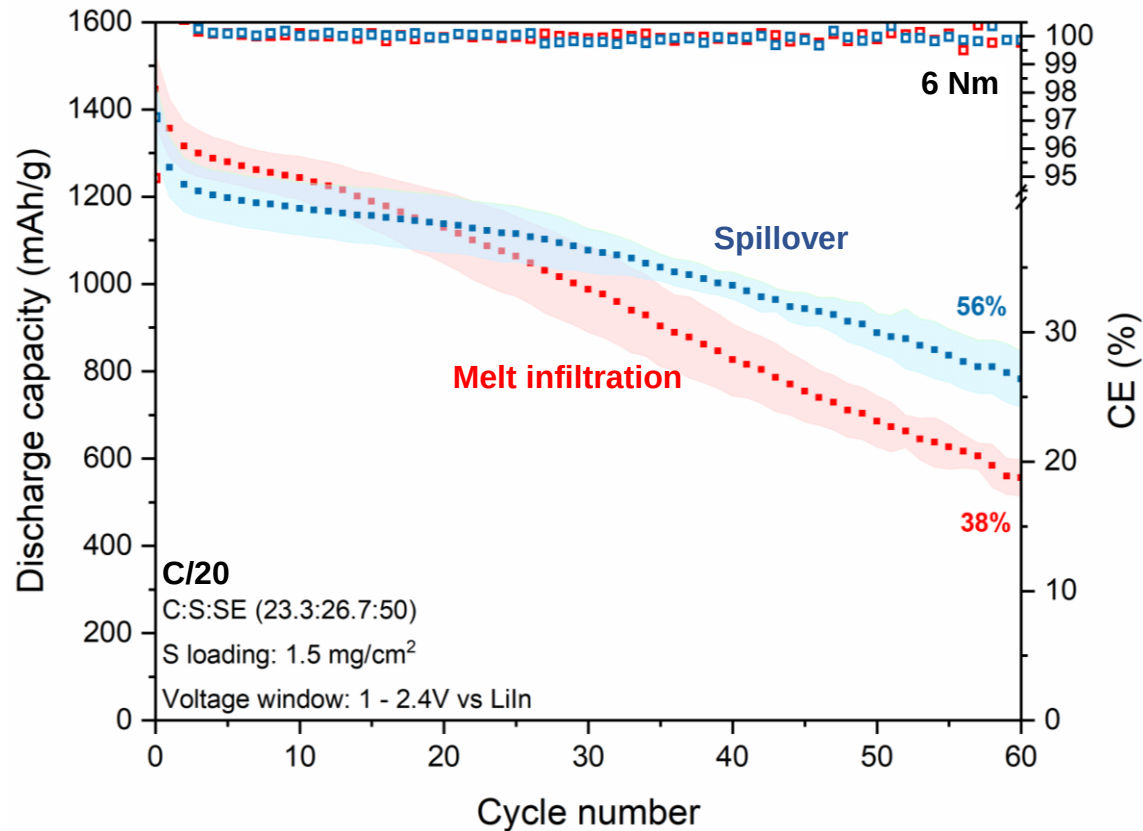


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EFFECT IN SOLID-STATE BATTERIES



EFFECT IN SOLID-STATE BATTERIES



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CONCLUSIONS

Causes and mechanism of spillover

- Physisorption process driven mostly by ΔS
- Strong evidences it is a solid-solid adsorption

Characterization

- Distinct final products were found for melt infiltration and spillover
- EPR shows melt infiltration has almost an order of magnitude higher radical amount
- NMR shifts higher for melt infiltration samples with less line broadening → Different interaction
- First-ever reported far-IR of sulfur confined in carbon (access to internal modes)

Effect on SSBs

- Easy and scalable preparation of sulfur-carbon composites
- Improved electrochemical performance of SSBs



Prof. Philipp Adelhelm

Dr. Stefano Tagliaferri

Dr. Francesco Piccolo

Dr. Katherine A. Mazzio

Changjiang Bai

Current and past group members

Collaboration partners

Prof. Marc Armbrüster

Jesus Andrade

Amanda Opis Basilio

Prof. Kallol Ray

Dr. Karsten Holldack

Confrence organizers



Prof. Stefan Kaskel

Dr. Holger Althues

Manja Hanke



Funding





THANK YOU FOR YOUR ATTENTION

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Dr. Stefano Tagliaferri

Dr. Francesco Piccolo

Dr. Katherine A. Mazzio

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