Modeling of Sulfur Based Polymer Cathodes for Li-S

Batteries:

Structural Analysis and Raman Characterization

Dissertation

zur Erlangung des Doktorgrades der Naturwissenschaften

(Dr. rer. nat.)

der

Naturwissenschaftlichen Fakultät II

Chemie, Physik und Mathematik

der Martin-Luther-Universität

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vorgelegt von

Frau Rana Kiani

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Submitted by

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Abstract

The optimization of lithium--sulfur batteries highly depends on the exploration of novel cathode materials. This thesis focuses on the development of sulfur/carbon co-polymers as a promising class of cathodes to replace crystalline sulfur. These co-polymers offer a flexible atomic structure and a potential for high reversible capacity. In particular, we dive into the investigation of poly(sulfur–n–1,3–diisopropenylbenzene) (S/DIB). Our exploration begins with a comprehensive analysis of the atomic structure of sulfur-n-1,3-diisopropenylbenzene co-polymers, using density-functional theory calculations. The primary goal was understanding the local structural properties, with a focus on identifying the optimal sulfur chain length (S_n with $n = 1 \cdots 8$) bridging two DIB units. Our findings reveal a preference for shorter sulfur chains $n \sim 4$ in DIB- S_n -DIB co-polymers. Subsequently, we complement our findings with ab initio Raman spectroscopy simulations and experimental Raman measurements. This combined approach facilitates the identification and characterization of various sulfur/carbon co-polymers with distinct sulfur contents. We demonstrate that S/DIB co-polymers featuring short and long sulfur chains exhibit distinguishable Raman activity in the 400-500 cm⁻¹ range, providing crucial insights into their structural composition. Significantly, the results presented herein apply to the fully charged state of the cathode. Furthermore, we extend our investigation to explain the discharge state of the battery, focusing on the transformation of sulfur co-polymer cathode materials upon lithiation. Specifically, we explore how sulfur chains evolve during lithiation and perform the same ab initio Raman spectroscopy methodology for their characterization.

Keywords: Li-S batteries, Polymer, Sulfur Cathodes, Quantum Chemistry, Spectroscopy

Acknowledgments

I express my deepest gratitude to my supervisor, Prof. Daniel Sebastiani, from whom I learned not just chemistry but, more profoundly, about humanity. I am indebted to him for his kindness and support during the challenging days of my Ph.D. He truly is a "Dr. Vater". Special appreciation also goes to Dr. Pouya Partovi-Azar, whose boundless patience and generosity paved the way for me. Without his guidance and support, this thesis would not have been possible. I would also like to express my gratitude to all the members of the Sebastiani research group throughout the years, specially, Luisa and Christian.

I extend my gratitude to Dr. Mehdi Amini for his invaluable support and guidance, helping me to reinvent myself over the past few years.

To my family, the most precious asset in my life: despite physical distance, their unconditional love and support were always in my heart. Heartfelt thanks go to my sister Bahareh, who shaped my character the most. Without her, I would not be the person I am today. My gratitude to her knows no bounds.

Last but certainly not least, I want to express my appreciation to my partner, Thomas, who made Germany a "home" to belong.

List of Publications

[1] Kiani, R., Sebastiani, D., and Partovi-Azar, P., "On the Structure of Sulfur/1, 3-Diisopropenylbenzene Co-Polymer Cathodes for Li-S Batteries: Insights from Density-Functional Theory Calculations," *ChemPhysChem*, Vol. 23, No. 1, 2022, e202100519

[2] Kiani, R., Steimecke, M., Alqaisi, M., Bron, M., Sebastiani, D., and Partovi-Azar, P., "Characterization of sulfur/carbon copolymer cathodes for Li-S batteries: A combined experimental and ab initio Raman spectroscopy study," 2023

[3] Kiani, R., Sheng, H., Held, T., Löhmann, O., Risse, S., Sebastiani, D., and Partovi-Azar, P., "Ab Initio Simulation of Raman Fingerprints of Sulfur/Carbon Copolymer Cathodes During Discharge of Li-S Batteries," *Chemphyschem: A European journal of chemical physics and physical chemistry*, e202400681

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Nomenclature

- *arb.u.* arbitary unit
- DFT Density functional Theory
- *DIB* 1,3–diisopropenylbenzene
- GTH Goedecker-Teter-Hutter
- Li S Lithium Sulfur
- MD Molecular Dynamics

Introduction

Jabir Ibn Hayyan (721 AD, Persia), also known as Geber in the Western world, who is often regarded as the father of chemistry, believed, 'The essential requirement in understanding of chemistry is the diligent engagement in practical work and the conduct of experiments. Those who refrain from such practical endeavors will never attain even the slightest degree of mastery.'⁴ Today, in the 21st century, we are in an era where computer modeling and computational frameworks have revolutionized our understanding of fundamental phenomena without stepping into the laboratory. I, personally, as a chemist who has experienced both worlds, believe that these two sides of chemical science complement one another and also one should be critical on both ends⁵.

Chemistry guides us to address fundamental questions about the world, ranging from the properties of substances like water to more complex ones. Quantum chemistry, in particular, empowers us to uncover the underlying reasons behind various phenomena. With quantum chemistry, we dive deep into each phenomenon, unraveling its atomic properties by studying its smallest constituents, such as electrons.

Theoretical chemistry is a field whose foundation is based on quantum mechanics. In this field the primary focus is around properties at the atomistic level. Therefore, it's useful to categorize theses properties into: structural, dynamics, and spectroscopic features.⁶

Computational chemistry being young in the sense that no technology in human history has developed at this pace that digital computers have over the last four decades, enabling us to address one of the greatest challenges of our century: the pursuit of green and renewable energy sources. Among all, Lithium Sulfur (Li-S) batteries emerging as promising competitor to fulfill this dream.

1.1 Lithium Sulfur Batteries

As oil production is anticipated to decline and the number of vehicles, along with their environmental impact, continues to rise worldwide, a shift in the transportation system becomes increasingly inevitable in our carbon-oriented world. The increasing demand for safe, cost-effective, high-energy-density, and long-lasting rechargeable batteries emphasizes the urgency to meet environmental requirements for energy storage systems compatible with renewable sources.^{7,8} Among the most

1

4 Newman, *Promethean ambitions: alchemy and the quest to perfect nature*, 2019.

5 Mata *et al.*, "Benchmarking quantum chemical methods: Are we heading in the right direction?," 2017.

6 Cramer, Essentials of computational chemistry: theories and models, 2013.

7 Winter *et al.*, "What are batteries, fuel cells, and supercapacitors?," 2004.

8 Bruce, "Energy storage beyond the horizon: Rechargeable lithium batteries," 2008.

promising candidates for energy storage devices is the lithium-sulfur cells. Lithium-sulfur (Li-S) cells have the potential to have substantially higher energy density, up to 2500 W.h.kg⁻¹, in comparison to Li ion ones (180 mA.h.g⁻¹). The cell in its simplest configuration consists of sulphur as the positive electrode (Cathode) and lithium as the negative electrode (Anode),^{9,10} Figure 1.1.



9 Rauh *et al.,* "A lithium/dissolved sulfur battery with an organic electrolyte," 1979.

10 Shim *et al.*, "The lithium/sulfur rechargeable cell: effects of electrode composition and solvent on cell performance," 2002.

Figure 1.1: Schematic of a Li-S cell. (Created by the author).

The overall electrochemical reaction during charge and discharge is shown in the following reaction:

$$S_8 + 16Li^+ + 16e^- \rightleftharpoons 8Li_2S \tag{1.1}$$

Despite its considerable advantages, were mentioned earlier, the sulfur cathode in Li–S cells face several challenges that hinder their widespread application. These challenges include:

a) Formation of an insulating layer consisting of insoluble Li_2S_2 and Li_2S structures on the sulfur cathode during discharge cycles. This results in poor utilization of the active material¹¹.

b) Dissolution of Li-polysulfides (Li_2S_n , 2 < *n* < 8) into the electrolyte before full reduction to Li_2S , leading to irreversible capacity fade¹¹.

c) Migration of Li-polysulfides to the anode (shuttle effect), their reaction with anode surface, and the eventual formation of an insulating layer of Li_2S_2 and Li_2S around the anode. This layer prevents the diffusion of Li^+ ions into the electrolyte^{12,11}.

d) Volume expansion in the sulfur cathode upon reaction with Li⁺ due to different densities between α -sulfur (2.07 g cm⁻³) and Li₂S (1.66 g cm⁻³). This not only results in weakened electrical contacts with the conductive substrate but also safety concerns¹¹.

To address these challenges, advancements in materials design, including the development of new electrolytes and protective films for the lithium anode, have been previously introduced.^{13–17} Nevertheless, the main problem still remains at the cathode, where the sulfur compounds are

11 Seh *et al.*, "Designing high-energy lithium–sulfur batteries," 2016.

12 Liang *et al.*, "A highly efficient polysulfide mediator for lithium–sulfur batteries," 2015.

13 Shin *et al.*, "Characterization of N-methyl-N-butylpyrrolidinium bis (trifluoromethanesulfonyl) imide-LiTFSI-tetra (ethylene glycol) dimethyl ether mixtures as a Li metal cell electrolyte," 2008.

14 Yuan *et al.*, "Improved dischargeability and reversibility of sulfur cathode in a novel ionic liquid electrolyte," 2006.

15 Ryu *et al.*, "Discharge behavior of lithium/sulfur cell with TEGDME based electrolyte at low temperature," 2006.

16 Wang *et al.*, "Sulfur–mesoporous carbon composites in conjunction with a novel ionic liquid electrolyte for lithium rechargeable batteries," 2008.

17 Chung *et al.*, "Lithium phosphorous oxynitride as a passive layer for anodes in lithium secondary batteries," 2004.

3

dissolving into the electrolyte, which lead to performance issues in the battery.

1.2 Polymeric Sulfur Cathode

Organic materials present a remarkable opportunity for advancing current energy storage systems. They can be incorporated into the sulfur cathode to improve conductivity, increase active material usage, and prevent dissolution. Among these, sulfur-rich copolymers derived from poly(sulfur-random-1,3-diisopropenylbenzene) (S-r-DIB) have recently emerged as cathode materials. It is typically synthesized through inverse vulcanization¹⁸, these co-polymer have demonstrated improved capacity retention and battery lifetime¹⁹. Moreover, the structural flexibility of polymeric cathodes can effectively overcome the volume expansion which occurs during lithiation.^{20,21} Li–S batteries using poly(S-r-DIB) copolymers as the active cathode material function similarly to traditional Li–S batteries that use S₈. The main difference is that during discharge, poly(Sr-DIB) copolymers form soluble organosulfur compounds (thiolated DIB units).

1.2.1 Inverse Vulcanization

In 2013, Pyun ^{20,18} and co-workers introduced a technique known as inverse vulcanization, allowing for the direct copolymerization of molten elemental sulfur with vinylic comonomers. The poly(S-r-DIB) copolymers are produced via inverse vulcanization, involving the direct dissolution and copolymerization of DIB within liquid sulfur. This process essentially comprises a bulk copolymerization of molten sulfur and DIB (solventfree), carried out at around 185 °C, allowing for the free radical ringopening polymerization (ROP) of S₈ (see Figure 1.2). This process leads to the formation of a highly cross-linked polymer network. At a current of 0.1C, displays a 1100 mA h g⁻¹ specific capacity on the first cycle and, importantly, retains 74.8% capacity after 100 cycles.¹⁸

18 Simmonds *et al.*, "Inverse vulcanization of elemental sulfur to prepare polymeric electrode materials for Li–S batteries," 2014.

19 Ji *et al.*, "Advances in Li–S batteries," 2010.

20 Chung *et al.*, "The use of elemental sulfur as an alternative feedstock for polymeric materials Nat," 2013.

21 Schon *et al.*, "The rise of organic electrode materials for energy storage," 2016.



Poly(Sulfur-random-1,3-Diisopropenylbenzene)copolumer

Figure 1.2: Synthetic scheme for the inverse vulcanization process yielding poly(sulfurrandom-1,3-diisopropenylbenzene) copolymers. (Created by the author based on lab work and samples personally synthesized).

However, a complete understanding of the redox mechanisms for these materials remains unknown, primarily because of the challenges associated with characterizing the amorphous structures of polymer cathodes and identifying individual ionic species.

In this thesis, our goal is to gain a deeper understanding of the structure of poly(S-r-DIB) copolymers, followed by investigating their discharge mechanism in the presence of Li ions. We aim to achieve this goal by employing a combination of density-functional theory-based calculations, ab-initio molecular dynamics simulations, and characterizing the Raman spectra of these copolymers.

1.3 Spectroscopy

Spectroscopy is a field of science that explores the interaction between external electromagnetic radiation and matter as a function of wavelength or frequency in order to extract valuable insights about the composition, structure, and properties of matter.²² In many cases, experimental spectroscopic measurements of materials such as NMR, IR, and Raman spectroscopy can be complemented by simulations using computational methods. This dual approach recognizes as a bridge between experimental and computational techniques, enabling a more comprehensive analysis of the fundamental aspects of a spectrum.

Each type of spectroscopy, such as electronic, X-ray, photoelectron, and vibrational spectroscopy, offers unique insights into the structure and properties of materials and molecules, making them essential tools across various scientific fields. Among these, vibrational spectroscopy is particularly valuable for studying the vibrational states of molecules, providing detailed information about molecular structure, bonding,

22 Press, *The Oxford American College Dictionary*, 2002.

and dynamics. By measuring the absorption or scattering of light at different frequencies, vibrational spectroscopy reveals important details about functional groups within a molecule and their interactions with the surrounding environment. Its ability to provide precise molecular fingerprints, coupled with non-destructive and versatile analysis across various states of matter, makes vibrational spectroscopy a preferred choice in many applications. Techniques like infrared (IR) and Raman spectroscopy are commonly used within this area.²³

In this thesis, specifically, Raman spectroscopy is employed as a key to enhance our understanding of poly(S-r-DIB) structures, by combining experimental measurements with *ab initio* molecular dynamics simulations.

A deeper exploration of the theory behind Raman spectroscopy and the methods which is used in this thesis for its simulation can be found in Chapter 2.

1.4 Thesis Outline

This doctoral research contains a series of investigations united by a common theme: the combination of density functional theory (DFT) and *ab initio* molecular dynamics (MD) simulations to explore novel sulfur-based cathode materials designed for advanced Lithium-Sulfur (Li-S) batteries. One project was carried out in collaboration with the experimental Raman laboratory led by Prof. Michael Bron at the Martin Luther University of Halle-Wittenberg, allowing for a direct comparison between theoretical and experimental results. Additionally, another collaboration was established with the Electrochemical Energy Storage department at Helmholtz-Zentrum Berlin für Materialien und Energie, Dr. Sebastian Risse's group, further enabling the integration of theoretical models with experimental data. The core of this thesis is based on the publications from this research, which have been published in international journals and are fully reproduced herein as a fundamental component of this work.

This cumulative thesis is structured as follows. Following the introductory section, in Chapter 2 we look into a comprehensive exploration of the theoretical frameworks, bases of the methods employed throughout this research. Chapter 3 provides an overview of the research conducted and presents the significant findings. Finally, Chapters 4–6 contain complete reproductions of the three published papers in peer–reviewed journals^{"1–3}. At the End, Chapter 7, we are presenting the conclusion of the thesis work.

23 Smith *et al.*, *Modern Raman spectroscopy: a practical approach*, 2019.

1 Kiani *et al.*, "On the Structure of Sulfur/1, 3-Diisopropenylbenzene Co-Polymer Cathodes for Li-S Batteries: Insights from Density-Functional Theory Calculations," 2022.

2 Kiani *et al.*, "Characterization of sulfur/carbon copolymer cathodes for Li-S batteries: a combined experimental and ab initio Raman spectroscopy study," 2023.

3 Kiani *et al.*, "Ab Initio Simulation of Raman Fingerprints of Sulfur/Carbon Copolymer Cathodes During Discharge of Li-S Batteries, .

2

Theoretical Framework

This chapter is dedicated to a discussion of the theoretical background of the methods used in this work.

2.1 Molecular Dynamics

Molecular Dynamics (MD) is a numerical simulation method to solve the classical many-body problem, specifically the movement of particles in time, which interact via a potential. The solution is derived through the numerical integration of the (Newtonian) equations of motion. In simpler terms, molecular dynamics explores the model and movements of particles (atoms) by solving classical equations of motion. This valuable technique has application in a wide spectrum, ranging from crystalline and amorphous solids to liquids and solutions.

2.1.1 Classical vs. Ab Initio Molecular Dynamics

Since we would like to probe a system, the obvious approach is to start from the equations of motion. Neglecting quantum effects, Newton's second law explains the motion of a I^{th} particle as follow:

$$m_I \ddot{\mathbf{R}}_{\mathbf{I}}(t) = \mathbf{F}_I(t) = -\nabla V(\mathbf{R}_1(t), \mathbf{R}_2(t), \dots, \mathbf{R}_{\mathbf{N}}(t)), \qquad (2.1)$$

Here, m_I represents the mass of the particle *I*, and $\mathbf{R}_{\mathbf{I}}(t)$ denotes its spatial coordinates at time *t*. *V* represents the system's potential as a function of the spatial coordinates of all *N* particles. The forces $\mathbf{F}_I(t)$ acting on the particles can be derived as the gradient of the potential *V*. There are various approaches to calculate forces $\mathbf{F}_I(t)$, resulting in different types of MD simulations. Classical MD involves dividing the energy of a molecular system into various contributions, and these contributions are parameterized based on nuclear positions. Following this approach, the total energy of a system and consequently, the forces are derived as the sum of individual contributions. This approach is computationally efficient, enabling the calculation of several thousand atoms up to hundreds of nanoseconds.

An alternative method for calculating forces on atomic nuclei involves an approximate solution of the Schrödinger equation. This approach, known as *ab initio* Molecular Dynamics (AIMD), is computationally more expensive. This method limits the system size to several hundred atoms and the time scale to usually less than one nanosecond. Although AIMD investigates smaller systems, it offers powerful predictive capabilities as forces are derived from an electronic structure method. In classical MD simulations, forces are based on previously parameterized processes, optimized for specific compound classes and properties, making them less transferable to other compound classes.

2.1.2 Numerical Integration of the Equations of Motion

The equation of motion (Eq (2.1)), describes a group of connected secondorder partial differential equations. There are different approaches to solve these kind of equations. The common approach is to use finitedifference integration, but not all algorithms fulfilling conditions like time-reversibility and conservation of energy and momentum. The Verlet algorithm is an appropriate method for numerically integrating the equations of motion.

The Verlet algorithm

We start by Taylor expansion, extending up to the second order, for the position of a particle at the time $t + \Delta t$:

$$\mathbf{r}_{i}(t+\Delta t) \approx \mathbf{r}_{i}(t) + \frac{d\mathbf{r}_{i}(t)}{dt}\Delta t + \frac{1}{2}\frac{d^{2}\mathbf{r}_{i}(t)}{dt^{2}}\Delta t^{2}$$
(2.2)

By using Newton's second law, we can replace the acceleration according to:

$$\mathbf{r}_{i}(t + \Delta t) \approx \mathbf{r}_{i}(t) + \frac{d\mathbf{r}_{i}(t)}{dt}\Delta t + \frac{\mathbf{F}_{i}(t)}{2m_{i}}\Delta t^{2}$$
(2.3)

The velocity term in equation (2.3) can be excluded by introducing a similar expression for $\mathbf{r}_i(t - \Delta t)$:

$$\mathbf{r}_{i}(t - \Delta t) \approx \mathbf{r}_{i}(t) - \frac{d\mathbf{r}_{i}}{dt}\Delta t + \frac{\mathbf{F}_{i}(t)}{2m_{i}}\Delta t^{2}$$
(2.4)

Summation of equation (2.3) and (2.4), results in:

$$\mathbf{r}_{i}(t+\Delta t) \approx 2\mathbf{r}_{i}(t) - \mathbf{r}_{i}(t-\Delta t) + \frac{\mathbf{F}_{i}(t)}{m_{i}}\Delta t^{2}$$
(2.5)

Equation 2.5 is the Verlet algorithm ²⁴. Starting from an initial state, equation (2.3) can create a set of coordinates at the time Δt . These coordinates can be further used along a trajectory of an arbitrary length correlation functions," 1968. using equation (2.5). The Verlet algorithm can not explicitly compute velocities. Velocities are obtained through post-processing of particle positions in the trajectory, as:

$$\mathbf{v}_{i}(t) = \frac{d\mathbf{r}_{i}}{dt} = \frac{\mathbf{r}_{i}(t + \Delta t) - \mathbf{r}_{i}(t - \Delta t)}{2\Delta t}$$
(2.6)

24 Verlet, "Computer" experiments" on classical fluids. II. Equilibrium

The Velocity-Verlet algorithm

The velocity-Verlet algorithm addresses the disadvantage of the Verlet algorithm and provides explicit formulae for both positions and velocities. It starts from the time reversibility of Newton's equations of motion and perform a Taylor expansion of $\mathbf{r}_i(t + \Delta t)$ from a time step $-\Delta t$ as follows:

$$\mathbf{r}_{i}(t) \approx \mathbf{r}_{i}(t + \Delta t) - \frac{d\mathbf{r}_{i}(t + \Delta t)}{dt}\Delta t + \frac{1}{2}\frac{d^{2}\mathbf{r}_{i}(t + \Delta t)}{dt^{2}}\Delta t^{2}$$
(2.7)

Combining this equation with equation (2.3), results in:

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)}{2m_i} \Delta t$$
(2.8)

The velocity-Verlet algorithm is formed by combining equations (2.3) and (2.8). It allows the simultaneous updating of positions and velocities, offering direct access to these values. This is particularly useful when implementing constant temperature algorithms.

Controlling the Temperature: Thermostats

The simulation procedure described, involves initiating a system with N particles in a fixed volume V where energy remains a constant, results in an NVE ensemble. However, it is often necessary to sample from different ensembles, such as the constant temperature (NVT) or constant pressure (NPT) ensemble, to reflect experimental conditions. In order to maintain constant temperature and pressure instead of energy, thermostats^{25–28} and barostats^{29–31} are employed, respectively. While various schemes exist in the literature, this thesis employs Canonical Sampling through Velocity Rescaling (CSVR) thermostat²⁷ for obtaining results.

The CSVR thermostat controls the temperature of a system by adjusting the velocities of particles at each simulation step using a rescaling factor, α , which depends on the system's kinetic energy.

$$\alpha = \sqrt{\frac{K_t}{K}},\tag{2.9}$$

where *K* is the system's current kinetic energy and K_t refers to the target kinetic energy drawn randomly from the kinetic energy distribution. However, if the velocities are rescaled too directly, it can cause large fluctuations, which can disturb the system's natural behavior. To minimize this effect, the rescaling is applied gradually over several steps, which smooths the process:

$$dK = (\bar{K} - K)\frac{dt}{\tau} + 2\sqrt{\frac{K\bar{K}}{N_f}}\frac{dW}{\sqrt{\tau}},$$
(2.)

where τ is a coupling constant, N_f refers to the number of degrees of freedom and dW is Wiener noise. By the assumption of ergodicity, this thermostat has been shown to accurately reproduce the NVT ensemble.²⁷

25 Marx et al., *Ab initio molecular dynamics: basic theory and advanced methods*, 2009.

26 Andersen, "Molecular dynamics simulations at constant pressure and/or temperature," 1980.

27 Nosé, "A molecular dynamics method for simulations in the canonical ensemble," 1984.

28 Hoover, "Canonical dynamics: Equilibrium phase-space distributions," 1985.

29 Bussi *et al.*, "Canonical sampling through velocity rescaling," 2007.

30 Parrinello *et al.*, "Crystal structure and pair potentials: A molecular-dynamics study," 1980.

31 Parrinello *et al.*, "Polymorphic transitions in single crystals: A new molecular dynamics method," 1981.

2.1.3 *Ab Initio* Molecular Dynamics (AIMD)

The efficiency of molecular dynamics simulations is primarily limited by the selected level of theory used to calculate atomic forces. Using pre-parametrized potentials for force calculations makes classical molecular dynamics a cost-effective option. In contrast, ab initio molecular dynamics (AIMD) is significantly more computationally demanding, due to solving the Schrödinger equation at each time step.

This thesis will employ AIMD due to the requirement for a more realistic representation of the electronic structure. Specifically, AIMD is chosen for its ability to accurately describe covalent bonds and as a result their associated vibrational modes to calculate Raman Spectra for the structures. This method will be further discussed in this chapter.

We use the term AIMD to refer to Born-Oppenheimer Molecular Dynamics (MD). In Born-Oppenheimer MD, the static electronic structure problem is solved within each MD step, with the nuclear positions held fixed at a given moment in time (Eq (2.12)). The nuclei move using classical equations of motion, and we calculate the forces by finding the gradient of the potential determined from solving the electronic structure problem. The electronic part of the total force on the atom is determined using Equation (2.11).

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \{ \langle \Psi_0, \hat{H}_{el} \Psi_0 \rangle \} + \mathbf{F}_{nn}$$
(2.11)

$$\hat{H}_{el}\Psi_0 = E_0\Psi_0 \tag{2.12}$$

In equation (2.12), \hat{H}_{el} denotes the electronic Hamiltonian, Ψ_0 denotes the ground state wave function, and E_0 denotes the ground state energy.

2.2 Electronic Structure

Electronic structure methods are employed to compute various properties of a many-body system³², based on the fundamental principles of quantum physics. The comprehensive description of a many-body particle system relies on its many-body wave function. Assuming negligible relativistic effects and time-independent external potentials, the many-body wave function can be derived from the stationary many-body Schrödinger equation:

$$\hat{H}\Psi = E\Psi \tag{2.13}$$

Here, the time-independent Hamiltonian (\hat{H}) is defined as:

32 McQuarrie, Quantum chemistry, 2008.

$$\hat{H} = \underbrace{\sum_{i=1}^{N} -\frac{1}{2} \nabla_{i}^{2}}_{\hat{T}_{e}} + \underbrace{\sum_{I=1}^{M} -\frac{1}{2M_{I}} \nabla_{I}^{2}}_{\hat{T}_{n}} + \underbrace{\sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|\vec{r}_{i} - \vec{r}_{j}|}}_{\hat{V}_{ee}} + \underbrace{\sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A} Z_{B}}{|\vec{R}_{A} - \vec{R}_{B}|}}_{\hat{V}_{nn}} + \underbrace{\sum_{i=1}^{M} \sum_{A=1}^{M} -\frac{Z_{A}}{|\vec{r}_{i} - \vec{R}_{A}|}}_{\hat{V}_{ne}} + \underbrace{\sum_{i=1}^{M} \sum_{A=1}^{M} \sum_{A=1}^{M} \sum_{A=1}^{M} \sum_{A=1}^{M} -\frac{Z_{A}}{|\vec{r}_{i} - \vec{R}_{A}|}}_{\hat{V}_{ne}} + \underbrace{\sum_{i=1}^{M} \sum_{A=1}^{M} \sum_{A=1}^{M$$

The indices *i* and *j* denote electrons, while *A* and *B* represent atomic nuclei. M_I signifies nuclear masses, and \vec{R}_A and \vec{r}_i stand for nuclear and electron positions, respectively, with Z_A referring to the atomic number. Also, Equation (2.14) is presented in atomic units, where *e*, \hbar , *m*, and $4\pi\varepsilon_0$ are considered to be equal to one.

The Hamiltonian *H* can be separated into contributions from the electron (\hat{T}_e) and the nuclear (\hat{T}_n) kinetic energy operators, the electron-electron repulsion (\hat{V}_{ee}) , the nucleus-nucleus repulsion (\hat{V}_{nn}) , and the electron-nucleus interaction (\hat{V}_{en}) .

Here, we will use this Hamiltonian to solve the electronic structure problem in a Born-Oppenheimer Molecular Dynamics given by equation (2.11). Practically, the precise quantum mechanical analysis of a many-body system is only possible for very small systems. The Born-Oppenheimer approximation simplifies the problem by expressing the complete many-body wave function $\Psi(\mathbf{r}, \mathbf{R})$ as the product of an electronic wave function $\Psi_{el}(\mathbf{r}, \{\mathbf{R}\})$ and a nuclear wave function $\phi_{nuc}(\mathbf{R})$,

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_{el}(\mathbf{r}, \{\mathbf{R}\})\phi_{nuc}(\mathbf{R})$$
(2.15)

Here, **r** represents the degrees of freedom of the electronic subsystem, and **R** denotes the degrees of freedom of the nuclear subsystem. As implied by equation (2.15), the states of electrons and nuclei can be treated independently. This allows for the calculation of the electronic wave function concerning fixed nuclear positions, denoted by the parametric dependence of $\Psi_{el}(\mathbf{r}, \{\mathbf{R}\})$ on the nuclear coordinates **R**. The Born-Oppenheimer approximation is theoretically justified by the significant mass difference of approximately three orders of magnitude between nuclei and electrons. Consequently, the electrons readily adjust to the positions of the slowly moving cores, behaving as if they are completely relaxed at any moment during atomic movement.

Instead of dealing with the entire many-body wave function, the manybody problem can be simplified to one involving electrons moving in an external field generated by stationary nuclei. The corresponding time-independent Hamiltonian for this simplified problem is given by:

$$\hat{H}_{el} = \sum_{i=1}^{N} -\frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N} \sum_{j>i=1}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^{M} \sum_{A=1}^{M} -\frac{Z_A}{|\vec{r}_i - \vec{R}_A|}$$
(2.16)

with:

$$\hat{H}_{el}\Psi_{el} = E_{el}\Psi_{el} \tag{2.17}$$

From this point onward, our focus will be on the electronic component of the total Hamiltonian. Various methods have been developed for the construction of approximate solutions of the equation (Eq (2.17)). A wavefunction based (Hartree-Fock) and a density based (Density Functional Theory) approach⁶. This thesis employs the Density Functional Theory (DFT) approach. In the subsequent sections, we mainly explore into this method.

2.2.1 Density Functional Theory

The computational demands of Hartree-Fock (HF) based methods increase significantly for large systems due to the requirement of calculating the many-body wave function. An alternative approach that reduces computational complexity is to utilize the electronic charge density instead of the wave function. This approach reduces the spatial variables from 3*N* to only 3 for an *N*-electron system. Density functional theory (DFT) employs the electron density as a fundamental quantity, allowing for more efficient computations compared to HF-based methods and enabling the investigation of larger systems. In DFT, the physical and chemical properties, such as the total energy, are expressed as functionals of the electronic charge density, which can be calculated as,

$$\rho(\mathbf{r}) = N \sum_{\sigma_1} \dots \sum_{\sigma_N} \int \dots \int |\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N|^2 d\mathbf{r}_1 \dots d\mathbf{r}_{N-1}.$$
(2.18)

Over the past decades, advancements in DFT-based methods have made it a widely used tool for studying various systems, including molecules, clusters, liquids, and solids. The concept of using electron density as a central quantity in materials modeling originated from the Thomas-Fermi model.

Hohenberg-Kohn Theorems

The foundations of modern Density Functional Theory (DFT) are based on the theorems formulated by Hohenberg and Kohn. The first theorem states that the electronic ground state contains all the necessary information in its electronic density. In other words, there is a one-to-one correspondence between the external potentials $v_{ext}(\mathbf{r})$ and the groundstate density $\rho_0(\mathbf{r})$. This allows the external potential to be expressed as a unique functional of the ground-state density $v[\rho_0](\mathbf{r})$, up to an arbitrary additive constant.

The second theorem states that the ground-state energy can be obtained using the Rayleigh-Ritz variational principle³³, where the exact ground-state density ρ_0 minimizes the total energy functional $E_{\nu_0}[\rho]$,

$$E_{\nu_0}[\rho] \ge E_0 \qquad \forall_\rho \tag{2.19}$$

and $E_{\nu_0}[\rho] = E_0$ if and only if $\rho = \rho_0$.

33 Ritz, "Über eine neue Methode zur Lösung gewisser Variationsprobleme der mathematischen Physik.," 1909. The Hohenberg-Kohn theorem was formulated for systems that can be described by a real physical potential, known as v-representable systems. Determining whether a given density is v-representable or not is generally a challenging task. However, the Levy-Lieb constrained search formalism offers a solution to this problem. Levy and Lieb^{34,35} introduced a functional similar to that of Hohenberg and Kohn but with a less restrictive condition on the density, known as N-representability. An electron density is considered N-representable if it originates from an N-electron antisymmetric wave function. This condition ensures the applicability of density functional theory (DFT).

Theoretically, the total-energy $E[\rho]$ can be expressed as a sum of kinetic energy functional $T[\rho]$ and the functionals of energy resulting from electron-electron and electron-nuclei interaction,

$$E[\rho] = T[\rho] + E_{en}[\rho] + E_{ee}[\rho]$$
(2.20)

This concept provides an accurate representation of the total energy of a system. However, the expression of its functional is not known. One particular problem is formulating the kinetic energy in terms of the electron density. To address this issue, Kohn-Sham Density Functional Theory (DFT) can be employed.

Kohn-Sham DFT

According to the Kohn-Sham (KS) approach, we can determine the electronic ground state density. Kohn and Sham proposed the use of a non-interacting reference system consisting of KS orbitals ϕ_m . These orbitals are chosen in such a way that the electron density of the Kohn-Sham auxiliary system, denoted as ρ_{KS} , equals the ground state density ρ_0 obtained from the fully interacting wave function,

$$\rho_0(\mathbf{r}) \stackrel{!}{=} \rho_{KS}(\mathbf{r}) = \sum_m (\phi_m^{KS}(\mathbf{r}))^* \phi_m^{KS}(\mathbf{r})$$
(2.21)

By replacing the many-body system with a system of N non-interacting electrons, we can express the total-energy functional within the framework of Kohn-Sham Density Functional Theory (KS-DFT) as follows:

$$E_{KS}[\{\phi_m^{KS}\}] = \underbrace{\sum_{m} \langle \phi_m^{KS}, -\frac{1}{2} \nabla^2 \phi_m^{KS} \rangle}_{T_s[\{\phi_m^{KS}\}]} + E_{en}[\rho] + E_H[\rho] + E_{xc}[\rho] \quad (2.22)$$

 $T_s[\{\phi_m^{KS}\}]$ denotes kinetic energy functional. $T_s[\{\phi_m^{KS}\}]$ represents an explicit function of the Kohn-Sham framework, while it serves as an implicit functional of the density orbitals $T_s[\rho] = T_s[\{\phi_m^{KS}[\rho]\}]$. The notation $[\{\phi_m^{KS}\}]$ represents the functional dependence on the set of occupied orbitals. In equation (2.22), $E_{en}[\rho]$ denotes the functional accounting for the repulsion between the nuclei and electrons,

34 Levy, "Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem," 1979.

35 Lieb, "Density functionals for Coulomb systems," 2002.

$$E_{en}[\rho] = \int \int v_{en}(\mathbf{r})\rho(\mathbf{r})d^3r \qquad (2.23)$$

The functional arising from electron-electron interaction can be decomposed into contributions from the classical Hartree potential (V_H), the energy functional ($E_H[\rho]$), and the exchange-correlation functional ($E_{xc}[\rho]$),

$$E_{ee}[\rho] = E_H[\rho] + E_{xc}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d^3r' d^3r + E_{xc}[\rho] \qquad (2.24)$$

$$=\frac{1}{2}\int\int\nu_{H}(\mathbf{r})\rho(\mathbf{r})d^{3}r'd^{3}r + E_{xc}[\rho] \qquad (2.25)$$

The exchange-correlation functional $E_{xc}[\rho]$ contains the difference between the independent-electron system and the real system of interacting electrons. We can define it as follows:

$$E_{xc}[\{\phi_m^{KS}\}] = T[\rho] - T_s[\{\phi_m^{KS}\}] + E_{ee}[\rho] - E_H[\rho]$$
(2.26)

An exact expression of the exchange-correlation functional would enable the calculation of exact ground-state energies. However, the precise form of $E_{xc}[\rho]$ is currently unknown, leading to significant efforts in finding efficient approximations to it. Numerous approximations have been developed, spanning from basic local density approximations based on the homogeneous electron gas to more sophisticated generalized gradient approximations and hybrid functionals that incorporate exact Hartree-Fock exchange.

It is important to note that the variational principle, which guarantees the minimum of the energy with respect to ground-state energies and densities, may not hold true for approximated energy functionals. However, despite this limitation, the variational principle is still applied in practice for current state-of-the-art approximated energy functionals. The resulting electron density obtained through these approximations is considered an approximation for the true ground-state density, serving as a useful approach for practical applications.

Differentiation of equation (2.22) with respect to the ϕ_m^{KS} eventually leads to the Kohn-Sham (KS) equations:

$$\underbrace{\left(-\frac{\hbar^2}{m}\nabla^2 + \nu_{ne}(\mathbf{r}) + \nu_H(\mathbf{r}) + \nu_{xc}(\mathbf{r})\right)}_{H_{KS}} + \phi_m^{KS} = \epsilon_m \phi_m^{KS}, \qquad (2.27)$$

where the Kohn-Sham potential, v_{KS} , is:

$$\nu_{KS}(\mathbf{r}) = \nu_{ne}(\mathbf{r}) + \nu_{H}(\mathbf{r}) + \nu_{xc}(\mathbf{r})$$
(2.28)

Similar to the Hartree-Fock equations, the KS equations must be solved in a self-consistent manner because the Kohn-Sham potential v_{KS} represents an effective potential that depends on the density itself.

2.3 Maximally localized Wannier functions

The electronic ground state of a periodic system is commonly expressed using extended Bloch orbitals. An alternative representation using localized "Wannier functions", introduced by Gregory Wannier in 1937, offers a different perspective. Since 1997, methods have been devised to iteratively transform the extended Bloch orbitals obtained from first-principles calculations into a distinctive set of maximally localized Wannier functions³⁶.

2.3.1 Bloch functions and Wannier functions

It is usually common to use periodic boundary conditions in electronicstructure calculations to investigate perfect crystals. This approach can also be extended to periodic supercells, facilitating the study of nonperiodic systems like liquids, interfaces, and defects. The one-particle effective Hamiltonian *H* commuts with the lattice-translation operator T_R , which allows for the use of Bloch orbitals, $|\psi_{nk}\rangle$, as common eigenstates:

$$[H, T_R] = 0 \Longrightarrow \psi_{nk}(r) = u_{nk}(r)e^{ik.r}, \qquad (2.29)$$

where $u_{nk}(r)$ has the periodicity of the Hamiltonian.

In a simplified model, we focus on *p*-like orbitals centered on each atom. We assume that this band is isolated, meaning it maintains a gap from the bands both below and above at all *k*. Due to the varying envelope functions, $e^{ik.r}$, of Bloch functions at different *k*, it is anticipated that a localized 'wave packet' can be constructed by combining Bloch functions from different *k*. To achieve a localized wave packet in real space, a broad superposition in *k* space is needed. However, since *k* is in the periodic Brillouin zone, the most effective approach is to assign equal amplitudes throughout the Brillouin zone. This allows us to construct:

$$w_0(r) = \frac{V}{(2\pi)^3} \int_{BZ} dk \psi_{nk}(r), \qquad (2.30)$$

Here, *V* represents the volume of the real-space primitive cell, and the integral is over the entire Brillouin Zone (BZ). Equation (2.30) can represent the Wannier function (WF) located in the reference unit cell. In general, we can introduce a phase factor, $e^{ik.R}$, into the integrand of Eq. (2.30) where *R* is a real-space lattice vector. This operation translates the real-space Wannier function by *R*, giving rise to additional Wannier functions such as w_1 and w_2 . Changing it to Dirac bra-ket notation and introducing the notation R_n to denote the Wannier function w_{nR} in the cell *R* associated with band *n*, Wannier functions can be constructed as follows:

$$|R_n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} dk e^{-ik.R} |\psi_{nk}\rangle.$$
(2.31)

It can be demonstrated that the $|R_n\rangle$ form an orthonormal set, and that two Wannier functions $|R_n\rangle$ and $|R'_n\rangle$ undergo a transformation into

36 Marzari *et al.*, "Maximally localized Wannier functions: Theory and applications," 2012.

each other under translation by the lattice vector R - R'. Equation (2.31) represents a Fourier transform, and its inverse transform will be:

$$|\psi_{nk}\rangle = \sum_{R} e^{-ik.R} |R_n\rangle.$$
(2.32)

Equations (2.31) and (2.32) represent a unitary transformation connecting Bloch and Wannier states. Therefore, both approaches describe an equally valid description of the band subspace. For instance, the charge density, obtained by summing the squares of either the Bloch functions $|\psi_{nk}\rangle$ or the Wannier functions $|R_n\rangle$, is identical. The similarity between the Bloch and Wannier representations becomes clear when we express the band projection operator *P* in both representations:

$$P = \frac{V}{(2\pi)^3} \int_{BZ} dk |\psi_{nk}\rangle \langle \psi_{nk}| = \sum_{R} |R_n\rangle \langle R_n|.$$
(2.33)

Therefore, Wannier functions are a good way to show the space covered by a Bloch band in a crystal. They are localized but still contain the same information as the Bloch functions.

2.3.2 Wannier Polarizability method

The critical factor in calculating a system's vibrational spectrum is its dipole moment. This dipole moment can be explicitly computed by utilizing maximally localized Wannier functions $^{37-39}$ (MLWFs). MLWFs are a special type of Wannier function that provides a localized representation of the electronic structure in periodic systems. MLWFs are constructed by applying a unitary transformation to minimize the spatial spread of the Wannier functions, making them highly localized in real space.³⁷ These functions assist in breaking down the total electronic density into smaller, localized fragments. Besides, recent studies have shown that changes in a molecule's polarizability are directly related to the volume of its electronic cloud in a linear manner⁴⁰. Since electronic properties play a crucial role in determining polarizability, we can assume that the overall isotropic polarizability of the system can be found by adding up the polarizabilities of individual Wannier functions. The polarizability assigned to the *n*th MLWF is expressed as follows:

$$A_n = \beta S_n^3, \tag{2.34}$$

where S_n is the spread of the *n*th MLWF and A_n is its associated polarizability^{41–43}. Based on Wannier function definition in equation (2.31), it is defined by:

$$S = \sum_{n} S_{n} = \sum_{n} (\langle R_{n} | r^{2} | R_{n} \rangle - \langle R_{n} | r | R_{n} \rangle^{2}), \qquad (2.35)$$

and β is a proportionality constant, which its optimized value for Wannier Polarizability (WP) method is β = 0.90. Therefore, the average polarizability of the system can be expressed as:

37 Marzari *et al.,* "Maximally localized generalized Wannier functions for composite energy bands," 1997.

38 Resta, "Quantum-mechanical position operator in extended systems," 1998.

39 Resta *et al., Theory of polarization: a modern approach,* 2007.

40 Murray *et al.*, "Relationships of critical constants and boiling points to computed molecular surface properties," 1993.

41 Partovi-Azar *et al.,* "Evidence for the existence of Li 2 S 2 clusters in lithium–sulfur batteries: ab initio Raman spectroscopy simulation," 2015.

42 Partovi-Azar *et al.*, "Efficient "On-the-Fly" calculation of Raman Spectra from Ab-Initio molecular dynamics: Application to hydrophobic/hydrophilic solutes in bulk water," 2015.

43 Partovi-Azar, "Efficient method for estimating the dynamics of the full polarizability tensor during ab initio molecular dynamics simulations," 2023.

$$\bar{A} = \frac{1}{3}Tr[\hat{A}] = \frac{1}{3}\sum_{n}^{N_{WF}} A_n = \frac{\beta}{3}\sum_{n}^{N_{WF}} S_n^3$$
(2.36)

This method enable us to calculate Raman spectra "on-the-fly" during AIMD simulations. This means that by calculating the spreads of each Wannier function and summing them up according to Equation (2.36), the average polarizability will be obtained. Consequently, one can determine the isotropic Raman spectrum at finite temperature by computing the autocorrelation between the polarizabilities of the system⁴³,

$$\sigma \langle \nu \rangle \propto C_{q/cl}(\nu) \int_0^\infty dt e^{i2\pi\nu t} \langle \bar{A}(0)\bar{A}(t) \rangle_{cl}, \qquad (2.37)$$

Here, $\sigma \langle v \rangle$ is the intensity of the isotropic Raman scattering as a function of the frequency, v, while $\langle ... \rangle_{cl}$ is statistical average in classical mechanics.

2.4 Raman Spectroscopy

In 1923, Smekal⁴⁴ introduced the idea of inelastic light scattering, a concept that was observed through the experiments conducted by C. V. Raman and K. S. Krishnan in 1928⁴⁵. This discovery, now known as Raman spectroscopy, earned Raman the Nobel Prize in Physics in 1930. In spectroscopy, we often use frequency ν or wavenumber ω instead of wavelength λ when discussing the interaction of radiation with molecules. This is because we are typically interested in the energy aspect. These scales are linearly related to energy, and their relationships are provided below:

$$\lambda = \frac{c}{\nu} \tag{2.38}$$

$$\nu = \frac{\Delta E}{h} \tag{2.39}$$

$$\omega = \frac{\nu}{c} = \frac{1}{\lambda} \tag{2.40}$$

Equations (2.38) to (2.40) indicate that energy is inversely proportional to wavelength.

When light interacts with matter, its photons can undergo absorption, scattering, or simply pass through the material without interaction. If an incident photon's energy matches the energy gap between a molecule's ground state and an excited state, absorption occurs, leading to the molecule transitioning to a higher energy state. Alternatively, photons can interact with molecules and scatter without requiring energy alignment with specific molecular energy levels⁴⁵.

When a light source radiates to a sample, a portion of the light scatters in various directions. Most of this scattered light has the same wavelength

44 Smekal, "Zur Quantentheorie der Streuung und Dispersion," 1925.

45 Graves *et al.,* "Practical raman spectroscopy," 1989.

 λ as the incident light, constituting elastic scattering. Rayleigh scattering is another term for elastic scattering. This interaction doesn't alter the energy state of the molecule, resulting in the scattered photon having the same wavelength λ as the incident photon. In a Raman spectrometer, it's necessary to filter out the Rayleigh scattered light from the collected light to ensure the visibility of Raman signals. However, a small fraction of the scattered light engages with the matter in a manner that involves the exchange of small energy quantities, known as inelastic scattering. Raman spectroscopy relies on the inelastic light scattering within a substance, where incident light transfer energy to molecular vibrations. This energy exchange leads to a modification in the frequency ν and wavelength λ of the scattered light. Elastic scattering in Raman spectroscopy is divided into two categories: Stokes and Anti-Stokes scattering. Stokes Raman scattering is the inelastic scattering process where energy is transferred from light to a molecular vibration, resulting in a scattered photon with lower energy and a longer wavelength than the incident photon. The energy transferred must precisely match the amount needed to excite a molecular vibration, making the composition of the scattered light unique to each molecule, like a fingerprint. While Stokes scattering is the most commonly utilized process for obtaining a Raman spectrum, it is much less likely to occur compared to Rayleigh scattering. Anti-Stokes Raman scattering involves the transfer of a specific amount of energy from a molecular vibration to the photon. The scattered photon has higher energy and a shorter wavelength than the incident photon. This process is less likely than Stokes scattering and is rarely used in Raman spectroscopy. Information from anti-Stokes scattered light is mostly equivalent to that from Stokes scattered light, and only specialized applications may require measuring both scattering processes^{23,4645}, Figure 2.1.





⁴⁶ Hollas, Modern spectroscopy, 2004.

Figure 2.1: Diagram of the Raman scattering processes. (Created by the author).

In Raman scattering, light interacts with a molecule, causing a tem-

porary polarization of the electron clouds around the nuclei, forming a short-lived "virtual state." This state is unstable, and the photon is quickly re-emitted. Raman spectroscopy identifies changes in a molecule's polarizability, focusing on vibrations where the polarizability alters during movement (known as Raman-active vibrations). Polarizability indicates how easily a molecule's electron cloud can be distorted, often influenced by changes in cloud size. For instance, symmetric stretching vibrations can lead to an increase in the local electron cloud size.
Summary of the Published Papers

3

3.1 On the Structure of Sulfur/1,3-Diisopropenylbenzene Co-Polymer Cathodes for Li-S Batteries: Insights from Density-Functional Theory Calculations

In this work the local bonding between 1,3-diisopropenylbenzene and sulfur chains has been investigated utilizing density functional theory calculations combined with classical molecular dynamics simulations. Here, the goal was to study the structure of poly(S-co-DIB) co-polymers, specifically, the most favorable length of a sulfur chain connecting two DIBs.

The importance of this investigation goes far beyond the interest of only computational methods, as understanding the structure of these sulfurbased co-polymers is crucial for energy-storage systems, particularly lithium-sulfur (Li-S) batteries. The chosen co-polymer, sulfur_{*n*}-1,3diisopropenylbenzen, represents an alternative cathode material for Li-S batteries. Recent evidence shows this sulfur co-polymer significantly improve the life cycle of Li-S batteries, as well as withstanding volumetric expansion of the cathodes during discharge.

Density functional theory (DFT) through the CP2K software package was used to perform all the structural optimizations. In some stages of this study, classical molecular dynamics (MD) simulations were carried out to improve structural sampling of the molecular structures.

In order to investigate how the sulfur chains and organic groups might affect the total stability of the mentioned sulfur co-polymer, we started with basic structures and gradually added chemical branches to reach the target ones. The procedure is depicted in figure 3.1.

Analysis demonstrated that short sulfur chains ~4 connecting carbonic groups with similar structure as DIB are preferable to form. Moreover, The stability of the co-polymer mostly depends on the length of the sulfur chain instead of its connection to different carbon types in the isopropenyl group, figure 3.2.

Another important finding of this study proved that a thermodynamically preferred structure of this sulfur co-polymer should contain 38 wt % of 1,3-diisopropenylbenzene. Among other benefits, this finding suggests

the enhancement of the electrical conductivity of the cathode due to the considerable amount of carbonic groups. The inverse vulcanization process is a usual synthesis method to produce this compound.



Figure 3.1: A schematic showing the steps taken in the present work from a simple $(\cdots \text{ S-CH}_2-\text{CH}_2-\text{S}_n-\text{CH}_2-\text{CH}_2-\text{S}\cdots)$ structure to the final $(\cdots \text{S-DIB-S}_n-\text{DIB-S}\cdots)$ structure. The groups which are added at each step are highlighted in red.



Figure 3.2: DFT energies as a function of number of sulfur atoms in the middle chain, n. Data shown in black circles, red triangles, and blue squares correspond to AA, AB, and BB connections between the middle sulfur chain and the DIBs. The energies are referenced with respect to the energy of the sample with (c, n) =(BB,4).

3.2 Characterization of sulfur/carbon copolymer cathodes for Li-S batteries: a combined experimental and ab initio Raman spectroscopy study

This work combines computational and experimental methods. It was done in collaboration with the Bron research group from the chemistry department of Martin Luther university. It is a continuation of the previous work on the structure of sulfur/1,3-diisopropenylbenzene co-polymer, but here, the focus was on the spectroscopical features of this co-polymer. The main concern was to identify structures with different sulfur chain lengths. Raman Spectroscopy is a powerful analytical technique used in chemistry to identify molecules, chemical bonds, and intermolecular interactions. It relies on the unique Raman signals produced by functional groups and substances, which are often referred to as chemical fingerprints. By analyzing the Raman spectra of compounds with different sulfur chain lengths, it is possible to identify differences in the vibrational modes and thus distinguish between different structures. For example, longer sulfur chains may exhibit different vibrational modes compared to shorter chains, leading to differences in the Raman spectra. The importance of this work relates to its direct application in the identification and characterization of sulfur co-polymers with different sulfur contents, particularly, in Operando Raman measurements of cathode in lithium-sulfur (Li-S) batteries.

The approach is based on *ab initio* Raman spectroscopy simulations combined with experimental Raman measurements. To simulate Raman spectra, we use the Wannier polarizability method, which is an efficient computational technique. The method assumes that the molecular polarizability changes linearly with the volume of the molecule, and instead of determining atomic volumes, it considers the volume of the Wannier functions. The total mean polarizability is expressed as a sum over the

polarizability assigned to each Wannier function in the system which are functions of the Wannier orbital volumes and Wannier spread.

The synthesis of sulfur/1,3-diisopropenylebenzene was done through the utilization of inverse vulcanization procedure. To vary the length of the sulfur chains, S/DIB samples were synthesized with different weight percentages of DIB, specifically 20, 25, 30, 40, and 50 wt %, which corresponded to average chain lengths of 11, 8, 6, 4, and 3 sulfur atoms, respectively. In order to confirm the presence of the connection between S chains and DIB molecules, we used liquid-state NMR spectroscopy.

By using a combination of quantum-chemical calculations and experimental Raman spectroscopy, we can identify a particular spectral activity that allows for discrimination between shorter and longer sulfur chains in the copolymer. We found that the Raman-active S--S stretching vibration at about 450 cm⁻¹ was absent in the Raman spectra of shorter sulfur chains, figure 3.3. In addition, we highlight the importance of synthesis strategies that facilitate the formation of S/DIB copolymers with short sulfur chains in a controllable way. As a result, by facilitating the formation of S/DIB copolymers with short sulfur chains, stable cycling for a greater number of cycles can be achieved due to the hindered formation of higher-order Li-polysulfides. All in all, by using Raman spectroscopy, it is possible to investigate the structural properties of S/DIB copolymers to provide a way to probe the presence and formation of short or long sulfur chains.



Figure 3.3: Calculated Raman Spectra of (a) DIB–S₄–DIB and (b) DIB–S₈–DIB in vacuum. Also shown in (a) and (b) are the computed Raman spectra of isolated S₄ and S₈ chains (black curve). Partial Raman spectra arising from sulfur chains within DIB–S₄–DIB and DIB–S₈–DIB systems are shown in red curves.

A comparison between experimental Raman spectra of S/DIB copolymers with different weight percentages of DIB is presented in Figure 3.4. Our theoretical results were supported by experimental measurements, which indicated that Raman activity at around 473, cm⁻¹ becomes less intense as the mass fraction of DIB increases.



Figure 3.4: Measured Raman spectra of S/DIB copolymers with different wt % of DIB.

3.3 Toward Ab initio Simulation of Operando Raman Spectroscopy: Application to Sulfur/Carbon Copolymer Cathodes in Li-S Batteries

This work continues previous research on the S/DIB co–polymer cathode material for Li–S batteries. Initially, we identified the optimal structure ¹, followed by its Raman characterization ². The primary focus here is to examine its Raman characterization during consecutive reaction with Lithium during discharge, facilitating Operando Raman analysis. This work represents the first attempt to compute *operando* Raman spectra using quantum-chemical calculations. It provides a comprehensive guideline for understanding Raman spectral changes of various electrodes during discharge. The approach aligns with the previous study and the procedures outlined in Chapter 2, involving state–of–the–art finite-temperature *ab initio* Raman spectroscopy simulations combined with experimental Raman measurements, utilizing the Wannier Polarizability method.

Sulfur–1,3–diisopropenylbenzene (S/DIB) copolymers, which consist of a network of DIB molecules linked by sulfur chains, have demonstrated effective performance as cathode materials in Li–S batteries. Despite this, their structural complexity and flexibility have made it challenging to fully understand their atomistic structural evolution during the discharge reactions. Figure 3.5 illustrates the detailed Raman spectral changes during the reaction with lithium, focusing on the frequency range of 0–1200 cm⁻¹ for S/DIB copolymers with short and long sulfur chains, specifically S₄ and S₈.

Our observations indicate that S/DIB copolymers with both short and long sulfur chains exhibit similar Raman characteristics at the full discharge state (100% depth of discharge). Additionally, the Raman

1 Kiani *et al.*, "On the Structure of Sulfur/1, 3-Diisopropenylbenzene Co-Polymer Cathodes for Li-S Batteries: Insights from Density-Functional Theory Calculations," 2022.

2 Kiani *et al.*, "Characterization of sulfur/carbon copolymer cathodes for Li-S batteries: a combined experimental and ab initio Raman spectroscopy study," 2023.



Figure 3.5: Computed Raman spectra of different stage of Lithiation for (a) DIB–Li_mS₄– DIB, (b) DIB–Li_mS₈–DIB, molecules in vacuum. The black curves represent the computed Raman spectra of the entire molecules, while the red curves represents the partial Raman spectra of (a) Li₆S₄ within the DIB–Li₆S₄–DIB molecule and (b) Li₁₄S₈ within the DIB–Li₁₄S₈–DIB molecule.

activities around 200 cm⁻¹ during the discharge process can differentiate between short and long sulfur chains. The band near 200 cm⁻¹ is exclusively present in fully discharged S/DIB copolymers with short sulfur chains. Conversely, we detected significant activity in the 200-250 cm⁻¹ range from 14% to 100% depth of discharge in copolymers with long sulfur chains.

Additionally, we have noted that the formation of lithium-sulfur structures may have significant implications. Specifically, the frequency range associated with C–H stretching vibrations widens as the depth of discharge increases. Figure 3.6 demonstrates the expansion of the C–H stretching bandwidth during the discharge process for both short (S₄) and long (S₈) sulfur chains. This broadening suggests that the incorporation of lithium and its subsequent interaction with sulfur atoms impacts the vibrations of C–H bonds, leading to non-identical oscillators.

Our theoretical predictions align well with experimental Raman measurements conducted on coin cells at various stages of discharge. Figure 3.7 shows the *ex-situ* Raman spectra measured for the synthesized SDIB10 sample, corresponding to an average sulfur chain length of 22 sulfur atoms. All intensities are normalized relative to the carbon D band at approximately 1350 cm⁻¹. The spectra represent different discharge depths: 0% (black), 66% (red), and 100% (blue). Despite variations in sulfur chain lengths, these spectra can be qualitatively compared with those of long sulfur chains (S₈), as shown in figure 3.5(b). Notably, in addition to contributions from the S/DIB copolymer, the experimental spectra also feature signals from the electrolyte, carbon black, and binder



Figure 3.6: C–H stretching bandwidth as a function of depth of discharge for DIB–S₄–DIB (circles) and DIB–S₈–DIB (squares).

materials. Therefore, the comparison between theory and experiment here remains primarily qualitative.



Figure 3.7: Experimental Raman measurement on SDIB10. DOD stands for depth of discharge.

4

Paper I: On the Structure of Sulfur/1, 3-Diisopropenylbenzene Co-Polymer Cathodes for Li-S Batteries: Insights from Density-Functional Theory Calculations

Rana Kiani, Daniel Sebastiani, and Pouya Partovi-Azar.

On the Structure of Sulfur/1, 3-Diisopropenylbenzene Co-Polymer Cathodes for Li-S Batteries: Insights from Density-Functional Theory Calculations.

ChemPhysChem 2022, 23, e202100519.

In concluding this research, I conducted all simulations and analyses with the supervision of Dr. Pouya Partovi-Azar and Prof. Dr. Daniel Sebastiani.

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On the Structure of Sulfur/1,3-Diisopropenylbenzene Co-Polymer Cathodes for Li-S Batteries: Insights from Density-Functional Theory Calculations

Rana Kiani,^[a] Daniel Sebastiani,^[a] and Pouya Partovi-Azar^{*[a]}

Sulfur co-polymers have recently drawn considerable attention as alternative cathode materials for lithium-sulfur batteries, thanks to their flexible atomic structure and the ability to provide high reversible capacity. Here, we report on the atomic structure of sulfur/1,3-diisopropenylbenzene co-polymers (poly (S-co-DIB)) based on the insights obtained from density-functional theory calculations. The focus is set on studying the local structural properties, namely the favorable sulfur chain length (S_n with $n = 1 \cdots 8$) connecting two DIBs. In order to investigate the effects of the organic groups and sulfur chains separately, we perform series of atomic structure optimizations. We start from simple organic groups connected via sulfur chains and

1. Introduction

With the ever growing global demand for energy, the quest for finding more efficient energy-storage systems has become more and more intensive. Recently, lithium-sulfur (Li-S) batteries have shown a superior performance over lithium-ion batteries in terms of the energy density.^[1,2] Additionally, abundance of the constituents makes the Li-S a promising candidate for the next-generation energy-storage devices. However, irreversible capacity fade observed in the Li-S batteries through cycling have so far prevented them from being used in electric devices.^[3] This is mainly due to the formation of Li-polysulfides during the discharge which could consume the active material and lead to a shuttle effect.^[4,5] Another problem which has hindered the commercial production of the Li-S batteries is the volumetric expansion of the sulfur cathode upon lithiation which can detach the electrode from the current collectors and even bring about safety issues.^[3,6,7]

In this regard, polymeric materials have been widely proposed and investigated as alternative cathodes for Li–S

gradually change the structure of the organic groups until we reach a structure in which two DIB molecules are attached via sulfur chains. Additionally, to increase the structural sampling, we perform temperature-assisted minimum-energy structure search on slightly simpler model systems. We find that in DIB- S_n -DIB co-polymers, shorter sulfur chains with $n \sim 4$ are preferred, where the stabilization is mostly brought about by the sulfur chains rather than the organic groups. The presented results, corresponding to the fully charged state of the cathode in the thermodynamic limit, have direct applications in the field of lithium-sulfur batteries with sulfur-polymer cathodes.

batteries.^[8-15] In particular, sulfur/carbon co-polymers, usually synthesized through an inverse vulcanization process, have recently attracted much attention.^[9,16] As sulfur cathode materials, they are not only able to withstand the volumetric expansion of the cathode during discharge, thanks to their structural flexibility, but they also have demonstrated a promising performance in improving the cycle life of Li-S batteries. Recently, sulfur/1,3-diisopropenylbenzene co-polymers (poly(S-co-DIB)) have been shown to substantially immobilize the Li-polysulfides during lithiation of the cathode.^[16,17] It has been shown that the improved cyclability stems from the organic moieties which act as anchors that fixate the Lipolysulfides to the polymeric network and, therefore, prevent them from diffusing into the electrolyte.^[17] However, the redox mechanisms of these materials are still not fully known. This is due to the difficulty in characterizing amorphous polymer cathode structures and identifying individual ionic species.

In this work, with the aim to gather insights onto the structure of poly(S-co-DIB) co-polymers, we combine density-functional theory-based calculations together with classical molecular dynamics simulations to study the local bonding between DIB and sulfur chains. We aim at finding the most favorable length of a sulfur chain connecting two DIBs and further use these information to gather insights onto the bulk structure of the whole poly(S-co-DIB).

2. Methodology

A 1,3-diisopropenylbenzene (DIB) molecule is shown in Figure 1(a). Through the inverse vulcanization process to synthesize poly(S-co-DIB) co-polymers, the non-aromatic double C=C

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cphc.202100519

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Figure 1. (a) A 1,3-diisopropenylbenzene molecule. (b) A local view of a poly (S-co-DIB) co-polymer during the inverse vulcanization process where two sulfur chains are connected to the organic moieties through a "quaternary" carbon C_q (connection A) and via CH_2 group (connection B).

bonds almost completely turn into single bonds resulting in two sp^3 hybridized carbon atoms (Figure 1(b)).^[16]

To be able to gather insights into the structure of poly(S-co-DIB) co-polymers, we concentrate on their local structure with the aim to find the most favorable length of the sulfur chains which form the poly(S-co-DIB) network. There are two factors which play important roles in thermodynamic stabilization of the DIB-S_n-DIB structures, namely the sulfur chain connecting the two DIBs and the interaction between the DIBs. In order to decompose these effects, first we start from a very simple compound as a product of the reaction 1 in which two C₂H₄ molecules react with a polymeric sulfur chain consisting of a large number of sulfur atoms (here, 40 in total) with the terminal sulfur atoms saturated with hydrogen atoms to prevent radical effects.



We change *n* from 1 to 8 while keeping the total number of sulfur atoms constant. The large total number of sulfur atoms are considered here to avoid finite-size effects. Afterwards, chemical branches are gradually added to the two C₂H₄ groups in the product structures until the structures of two DIBs are reached. To this end, first the hydrogen atoms bonded to $C-S_n$ are both replaced with a methyl group. In a next step, we replace the other hydrogens bonded to the same carbons with methyl groups as well. In next steps, two benzene rings are added to the structure and finally, the obtained structure is further modified to reach the target (---S-DIB-S_n-DIB-S---), $n = 1 \cdots 8$ structures. The above steps are schematically shown in Figure 2. In order to focus mainly on the effect of the additional carbon groups, at each step we start the structural optimization from the optimized structures obtained in the last step. Additionally, in order to further avoid the effects of structural flexibility of sulfur side chains we also perform structural optimizations under periodic boundary conditions.

All structural optimizations are carried out at density-functional theory (DFT) level using the CP2 K software package.^[18] A DZVP-MOLOPT basis set,^[19] along with Perdew-Burke-Ernzerhof (PBE)^[20,21] exchange-correlation energy functional and Geo-



Figure 2. A schematic showing the steps taken in the present work from a simple (...S– CH_2 – CH_2 – S_n – CH_2 – CH_2 – S_m) structure to the final (...S–DIB-S_n-DIB-S…) structure. The groups which are added at each step are highlighted in red.

decker-Teter-Hutter (GTH) pseudopotentials^[22] are employed. Moreover, for the long-range dispersion interactions, the semiempirical DFT-D3 method^[23] is used. The synthesis of poly(S-co-DIB) co-polymers is a solvent-free process and the DIBs are added to the molten sulfur after ring-opening polymerization.^[16] Therefore, all calculations in this work are performed in vacuum.

Moreover, to have a better structural sampling we adapt a temperature-assisted minimum-energy structure search on simpler structures consisting of two DIB molecules and a connecting S chain only, namely DIB-S_n-DIB. The initial configurations are selected based on possible ways a sulfur chain can attach to two DIB molecules. There are two connection possibilities; (A) the S chain directly connects to the doubly bonded carbon, and (B) it connects to the DIB via a methyl group (Figure 1(b)). The former results in a carbon atom which is covalently bonded to four non-hydrogen atoms. Here, they are referred to as "quaternary" carbons, C_{qr} and are shown in Figure 1(b). As a result, three possible connections are considered, i.e. c = AA, AB, BB. In order to find candidates for the lowest-energy structure of DIB-S_n-DIB, $n = 1 \cdots 8$, with different connections c, first for each (c, n) 10 ns classical molecular



dynamics (MD) simulations at 300 K using General Amber Force Field (GAFF)^[24] as implemented in the GULP code^[25-27] are carried out. The atomic charges are calculated using the RESP method at DFT^[28] level employing the sphere sampling of the fitting points for molecular structures^[29] together with the REPEAT method.^[30] A time step of 0.5 fs is considered in all simulations while the temperature is controlled using a Nosé-Hoover thermostat.^[31,32] For each (c, n), 10 uncorrelated snapshots are extracted from the MD trajectories roughly every 1 ns, resulting in total 240 sample structures. DFT-based geometry optimizations are then performed for all these structures.

3. Results and discussion

As mentioned above, in order to investigate how the sulfur chains and organic groups affect the total stability of poly(S-co-DIB) copolymers, we gradually change the organic moieties towards the target structure (...S-DIB-S_n-DIB-S...) (see Figure 2). The optimized structures and the respective DFT energies are shown in Figure 3(a)-(I) (the energies are referenced with respect to n = 4 in all cases.) Here, we use the DFT energies since the entropic contribution to the free energy is found to be very small in the samples considered here (please see the SI). Figure 3(a) shows the lowest energy structure of $S_{18}-C_2H_4-S_n-C_2H_4-S_{18}$ with n = 4. The total number of sulfur atoms in all samples in Figure 3 is constant (i.e. 40). Therefore, the total DFT energies can be directly considered as a stability measure. Here, the middle sulfur chains with n = 4,8 show the lowest energies. Explicit check for n = 9 in the case of S₁₈-C₂H₄-S_n-C₂H₄-S₁₈ reveals less favorable structures for longer middle chains with n > 8. To see whether n = 4, 8 truly represent the most favorable number of sulfur atoms on the middle sulfur chain, we slightly modify the structures in the following way: while the total number of S atoms in the middle chain is kept fixed, the carbon groups from both sides are equally moved in one direction by several bonds. Afterwards, the structures are re-optimized. We see that in such a modification,

n = 4 still remains to be the most favorable number of S atoms for the middle chain. However, small structural changes around n = 8 lead to structures with higher energies (please see the SI for more detail). The results in Figure 3 also indicate that the stability of the poly(S-co-DIB) is mainly brought about by the sulfur middle chains rather than the interaction between the organic groups. Therefore, although the interaction between the two DIBs could be different when different carbons engage in their connection to the middle sulfur chain (Figure 1(b)), as will be shown later, the local connection of the middle S chain to the DIBs could only play a minor role in specifying the length of the middle S chain, n.

To study electronic contributions to the thermodynamic stability of DIB-S_n-DIB systems, we decompose the total energy of all (...S-DIB-S_n-DIB-S...) systems (Figure 3(k) and (l)) into nuclear and electronic parts. Our specific inspection reveals that, within the electronic part, only the exchange-correlation and the dispersion (also a correlation effect) contributions approximately follow the same trend as the total energy (see the SI). Therefore, we conclude that the electronic properties play an important role in the thermodynamic stability of the DIB-S_n-DIB and these effects are mostly of quantum mechanical nature.

In a next step, in order to minimize the effects corresponding to the geometrical flexibility of sulfur side chains on the energies of the (...S-DIB-S_n-DIB-S...) structures, we consider periodic samples. An optimized structure for (--S-DIB-S₄-DIB-S--) is shown in Figure 4(a). The corresponding energies are presented in Figure 4(b). Here, we also study the possible effect of different connections between the middle sulfur chain and the DIBs, namely c = AA, AB, and BB. The unit cell size is set to 30 $\text{Å} \times 63$ $\text{Å} \times 30$ Å, the structure lies along the y-axis, and each side chain consists of 22 sulfur atoms. The cell sides along the x- and z-axes together with the unit cell angles are kept fixed. They are long enough to ensure a negligible interaction between the atoms in the unit cell and those in the cell replicas. The cell size along y-axis was obtained after a full (atomic coordinates and cell parameters) optimization of an isolated



Figure 3. (a) Optimized structures of $S_{18}-C_2H_4-S_n-C_2H_4-S_{18}$, n = 4. (b) Corresponding DFT energies for the optimized structures $S_{18}-C_2H_4-S_n-C_2H_4-S_{18}$ with n = 1...8. The energies are referenced with respect to n = 4 in all cases. (c)–(l) show the same for the optimized structures obtained by step-wise modifications shown in Figure 2. The gray circles show the energies for n = 8 samples. However, these samples do not represent stable structures (see text).

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Figure 4. (a) The optimized periodic structure of (...S-DIB-S₄-DIB-S...) with 4 sulfur atoms in the middle chain. The unit cell is shown in blue. (b) DFT energies as a function of number of sulfur atoms in the middle chain, *n*. Data shown in black circles, red triangles, and blue squares correspond to AA, AB, and BB connections between the middle sulfur chain and the DIBs. The energies are referenced with respect to the energy of the sample with (c, n) = (BB, 4).

sulfur chain consisting of 48 atoms. The target pressure was set to 0.1 GPa. As can be seen in Figure 4(b), the structures with n = 4 again show lowest energies (apart from (c, n) = (AA, 8)which shows a comparable energy to (AA,4)). Additionally, different connections between the middle sulfur chain and the DIBs do not appear to have a considerable effect on the stability of the samples. n = 4 approximately corresponds to a poly(Sco-DIB) network with an average DIB mass fraction of ~38 wt%. This mass fractions nearly correspond to the S-DIB-40 samples studied in Refs. [16,17]. The predicted sulfur chain lengths in the present work perfectly match the experimental assignments using ¹³C NMR chemical shifts^[17] and electrochemical measurements^[16] ($n \approx 3, 4$). Therefore, with the poly(S-co-DIB) co-polymers as cathode materials for Li-S batteries, the formation of higher-order Li-polysulfides could considerably be hindered during the discharge due to the preferred shorter sulfur chains in the cathode structure. In fact, this has been previously shown through electrochemical measurements that the poly(S-co-DIB) co-polymers with comparable DIB mass fraction exhibit an almost plateau-free voltage curve as a function of the state of discharge at high voltages.[16,17] However, low mass fraction of the active material could lead to a limited cathode capacity.

Finally, in order to enhance the structural sampling and further assess the results obtained from the geometry optimizations above, we perform a temperature-assisted minimumenergy structure search (for details see Sec. 2) on slightly simpler samples of DIB-S_n-DIB without sulfur side chains. To this end, we consider the following hypothetical reaction,

$$\mathsf{DIB} - \mathsf{S}_1 - \mathsf{DIB} + \frac{1}{8}(n-1)\mathsf{S}_8 \to \mathsf{DIB} - \mathsf{S}_n - \mathsf{DIB} \tag{2}$$

which would correspond to a situation where an infinitely large reservoir of S_8 molecules with zero chemical potential is available for the DIB molecules. Moreover, here we also study the effect of different connections between the middle sulfur chain and the DIBs. Based on the above reaction, we define the formation energy per sulfur atom for each DIB-S_n-DIB structures with a given connection *c*, as

$$E_{\text{form}}^{(c,n)} = \frac{1}{n} \left[E_{\text{tot}}^{(c,n)} - \frac{1}{8} (n-1) E_{\text{tot}}^{(S_8)} - E_{\text{tot}}^{(c,1)} \right],$$
(3)

where E_{tot} denotes the total DFT energy. $E_{tot}(S_8)$ represents an average energy for a typical S₈ molecule. Additionally, with the above definition for the formation energy, we assume that the reaction always takes place with the elemental sulfur, S₈, as suggested experimentally for inverse vulcanization.^[16] The formation energy defined in Eq. 3 is considered here as a measure for thermodynamic stability of DIB-S_n-DIB structures with respect to n = 1. The formation energies per sulfur atom for the lowest-energy structures are shown in Figure 5. The dashed lines in the figure which connect the data points for n = 1 and n = 2 are guides to the eye. The standard deviation of the $E_{\text{form}}^{(c,n)}$ calculated for the ten structures for each (c, n) are displayed in the figure as error bars. For all connections c, the sulfur chains with n > 1 show lower formation energies than n = 1. Moreover, shorter sulfur chains (2 < n < 4) are found to be somewhat more favorable, in agreement with the results in Figures 3 and 4. In this range, all connections show comparable formation energies. However, DIB-S_n-DIB structures where the sulfur chain connects to the quaternary carbons of DIBs (c =AA) exhibit slightly lower formation energies. To further validate the results in Figure 5, we additionally re-optimize DIB-S_n-DIB structures with AB connection through temperature-assisted minimum-energy search at an elevated temperature, namely 500 K. The minimum-energy structure is again found to be the one with n = 3 confirming the previous results above.

4. Conclusions

In summary, we have used density-functional theory calculation to study the local bonding between sulfur chains and the



Figure 5. The formation energies of DIB-S_n-DIB systems with different connections between the sulfur chain and the DIBs. The data points correspond to the formation energies calculated for the lowest-energy structures obtained after the simulated quenching. The error bars are the standard deviations of the formation energies calculated for all 10 uncorrelated snapshots taken from the classical MD trajectories. The dashed lines connecting the curves to the corresponding reference points, n = 1, serve as guides to the eye.

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organic moieties in sulfur/1,3-diisopropenylbenzene co-polymers. We find that sulfur chains with 4 atoms are more likely to form between the diisopropenylbenzenes. We also find that the stabilization of the sulfur/1,3-diisopropenylbenzene co-polymers is brought about by the sulfur chains connecting the diisopropenylbenzene molecules and forming the polymer network. Therefore, based on our investigations, we could anticipate that the short sulfur chain with 4 atoms should also be favorable in any other sulfur/carbon co-polymers with comparable structures. We have also observed that the connection of the sulfur chain to the different carbon types in the isopropenyl groups does not have any noticeable preference.

Based on our findings on their local structure, we have shown that a thermodynamically preferred structure of a sulfur/ 1,3-diisopropenylbenzene co-polymer should contain about 38 wt % diisopropenylbenzene. This means that even compounds with lower organic mass fraction, which has been experimentally demonstrated to have a better electrochemical performance as cathode materials for lithium-sulfur batteries, would show a tendency towards the above-mentioned mass fraction and shorter sulfur chains after cycling. This, in turn, could mean that despite a lower cathode capacity, the sulfur/ 1,3-diisopropenylbenzene co-polymers with around 38 wt % of diisopropenylbenzene could maintain their capacity over a larger cycle numbers. Besides, a considerable amount of mass fraction of the carbon material could, in principle, enhance the electrical conductivity of the cathode.

Acknowledgement

The authors gratefully acknowledge DFG funding via projects PA3141/3-1 (Project number 420536636) and PA3141/5-1 (Project number 446879138). This research was also financially supported by the European Social Funds (ESF) and the State of Saxony-Anhalt through the graduate school AgriPoly. The computations have been mostly performed on a Bull Cluster at the Center for Information Services and High Performance Computing (ZIH) at TU Dresden via the project 'p_oligothiophenes'. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Li–S batteries · sulfur cathodes · polymers molecular dynamics · density functional calculations

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Manuscript received: July 8, 2021 Revised manuscript received: September 13, 2021 Accepted manuscript online: September 29, 2021 Version of record online: October 22, 2021

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Paper II: Characterization of sulfur/carbon copolymer cathodes for Li-S batteries: a combined experimental and ab initio Raman spectroscopy study

Rana Kiani, Matthias Steimecke, Marah Alqaisi, Michael Bron, Daniel Sebastiani, and Pouya Partovi-Azar.

Characterization of sulfur/carbon copolymer cathodes for Li-S batteries: a combined experimental and *ab initio* Raman spectroscopy study. *RSC Adv.*, 2023,13, 27756-27763

In concluding this research, I performed all simulations and analyses using the methodology developed by Dr. Pouya Partovi-Azar. Additionally, with the guidance of Mara Alqaisi, I synthesized the sulfur co-polymer. Experimental Raman measurements were conducted by Dr. Matthias Steimecke in Prof. Dr. Michael Bron's laboratory. This work was supervised by Dr. Pouya Partovi-Azar and Prof. Dr. Daniel Sebastiani.

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Cite this: RSC Adv., 2023, 13, 27756

Received 5th May 2023 Accepted 12th September 2023

DOI: 10.1039/d3ra02980h

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Introduction

Characterization of sulfur/carbon copolymer cathodes for Li–S batteries: a combined experimental and *ab initio* Raman spectroscopy study⁺

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Optimization of lithium–sulfur batteries highly depends on exploring and characterizing new cathode materials. Sulfur/carbon copolymers have recently attracted much attention as an alternative class of cathodes to replace crystalline sulfur. In particular, poly(sulfur-*n*-1,3-diisopropenylbenzene) (S/DIB) has been under considerable experimental and theoretical investigations, promising a good performance in mitigating the so-called shuttle effect. Here, combining *ab initio* Raman spectroscopy simulations with experimental measurements, we show that S/DIB copolymers containing short and long sulfur chains are distinguishable based on their Raman activity in 400–500 cm⁻¹. This frequency range corresponds to S–S stretching vibrations and is only observed in the Raman spectra of those copolymers with longer sulfur chains. The results reported in this study have direct applications in identification and characterization of general sulfur/carbon copolymers with different sulfur contents.

Lithium–sulfur (Li–S) batteries are considered as one of the candidates for next-generation energy-storage devices. Despite their very high specific energy, commercialization of Li–S batteries is negatively affected by few drawbacks, such as irreversible capacity fade and volumetric expansion of the crystalline sulfur during the discharge. Recently, a huge amount of studies has been concentrated on using polymeric sulfur cathodes to overcome these problems. In particular, sulfur/carbon copolymers such as poly(sulfur-*n*-1,3-diisopropenylbenzene) (S/DIB) have attracted much attention. Thanks to a straightforward synthesis procedure,^{1,2} S/DIB copolymers could be produced in large quantities relatively easily. In addition, it has been demonstrated that S/DIB copolymers show a promising performance in alleviating the shuttle effect and therefore, can result in a stable cycling performance of a Li–S battery.^{3,4}

Nevertheless, to this day neither the lithiation mechanism of S/DIB copolymer cathodes has been entirely resolved at an atomistic level, nor their structural evolution during the discharge has been fully understood. A first step towards

understanding the discharge mechanism of the S/DIB copolymers is to decipher their structural properties at the fully charged state of the battery, where no lithiation reaction has occurred. It has been recently found that short S_n chains $(n \approx 4)$ show a higher formation probability compared to other sulfur chain lengths. It has also been observed that the stability of S/ DIB copolymers is brought about by the formation of short S chains.⁵ In addition, short S chains have been predicted^{6,7} and reported^{8,9} to be more favorable in other sulfur/carbon copolymer materials involving organic groups interconnected via sulfur chains. The formation of Li-polysulfides during discharge has been shown to be largely hindered in S/DIB copolymer cathode involving short S chains and therefore, they exhibit a much better performance in terms of cycle life. It has been argued that even copolymers involving longer S chains (lower organic mass fraction), would show a tendency towards around 40% mass fraction (SDIB40) and shorter sulfur chains after cycling.⁵ Therefore, a strategy for the synthesis of S/DIB copolymers as well as their structural modification is highly called for, in which the formation of S_n chains with short lengths ($n \le 4$) has the highest probability.

However, in order to reach this goal first it must be understood how physical and chemical properties of S/DIB copolymers involving short and long sulfur chains are different. For example, vibrational spectroscopic signatures of "local" DIB- S_n -DIB structures and their contribution to the total spectra of S/ DIB copolymer are not yet known. Moreover, up to now any estimation on the sulfur chain length distribution in S/DIB

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[†] Electronic supplementary information (ESI) available: Further remarks on Raman spectroscopy simulations and measurements, structural analysis using ¹H NMR spectroscopy of the S/DIB copolymers. See DOI: https://doi.org/10.1039/d3ra02980h

systems have been based on the sulfur (or DIB) mass fraction used in the synthesis process.^{10–12} Therefore, a question which remains to be answered is whether it is possible to distinguish between short and long sulfur chains in sulfur/carbon copolymers.

In this article, we address the above question by combining experimental Raman spectroscopy measurements with ab initio Raman spectroscopy simulations at room temperature. Raman spectroscopy is a powerful tool for analyzing sulfur-containing materials due to strongly polarizable S-S covalent bonds. It is particularly suitable for *in situ* experiments, providing valuable insights on structural modifications during reactions and has been successfully used to study the lithiation mechanism of sulfur cathodes in Li-S batteries.13-16 In this article, we focus on S/DIB copolymer cathodes at the fully charged state of the battery, meaning the point at which there is no ongoing reaction with lithium and the cathode material only contains the sulfur/carbon copolymer. In the next section, we introduce our computational and experimental methods as well as the synthesis procedure. This will be followed by presentation of the results and concluding remarks.

Methodology

Computational details

As it has been shown earlier,⁵ DIB molecules are preferably connected *via* short sulfur chains ($n \approx 4$). Here, we consider DIB-S₄-DIB and DIB-S₈-DIB as target molecules in vacuum, representing local structures of poly(sulfur-*n*-1,3-diisopropenylbenzene) containing short and long S chains, respectively. The connection of the sulfur chains and the DIB molecules are assumed to be *via* a quaternary carbon. For the sake of comparison, we also consider gas-phase S₄ and S₈ chains with terminal sulfur atoms saturated with hydrogens. Additionally, sulfur-free 1,3-diisopropenylbenzene and 1,3-diisopropylbenzene molecule are studied.

Following our previous work,⁵ a temperature-assisted minimum-energy structure search is carried out: first, classical molecular dynamics (MD) simulations at 300 K using General Amber Force Field (GAFF)¹⁷ as implemented in the GULP code¹⁸⁻²⁰ is performed for 10 ns in canonical ensemble. The atomic charges are calculated using the RESP method²¹ at density functional theory (DFT) level employing the sphere sampling of the fitting points for molecular structures²² together with the REPEAT method.²³ A time step of 0.5 fs is considered in all simulations while the temperature is controlled by a Nosé–Hoover thermostat.^{24,25} For each system, 10 uncorrelated snapshots were extracted from the classical MD trajectories, roughly every 1 ns. Afterwards, minimum-energy structures are obtained through geometry optimizations at DFT level.

All DFT calculations are performed using the CP2K/ QUICKSTEP software package²⁶ in conjunction with a DZVP-MOLOPT basis set,²⁷ as well as Perdew-Burke-Ernzerhof (PBE)²⁸ exchange-correlation energy functional and Geodecker-Teter-Hutter (GTH) pseudopotentials.^{29,30} The semi-empirical DFT-D3 (ref. 31) method is used to correct for the long-range dispersion interactions. All calculations in this work are performed in vacuum.

The efficient Wannier polarizability method is used to simulate Raman spectra.^{15,32} In this method, the mean polarizability is expressed as a sum of isotropic polarizabilities attributed to each Wannier function in the system, $\overline{A} = \beta/3 \sum_{i=1}^{N_{WF}} S_i^3$, where S_i are the Wannier spreads and the proportionality constant is obtained to be $\beta \approx 0.9$. Such an expression for the mean polarizability also allows for the decomposition of the total Raman spectra into local contributions³³ and provides a straightforward way for the assignment of Raman peaks (see ESI[†]).

All Raman spectra are obtained by performing 20 ps *ab initio* molecular dynamics (AIMD) simulations in the canonical ensemble to achieve equilibrium at 300 K, followed by 80 ps AIMD simulations in the micro-canonical ensemble to remove thermostat effects and sample the polarizabilities. A time step of 1 fs is used in these simulations and polarizabilities are sampled every 5 fs. The AIMD simulations are also performed using the CP2K software with the same simulation setup as mentioned earlier. Power spectra have been calculated using the TRAVIS program.^{34,35} The power spectra are normalized in a way that the sum of partial spectra gives the total power spectrum.

Material and synthesis

The S/DIB samples are synthesized with different weight percentages of DIB, namely 20, 25, 30, 40, and 50 wt%, following the method presented in ref. 36 and 37. Elemental solid sulfur (99.5%, Sigma Aldrich) is used without further treatment. Sulfur in the powder form is heated to 185 °C using a thermostated oil bath under the fume hood until a clear yellowish molten sulfur is formed. DIB (97%, Sigma Aldrich) is passed through an activated, basic aluminum oxide column to remove 4-tert-Butylcatechol (TBC) as a stabilizer. Afterwards, pure DIB is directly added through a syringe to the molten sulfur. The mixture is stirred by a magnetic stir bar for 10 minutes at 185 °C to enhance the ring-opening polymerization of sulfur and to obtain chemically stable copolymers. Afterward, each sample is placed in a vacuum oven for approximately 15 minutes at 176 °C to complete the reaction and reduce the amount of remaining monomers. Then, they are cooled down to room temperature. Within a few minutes, this results in a vitrified red polymer. We assume that the sulfur content remains nearly unchanged after the heating process since the synthesis involves heating at temperatures below the boiling point of sulfur. Additionally, the inverse vulcanization is a solvent-free synthesis procedure. This also ensures that the sulfur content is not altered during the synthesis process due to solvent evaporation. Elemental analysis on S/DIB samples also confirms the above conclusion (please see the ESI[†]). The samples are further investigated using NMR spectroscopy in order to confirm the formation of desired copolymers. Since low solubility of the S/DIB copolymers in organic solvents is a challenging factor, here we grind the samples using a mortar to increase sample surface, and then

dissolve them in deuterated chloroform (CDCl₃) and place them in ultrasonication water bath to accelerate their solubility. ¹H NMR is carried out afterwards. Further information is provided in the ESI.[†]

Instrumentation and methods

NMR spectra are recorded using Varian Gemini 400 MHz NMR spectrometer. Deuterated chloroform is used as solvent. Chemical shifts are given in parts per million (ppm). MestRe-Nova 14.2.1-27684 is used for spectra interpretation and analysis.

Raman spectra of all samples are recorded by a confocal Raman microscope setup (inVia, Renishaw) consisting of a 532 nm laser as excitation source, notch filter, a turnable grating (1800 lines mm⁻¹), a CCD camera and a light microscope (Leica, DMI2500). The microscope is equipped with a ×100 objective (Leica) to focus the laser spot (*ca.* 1 μ m) on the sample as well as to collect the scattered Raman light. Before the measurements, the instrument is calibrated to a band at 520.4 cm⁻¹ of a polycrystalline silicon disk. All samples are prepared onto a glass slide and several single spectra are recorded between 100–2000 cm⁻¹. In all cases, the laser power is adjusted to 0.1 mW and each sample spot illuminated for 10 s. Several spectra are recorded at various positions at the samples to ensure homogeneity.

Results and discussion

First, we start by calculating *ab initio* Raman spectra of a 1,3diisopropenylbenzene (DIB) and a 1,3-diisopropylbenzene molecule at 300 K in vacuum. The Raman spectra are shown in Fig. 1a and b, respectively.

The Raman spectra presented here agree well with the previous studies,^{38,39} with an overall mean relative error of about 10% in dominant peak positions. In comparison to the Raman spectrum of 1,3-diisopropenylbenzene in Fig. 1a, 1,3-diisopropylbenzene shows similar Raman activities [Fig. 1b], the main difference being the activities around 1560 and 1640 cm⁻¹ related to the C=C stretching vibration in propenyl groups. The Raman activities in the range of 650–1500 cm⁻¹ are mainly

dominated by aromatic ring vibrations, while the activities around 3000 cm⁻¹ arise from C–H stretching vibrations in both Fig. 1a and b.⁴⁰ Another difference in the Raman spectra presented in Fig. 1a and b is the activity at ~450 cm⁻¹. This peak corresponds to a CH₃ vibration in the propyl group in 1,3-diisopropylbenzene⁴¹ and is much less intensive in 1,3-diisopropenylbenzene spectrum (see ESI[†]).

Calculated Raman spectra of a DIB-S₄-DIB and a DIB-S₈-DIB at 300 K are shown in Fig. 2a and b in blue curves, respectively. For comparison, Raman spectra of isolated S₄ and S₈ chains, where the terminal S atoms are saturated with hydrogens, are also calculated. These spectra are shown in black curves in Fig. 2a and b, respectively. The red curves in Fig. 2a and b show partial Raman spectra corresponding to the vibrations of S₄ and S₈ chains within DIB-S₄-DIB and DIB-S₈-DIB structures.

Comparison between the spectra shown in black and red curves in Fig. 2a indicates that the characteristic vibrations of S_4 chain are almost fully suppressed in DIB-S₄-DIB due to the presence of DIB molecules. In particular, despite S–S bonds being present, Raman activities at ~165 cm⁻¹ and 400-500 cm⁻¹, which are assigned to S–S–S deformation and S–S stretching vibrations in free S_4 chain respectively (see ESI†), are absent in the partial spectrum of S_4 in DIB-S₄-DIB. However in Fig. 2b, although Raman activities below 200 cm⁻¹ are absent in the partial spectrum of S_8 chain within DIB-S₈-DIB, a Raman peak corresponding to the characteristic S–S stretching vibration at 455 cm⁻¹ is seen. Moreover, this activity appears to mainly arise from the S_8 chain between two DIBs [red curve in Fig. 2b].

To further assess the above observation, we calculate power spectra of the same systems [Fig. 2c and d]. In Fig. 2c, a peak is observed at around 450 cm⁻¹ in the power spectrum of DIB-S₄-DIB system (blue curve). Note that there is no activity around 450 cm⁻¹ in the partial power spectrum of the S₄ chain within DIB-S₄-DIB in Fig. 2c shown in dotted red curve. As mentioned earlier, this activity corresponds to a Raman-active CH₃ vibration in 1,3-diisopropylbenzene [Fig. 1b]. This vibration becomes Raman inactive in DIB-S₄-DIB as no Raman activity is observed around its corresponding frequency in Fig. 2a. This could be due to the fact that the change in the total polarizability due to this vibration is minimal in a DIB-S₄-DIB molecule. Moreover,



Fig. 1 Calculated Raman spectra of (a) 1,3-diisopropenylbenzene (DIB) and (b) a 1,3-diisopropylbenzene in vacuum. Corresponding atomic structures are also shown in the insets.



Fig. 2 Calculated Raman spectra of (a) $DIB-S_4$ -DIB and (b) $DIB-S_8$ -DIB in vacuum. Also shown in (a) and (b) are the computed Raman spectra of isolated S_4 and S_8 chains (black curves). Partial Raman spectra arising from sulfur chains within $DIB-S_4$ -DIB and $DIB-S_8$ -DIB systems are shown in red curves. (c) and (d) show the computed power spectra of $DIB-S_4$ -DIB and $DIB-S_8$ -DIB, respectively (blue curves). Power spectra of isolated S_4 and S_8 chains are shown in black, while partial power spectra of sulfur chains are shown in red curves. Minimum-energy structures of isolated S_4 and S_8 chains as well as those of $DIB-S_4$ -DIB and $DIB-S_8$ -DIB molecules are shown also in the lower panel.

in contrast to the partial power spectrum of the isolated S_4 chain, almost no activity is observed in the partial power spectrum of the S_4 chain within DIB- S_4 -DIB in 400–450 cm⁻¹ and below 250 cm⁻¹ in Fig. 2c. However, although the low-frequency vibrations of the partial S_8 chain within DIB- S_8 -DIB are insignificant, the peak corresponding to the characteristic S–S stretching vibration at 455 cm⁻¹ is clearly visible [red curve in Fig. 2d].

Fig. 3 shows how the Raman peaks corresponding to the S–S stretching vibrations change as the S chain becomes longer.

In the case of S_4 chain, both peaks attributed to the symmetric and antisymmetric S–S stretching are nearly absent. As the chain length increases to six sulfur atoms in DIB-S₆-DIB, the Raman peak corresponding to the antisymmetric vibration appears, whereas that attributed to the symmetric stretching remains unnoticeable. As the S chain length further increases to S_8 , both symmetric and antisymmetric peaks become distinct.



Fig. 3 Calculated partial Raman spectra of S4, S6, and S8 chains in DIB-S4-DIB, DIB-S6-DIB, and DIB-S8-DIB systems.

Based on the above observations, we conclude that in S/DIB copolymers consisting of short S chains, the total Raman spectrum is fully dominated by the Raman activities of the organic molecules. However, in S/DIB copolymers involving longer S chains, Raman activities arising from the symmetric and antisymmetric S-S stretching vibrations in 400-500 cm⁻¹ are found to be present. The observed effect has to do with the fact that polarizability of a typical S-S bond in a short S chain becomes strongly affected by the DIB molecules. The characteristic frequency for S-S stretching vibration is clearly reflected in the time-dependent variations of the spread of Wannier functions centered along S-S bonds (Fig. S1 in ESI[†]). Here, in order to identify differences between these time-dependent variations in short and long S chains, we calculate the autocorrelation function of the polarizability (expressed as $A = S^3$ in the Wannier polarizability method) attributed to a typical S-S bond in free S4 and S8 chains, as well as that in DIB-S4-DIB and DIB-S8-DIB molecules.

Fig. 4 shows the autocorrelation functions of S–S bond polarizabilities, $C_{AA}(t)$, in free S_n chains (black curves) and DIB-S_n-DIB (red curves) for (a) n = 4, and (b) n = 8. Although C_{AA} decays much slower in the case of free S₄ chain compared to DIB-S₄-DIB [Fig. 4a], its values for the free S₈ chain and DIB-S₈-DIB are comparable. Therefore, we conclude that the presence of massive DIB molecules leads to S–S bond polarizabilities in S/ DIB copolymers containing short S chains which decline much faster than those in free S chains. However, this is not the case when the S chains are longer, and the periodic patterns in the time evolution of a typical S–S bond polarizability are found to be comparable to those in free S chains with the same length.

The observed difference in the Raman spectra can be used to distinguish between short and long sulfur chains in S/DIB copolymers, for example in the synthesis process or during cycling of the battery. To validate the above theoretical observation, first five S/DIB copolymers are synthesized with different mass fractions of DIB (and consequently varying S chain lengths) using inverse vulcanization.^{3,36} Here, we refer to them as SDIB*w* in which *w* is the wt% of DIB, namely 20, 25, 30, 40, and 50%. These mass fractions correspond stoichiometrically to average chain lengths of 11, 8, 6, 4, and 3 sulfur atoms, respectively. Presence of the connection between S chains and DIB molecules is confirmed in all synthesized samples by liquid-state NMR spectroscopy while crystal formation is ruled out by X-ray diffraction measurements (see ESI†). In a second step, Raman spectra of the synthesized sulfur copolymers are measured. Fig. 5 shows a comparison between experimental Raman spectra of S/DIB copolymers with different wt% of DIB.

The intensities are normalized with respect to that of the peak at $\sim 1000 \text{ cm}^{-1}$ in SDIB20 sample. This peak is present in all Raman spectra and corresponds to an aromatic ring vibration. The Raman peak for the characteristic S–S stretching is



Fig. 5 Measured Raman spectra of S/DIB copolymers with different wt% of DIB.



Fig. 4 Autocorrelation functions of S–S bond polarizabilities in free S_n chains (black curves) and DIB-S_n-DIB (red curves) for (a) n = 4, and (b) n = 8.

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observed at 473 cm⁻¹, which is about 4% higher than the theoretically predicted value. The presence of peaks in 1560-1640 cm⁻¹ region indicates partially unsaturated propenyl groups. It is observed that these peaks become more intensive with increasing w. This is in agreement with our NMR measurements (see ESI[†]), where the residual C=C bonds are confirmed by the presence of NMR peaks in the range of 5.0-5.5 ppm. Nevertheless, the observed NMR peaks at chemical shift of 2.2 ppm ensure the formation of C-S bonds in all samples. The C-S bond formation is also seen in the calculated Raman spectrum of DIB-S₈-DIB in 560–575 cm⁻¹ range [Fig. 2b]. In agreement with our theoretical prediction, the experimental measurements show that as the mass fraction of DIB increases (or similarly, as the average S chain length decreases), the Raman activity at around 473 cm⁻¹ becomes less intensive. In a recent in operando FTIR study during discharge,42 it has also been observed that the characteristic S-S stretching vibration is absent in S/DIB copolymers containing short S_n chains ($n \le 4$) throughout discharge. However, this peak evolves as a function of cell voltage in S/DIB copolymers with longer chains, clearly indicating the formation of different Li-polysulfides. In addition, in Fig. 5 we observe Raman activities at $\sim 165-200$ cm⁻¹ assigned to the sulfur chain deformation and S-S-S bending [see Fig. 2a and b], which gradually disappear with increasing wt% of DIB (shorter sulfur chains).

The Raman spectra of samples with more than 50 wt% DIB should effectively be identical to that of DIB molecules, as the only possible sulfur vibration, that is S–S stretching, is observed to be fully suppressed by the carbon moieties. Moreover, NMR analysis shows $\delta = 5.0-5.5$ ppm, indicating the presence of unreacted propenyl groups in 1,3-diisopropenylbenzene as a monomer (see ESI†). It is therefore expected that at DIB mass fractions above 50%, Raman spectroscopic signatures of 1,3-diisopropenylbenzene monomers above 600 cm⁻¹ become more prominent (Fig. 1 and S2†).

Conclusions

We have studied Raman spectra of sulfur/organic copolymers, which are presently discussed as interesting candidates for cathode materials for Li–S batteries, with a particular focus on the spectral response to variations of the length of the sulfur segments. In particular, we have chosen sulfur/1,3-diisopropenylbenzene (S/DIB) copolymers, which have recently shown a promising performance in mitigating the shuttle effect during discharge.

The comparison of quantum-chemical calculations of Raman signals with corresponding experimental spectra shows that there is a particular spectroscopic fingerprint at about 450 cm⁻¹ which allows for discriminating between shorter S_n chains ($n \le 4$) and longer ones (n > 4) in the copolymers at the fully charged state of the battery. This fingerprint, which corresponds to the Raman-active S–S stretching vibration, is absent in the Raman spectra of shorter sulfur chains. We attribute this effect to the confinement of shorter sulfur chains by the organic parts of the copolymer, which leads to a suppression of the net polarizability change during the vibrational motion.

It has been demonstrated that formation of short sulfur chains connecting DIB molecules are thermodynamically more favorable.⁵ As a result, the initial reactions primarily occur with the shorter sulfur chains, leading to a shuttle effect reduction. It has also been observed experimentally that formation of higherorder Li-polysulfides which can dissolve in the electrolyte is largely hindered during discharge in S/DIB copolymers containing short sulfur chains.4 Therefore, a stable cycling for 1500 cycles has been reported.42 This clearly emphasizes the need for a strategy for the synthesis of S/DIB copolymers with controllable S chain lengths. The present study shows that Raman spectroscopy is a powerful tool to investigate structural properties of S/DIB copolymers and provides a way to probe the presence and formation of short or long sulfur chains by focusing on the frequency range attributed to the characteristic S-S vibration.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge DFG funding *via* projects PA3141/3 (Project number 420536636) and PA3141/5 (Project number 446879138). This research was also financially supported by the European Social Fund (ESF) and the State of Saxony-Anhalt through the graduate school AgriPoly. The computations have been mostly performed on a Bull Cluster at the Center for Information Services and High Performance Computing (ZIH) at TU Dresden *via* the project 'p_oligothiophenes'. We also gratefully thank Wolfgang Binder for the synthesis supervision, Karsten Busse for the XRD measurements, and Matthias Vogt for elemental analyses.

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Paper III: Toward Ab initio Simulation of Operando Raman Spectroscopy: Application to Sulfur/Carbon Copolymer Cathodes in Li-S Batteries

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Toward Ab initio Simulation of Operando Raman Spectroscopy: Application to Sulfur/Carbon Copolymer Cathodes in Li-S Batteries. *ChemPhysChem* 2024, e202400681.

In concluding this research, I performed all simulations and analyses, utilizing the methodology developed by Dr. Pouya Partovi-Azar. Timo Held carried out the structural analysis. Huiying Sheng synthesized the S/DIB co-polymer. Under the guidance of Oliver Löhmann, the experimental Raman measurements were performed in Dr. Sebastian Risse's group at Helmholtz-Zentrum Berlin for Materials and Energy. This work was supervised by Dr. Pouya Partovi-Azar and Prof. Dr. Daniel Sebastiani.

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Ab Initio Simulation of Raman Fingerprints of Sulfur/Carbon Copolymer Cathodes During Discharge of Li-S Batteries

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Sulfur/carbon copolymers have emerged as promising alternatives for conventional crystalline sulfur cathodes for Among these, sulfur-n-1,3lithium-sulfur batteries. diisopropenylbenzene (S/DIB) copolymers, which present a 3D network of DIB molecules interconnected via sulfur chains, have particularly shown a good performance and, therefore, have been under intensive experimental and theoretical investigations. However, their structural complexity and flexibility have hindered a clear understanding of their structural evolution during redox reactions at an atomistic level. Here, by performing state-of-the-art ab initio molecular dynamics-based Raman spectroscopy simulations, we investigate the spectral fingerprints of S/DIB copolymers arising from local structures during consecutive reactions with lithium. We discuss in detail Raman spectral changes in particular frequency ranges which are common in S/DIB copolymers having short sulfur chains and those consisting of longer ones. We also highlight those distinctive spectroscopic fingerprints specific to local S/DIB structures containing only short or long sulfur chains. This distinction could serve to help distinguish between them experimentally during discharge. Our theoretically predicted results are in a good agreement with experimental Raman measurements on coin cells at different discharge stages. This work represents, for the first time, an attempt to compute Raman fingerprints of sulfur/carbon copolymer cathodes during battery operation including quantum-chemical and finite-temperature effects, and provides a guideline for Raman spectral changes of arbitrary electrodes during discharge.

Introduction

The remarkable theoretical specific capacity of elemental sulfur ($\simeq 1675$ mA h/g), its eco-friendly nature, and its abundance make lithium-sulfur (Li-S) batteries an

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attractive alternative to current lithium-ion batteries.^[1,2] Nevertheless, their cycle life has so far been limited due to certain drawbacks. A notable challenge is the formation of long-chain, soluble lithium poly-sulfides during the discharge and their shuttling through the conventional electrolytes, $^{[3,4]}$ which leads to a depletion of the active material and formation of an insulating layer around the anode. All these processes result in an irreversible capacity fade in Li-S batteries. [5-8] To tackle these issues, numerous studies have focused on structural optimization of sulfur cathodes including utilization of sulfur/carbon copolymers. In order to synthesize S/C copolymers, many researchers have employed the inverse vulcanization reaction as a facile synthesis method which provides a straightforward way for controlling sulfur content. Among others, sulfur-n-1,3-diisopropenylbenzene (S/DIB) copolymer has shown a promising performance as an active cathode material for Li–S batteries.^[9,10]

Structural characterization of S/DIB copolymers has been the subject of several studies so far.^[10–13] For example, similar to other S/C copolymers involving sulfur chains,^[14–20] thermodynamically preferred S/DIB structures consist of short S_n chains, $n \simeq 4$.^[12] The shorter sulfur chains are expected to result in a hindrance in the formation of higher-order Li-poly-sulfides and consequently a stable cycling of 1500 cycles has been reported.^[21] Despite qualitative descriptions of the discharge mechanism of S/DIB copolymer cathodes,^[10,21] an atomistic view on their structural evolution during the lithiation reactions is still lacking. Such an insight can lead to morphology optimization of sulfur/carbon copolymers toward more efficient cathodes.

In this study, we aim to address the structural evolution of S/DIB copolymers during discharge by performing finite-temperature Raman spectroscopy simulations, combining quantum-chemical calculations with ab initio molecular dynamics simulations on model S/DIB systems. Here, we study the lithiation reactions of $DIB-S_n-DIB$ with two different sulfur chain lengths, namely n = 4 and 8, and focus on Raman spectroscopic fingerprints of the final structures at different stages of discharge. The huge computational effort of such an investigation is substantially reduced by the efficient Wannier polarizability method for the estimation of the dynamics of polarizability tensors during ab initio molecular dynamics simulations,^[22-25] fully bypassing the time-consuming linear response calculations. We demonstrate common spectroscopic trends occurring during discharge of Li-S batteries based on S/DIB copolymer cathodes involving both short and long sulfur chains. Moreover,

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we predict spectroscopic fingerprints during discharge specific to the copolymers having short sulfur chains or those consisting of long ones. Our theoretical predictions are validated against Raman spectroscopy measurements on coin cells at different discharge states. These findings serve as an important step towards simulation of contributions from the local copolymer cathode structures to the Raman spectrum during discharge and will contribute to the advancement of material analysis and, thereby, can lead to an enhanced performance of Li-S batteries.

Computational Details

We consider DIB–S_n–DIB as target molecules in vacuum as a local structure of poly(sulfur-n-1,3-diisopropenylbenzene), where n = 4 and 8, representing local structures of the S/DIB copolymers consisting of short and long sulfur chains, respectively. In S/DIB copolymers, the terminal sulfur atoms forming C–S bonds are usually referred to as organic sulfur atoms. The C–S bonds remain stable during reactions with lithium,^[10] resulting in lithium-saturated chains where the number of lithium atoms reacting with the sulfur chain is twice the number of sulfur atoms minus two. Therefore, consecutive lithiation reactions of S/DIB copolymers are described here by

DIB-S_n-DIB +
$$m$$
 Li⁺ + m e⁻ \longrightarrow DIB-Li_mS_n-DIB, (1)
 $m = 2, 4, ..., 2n - 2.$

In our computations, we treat the Li^+ and e^- pair as a single lithium atom. The initial structures are prepared by adding Li atoms along the S chain at distinct positions. These structures then go through atomic coordinate optimizations. In total, about 360 initial structures and optimizations are carried out. At each lithiation step, the lowest-energy product structure is considered as a candidate for the actual lithiation product. As indicated in Eq. (1), we continue with sequential lithiation reactions until the saturation of the sulfur chain with lithium atoms is achieved. For simplicity, we specifically consider even numbers of lithium atoms in each reaction.

All coordinate optimizations are performed at density-functional theory (DFT) level using the CP2K/QUICKSTEP software package^[26] in conjunction with a DZVP-MOLOPT basis set^[27], as well as Perdew-Burke-Ernzerhof (PBE)^[28] exchange-correlation energy functional and Geodecker Teter-Hutter (GTH) pseudopotentials.^[29,30] The semi-empirical DFT-D3^[31] method is also used to correct for the long-range dispersion interactions.

After identifying the minimum-energy structure at each lithiation step, we study its structural stability by carrying out a 20 ps DFT-based *ab initio* molecular dynamics (AIMD) simulation in the canonical ensemble (NVT), specifically a canonical sampling through velocity rescaling (CSVR) thermostat^[32] with a time constant of 10.0 fs, at an elevated temperature of 500 K. In rare cases where an unexplored structure is formed at the elevated temperature, new geometry optimization is performed and the energy is compared to the previously found product structure at the corresponding lithiation step. In a following step, another round of AIMD simulations is performed on the structurally stable products for 20 ps in the NVT ensemble to achieve equilibrium at 300 K. This is followed by 20 ps of AIMD

simulations in the micro-canonical ensemble (NVE) to sample the polarizabilities needed for the simulation of Raman spectra. A time step of 1 fs is used in the AIMD simulations, while the polarizabilities are sampled every 5 fs. The AIMD simulations are also performed using the CP2K software with the same simulation setup as mentioned earlier.

The Raman spectroscopy simulations are performed using the efficient Wannier polarizability method.^[22–25] This method allows for a very efficient estimation of the dynamics of the polarizability, which can be about 1000 times faster compared to the conventional approaches, for example those based on linear response theory.^[25] Such an efficiency can allow for performing *ab initio* Raman spectroscopy simulations on many intermediate electrode structures during battery operation.

The interaction energies are corrected for the basis set superposition error based on the counterpoise correction of Boys and Bernardi. $^{[33]}$

In a lithium-sulfur battery sporting an S/DIB copolymer as cathode, reactions occur at the interface between the electrolyte and the three dimensional network of the copolymer. As such, only those local S/DIB structures are exposed to the electrolyte which happen to be on the surface. Therefore, adding a solvent to the molecular systems considered here for the local structures, where the solvent fully surrounds the molecules, might not be fully realistic. Nevertheless, we check the effect of solvent around Li-saturated DIB-Li₆S₄-DIB using an implicit solvent model.^[34] We find that the change in the bond lengths remain below 3% (please see the Supplementary Information). Moreover, as will be discussed later, the agreement between the calculated and experimental spectra is found to be remarkable. This ensures that, although the effect of the electrolyte cannot be completely neglected, in the frequency range of sulfur activity (below 1100 cm^{-1}), the observed Raman peaks and their evolution mostly arise from the Li-S structures which emerge during discharge. Therefore, all calculations in this work are performed in vacuum.

Results and Discussion

During structure optimizations and AIMD simulations at 500 K and 300 K, we do not observe any C-S bond breaking, irrespective of the sulfur chain length and the depth of discharge. However, we see a gradual breaking of S–S bonds in the course of discharge. This implies that the organic sulfur atoms play an important role in keeping the emerging lithium-sulfur structures connected to the organic groups via C-S bonds. This has also been argued earlier to be one of the factors contributing to the good electrochemical performance of S/DIB copolymers by anchoring the emerging lithium-sulfur structures to the organic groups.^[10] In fact, here we find the interaction energies between the lithiumsulfur structures and the organic groups (DIB molecules together with organic sulfur atoms) at 100% depth of discharge to be about 1.4 times as high as a typical C–S covalent bond $(E_{\text{C-S}} \simeq 7.2 \text{ eV})^{[35]}$ both in DIB-Li₆S₄-DIB and DIB-Li₁₄S₈-DIB.

Calculated room-temperature *ab initio* Raman spectra of DIB–S₄–DIB and DIB–S₈–DIB molecules at different stages of discharge are shown in Fig. 1 and Fig. 2, respectively. The corresponding lithiated structures are also shown in the insets. By decomposing the total Raman spectra into local contributions, ^[23–25] we find that among all Raman activi-

affected by the presence of binder material and/or carbon Furthermore, we observe that the formation of lithiumsulfur structures could have a far-reaching effect. For example, as shown in Fig. 1(b), we see that the frequency range attributed to the C-H stretching vibrations becomes broader as a function of the depth of discharge. For clarity, the intensities are scaled up ten times compared to Fig. 1(a). A redshift is seen in the frequency of the dominant peak at $\sim 3065 \,\mathrm{cm}^{-1}$ [Fig. 1(b), panel (I)] towards $\sim 3048 \,\mathrm{cm}^{-1}$ [Fig. 1(b), panel (IV)] in the course of discharge. The decomposition of the spectra reveals that the observed redshift corresponds to the weakening of the C-H bonds proximal to the lithiation center (see Fig. S2 in the Supplementary In-Long Sulfur Chains The calculated Raman spectra of a $DIB-Li_mS_8-DIB$ molecule at different stages of discharge are presented in Fig. 2(a), panels (I)–(VIII). The Raman spectrum of DIB– S_8 -DIB structure [Fig. 2(a), panel (I)] agrees well with our previous investigations on S/DIB copolymers with long sulfur chains.^[13] In the range of $100-180 \,\mathrm{cm}^{-1}$, two prominent peaks are observed. In our previous study, these activities in copolymers with longer sulfur chains have been attributed to sulfur chain deformation and S-S-S bending, and they gradually decline with increasing weight percentage of DIB. At a discharge state of approximately 14% [Fig. 2(a),

panel (II)], we observe a structure with one broken S-S bond, resulting in two shorter chains, namely S_3 and S_5 . As lithiation continues, an additional sulfur bond is broken [Fig. 2(a), panel (III)]. Similar to the case of $DIB-S_4-$ DIB, this pattern continues during further lithiations up to the final stage of discharge, where there is no S-S covalent bond remaining in DIB-Li₁₄S₈-DIB [Fig. 2(a), panel (VIII)]. Here, we also observe that S–S bond breaking can be reversible as well.

Upon splitting of the S_8 chain in DIB-S₈-DIB at early stages of discharge [Fig.,2(a), panel (II)], we observe rather intensive Raman activities in the range of $100-250 \,\mathrm{cm}^{-1}$, resembling those previously observed in free (isolated) S_4 and S_8 chains.^[13] This shows that the S/DIB copolymer cathode should involve quasi-free S chains at low depths of discharge. Here, these activities are attributed to S-S-S bending within the S₅ unit of DIB-Li₂S₈-DIB (see Fig. S3 and S4 in the Supplementary Information for further details).

As the system gets further lithiated, a significant Raman activity is observed at around $200 \,\mathrm{cm}^{-1}$ [Fig. 2(a), panels (II)-(VIII)]. Similar to the case of $DIB-Li_mS_4-DIB$ [Fig. 1(a)], this activity can generally be assigned to the emerging lithium-sulfur structure.

Similarly, Raman activities in the 320-400 and 420- $600 \,\mathrm{cm}^{-1}$ ranges arise from the lithium-sulfur structure. These activities become more noticeable with increasing number of lithium atoms. At 100% depth of discharge [Fig. 2(a), panel (VIII)], the dominant Raman activity in $320-400 \,\mathrm{cm}^{-1}$ range coincides with the characteristic Raman activity of Li_2S solid.^[37]

The Raman activity around $450 \,\mathrm{cm}^{-1}$ predominantly originates from S–S stretching vibration in longer sulfur chains. As previously discussed, ^[13] this activity is a key factor in distinguishing between long and short sulfur chains. The activity at $\sim 450 \,\mathrm{cm}^{-1}$ is found to be absent at 100%

ties spanning $0-3300 \,\mathrm{cm}^{-1}$ range, the signals in $0-1200 \,\mathrm{cm}^{-1}$ predominantly arise from the emerging lithium-sulfur structure between two DIB molecules [Fig. 1(a), panel (IV) and Fig. 2(a), panel (VIII)]. The observed signals in the higher frequency range $(1200-3300 \text{ cm}^{-1})$ mostly correspond to vibrations of the DIB molecules (see Fig. S1 in the Supplementary Information). Here, we particularly focus on the activities arising from lithium-sulfur structures.

black.

formation).

Short Sulfur Chains

The Raman spectra obtained for the DIB-S₄-DIB structure [Fig. 1(a), panel (I)] agrees well with earlier investigations.^[13] The activities observed at around $100 \,\mathrm{cm}^{-1}$ and $350 \,\mathrm{cm}^{-1}$ in Fig. 1(a), panel(I), are attributed to S₄ chain deformations in the DIB-S₄-DIB structure. However, as seen in Fig. 1(a), these activities become unnoticeable upon reaction with lithium due to the breaking of S-S bonds along the chain. Based on our observation, as the copolymer is discharged to around 33% [Fig. 1(a), panel (II)], the S₄ chain splits at the mid-bond, resulting in the formation of two shorter S_2 chains. As the lithiation continues, another sulfur bond is broken [Fig. 1(a), panel (III)]. The same pattern is observed until the final lithiation stage, where no S-S covalent bond is present anymore [Fig. 1(a), panel (IV)]. Additionally, the lithiation reactions appear to be reversible. The reversibility of the reactions is particularly checked by removing two lithium atoms from the optimized DIB-Li₄S₄-DIB structure [Fig. 1(a), panel (III)] followed by an atomic coordinate optimization on the resulting structure. We observe a restoration of a broken S-S bond leading to a DIB- Li_2S_4 -DIB structure, similar to the one shown in Fig. 1(a), panel (II).

At 100% depth of discharge, where the system contains the highest possible number of lithium atoms, a notable Raman activity is observed around $200 \,\mathrm{cm}^{-1}$, as shown in Fig. 1(a), panel (IV). This activity can be attributed to the lithium-sulfur structure.^[36]

Moreover, in agreement with previous studies $^{[23]}$ where the Raman activities in the range of $350-500\,\mathrm{cm}^{-1}$ have predominantly been attributed to lithium-sulfur structure, our results reveal a gradual increase in Raman activities within the $400-500 \text{ cm}^{-1}$ range as more lithium atoms react with sulfur [Fig. 1(a)]. In the range of $480-580 \,\mathrm{cm}^{-1}$, specifically at $520 \,\mathrm{cm}^{-1}$, a broad Raman activity is observed as the depth of discharge reaches 100%, which should also arise from the formation of the lithium-sulfur structure.^[36]

Based on partial Raman analysis, the activity at ${\sim}575\,\mathrm{cm}^{-1}$ can be assigned to the C–S bond stretching [see Fig. S5 in the Supplementary Information].^[13] In agreement with our observation, it has been shown before^[21] that this peak gets slightly blue-shifted during the discharge.

The activity in about 650, 710, 790, 870, and $900 \,\mathrm{cm}^{-1}$ Raman shifts can be due to collective Raman-active vibrations of lithium-sulfur structures and the DIB groups. These vibrations are observed in all lithiated samples of DIB-S₄-DIB and DIB-S₈-DIB. This also holds for the activities seen around $1100 \,\mathrm{cm}^{-1}$ (see Fig. 1(a), panel (IV) and the Supplementary Information).

The vibrational mode around $1000 \,\mathrm{cm}^{-1}$ is a strong indicator of a benzene ring breathing vibration in all systems. Here, we observe that the intensity of this mode fluctuates non-monotonically with the depth of discharge. As will be discussed later, the intensity of this band could be heavily



Figure 1. Computed Raman spectra for (I) $DIB-S_4-DIB$, (II) $DIB-Li_2S_4-DIB$, (III) $DIB-Li_4S_4-DIB$, and (IV) $DIB-Li_6S_4-DIB$ molecules in vacuum. (a) Spectra in the range of 0–1200 cm⁻¹ and (b) Spectra in the range of 2950–3150 cm⁻¹. The black curves represent the computed Raman spectra of the entire $DIB-Li_mS_4-DIB$ molecule, while the red curve represents the partial Raman spectra of Li_6S_4 within the $DIB-Li_6S_4-DIB$ molecule. The intensities in 2950–3150 cm⁻¹ in (b) are multiplied by a factor of ten for clasity. The purple, yellow, black, and white colors in the atomic structures indicate lithium, sulfur, carbon, and hydrogen atoms, respectively.



Figure 2. Computed Raman spectra for (I) DIB– S_8 –DIB, (II) DIB– Li_2S_8 –DIB, (III) DIB– Li_4S_8 –DIB, (IV) DIB– Li_6S_8 –DIB, (V) DIB– Li_6S_8 –DIB, (V) DIB– $Li_{12}S_8$ –DIB, (VI) DIB– $Li_{12}S_8$ –DIB, and (VIII) DIB– $Li_{14}S_8$ –DIB molecules in vacuum. (a) Spectra in the range of 0–1200 cm⁻¹ and (b) Spectra in the range of 2950–3150 cm⁻¹. The black curves represent the computed Raman spectra of the entire DIB– Li_mS_8 –DIB molecule, while the red curve represents the partial Raman spectra of $Li_{14}S_8$ within DIB– $Li_{14}S_8$ –DIB molecule. The intensities in (b) are multiplied by a factor of ten for clarity. The atomic colouring scheme is the same as Fig. 1.

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depth of discharge as there is no S–S covalent bond present in the DIB-Li₁₄S₄–DIB molecule anymore. Instead, a broad activity emerges at 100% depth of discharge at 470-550 cm⁻¹ which seems to come almost entirely from the formed lithium-sulfur structure [see the red curve in Fig. 2(a), panel (VIII)]. However, our analysis based on partial Raman spectrum of the S₈ chain within DIB–S₈–DIB shows that the activity at ~480 cm⁻¹ should partially arise from the DIB molecules as well. It is worth noting that this activity arising from the organic molecules should be present at all stages of discharge.

Similar to the case of DIB–S₄–DIB, the activity at ~575 cm⁻¹ can be attributed to the C–S bond stretching [see Fig. S5 in the Supplementary Information].^[13] In qualitative agreement with previous studies,^[21] this peak undergoes a blueshift from ~575 cm⁻¹ to ~585 cm⁻¹ during discharge.

The activity in the $600-900 \,\mathrm{cm}^{-1}$ range can also be attributed to collective Raman-active vibrations of sulfur (either lithiated or otherwise) and the organic groups. As in the case of DIB-S₄-DIB, the activities seen around $1100 \,\mathrm{cm}^{-1}$ should also arise from similar coupled Li-S/DIB vibrations (see the Supplementary Information).

We also observe a similar behavior in the C–H stretching frequency range as in DIB–S₄–DIB. As shown in Fig. 2(b), the frequency range associated with C–H stretching bandwidth broadens with increasing depth of discharge. However, in the case of DIB–S₈–DIB, no meaningful



Figure 3. C–H stretching bandwidth as a function of depth of discharge for DIB–S₄–DIB (circles) and DIB–S₈–DIB (squares).

frequency shift is observed. Figure 3 illustrates how the C–H stretching bandwidth increases during the discharge process for both sulfur chain lengths (S_4 and S_8). This broadening indicates that the introduction of lithium into the system and hence its interaction with sulfur atoms affects C–H bonds vibrations, resulting in nonidentical oscillators (see Fig. S2 in the Supplementary Information for partial Raman analysis).

Comparing panel (IV) in Fig. 1(a) with panel (VIII) in Fig. 2(a), we observe that S/DIB copolymers containing short chains and those having long ones show similar Raman features at 100% depth of discharge. The main difference is that the bands are broader in the case of DIB–S₈–DIB. This is due to the fact that in lithiated DIB–S₈–DIB structure, the number of nonidentical oscillators with Raman activities at certain frequency ranges are higher than that in the DIB–S₄–DIB system in the same frequency ranges. However, the Raman activity at ~450 cm⁻¹ corresponding to

the S–S stretching mode could still serve as a fingerprint for distinguishing between local copolymer structures consisting of short and those having long sulfur chains. Although the corresponding band shows an insignificant intensity at 0% depth of discharge in DIB-S₄-DIB [Fig. 1(a), panel (I)], it exhibits an intensive band in DIB–S₈–DIB from 0% up to 86% depth of discharge [Fig. 2(a), panels (I)-(VII)]. At 100% depth of discharge, where no S–S covalent bond is present, the intensity of this band becomes negligibly small in both $\rm DIB\text{--}Li_6S_4\text{--}DIB$ and $\rm DIB\text{--}Li_{14}S_8\text{--}DIB$ structures. In addition to this band, the Raman activities at $\sim 200 \,\mathrm{cm}^{-1}$ during discharge can also be used to distinguish between short and long sulfur chains. While the band at $\sim 200 \,\mathrm{cm}^{-1}$ only appears at fully discharged DIB-S₄-DIB [Fig. 1(a)], our results show a rather intensive activity in $200-250 \,\mathrm{cm}^{-1}$ range at 14% to 100% depth of discharge of DIB-S₈-DIB [Fig. 2(a), panels (II)-(VI)].

Comparison with Raman Measurements

Figure 4 shows the *ex-situ* measured Raman spectra of the synthesized SDIB10 sample which corresponds to an average sulfur chain length of 22 sulfur atoms. All the intensities are normalized with respect to the carbon D band at $\sim 1350 \text{ cm}^{-1}$. The spectra are obtained at different depths of discharge, namely %0 (black), %66 (red), and 100% (blue). Despite differing sulfur chain lengths, these spectra can be



Figure 4. Experimental Raman measurement on SDIB10. DOD stands for depth of discharge.

qualitatively compared with those presented in Fig. 2(a) for DIB–S₈–DIB. It is worth noting that apart from activities coming from the S/DIB copolymer, those from the electrolyte, carbon black, and binder material are also present in the experimental spectra.

Although the relative intensities in the spectrum corresponding to 0% depth of discharge in Fig. 4 (black curve) do not fully match with those in panel (I) of Fig. 2(a), the peak positions agree well. As discussed earlier, the activity at around $200 \,\mathrm{cm}^{-1}$ in Fig. 4 should come from sulfur chain deformation at early stages of discharge. The collective vibrations in the lithium-sulfur structure toward the end of discharge also have an activity around the same frequency. The activity in $300-400 \,\mathrm{cm}^{-1}$ in the black curve in Fig. 4 (0% depth of discharge) can also be attributed to sulfur chain deformation, as has been revealed in our previous study.^[13] This activity, similar to the one at $\sim 200 \,\mathrm{cm}^{-1}$ also arises from lithium-sulfur vibrations at higher depths of discharge [Fig. 2(a), panel (VIII)]. As discussed earlier, the activity at ${\sim}450\,\mathrm{cm}^{-1}$ can be assigned to S–S stretching, the one at $\sim 500 \,\mathrm{cm}^{-1}$ to DIB vibrations, $\sim 560 \,\mathrm{cm}^{-1}$ to C–S stretching, and finally those at ~650 cm⁻¹ to coupled (lithium-)sulfur/DIB vibrations. These assignments can be further justified based on the fact that, for example, the peak at ~450 cm⁻¹ is found to become unnoticeable at 100% depth of discharge (blue curve), while the ones at ~500 cm⁻¹, ~560 cm⁻¹, and ~650 cm⁻¹ are found at all stages of discharge. A clear broad activity is observed in Fig. 4 in 450-500 cm⁻¹ range. Our calculations show that this broad activity arises mostly from the emerging lithium-sulfur structure and is found to occur in a comparable frequency range, namely 470-550 cm⁻¹.

It should be noted here that although the spectral fingerprints of the local structures and their evolution during discharge are well predicted in our calculations, an in situ/operando Raman spectrum of a realistic S/DIB copolymer cathode should, in general, be calculated by adding the local contributions weighted by their formation energies.^[12,19] However, as demonstrated here, the spectral evolution of the cathode during discharge occurs at around the same frequencies, namely $\sim 200 \,\mathrm{cm}^{-1}$, $300\text{-}400 \,\mathrm{cm}^{-1}$, and $\sim 450 \,\mathrm{cm}^{-1}$, irrespective of the sulfur chain length in the local structures. The same behavior could be expected in local S/DIB structures containing intermediate sulfur chain lengths. Therefore, the cathode contribution to the Raman spectrum in the frequency range of sulfur activity computed through the weighted sum of local contributions should appear approximately similar to any individual contribution.

Conclusions

In summary, we have investigated the spectral evolution of sulfur/1,3-diisopropenylbenzene (S/DIB) copolymers as a function of depth of discharge by performing *ab initio* finite-temperature Raman spectroscopy simulations. The focus has been set on the spectroscopic fingerprints arising from local S/DIB structures containing low and high sulfur content, corresponding to short and long sulfur chains, respectively. This study, represents an important step toward quantum-chemical simulation of Raman spectroscopy based on *ab initio* molecular dynamics simulations on battery electrodes during operation. This has been facilitated by using the Wannier polarizability method ^[22–25] to efficiently estimate the polarizability dynamics in many intermediate lithiated structures.

Our current study dives deeper into understanding of the complex discharge mechanism of S/DIB copolymer cathodes. We have observed that local S/DIB structures containing short and those consisting of long sulfur chains show similar Raman features at 100% depth of discharge. However, we have found frequency ranges in which short- and long-sulfur chain containing local structures have distinctive Raman activities during discharge. For example, the Raman activity at $\sim 450 \,\mathrm{cm}^{-1}$ (S–S stretching) can serve as a fingerprint for distinguishing between local copolymer structures consisting of short and those having long sulfur chains. Although the corresponding band shows an insignificant intensity at early to mid stages of discharge in structures with short sulfur chains, it shows an intensive band from 0% up to 86% depth of discharge in those containing long sulfur chains. At 100% depth of discharge, where no S–S covalent bond is present, the intensity of this band can become negligibly small irrespective of the sulfur chain length in the local copolymer structure. In addition to this, the Raman activities at $\sim 200 \text{ cm}^{-1}$ during the discharge can also be used to distinguish between short and long sulfur chains. The band at $\sim 200 \text{ cm}^{-1}$ only appears at fully lithiated local S/DIB structures with short sulfur chains. However, we have found a rather intensive activity in 200-250 cm⁻¹ range from 14% to 100% depth of discharge of those local copolymer structures consisting of long sulfur chains. These theoretical predictions have been validated against *ex-situ* Raman measurements on S/DIB cathodes at different stages of discharge and provide practical insights into designing and characterizing sulfur/carbon copolymers cathode materials.

Supporting Information

Supporting Information is available on Raman peak assignments based on partial Raman analysis, solvent effects, and lithiation reaction energies.

Experimental

Materials and Synthesis

Chemicals

All reagents, namely sulfur ($\geq 99.5\%$, Sigma-Aldrich), 1,3-diisopropenylbenzene (DIB, 97%, TCI), sodium carboxymethyl cellulose (CMC, MW 250,000, Sigma-Aldrich), polyacrylic acid (PAA, MW 450,000, Sigma-Aldrich), electrolyte (purchased from E-lyte) consisting of lithium bis(trifluoromethane)sulfonimide and 2 wt% lithium nitrate in a 1:1 v/v mixture of 1,3-dioxolane and 1,2-dimethoxy ethane, metallic lithium chips (99.95%, China Energy Lithium), polypropylene separator (Celgard-2700), and carbon black (super p, Macklin) are used directly.

Synthesis of SDIB10

SDIB10 is synthesized using the previously reported method. $^{[10,11,13,38]}$ 10 wt% sulfur is added into a glass vial equipped with a magnetic stir bar and heated to 130 °C in a thermostated oil bath. DIB is added to the fully molten sulfur using a syringe and stirred for 10 minutes to achieve a homogeneous mixture.

SDIB10 Cathode Preparation

The synthesized S/DIB is further heated to 185 °C for 8-10 minutes, which results in vitrification of the mixture. The product is then cooled down to room temperature. The obtained product is mixed with carbon black and binder mixture of CMC/PAA (1/1 w/w) in a mass ratio of 75:20:5 in water. The slurry is then ball milled and blade cast onto carbon coated aluminum foil. The areal mass loading of sulfur inside the electrode is around 3 mg/cm^2 . After getting completely dried, the prepared electrode is cut into disks with 12 mm diameters to be used as cathode in a coin cell.

Instrumentation and Measurements

The prepared cathodes are assembled into CR2032 coin cells with electrolyte, a polypropylene separator, and a lithium foil anode in an argon filled glove box. Cells are tested in a VMP3 potentiostats from 0.8-3.0 V at 0.1 C for 4 cycles. A

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renishaw QONTOR instrument with a 532 nm laser is employed for the *ex-situ* Raman spectroscopy in the range from 0-4000 cm⁻¹ with a resampling interval of 1 cm^{-1} . Cycled cathodes at 0%, 66%, and 100% depth of discharge and a cathode without cycling are measured.

Acknowledgements

The authors gratefully acknowledge DFG funding via projects PA3141/3 (Project number 420536636), PA3141/5 (Project number 446879138), and SPP 2248 "Polymer-based Batteries". Additionally, H.S. kindly acknowledges the financial support from the China Scholarship Council (No. 202308080034). The computations have been mostly performed on a Bull Cluster at the Center for Information Services and High Performance Computing (ZIH) at TU Dresden via the project 'p_oligothiophenes'.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Li-S battery \bullet sulfur/carbon copolymer \bullet Raman spectroscopy \bullet density functional theory \bullet ab initio molecular dynamics

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Conclusions

7

In this doctoral research, I conducted studies focused on the sulfur-1,3diisopropenylbenzene (S/DIB) cathode material for Li–S batteries, which has recently demonstrated promise in reducing the shuttle effect during discharge. My investigations employed quantum chemical calculations using Density Functional Theory (DFT) and *ab initio* finite-temperature Raman spectroscopy simulations with the Wannier Polarizability method. In this work, I began by investigating the local structure of the sulfur copolymer to determine the optimal number of sulfur atoms required to connect two DIB molecules. Following this, I characterized these structures through Raman spectroscopy simulations, which were supported by experimental synthesis of the sulfur copolymer and corresponding Raman measurements. Finally, I introduced lithium into the system to further explore the structural behavior during the battery's discharge process.

In the first study, I employed density–functional theory calculations to examine the local bonding in S/DIB copolymer. I discovered that sulfur chains consisting of four atoms are more likely to form between diisopropenylbenzene molecules, contributing to the stabilization of the polymer network. This suggests that short sulfur chains are favorable in similar sulfur/carbon copolymers. Additionally, I found no significant preference for the sulfur chain connection to different carbon types in the isopropenyl groups. My findings indicate that a thermodynamically preferred structure of S/DIB copolymers should contain approximately 38 wt% diisopropenylbenzene. This implies that despite a lower initial cathode capacity, S/DIB copolymer with around 38 wt% diisopropenylbenzene, a higher carbon content can potentially enhance the electrical conductivity of the cathode.

In the second study, I investigated the Raman spectra of S/DIB copolymer, previously explored, with a focus on how the length of sulfur segments affects the spectral response. By comparing quantum-chemical calculations of Raman signals with experimental spectra, I identified a specific spectroscopic fingerprint at around 450 cm⁻¹. This fingerprint, corresponding to the Raman-active S–S stretching vibration, is key to distinguishing between shorter sulfur chains ($n \le 4$) and longer ones (n > 4) in the fully charged state of the battery. Notably, this feature is absent in the Raman spectra of shorter sulfur chains, which we attribute

to the confinement of these chains by the organic components of the copolymer. This confinement suppresses the net polarizability change during vibrational motion.

In the third study, I go further to examine the spectral evolution of S/DIB copolymer during discharge using ab initio finite-temperature Raman spectroscopy simulations. I focused on the spectroscopic fingerprints of local S/DIB structures with varying sulfur content to better understand the complex discharge mechanisms of S/DIB copolymer cathodes. My findings reveal that while S/DIB copolymers with short and long sulfur chains exhibit similar Raman features at full discharge, they display distinct Raman activities in specific frequency ranges during the discharge process. For instance, the Raman activity at 450 cm⁻¹ (S–S stretching) serves as a key identifier, showing intense bands in long sulfur chains from 0% to 86% depth of discharge, but becoming negligible at 100% discharge. Additionally, the Raman activity around 200 cm⁻¹ distinguishes fully discharged S/DIB copolymers with short sulfur chains, whereas long sulfur chains exhibit significant activity in the 200-250 cm⁻¹ range from 14% to 100% discharge. These theoretical predictions have been validated by ex-situ Raman measurements, offering practical insights for designing and characterizing sulfur/carbon copolymer cathode materials.

The findings from my PhD research will assist future battery scientists in selecting the optimal sulfur content for synthesizing cathode materials with superior performance. Additionally, by conducting operando Raman spectroscopy and characterizing the cathode structure at each stage of the discharge process, this work provides valuable insights into the structural evolution of the material, enabling more informed decisions in battery design and development.

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Appendices

A

Academic Curriculum Vitae

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Eidesstattliche Erklärung / Declaration under Oath

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