

Lithium Bonds

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Lithium Bonds in Lithium Batteries

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Abstract: Lithium bonds are analogous to hydrogen bonds and are therefore expected to exhibit similar characteristics and functions. Additionally, the metallic nature and large atomic radius of Li bestow the Li bond with special features. As one of the most important applications of the element, Li batteries afford emerging opportunities for the exploration of Li bond chemistry. Herein, the historical development and concept of the Li bond are reviewed, in addition to the application of Li bonds in Li batteries. In this way, a comprehensive understanding of the Li bond in Li batteries and an outlook on its future developments is presented.

The existence of lithium (Li) bonds, which are analogous to hydrogen (H) bonds, was first suggested as a possibility by Shigorin in 1959 based on the rationale that both Li and H are monovalent electropositive elements and exhibit similar interactions between molecules.^[1,2] However, this concept was not accepted until 1970. The paper entitled „The Lithium Bond“ was influential in delineating the analogy with the H bond, in which the characteristics of H and Li bonding were confirmed by theoretical infrared (IR) spectroscopy frequency shifts and intensity enhancements.^[3] Subsequently, the first experimental proof of the existence of Li bond complexes $X \cdots Li-Y$ ($X = NH_3$, Me_3N , H_2O , Me_2O ; $Y = Cl$, Br) was obtained in a matrix isolation IR study in 1975.^[4] The Li bond theory has developed continuously since these reports.^[2,5,6]

Although the Li bond shares some common characteristics with the H bond (Figure 1), they have several distinguishing differences. Firstly, the typical H bond ($X \cdots H-Y$, $X/Y = N, O, F$ etc.) is formed between proton acceptors and donors with saturation and directionality. In contrast, Li is not restricted to the dicoordination case and the Li bond has no saturation or directionality limitations owing to the large radius and metallic nature of Li. X-ray studies show that Li tends to engage in multicenter interactions with donor solvents or ligands.^[2,7] However, some early reports have argued that the designation of the Li bond should specially refer to the dicoordinated $X \cdots Li-Y$ arrangement.^[2,3] Secondly,

the H bond has partial covalent bond character, as confirmed by 1H NMR spectroscopy,^[8] while the Li bond is more electrostatic owing to the metallic nature of Li. Thirdly, the Li bond (e.g., Li_2S_8 @ pyridinic nitrogen in graphene, bonding energy: 0.64 eV) is much stronger than the H bond (bonding energy: 0.04–0.22 eV) because of the larger dipole moment of the Li bond.^[9] Besides, the bonding energy of the Li bond is much smaller than that of typical Li–O (341 kJ mol^{-1}) and Li–F (573 kJ mol^{-1}) bonds, differentiating the former from ionic bonds. Fourthly, while the H bond distances of $H-Y$ and $H \cdots X$ differ significantly, the Li atom in Li bond complexes is more shared between the coordinated atoms.^[5] Fifthly, Li transfer in Li bonds is different from the H transfer in H bonds. As Li is more shared between X and Y, the Li transfer barrier is smaller than that of H, although the Li bond is stronger than the H bond. Besides, compared to H transfer in H bonds, the Li transfer barrier is less sensitive to the properties of X/Y and angular distortion, which is consistent with the greater ionic nature of Li bond.^[10]

One of the most important applications of Li element is in lithium batteries, which power modern portable electronic devices and electric vehicles.^[11] Although Li batteries were developed in the last century and Li ion batteries were commercialized by the Sony Corporation in 1991,^[12] Li bond chemistry was not considered in Li battery research until the 2010s. A fundamental and deep understanding of lithium bond chemistry in batteries is crucial for building safe, high-performance Li batteries. Additionally, Li battery research can promote the development of Li bond theory. In 2015, Goodenough and co-workers^[13] explained the interaction between Li polysulfides (LPSs) and electron-donating functional groups in a polymer matrix in terms of the Li bond, which is supposed to resist the dissolution of LPSs in electrolytes and thus ease the shuttle effect in lithium–sulfur (Li–S) batteries. Furthermore, Li bond chemistry in Li batteries was comprehensively proven for the first time by

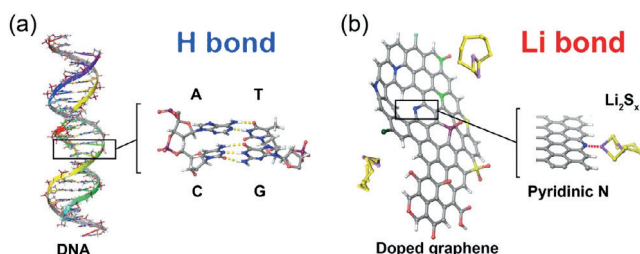


Figure 1. Schematic diagrams of a) H bonds in deoxyribonucleic acid (DNA) and b) Li bonds in Li–S batteries. Reproduced with permission.^[9] Copyright 2017, Wiley-VCH.

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Zhang and co-authors through density functional theory calculations and experiments, including geometrical structure, bonding energy, Bader charge, dipole moment, and experimental/theoretical ^7Li NMR analyses.^[9,14] The Li bond between LPSs and electron-rich donors (e.g., pyridinic nitrogen) was validated as a dipole–dipole interaction. It is worth noting that the formation of the Li bond induces an upfield shift of the ^7Li signal to lower field in the NMR spectrum, which is also a typical characteristic of H bonds. Li bonds have been widely used to explain the interactions between LPSs and sulfur hosts.^[15]

Although Li bonds in batteries were initially evoked to understand the host–guest interactions in sulfur cathodes, they may also be applied to Li-containing clusters in batteries, the Li solvation structure in liquid electrolytes, and Li nucleation in Li metal anodes (Figure 2). Further, it is argued that the analogy between Li and H bonds is not appropriate in the solution and solid states as Li is solvated or associated, and considerations of the Li bond should be limited to the three-center $\text{X}\cdots\text{Li}\cdots\text{Y}$ model. The concept of the Li bond allows us to understand the nature of bonding involving Li in these cases.^[2] Nevertheless, the rationality of such design limitations to dicoordinated Li are still being debated. Therefore, it is reasonable to explain the nature and behavior of Li bonds in batteries using the Li bond theory, and gain insight into fundamental Li chemistry in batteries.

In sulfur cathodes, S_8 molecules are reduced to produce various LPSs ranging from Li_2S_8 to Li_2S_2 . In these LPSs, Li can coordinate with two or even more S atoms (Figure 3). Although different structures have been reported for the

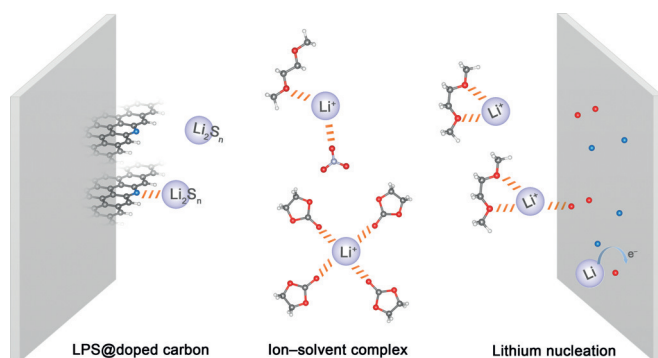


Figure 2. Schematic representation of the Li bond in Li batteries. LPS: Lithium polysulfide.



Qiang Zhang received his Bachelor's and PhD degrees from Tsinghua University in 2004 and 2009, respectively. After a stay at Case Western Reserve University (USA) and the Fritz Haber Institute of the Max Planck Society (Germany), he joined the faculty of Tsinghua University in 2011. His current research interests are advanced energy materials, including Li metal anodes, solid-state electrolytes, Li–S batteries, and electrocatalysts.

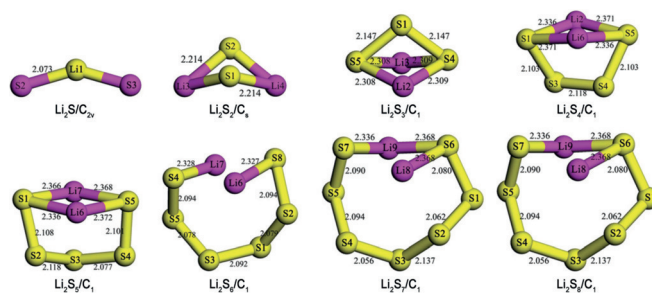


Figure 3. Optimized structure of Li_2S_x ($1 \leq x \leq 8$) clusters. The Li–S and S–S bond lengths (in Å) are also provided. Reproduced with permission.^[16] Copyright 2013, Elsevier.

same LPS and it is not easy to determine the ground state,^[16–18] the S–Li–S interactions in polysulfide clusters can be explained by Li bond theory, similar to intramolecular H bonds. The stability of LPSs is strongly associated with the Li bond. For example, compared to linear Li_2S_8 , cyclic Li_2S_8 can form more Li bonds and is predicted to have a lower energy under various conditions, including under vacuum and in tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO).^[19] Besides, the lack of saturation and directionality of Li bonds results in tremendous structural diversity for LPSs. LPSs and Li_2S can even form complicated clusters connected by Li bonds, which can further regulate the physical and chemical properties of LPSs and Li_2S .^[18] For example, lower order polysulfides prefer to form large clusters in electrolytes, resulting in their poor solubility. In contrast, higher order polysulfides show good solubility as the LPS–solvent interactions are increased, and the interaction between Li and polysulfide anions is weakened.^[20] Consequently, the Li bond can regulate the structure and clustering behavior of LPSs as well as their interactions with sulfur hosts and electrolytes, similar to organolithium compounds. Besides sulfur cathodes, the Li bond is also expected to explain the interaction between Li and organic cathodes in Li ion batteries and provide insights into the charge/discharge mechanisms.

In aqueous solutions, numerous H bonds exist between water molecules, and proton transfer via the H bond has a low barrier, which explains the high proton conductivity. This situation is different for Li bonds in solutions. Li ions are often solvated by several solvent molecules. Li can coordinate with up to six atoms from solvents or anions and it is hard to designate a Li bond in Li^+ solvation structures. However, the concept of the Li bond can help understand the interaction between Li^+ and coordinated solvents/anions, and explain Li ion diffusivity and regulate electrolyte stability. Although Li^+ transfer in a Li bond is easier than proton transfer in a H bond, such Li^+ transfer has a small contribution to the Li ion conductivity in electrolytes. A large Li bond energy also prevents the exchange between solvents in the Li ion solvation shell and free solvents in electrolytes, impeding Li ion diffusion. Besides Li ion diffusivity, the Li bond can also regulate electrolyte stability by forming ion–solvent complexes, which can lower the lowest unoccupied molecular orbital (LUMO) energy level of solvents and thus promote the decomposition of the electrolytes.^[21] The role of the Li

bond in regulating electrolyte stability can be explained by two mechanisms in ester and ether electrolytes.^[22] In ester electrolytes, the coordinated Li can regulate the contribution of the carbon atomic orbital to the LUMO to decrease the LUMO energy level. In ether electrolytes, the coordinated Li can completely change the composition of LUMO and also decrease the energy level. Simultaneously, the coordination with Li lengthens the C–O bond in both ester and ether solvents. The decreased LUMO energy level and stretched C–O bond indicate that the solvents can acquire electrons from the anode with ease and electrolyte reduction is promoted. Different from dilute electrolytes, anions participate in the solvation shell of Li ions and change the Li bonding in the solvation structure in concentrated electrolytes, which can further regulate the electrolyte stability.^[23] Besides, anions such as NO_3^- can connect two Li ions and thus produce multicenter complexes.^[24] The role of anions in the Li^+ solvation shell and the regulation of electrolyte–anode interface is an interesting topic in batteries and requires further investigations. Therefore, the Li bond offers an opportunity to understand Li–solvent/anion interactions in electrolytes.

The H-bonding network plays an important role in promoting hydrogen and oxygen evolution in solutions.^[25] The Li bond is similarly expected to regulate Li conversion in batteries. In Li metal anodes, Li stripping and deposition are strongly related to Li bond evolution. During Li^+ reduction, Li^+ from the electrolyte loses contact with the solvent gradually, obtains electrons from the anode, and forms new bonds with the anode framework simultaneously. A dedicated framework can induce a different interaction with Li and thus regulate Li nucleation, resulting in varied nucleation and deposition overpotentials. For instance, heteroatom-doped carbon materials, such as N-doped graphene, are often used as Li metal anode frameworks.^[26] Different doping atoms and functional groups have different affinities with Li and this difference can be explained by lithiophilicity chemistry, in which the fundamental interaction between nucleated Li and the anode host is the key issue (Figure 4).^[27] Therefore, the Li bond supposedly regulates Li conversion in Li batteries.

Previous studies on the Li bond have mainly focused on lithium halides or organolithium systems. Even among recent reports of Li batteries, the existence of the Li bond is only proven in the LPSS–host case. A comprehensive investigation of Li bonds in batteries must include organic cathodes,

electrolytes, and Li metal anodes. In this aspect, the Li bond theory for Li batteries is still being developed and requires further research. Firstly, a clear designation of the Li bond in batteries should be achieved, including comparison with H bonds and the differences between Li ionic bonds and metallic bonds. Then, geometrical and electronic structures and related properties of Li bonds in various cases should be studied carefully, based on which the role of Li bond in Li batteries may be understood. Thus, a well-established Li bond theory in batteries can shed light on the Li working mechanism in batteries and enable the fabrication of a safe, high-performance Li batteries.

In conclusion, we have briefly summarized the historical development of the Li bond. Especially, the similarities and differences between the Li and H bonds were discussed. Subsequently, the Li bond was described in the context of Li batteries, including discussions of sulfur cathodes, liquid electrolytes, and Li metal anodes. Such discourse on the chemistry of the Li bond can provide fruitful insight into the fundamental interactions within Li batteries and thus deliver a deeper understanding of their working mechanism. Nevertheless, further investigations are necessary for a comprehensive understanding of Li bond chemistry, including its clear designation, geometrical and electronic structures, features that differ from other bonds involving Li, and their typical functions in Li batteries.

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Conflict of interest

The authors declare no conflict of interest.

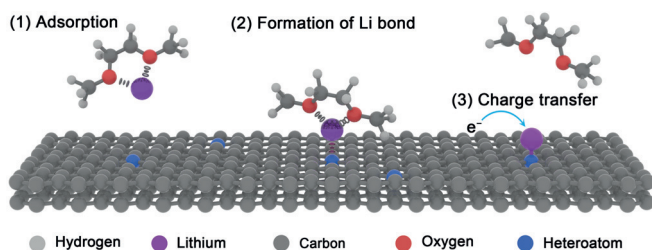


Figure 4. Schematic representation of Li nucleation on a conductive framework. Li bond evolution plays an important role in regulating the Li nucleation process. Reproduced with permission.^[27] Copyright 2019, AAAS.

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