Lithium interaction with polyaromatic hydrocarbons and properties of lithium solvated electron solutions

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2019

Liu, Z. (2018). Lithium interaction with polyaromatic hydrocarbons and properties of lithium solvated electron solutions. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/106506>

<https://doi.org/10.32657/10220/48104>

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**LITHIUM INTERACTION WITH
POLYAROMATIC HYDROCARBONS AND
PROPERTIES OF LITHIUM SOLVATED
ELECTRON SOLUTIONS**

LIU ZHIHAO

**SCHOOL OF MATERIALS SCIENCE AND
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ELECTRON SOLUTIONS**

LIU ZHIHAO

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

06/may/2019

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

06/may/2019

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Authorship Attribution Statement

This thesis contains materials from papers published in the following peer-reviewed journals where I was the first author or co-author.

Chapter 4 contains materials published at journal ACS Omega with title "Electrochemical Properties of Anthracene-Based Lithium-solvated Electron Solutions" with DOI 10.1021/acsomega.8b03621.

The contributions are as follows:

- I co-designed the study with Prof Su Haibin and Prof Andrew.
- Andrey.V. Luncheva performed the experiments;
- I performed the DFT calculation and analysed the experimental data;
- I modelled the properties of the solutions and prepared the manuscript;
- Prof Su Haibin, Prof Rachid and Prof Andrew injected ideas on the topic revised the manuscript.

06/may/2019

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Abstract

Lithium batteries have been widely used in handheld consumer devices and electric vehicles for their high energy density and portability. They also produce relatively less pollution compared with traditional batteries. To improve their performance, a lot of attentions have been paid to the fundamental level of lithium batteries, especially the properties of anode materials. Current anode materials include solid-state and semi-solid state materials like graphite, carbonaceous materials and alkali metals. However, these materials either have safety problem or have slow recharge rate. In addition, performance of batteries based on these materials is reaching a limit. Recently, researcher has found that lithium solvated solutions (LISES) based on polyaromatic hydrocarbons (PAH) could be achieved by adding metallic lithium to tetrahydrofuran (THF) solution of PAH. These solutions have been proved to have potential application in rechargeable lithium batteries for their low cost, fast recharge rate and good safety. We modeled the interactions between lithium atoms and PAH molecules in the solutions using density functional density theory (DFT) and studied the properties of LISES based on various PAH species. The interaction of lithium atoms with anthracene, p-terphenyl and triphenylene monomers is correlated with the open circuit voltage (OCV) and conductivity of the solutions. Interactions between lithium atoms and anthracene, p-terphenyl and triphenylene clusters were studied to predict the behavior of the systems when depositing lithium into corresponding solids and highly concentrated LISES. The interactions between lithium atoms and nitrogen substituted biphenyl, naphthalene, anthracene were studied to understand the effect of nitrogen in the PAH on the properties of corresponding LISES. The investigation shows LISES could be a good anode material for lithium batteries by increasing lithium loading and reducing electron affinity of the PAH and molecular modeling could be a powerful tool to find better PAH alternatives.

Lay Summary

Lithium batteries have been a very popular power resource for portable devices like laptops, hand phones, calculators and so on. The advantages of lithium based batteries over other batteries are their high energy density, light weight and low pollution. It is an important topic to design new lithium based batteries with higher performance. One potential anode material for good lithium batteries was found to be lithium solvated solutions (LISES) based on polyaromatic hydrocarbons (PAH). The solutions were made by adding metallic lithium to tetrahydrofuran (THF) solution of the PAH. In this research project, we studied the interactions between lithium atoms and PAH molecules in the solutions with usage of density functional density theory (DFT) and the properties of LISES based on various PAH species. The interaction between lithium atoms and anthracene, p-terphenyl, triphenylene monomers or clusters were investigated to enhance understanding of provide guidance on designing more promising LISES. The interactions between lithium atoms and nitrogen substituted biphenyl, naphthalene, anthracene were also studied to understand the effect of nitrogen in the PAH on the properties of corresponding LISES.

Acknowledgements

This research project would not have been possible without funding from Ministry of Education of Singapore. I would like to thank my research project supervisors, Prof Su Haibin and Prof Dong Zhili for their helpful and inspiring guidance on my project. I am grateful Prof Andrew and Prof Rachid for their supports on my work. I appreciate the help from the discussion with my colleagues, Lu Yihua, Wu Can, Zhou Feng and Wang Qiang. I was fortunate for the generosity of Andrey.V. Luncheva for sharing his experimental data with me.

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List of Abbreviations

LISES	lithium solvated electron solution
THF	tetrahydrofuran
PAH	polyaromatic hydrocarbon
DFT	density functional theory
OCV	open circuit voltage
MPM	mol percentage of metal
MNMT	metal-nonmetal transition
LDA	local density approximation
GGA	generalized gradient approximation
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital

Chapter 1

Introduction

Lithium based battery has been widely used in many applications. It is an important power resource for portable devices. The performance of the lithium battery is determined by the properties of the electrode and electrolyte. A major limiting factor is the anode material. Lithium solvated electron solutions (LISESs) with metallic lithium dissolved in tetrahydrofuran (THF) solution of polyaromatic hydrocarbon (PAH) have potential application in rechargeable lithium battery as liquid anode. We aim to investigate the properties of the LISESs based on various types of PAH and model the interactions between lithium atoms and PAH molecules using density functional theory (DFT). In this chapter, we presented our motivations, objectives and major discoveries.

1.1 Problem Statement

Lithium based batteries play an irreplaceable role in today's information age. They are widely used in various portable devices like laptop, hand phone, calculator, cameras and so on. Another important application of lithium batteries is that they are used in power tools like saws and whipper-snipers. Also, they have a wide-spread usage in electric vehicles such as aircraft and electric cars[1]. Each year, more than 1 billion lithium cells are manufactured[2]. Lithium and lithium based batteries are so attractive because of the unique advantages of lithium over other metal elements. The electronegativity of lithium is 0.98 based on the Pauling scale[3] and this makes it the least electronegative metal. Meanwhile, lithium is the lightest metal. These two fantastic properties make lithium a promising material to be the anode for high energy density battery.

Since the first assembly of primary lithium cell in the 1970s[4], researchers have put in a lot of efforts to improve the performance of the lithium based batteries[5–7]. At the applied level, researchers tried to modify the electrodes and electrolytes of the lithium based batteries. For example, carbonaceous materials like graphite was proposed by a group of Japanese scientists as the anode intercalation host[8, 9]. The problem of dendrite formation of metallic lithium anode[10–12] was solved and the idea of lithium ion battery was introduced. Also, new types of electrolytes like the polymer electrolyte was introduced[13]. At the fundamental level, the coordination of lithium cations [14] with the host, lithium cation solvation and diffusion in organic solutions[15] and a lot of others were studied[16–18]. The coordination number of lithium ion and corresponding structure minimal radius of enclosed cavity formed by the solvent molecules change with solvent species. Lithium cations favour to be solvated by organic solvent with high dielectric constant and diffuse faster in solvent with low viscosity and so on. Researchers also build models to understand the performance of lithium based batteries[19–22].

The properties of the anode material plays a crucial role in the performance of lithium based batteries. The open circuit voltage (OCV) and its electric conductivity of the material are two of the key factors to evaluate the performance of the material as anode. The OCV of the material directly determines the power supply and energy capacity. A larger electric conductivity of the material allows energy stored in the electrodes of the batteries to be released at a faster speed and hence increases the power output of the batteries. Current research interests mainly focus on solid-state such as graphite, carbonaceous materials and carbon-silicon composites[2, 23–26]. Alkali metals like lithium and sodium were applied in semi-solid redox flow batteries[27–29]. However, the semi-solid lithium flow cells have very poor conductivity so that large quantity of additives was required to improve the conductivity. While those solid-state anode material such as metallic lithium has slow recharge rate and would induce serious safety problem. In addition, the performance of batteries based on these materials is reaching a limit. Recently, a liquid-state material, lithium solvated electron solutions (LISES) based on polyaromatic hydrocarbon (PAH) has been found to have potential application in rechargeable lithium batteries[30–32]. The solutions were made by dissolving metallic lithium into tetrahydrofuran (THF) solution of PAH.

In this work, we extent the study of LISES in Ref. 30 and 31. We studied the properties LISES based on various PAH with more benzene rings (anthracene, p-terphenyl and triphenylene) and PAH with carbon atom replaced by nitrogen atom and modelled the interactions between lithium atoms and corresponding molecules. Anthracene, p-terphenyl and triphenylene were chosen to see the whether the sigma bond between benzene rings and number of benzene rings would affect the properties of LISES. Another practical reason is that they are of low cost, which is also an important factor for anode material. The study helps us to understand the behaviour of LISES from molecular perspective and to find a solution to improve the reduction potential and conductivity of LISES.

1.2 Research Scope

The aim of this research project is to model the interaction between lithium atoms and PAH molecules and study the properties of LISES based on corresponding PAH species. The project deals with anthracene, p-terphenyl and triphenylene, as well as phenylpyridine, nitrogen substituted naphthalene and anthracene. We studied the interactions between lithium atoms and PAH monomers in dilute LISES solutions based on anthracene, p-terphenyl and triphenylene and correlated the binding properties to the OCV and conductivity of the solutions; investigated the interactions between lithium atoms and clusters formed by anthracene, p-terphenyl, triphenylene molecules in concentration solutions or solids; and predicted the effect of nitrogen atoms on the properties of corresponding LISES by modeling the interaction between nitrogen substituted biphenyl, naphthalene and anthracene.

For PAH monomers, the geometrical structures of the Li-PAH adducts with different lithium positioning were obtained for anthracene, p-terphenyl and triphenylene. The binding energy between lithium atoms and PAH molecules was calculated and molecular orbitals of the systems were investigated. The cell reaction during OCV measurement was modelled as a binding process of lithium atoms to PAH molecules. The internal energy change of the system was compared with the enthalpy change measured from experiment. The molecular orbitals of the adducts was analysed to study the electronic structures of the systems. Dissociation of lithium cation from the Li-PAH adducts was studied and applied to conductivity analysis.

Formation of clusters in highly concentrated LISES and solids was studied for anthracene, p-terphenyl and triphenylene. The interactions between lithium atoms and clusters with 2 and 3 PAH molecules were modeled and compared to understand the deposition of lithium into corresponding solids and concentrated

LISES. The geometries reveal the way lithium atoms bind to the clusters and binding energy characterizes the binding strength.

For the effect of nitrogen atom, we compared the properties of the phenylpyridine based LISES with biphenyl based LISES and studied the binding properties between lithium atoms and phenylpyridine or biphenyl molecules. The properties of nitrogen substituted naphthalene and anthracene were also theoretically investigated to predict the properties of the corresponding LISESs.

1.3 Dissertation Overview

Chapter 1 provides an introduction of the research, including the rational, scope and an overview.

Chapter 2 reviews some literature concerning the background of the research project. It includes the concept of solvated electrons, interactions between lithium atoms and ammonia molecules in lithium-ammonia solutions, properties of biphenyl and naphthalene based LISESs. This chapter provides a basis insight to the systems studied in the research.

Chapter 3 presents the computational and theoretical methods applied in the subsequent chapters. For computational methods, We introduced the basic concept of density functional theory, the M06 functional and SMD model for solvent effect. For theoretical analysis, introduced the ion transport and electron transport which contribute to the conduction of the LISESs based on PAH.

Chapter 4 discusses the interactions between lithium atoms and various PAH monomers and the electrochemical properties of the corresponding LISESs. We studied the binding and electronic properties of the Li-PAH adducts and correlated it to the LISESs properties.

Chapter 5 discusses the interaction between lithium atoms and PAH clusters. It deals with the formation of clusters in highly concentrated LISESs and solids and binding of lithium atoms to the clusters.

Chapter 6 discusses the effect of nitrogen atom on the systems. We compared the properties of phenylpyridine based LISESs with biphenyl based LISESs. The binding properties and electronic structures of the systems were investigated and compared. We extend the study to nitrogen substituted naphthalene and anthracene to predict the properties of corresponding LISESs.

Chapter 7 is an overall discussion of the whole thesis and some future works.

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Chapter 2

Literature Review

In this research project, we focus on the LISEs based on various types of PAH and the interaction between lithium atoms and PAH molecules. This chapter reviews the concept of solvated electrons, interaction between lithium atom and ammonia molecules in lithium-ammonia solution and properties of LISEs based on biphenyl and naphthalene to give an insight on background of our research work.

2.1 Solvated Electron

A solvated electron, as its name suggests, is a free electron solvated in a solvent. It is the smallest possible anion. The lifetime of solvated electrons is usually very short in most solvents[1], hence making it very difficult to observe them directly. Since the discovery of solvated electron, lots of attention has been paid to this phenomenon[1–10]. The most widely discussed solvated electrons were electrons solvated in liquid ammonia because they have a relatively long stable time, a few days[10–13]. In fact, solvated electron is a very common phenomenon. Other than ammonia, it also occurs in many other solvents that mediate outer-sphere electron transfer. For example, excess electrons in water is another type of solvated electrons that are frequently mentioned[5, 6, 14–17].

The earliest description on the nature of solvated electron was made by Kraus around a century ago[18]. He dissolved alkali metals in liquid ammonia and studied the properties of the solutions. With careful investigation, the primary charge carrier which leads to electric current in the solutions was determined to be a new specie of ion. The ion is of negative charge and massless by chemical standards. Soon after that, the term "solvated electron" appears[2] and received lots of attention because of their fantastic physical and chemical properties. Researchers studied on the spectrum of the metal-ammonia solution, discovered the transition of liquid electrolyte to liquid metal induced by composition of the solutions and noticed the liquid-liquid phase separation in the solutions. On the theory level, models that describes residential and motion of the electrons were established[19–26].

When small amount alkali metal is dissolved in ammonia solvent, the solutions express a blue colour. The absorption spectra of the ammonia solutions shows the same peak at 0.85 eV with a tail extending into the visible range when different alkali metals were used, which suggests that the blue colour of the solutions was not caused by the metals. Scientist further changed solvents into methylamine or

ethylamine, and the spectra was found to produce the same blue colour, which suggests that the blue colour was also not caused by the solvent species. Indeed, it is due to the common specie in these different solutions, solvated electrons[27, 28].

The amount of metal added to the solution would greatly affect the characteristics of the solutions. Considering the lithium ammonia solution as an example, it saturates at around 16 mol percentage of metal (MPM). At low MPM, the solution exhibits a blue colour[19, 20]. It expresses paramagnetic properties. When MPM is increased to 0.5, all electrons in the solution are paired up, hence producing a diamagnetic material. When amount of lithium increases to 4 MPM, the liquid-liquid phase separation would be observed as shown in Figure 2.1. A new gold-colour phase would appear. The newly formed phase has lower density than the original blue-colour phase and the two phases are immiscible, which results in the phenomenon referred as phase separation[22, 23]. When the lithium amount increases further to 8 MPM, the solution expresses a gold colour. In many aspect, the solution behaves like liquid metal and this phenomenon is referred as "metal-nonmetal transition" (MNMT)[21].

Lithium ammonia solutions

FIGURE 2.1: The colour of dilute lithium ammonia solution, phase separation and concentrated lithium ammonia solution[29].

Another interesting phenomenon about the solution is its large volumetric expansion accompanied with dissolution of metal. The phase separation phenomenon suggests that the density of the gold-colour phase is lower than the blue-colour

phase. In deed, the density difference of the two phases is as large as 30% in the same concentration range. The large volumetric expansion is associated with the molecular structures of the solvated electrons. In ammonia solutions of alkali metals, the metal atoms dissociates into metallic cations and electrons through the process

The resulted cations are solvated by ammonia molecules and the resulted electrons reside in a cavity form by ammonia molecules with radius around 3 Å[30] as illustrated in Figure 2.2.

FIGURE 2.2: Schematic representation of the solvated electron in dilute lithium-ammonia solutions[26]. The solvated electron has a 1s-like wave function which is delocalized over the solvation shells of ammonia molecules. The radial probability distribution of the electron is qualitatively described by the lower part of the figure[31].

The optical spectrum of the solution is caused by the transition of the solvated electron from its 1s orbital to 2p orbital. The surrounding ammonia molecules on the solvation shells, especially on the first solvation shell, were polarized by the electron in the cavity. This model of solvated electrons developed by Jortner

also provides an explanation on the large expansion of volume when alkali metal was dissolved in liquid ammonia with the solvation process illustrated in Figure 2.3.

FIGURE 2.3: Schematic description of electron solvation process in meta-ammonia solutions[26]. a. Normal ammonia structures with molecules bonded by hydrogen bonds; b. Cavity formed by ammonia molecules surrounding vacancy defect; c. Trapping of electron in the vacancy cavity; d. Solvation shell redistribution to minimize Bjerrum effect.

In the metal-ammonia solutions, there initially exists normal liquid ammonia structures where the molecules are bonded by hydrogen bonds. Cavities of vacancy defect are also formed in the solution. The electrons produced from dissociation of metal atoms in the solution is then trapped by the vacancy cavities. This trapping process does not cause any volumetric change of the solutions, but the subsequent solvation shell redistribution does. With a negatively charged electron in the cavity, the ammonia molecules on the solvation shell would be highly polarized. The polarization process creates high energy Bjerrum defects due to proton-proton interaction. To minimize the Bjerrum effect, some ammonia molecules would be excluded from the solvation shell, leading to a much looser structure[32, 33]. The loosening effect of the solvation shell in the solutions accounts for the large volume expansion during the solvation of alkali metals.

The location of the solvated electrons in cavities also captured researchers' interests. The lower part of Figure 2.2 qualitatively describes the distribution of the electrons over the solvation shells. A more detailed study on the location of the solvated electron inside the cavity enveloped by ammonia molecules was presented in Figure 2.4. It explicitly shows probability distribution of the solvated electron over a distance r from the cavity center. The probability distribution exhibits a hill-like shape. It suggests that the electron is never at the center of the cavity. Instead, it is most likely to be located at a distance around 3.8 Å from the cavity center, which lies between the nitrogen and hydrogen atoms.

FIGURE 2.4: The normalized probability distribution of solvated electron over a distance r from center of the cavity[35].

An investigation on the excess electron in water reveals interesting electron distribution. Figure 2.5 presents the iso-surface of the reduced electron density for various water clusters which carrier an excess electron. The structures labelled as 12b, 13a, 20e, 20f and 24b are identified as dipole bound states where the electron cloud associated with the excess electron mainly locates at the surface of the water clusters. The electron interacts electrostatically with the substantial dipole moment of the clusters. The 24c and 24d structures were determined to be cavity bound states where the electron cloud locates inside the cavity enveloped by the water molecules. Some other structures have their electron cloud located

outside the cavity while charge of the systems was found to be distributed inside the cavities.

FIGURE 2.5: The distribution of excess electron in various water clusters[34]. The Iso-surface of the reduced electron density were obtained from CI wave function. The label of the structures indicates the number of water molecules in the cluster.

The transport of solvated electrons in the solution is a complicated process. The mechanism differs with its solvent species. When solvated in liquid tert-butanol, the solvated electrons were found to propagate by a hopping mechanism with a mobility of $\mu_e = 4.1^{-8} m^2 V^{-1} s^{-1}$. While solvated in ethanol and methanol, the electrons behave like ions and diffuse through the solution[35]. In some other solvent, the electrons were firmly trapped by the solvent molecules and propagate by tunnelling mechanism[27].

Naturally, solvated electrons are good electron donor and usually used as reducing agents. When it react with oxygen, super-oxide radical could be formed[36]. When interacting with nitrous oxide, hydroxyl radicals would be produced[37]. Other example of usage of solvated electrons are Birch-reduction where sodium-ammonia solution is involved and Bouveault–Blanc reduction where sodium-ethanol solution is used.

To better understand solvated electron solutions, we will introduce the interaction between lithium and ammonia in lithium-ammonia solution so that we could have a closer look at what is taking place in the solution. Also, a new type of solvated electron solution which is based on THF solution of PAH will be introduced.

2.2 Li-Ammonia Interaction

Lithium-ammonia solution has been studied by many researchers[24–27, 38–40]. It was noticed that Hoffmann has performed a systematic study on the properties of lithium-ammonia solution. The physical and chemical properties of lithium-ammonia solution was reviewed, which enhance our understanding of solvated electrons. The lithium-ammonia interactions in the solution were investigated at molecular level with DFT calculation, which provide a guidance for us to study the interaction between lithium and various polyaromatic hydrocarbons. In this section, we would review the interaction between lithium and ammonia molecules in the solution.

Hoffmann’s study on the lithium-ammonia solution begins with the properties of ammonia. He then explore the solvated lithium cation, solvated neutral lithium atom, and solvated electron as well as the aggregations of the basic structures in the Lithium-Ammonia solutions which will not be addressed here. He carefully examined the geometry structure, binding properties and molecular orbitals for those species.

Ammonia serves as the solvent in lithium-ammonia solution. A picture of the eight valence electrons and the a_1 orbitals of ammonia is presented in Figure 2.6. The valence electrons fill four orbitals, $1a_1$, $1e$ and $2a_1$, with coupled spin and leave three higher orbitals empty.

FIGURE 2.6: A valence-electron basis picture of ammonia[27]. The left column is the orbital occupation with the spin of the eight valence electrons and three empty orbitals; the middle column is the traditional iconic representations; the right column is the calculated contour diagrams of the a_1 orbitals.

The ionization energy of ammonia was determined to be 10.85 eV[41]. For ammonia, there exists two excited states below this ionization energy which are results of transitions of electron from the $2a_1$ orbital to the empty orbitals $3a_1$ and $2e$.

Among the valence electrons of ammonia, the electrons in a_1 orbital are of crucial importance as they are responsible for the interaction between lithium and ammonia. The right column presents the calculated contour diagrams of this a_1 orbitals. It is mainly contributed by the $2s$ orbital of the nitrogen atom. The $2a_1$ orbital exhibits a $2p_z$ shape, $3a_1$ exhibits a $3s$ shape of the united atom, which agrees with the characteristics discovered by K. S. Pitzer[42].

Ammonia, being a polar molecule, form hydrogen bonds between the molecules. With the solvation of lithium cation, neutral lithium atom and electron, some of the hydrogen bonding in ammonia liquid would be broken and new bonds

FIGURE 2.7: Optimized geometries of two ammonia molecules with hydrogen bonding[27]. ΔE are the energy change for dimer formation $2NH_3 \rightarrow (NH_3)_2$ in gas phase and solution phase.

would be formed. An illustration of the hydrogen bonding between two ammonia molecules was presented in Figure 2.7. The angle formed by H1, N1 and N2 is found to be 8.7° , smaller than value reported by Marx[43]. The hydrogen bond length is $2.47 \text{ \AA}$. The negative value of ΔE indicate that the dimer structure is more stable than isolated ammonia molecules. The difference of ΔE between gas phase and solvent phase comes from the solvation energy.

When lithium is dissolved in ammonia, its sole valence electron is ionized into the solvent. This process results in the many species existing in the lithium-ammonia solution. For the lithium cation, it forms different structures with various number of ammonia molecules. The geometries of these lithium cation-ammonia structures are presented in Figure 2.8. It was also shown that the lithium-nitrogen bond distance increases slightly with increasing ammonia molecules coordinated to the lithium cation. Also, from the geometries, it is noted that when the number of coordinated ammonia molecules increases up to 5, the fifth ammonia molecule is at a long distance from the lithium cation. This indicates that the fifth ammonia molecule is only weakly associated to the lithium cation and the corresponding structure is not stable.

An investigation on the binding energy of the structures shows that the binding energy per lithium-nitrogen bond decreases with ammonia molecule number n . This is consistent with the increasing bond length shown in Figure 2.8. When number of coordinated ammonia molecule increases, the binding strength between

FIGURE 2.8: Optimize geometries of $\text{Li}(\text{NH}_3)_n^+$ with $n =$ varies from 1 to 5. The Lithium Nitrogen bond distance are provided for gas phase[27].

lithium cation and nitrogen atom becomes weaker with longer bond length. In solvent phase, an increase in the total binding energy was noticed when the coordination number increase from 4 to 5. It implies that there exists an barrier for the binding process and the $\text{Li}(\text{NH}_3)_5^+$ structure is not stable. In the solution, various lithium cation structures coexist while the dominant specie in the solution has been verified to be $\text{Li}(\text{NH}_3)_4^+$ [24, 25, 44, 45].

As introduced in the previous section on the concept of solvated electrons, 2s electron of lithium atoms would be trapped by a cavity form by ammonia molecules. The capture of the electron leads to ammonia anions (NH_3^-). The 2s electron of lithium atom would fill the $3a_1$ orbital which is empty for ammonia molecules as shown in Figure 2.6.

The calculation of the $[\text{e}^-(\text{NH}_3)_n]$ cluster was performed for $N = 1 - 14$. Figure 2.9 shows the optimized geometries with $n > 5$. With ammonia molecules in the range of 5-8, the structures exhibit a single cavity. When n exceeds 8, ammonia molecules starts to appear inside the cavity, which means the structures could be treated as combination of several cavities. For the cavities with less than 5 ammonia molecules, an examination on the energy of cavity formation shows

FIGURE 2.9: The geometrical configurations and symmetries of electron cavity clusters with number of ammonia molecules ranging from 5 to 14[27].

they are not stable. The optimal number of ammonia molecules on the cavity was suspected to be 5-8.

In the lithium ammonia solution, there still exists a lot of other coupled structures, formation of ion pairs for example. We would not go into further details on the lithium-ammonia interactions here. These interactions helps to enhance the understanding of solvated electron solutions and provides an insight for us to investigate the lithium polyaromatic hydrocarbon interactions in corresponding LIESE.

2.3 Lithium Solvated Electron Solution Based on Biphenyl and Naphthalene

Recently, researchers have synthesized a new type of solvated electron solution[46]. They used THF as the solvent and polyaromatic hydrocarbons like biphenyl and naphthalene as electron acceptor. Lithium metal was used as electron donor. Biphenyl or naphthalene molecules were first dissolved in THF solvent to form a non-conducting solution. After which metallic lithium was then added to the

solutions to make corresponding PAH based LISES. Such kind of solutions have been found to have potential application in rechargeable lithium battery as liquid anode material. The physical and electrochemical properties of LISES based on biphenyl and naphthalene was studied and reported[46, 47].

The properties of the solutions were affected by a lot of factors. Without adding lithium metal into the THF solution of biphenyl or naphthalene, the solutions were found to be good insulators. And the volume of the solution has been found to increase linearly with the ratio between biphenyl (naphthalene) and THF solvent. When metallic lithium is added into the solutions, they become conductive and the viscosity of the solutions were greatly affected by the amount of lithium and biphenyl (naphthalene) in the solutions. Figure 2.10 presents the viscosity profile of the naphthalene based LISES.

FIGURE 2.10: The viscosity profile of the naphthalene based LISES[47].

It was noticed that the logarithm of the viscosity of the solutions increase linearly with the amount of lithium added into the solutions. While the overall concentration of the solutions is another impact factor. The solutions become more viscous as they get more concentrated. The viscosity behaviour of the solutions

resembles that of glass and polymers which are amorphous materials. It follows the Arrhenius Law:

$$\eta = Ae^{-\frac{E_a}{kT}}. \quad (2.2)$$

A is a constant which describe the mass transport properties of the system when the transport is barrier-less. E_a is the activation energy which triggers the mass transport in the solutions. The activation energy which leads to non-linear viscosity was resulted from the complicated molecular interactions in the solutions. For instance, electron-electron interactions, electron-dipole interactions and ion pairings.

Biphenyl

Naphthalene

FIGURE 2.11: Electric conductivity of the lithium solvated electron solution against the lithium amount and solvent composition for biphenyl case and naphthalene case[46, 47].

The conductivity of the solutions has been found to depend on the overall concentration of the solutions. Generally, higher concentration (smaller n) would lead to higher carrier density in the solutions, hence higher conductivity. The carrier density would eventually saturate when the concentration is high enough and the conductivity of the solution would not increase further. Another important factor that affects the conductivity of the solutions is the ratio between lithium and biphenyl or naphthalene. The conductivity of the solutions first increases with

the ratio and peaks at lithium-biphenyl (lithium-naphthalene) ratio of 1:1 for dilute solutions and eventually falls. For more concentrated solutions, the peak appear at a ratio between 0.5:1 and 1:1. The researchers also correlated the viscosity increase accompanied with rising lithium-biphenyl (lithium-naphthalene) ratio with the conductivity change and suspected that the larger viscosity of the solutions might account for the downward trend of conductivity. A comparison between the conductivity profile of the LISES based on biphenyl and naphthalene reveals that the two solutions have quite similar conductivity. It varies from a few mS/cm to around $12 mS/cm$ according to the lithium-PAH ratio and overall concentration.

FIGURE 2.12: Conductivity versus temperature profile for Naphthalene based LISES with overall molecular formula $Li_x(\text{naphthalene})(\text{THF})_{10.4}$ [47].

An investigation on the temperature dependence of the conductivity of the solutions based on naphthalene exhibits a metal like behaviour where the conductivity of the solutions decrease linearly with temperature. In the solutions, both ions and electrons are effective charge carriers. The negative temperature dependence suggests that electron transport would be the dominant conducting mechanism

FIGURE 2.13: Open circuit voltage of the naphthalene based Lises with lithium-naphthalene ratio of 1:1[47].

in the solutions. The conductivity was found to be at maximum when lithium-naphthalene ratio is 1:1. This is consistent with the results presented in Figure 2.11. The slope of the conductivity profile also changes with lithium-naphthalene ratio. The most negative slope was achieved at a ratio of 0.5.

Researchers also tested the open circuit voltage of the solutions in half cell experiment where lithium metal was used as the counter electrode. The experiment was designed in such a way that lithium metal was the anode. tested Lises was the cathode and 1M 1:1 EC/EMC solution of LiPF_6 was the electrolyte connecting the two electrode with a ceramic membrane as separator. During the experiment, lithium metal lost its 2s electrons and was dissolved into the electrolyte as lithium cations while the tested Lises received electrons donated by lithium atoms and absorb lithium cations from the electrolyte to form binding adducts. The resulted potential difference from the cell reaction was measured to be the OCV of the Lises. Figure 2.13 shows that the OCV of the naphthalene based Lises decreases with temperature, suggesting a entropy decrease during the cell reaction. The entropy change of the system was determined to be $-290 \text{ JK}^{-1}\text{mol}^{-1}$ which

is much more significant than the lithium-graphite system[48] or lithium-Cobalt Oxide system[49]. The enthalpy change of the system was also obtained at the value of -159 kJ/mol .

2.4 Summary

In this chapter, we reviewed the concept of solvated electrons so that we have a basic idea on its history, fantastic characteristics, and application in experiments. We also reviewed the interaction between lithium and ammonia molecules in lithium-ammonia solutions to enhance our understanding and provide guidance on our investigation on the lithium polyaromatic hydrocarbon interactions. The properties of the LISES based on biphenyl and naphthalene was introduced to provide an overall view on LISES systems based on other PAH species to be studied in the project.

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Chapter 3

Methodology

The research project involves lots of computational work on the interaction between lithium atoms and polyaromatic hydrocarbon molecules. The computations were performed with density functional theory (DFT) with M06 functional. The solvent effect was accounted using SMD model. In the analysis conducting mechanism, the concept of ion transport and electron transport were applied.

3.1 Density Functional Theory

Density functional theory (DFT) is a quantum mechanical modelling method used in physics, chemistry and material science to investigate the electronic structure of many-body systems such as atoms, molecules and condensed phases[1–12]. This microscopic first-principle theory introduced a exchange-correlation term in the functional of electronic density. Through usage of functional, which describes the spatial distribution of electron density, the properties of many-electron system could be determined. Contemporary DFT techniques evaluates the electronic structure by using a potential acting on the electrons of the systems where this potential is the sum of the external potential coming from the nucleons in the system and inter-electronic interactions. The n electron problem is indeed treated as a set of n one-electron Schrodinger equations, which is also know as Khon-Sham equations[13].

DFT has been very popular for calculations in solid-state physics since 1970s because of its relatively low computational cost compared with traditional computational methods such as Hartree-Fock theory. It was not until the 1990s, DFT was considered to be accurate for calculations in quantum chemistry[14]. With huge improvements on the approximations used in the theory, the exchange and correlation interactions in the system were modeled in a much better way[15–19].

The calculation of electronic structure of many-body system is carried out with basic quantum mechanical considerations. The stationary state of the system could thus be described by a time-independent Schrodinger equation:

$$H\psi(\mathbf{x}_1, \dots, \mathbf{x}_n; \mathbf{X}_1, \dots, \mathbf{X}_N) = E\psi(\mathbf{x}_1, \dots, \mathbf{x}_n; \mathbf{X}_1, \dots, \mathbf{X}_N), \quad (3.1)$$

where $\mathbf{x}_1, \dots, \mathbf{x}_n$ represent the coordinates of the electrons and $\mathbf{X}_1, \dots, \mathbf{X}_N$ represent the coordinates of the nuclei in the system. The Hamiltonian of the system could be decomposed into five term, the kinetic energy of electrons (T_e) and

nucleons (T_n), the electron-electron interaction energy (V_{ee}), nucleon-nucleon interaction energy (V_{nn}) and electron-nucleon interaction energy (V_{en}). The kinetic energy could be expressed as:

$$T_e = -\frac{\hbar}{2m_e} \sum_{u=1}^n \nabla_u^2; \quad T_n = -\sum_{k=1}^N \frac{\hbar}{2m_k} \nabla_k^2. \quad (3.2)$$

The interaction between nucleon and electron could be treated as the coulomb repulsion or attraction between the charged particles. The interaction energy hence could be written as:

$$V_{ee} = \sum_{u=1}^n \sum_{v>u}^n \frac{e^2}{4\pi\epsilon_0 |\mathbf{x}_u - \mathbf{x}_v|}; \quad (3.3)$$

$$V_{en} = \sum_{k=1}^N \sum_{l>k}^N \frac{Z_k Z_l e^2}{4\pi\epsilon_0 |\mathbf{X}_k - \mathbf{X}_l|}; \quad (3.4)$$

$$V_{en} = \sum_{u=1}^n \sum_k^N \frac{Z_k e^2}{4\pi\epsilon_0 |\mathbf{x}_u - \mathbf{X}_k|}. \quad (3.5)$$

Where Z refers to the number of protons in each nuclei. Considering that the electron mass is negligible compared with the mass of the nuclei, the impact of its motion on the nuclei could be neglected. With the separation of wave function for electrons and nuclei, the problem could be reduced to solve the electron wave function with Hamiltonian at fixed nuclei coordinates (Born-Oppenheimer approximate). The new Hamiltonian is thus:

$$H = \hat{T} + \hat{U} + \hat{V} = -\frac{\hbar}{2m_e} \sum_{u=1}^n \nabla_u^2 + \sum_{u=1}^n \sum_{v>u}^n \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_u - \mathbf{r}_v|} + V_{ext}. \quad (3.6)$$

The first term describes the kinetic energy; the second term describes the electron-electron coulomb interactions in the system while the last term describes the overall effect of nuclei on the electron. The operator $\hat{T}$ and $\hat{U}$ were called the universal operators since they do not change for any n-electron systems. $\hat{V}$ is

highly dependent on the structures of the system. The above many-body Hamiltonian equation could not be separated further into single-particle equations due to the existence of interactions between particles.

The wave function of a multi-fermionic system which satisfies anti-symmetry requirement and Pauli Principle could be approximated by the Slater determinant. Based on this, many methods have been developed to solve the many-body Schrodinger equation. The simplest one is the Hartree-Fock method where the wave function expressed by Slater determinant is substituted into the Hamiltonian equation. The problem ended up with solving n equations. Hartree-Fock method and post-Hartree-Fock methods involve large volume of computation. They have significant disadvantages when the system becomes larger and more complicated.

DFT provides an appealing alternative which is faster and requires less computational efforts. The idea of DFT is to map the many-body system with interactions between electrons to single-body systems by introducing fictitious reference systems with non-interacting electrons and same electron density distribution. A system with normalized wave function Ψ is given by

$$n(\mathbf{r}) = N \int d^3\mathbf{r}_1 \dots \int d^3\mathbf{r}_N \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (3.7)$$

Vice versa, the wave function of the ground state could be derived from the ground state density $n_0(\mathbf{r})$ since the ground state density uniquely determines the potential and properties of the system. This accounts for one aspect of the so called Hohenberg-Kohn theorems. The corresponding wave function Ψ would be a unique function of $n_0(\mathbf{r})$. The ground-state energy of the system is thus

$$E_0 = \langle \Psi(n_0) | \hat{T} + \hat{U} + \hat{V} | \Psi(n_0) \rangle. \quad (3.8)$$

Generally, the contribution of the external potential could be expressed as a function of the electron density $n(\mathbf{r})$:

$$V(n) = \langle \Psi(n) | \hat{V} | \Psi(n) \rangle = \int V(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}. \quad (3.9)$$

Thus the energy of the system could be written in the form of

$$E(n) = F(n) + \int V(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad (3.10)$$

with $F(n)$ being the sum of the kinetic term and electron-electron interaction term. This accounts for another aspect of the Hohenberg-Kohn theorems and $F(n)$ is the so called density functional.

To solve the many-body problem, a reference system without electron-electron interactions was introduced. The energy of the reference system would be

$$E_S = \langle \Psi_S(n) | \hat{T} + \hat{V}_S | \Psi_S(n_0) \rangle. \quad (3.11)$$

In the equation, $\hat{V}_S$ describes the effective external potential consisting of electron-nuclei and nuclei-nuclei interactions. The electrons of the reference system move in $\hat{V}_S$. The Schrodinger equation of the non-interacting system is also called the Kohn-Sham equation and could be solved explicitly.

$$\left[-\frac{\hbar}{2m} \nabla^2 + V_S(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (3.12)$$

To recover the properties of the many-body system, the electron density of the non-interacting reference system is required to be the same as that of the many-body system, $n_S(\mathbf{r}) = n(\mathbf{r})$. The external potential in which the electrons of the reference system move in should account for interaction term, correction to the kinetic energy and exchange correlation potential. A detailed expression of the

single-particle potential could be given as:

$$V_S(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}')e^2}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + V_{xc}(n(\mathbf{r})). \quad (3.13)$$

The first term accounts for the external potential of the original many-body system; the second term accounts for the electron-electron repulsion in the original system and the third term is the exchange correlation which accounts for all many-particle interactions.

The Kohn-Sham equation is much simplified compared with the original Schrodinger equation of the many-body system. The major difficulty is that the exact functional form of the exchange correlation potential is not known. It was noticed that the solution of the Kohn-Sham equation must be self-consistent because the exchange correlation potential depends on V_S and V_S is determined to be a function V_{XC} . This provides a way to solve the Kohn-Sham equation by substituting the ansatz of electron density into V_S and in turn solve the Kohn-Sham equation to obtain an updated electron density. The procedure continues until convergence is reached. In calculation, local density approximation (LDA) or generalized gradient approximation (GGA)[20] is usually used. Both assume that the functional only depends on the electron density at the point under evaluation while GGA takes into account of the gradient effect. In this project, the GGA method is applied.

The functional used in this project was the M06 functional. M06 functional was developed by Zhao Yan and Truhlar in 2008 based on the M05 and VSXC functional[19, 21–24]. There are three key variables for the local part of the functional, spin density (ρ_σ), reduced spin density gradient (x_σ) and spin kinetic energy density (τ_σ) of the system where

$$x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}} \quad \tau_\sigma = \frac{1}{2} \sum_i^{occup} |\nabla \Psi_{i\sigma}|^2. \quad (3.14)$$

In the equation, σ refers to the electron spin angular momentum along any arbitrary fixed axis in space phase.

The M06 exchange functional could be treated as a linear combination of the exchange functional of M05 and VSXC. The expression could be written as

$$E_X^{M06} = \sum_{\sigma} \int dr [F_{X_{\sigma}}^{PBE}(\rho_{\sigma}, x_{\sigma})f(\omega_0) + \varepsilon_{X_{\sigma}}^{LSDA}h_X(x_{\sigma}, z_{\sigma})]. \quad (3.15)$$

$F_{X_{\sigma}}^{PBE}(\rho_{\sigma}, x_{\sigma})$ is the exchange energy density of the PBE[20] exchange model and $h_X(x_{\sigma}, z_{\sigma})$ is a working function in VSXC model. An explicit expression of this function is given by

$$h(x_{\sigma}, z_{\sigma}) = \left(\frac{d_0}{\gamma(x_{\sigma}, z_{\sigma})} + \frac{d_1 x_{\sigma}^2 + d_2 z_{\sigma}}{\gamma_{\sigma}(x_{\sigma}, z_{\sigma})} + \frac{d_3 x_{\sigma}^4 + d_4 x_{\sigma}^2 z_{\sigma} + d_5 z_{\sigma}^2}{\gamma_{\sigma}^3(x_{\sigma}, z_{\sigma})} \right) \quad (3.16)$$

$$\gamma(x_{\sigma}, z_{\sigma}) = 1 + \alpha(x_{\sigma}^2 + z_{\sigma}) \quad z_{\sigma} = \frac{2\tau_{\sigma}}{\rho_{\sigma}^{5/3}} - \frac{3}{5}(6\pi^2)^{2/3} \quad (3.17)$$

The d_i in the equation are working coefficients. $\varepsilon_{X_{\sigma}}^{LSDA}$ describes the approximation of local spin density[25] for exchange:

$$\varepsilon_{X_{\sigma}}^{LSDA} = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3} \rho_{\sigma}^{4/3}, \quad (3.18)$$

and $f(\omega_{\sigma})$ is an enhancement factor for the kinetic energy density with

$$\omega_{\sigma} = \frac{\tau_{\sigma}^{LSDA}/\tau_{\sigma} - 1}{\tau_{\sigma}^{LSDA}/\tau_{\sigma} + 1} \quad \tau_{\sigma}^{LSDA} = \frac{3}{10}(6\pi^2)^{2/3} \rho_{\sigma}^{5/3}. \quad (3.19)$$

The correlation functional of M06 is also based on the M05 and VSXC functional with a different treatment in the opposite and parallel spin. The correlation energy of opposite spins is given by

$$E_c^{\alpha\beta} = \int e_{\alpha\beta}^{UEG}[g_{\alpha\beta}(x_{\alpha}, x_{\beta}) + h_{\alpha\beta}(x_{\alpha\beta}, z_{\alpha\beta})]dr \quad (3.20)$$

with $x_{\alpha\beta}$ and $z_{\alpha\beta}$ defined as

$$x_{\alpha\beta}^2 \equiv x_{\alpha}^2 + x_{\beta}^2; \quad z_{\alpha\beta} \equiv z_{\alpha} + z_{\beta}. \quad (3.21)$$

The first part of the correlation has an explicit expression of

$$g_{\alpha\beta}(x_{\alpha}, x_{\beta}) = \sum_{i=0}^n cC_{\alpha\beta,i} \frac{\gamma C_{\alpha\beta}(x_{\alpha}^2 + x_{\beta}^2)}{1 + \gamma C_{\alpha\beta}(x_{\alpha}^2 + x_{\beta}^2)}. \quad (3.22)$$

For parallel spins, the correlation energy has a similar expression

$$E_c^{\sigma\sigma} = \int e_{\sigma\sigma}^{UEG} [g_{\sigma\sigma}(x_{\sigma}) + h_{\sigma\sigma}(x_{\sigma}, z_{\sigma})] \cdot D_{\sigma} dr. \quad (3.23)$$

The extra term refers to the self-interaction term with expression

$$D_{\sigma} = 1 - \frac{x_{\sigma}^2}{4(z_{\sigma} + 3(6\pi^2)^{2/3}/5)}. \quad (3.24)$$

The total correlation energy of the M06 functional could be determined by adding up the opposite-spin energy and parallel-spin energy[26].

3.2 SMD Model of Solvent Effect

The SMD model was developed by Marenich, Cramer and Truhlar in 2009 to deal with solvation problems[27]. In SMD model, the solvent was treated as continuum dielectric medium with surface tension at the solute-solvent boundary. The model uses full electron density of the solute without defining partial atomic charges and could be applied to any systems with some key characteristics of the material known. In the model, the solvation free energy is decomposed into to main parts, the bulk electrostatic contribution and cavity dispersion contribution.

When the solute is solvated by the solvent molecules, the solute particles are transferred from gas phase to condensed phase. The standard free energy of

solvation could thus be partitioned as

$$\Delta G_S^0 = \Delta G_{ENP} + \Delta G_{CDS} + \Delta G_{conc}. \quad (3.25)$$

The first term represents the electrostatic contribution which consists of electronic, nuclear and polarization components. The nuclear relaxation energy could be neglected when the geometries of the system does not change under transformation of gas-phase to liquid-phase. The second term represents the contribution from solvent cavitation, changes in dispersion and any possible changes in local solvent structures. The third term represents the contribution from concentration change between gas-phase and liquid-phase.

For a homogeneous dielectric medium with relative permittivity ε , the electric potential should satisfy Poisson's equation

$$\varepsilon \nabla^2 \Phi = -4\pi \rho_f \quad (3.26)$$

where ρ_f refers to the free charge density. When the medium is non-homogeneous, the equation is modified into[28]

$$\nabla \cdot (\varepsilon \nabla \Phi) = -4\pi \rho_f, \quad (3.27)$$

which is a generalized form of the Poisson's equation. The reaction field during solvation is a result of polarization of the dielectric medium (solvent) and solute. It could be obtained as the difference of the total electric potential (Φ) and the electric potential of the gas-phase molecule. With the assumption of rigid solute, the solvation free energy from electrostatic interaction could be obtained as

$$\Delta G_{EP} = \langle \psi | H^0 - \frac{e\phi}{2} | \psi \rangle + \sum_k \frac{Z_k e \phi_k}{2} - \langle \psi^0 | H^0 | \psi^0 \rangle. \quad (3.28)$$

where ϕ refers to the reaction field, H^0 and $|\psi^0\rangle$ represent gas-phase electronic

Hamiltonian of the solute and the corresponding eigenstate and $|\psi\rangle$ is the eigenstate of the polarized solute in the solution[29].

The free energy of solvation contributed from the cavitation, dispersion and solvent structure change could be expressed as

$$\Delta G_{CDS} = \sum_k \sigma_k A_k(\mathbf{R}, R_{z_k} + r_s) + \sigma^M \sum_k A_k(\mathbf{R}, R_{z_k} + r_s). \quad (3.29)$$

σ_k and σ^M are the atomic surface tension and molecular surface tension. The solvent accessible surface area (A_k) is jointly determined by the geometry $\mathbf{R}$, the Van der Waals radii R_{z_k} and the radius of the solvent molecules (r_s).

3.3 Carrier Transport

The Carrier transport involved in the project includes ion transport and electron transport in solutions. For ionic transport, the mobility of the ions is correlated to their diffusive properties.

When the solution is exposed to an external electric field, the ions experience an electric force. under the effect of the force, cations in the solutions would move in the direction of electric field while anions would move in the opposite direction. This directional motion of charge carriers in solutions leads to the current in the media. During this directional motion, ions collide with the solvent molecules and the net averaged velocity along the direction of motion is the so called "drift velocity" and is determined as

$$v_d = \frac{1}{2} a \tau_c = \frac{q E_{eff}}{2m} \tau_c. \quad (3.30)$$

With the relation $v_d = \mu E$, the mobility of the charge carrier is indeed $q \tau_c / 2m$. A smaller mass and larger charge of the carrier would both boost the electric mobility while the mean collision time depends on the size of the charge carriers

as well as the density of the surrounding particles. In the solutions, directional motion of carriers under electric field would create an inhomogeneous carrier distribution. More cations would be located at the side to which electric field points to and anions would aggregate on the other side. The drift current caused by electric field and diffusive current due to concentration redistribution could be written as

$$J_{diff} = -Dq \frac{d\rho(x)}{dx} \quad (3.31)$$

$$J_{drift} = q\rho(x)\mu \left(-\frac{dU(x)}{dx} \right) \quad (3.32)$$

respectively. Where D is the diffusion coefficient of the carrier, q is the charge carried by the carrier, $\rho(x)$ is the carrier distribution over space, μ is the electric mobility and $U(x)$ is the potential generated by the applied field. When the system is at equilibrium, the two current would be balanced with $J_{diff} + J_{drift} = 0$ and the distribution of charge carrier follows the Boltzmann distribution

$$\rho(x) = Ae^{-(qU(x)+E)/kT}. \quad (3.33)$$

Where A is a particle population constant and E is the thermal energy level of the charge carrier excluding the electric potential energy due to external electric field. A relation between the electric mobility and diffusion coefficient could be derived as

$$Dq \cdot \left(A \frac{q}{kT} e^{-(qU(x)+E)/kT} \frac{dU(x)}{dx} \right) - qAe^{-(qU(x)+E)/kT} \mu \frac{dU(x)}{dx} = 0$$

$$D = \frac{\mu kT}{q}. \quad (3.34)$$

The diffusion coefficient is related to the viscosity of the solution by Stokes-Einstein relation

$$D = \frac{kT}{6\pi\eta r} \quad (3.35)$$

where r is the effective radius of the charge carriers. The electric mobility of the carrier is thus expressed as the properties of the solution and carrier itself as

$$\mu = \frac{q}{6\pi\eta r}. \quad (3.36)$$

Electron transport consists of many different types of mechanisms like electron scattering, tunnelling and hopping. In this section, we will introduce the scattering process during electron transport which are related to our project.

Electron scattering is a very general phenomenon solid conductors, semiconductors and insulators. The free electrons moving in the materials experience electrostatic forces exerted by surrounding atoms or ions. The original trajectory of the electrons would be deviated due to the electrostatic interactions. The scattering of electrons greatly reduces the average velocity when the materials are exposed to electric field. It acts as a limiting factor in integrated circuits and transistors.

A schematic illustration of the electron scattering process is illustrated in Figure 3.1. In particular, it could be used to understand the working principle of detectors which measure the number of particles (electrons) per unit time scattered into an element of a solid angle in a specified direction. Consider the intensity of the incident electron beam being I , using conservation of particle number, the electrons scattered into a solid angle $d\Omega = \text{area}/R^2 = 2\pi \sin \theta d\theta$ would be

$$dN = I d\sigma = I \left[\frac{d\sigma}{d\Omega} \right] d\Omega. \quad (3.37)$$

where σ is the cross section area with $\sigma = 2\pi b db$. The differential cross section which characterize the collision could thus be express as

$$\frac{d\sigma}{d\Omega} = \frac{b}{\sin \theta_s} \left| \frac{db}{d\theta} \right| \quad (3.38)$$

with θ_s being the angle of scattering and parameter b is called the impact parameter.

FIGURE 3.1: Scheme of electron scattering by a target atom and illustration of solid angle.

To solve the classical coulomb scattering problem, three assumptions were made.

1. Coulomb force exerted by the target atom is central and conservative; 2. The collision is elastic so that energy is conserved during the scattering process; 3. The velocity of incident electrons is relatively low such that the system is non-relativistic. The velocity of the electrons can be expressed as $\mathbf{v} = \dot{r}\hat{r} + r\dot{\theta}\hat{\theta}$. Introduce the angular momentum as

$$\left| \frac{\mathbf{L}}{m} \right| = |\mathbf{r} \times \mathbf{v}| = r^2 \dot{\theta} = l. \quad (3.39)$$

For convenience, $u = 1/r$ is introduced. The energy conservation is thus

$$\frac{1}{2}ml^2 \left[\left(\frac{du}{d\theta} \right)^2 + u^2 \right] + V(r) = E. \quad (3.40)$$

The relation between $d\theta$ and du is obtained as

$$d\theta = \frac{ml}{\sqrt{2m(E - V) - (mlu)^2}} du. \quad (3.41)$$

With initial conditions of

$$\begin{aligned} l &= bv_0; & E &= \frac{1}{2}mv_0^2; & V(r) &= ku; \\ \theta_0 &= 0; & u_0 &= 0; \end{aligned}$$

and boundary conditions of

$$u_{max} = \frac{1}{2b^2} \left[-\frac{2k}{mv_0^2} + \sqrt{\frac{4k^2}{m^2v_0^4} + 4b^2} \right]; \quad \theta_{u_{max}} = \theta_s/2$$

equation (3.34) could be integrated such that the impact parameter is expressed as a function of the scattering angle

$$b^2 = \frac{k^2}{m^2v_0^4} \frac{1}{\sin^2(\theta_s/2)} - \frac{k^2}{m^2v_0^4}. \quad (3.42)$$

By taking the differential form of equation (3.35), we arrived at the Rutherford cross section:

$$\frac{d\sigma}{d\Omega} = \frac{k^2}{16E^2} \frac{1}{\sin^4(\theta_s/2)}. \quad (3.43)$$

The total cross section area obtained by integrating equation (3.43) describes the effective projected area along the path of the electron. The scattering problem could be thought as the deviation of moving direction of the electron if it passes through the effective projective area. An immediate example is the elastic scattering process from a hard sphere. The differential cross section is $\frac{d\sigma}{d\Omega} = \frac{R^2}{4}$. The total cross section area is thus πR^2 , which is exactly the projected area of the hard sphere.

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Chapter 4

Lithium Interaction with Anthracene, P-terphenyl and Triphenylene Monomers

Lithium solvated electron solutions based on polyaromatic hydrocarbon could be achieved by adding metallic lithium to corresponding PAH solution in THF. The properties of lithium solvated electron solutions based on biphenyl and naphthalene has been reported. In this chapter, we studied the electrochemical properties of 0.1 M LiSES based on anthracene, p-terphenyl and triphenylene with various lithium-PAH ratio and modeled the interaction between lithium atoms and anthracene, p-terphenyl and triphenylene monomers through first principle density functional theory calculation.

4.1 Electrochemical Properties of Lithium Solvated Electron Solutions

Anode material for lithium based batteries has been a long standing problem. Current research mainly focus on solid-state and semi-solid state anode materials such as graphite, carbonaceous materials[1–3] and Alkali metals like lithium[4, 5] which have very poor conductivity[6] or would induce some safety problem. A potential alternative material for anode was the Lithium Solvated Electron Solution based on polyaromatic hydrocarbons. It is a liquid-state anode material where polyaromatic hydrocarbons were dissolved in THF solvent and metallic lithium was added to the solution. The lithium PAH ratio could be controlled to manipulate the electrochemical properties of the lithium solvated electron solution. It has been experimentally verified that lithium dissolved in THF solution of biphenyl and naphthalene could be used as the anode material in full cells to replace solid state graphite[7]. The electrical properties of biphenyl and naphthalene based LiSES were reported[8, 9]. A main feature of LiSES is that they show metal-like conductivity behaviour – the conductivity of LiSES decreases with increasing temperature. Such metal-like conductivity correlates to the delocalization of electrons in solvated PAH anions. Other than conductivity, the energy storage capacity is another vital factor for the potential application of LiSES as anode material in lithium based batteries. Theoretical study on interaction between lithium and biphenyl and naphthalene has shown that the lithium atom would bind to the benzene rings of the PAH molecules[10, 11] which suggests enlarged PAH molecules with more benzene rings could possibly bind with more lithium atoms to produce higher energy density and capacity. An investigation on the electrochemical properties of Lises based on anthracene, para-terphenyl and triphenylene molecules (Figure 4.1) was carried out.

Some basic information about anthracene, p-terphenyl and triphenylene was revealed. Anthracene is a solid polyaromatic hydrocarbon with formula $C_{14}H_{10}$, consisting of three fused benzene rings which melts at temperature of $215.76\text{ }^{\circ}\text{C}$.

FIGURE 4.1: The molecular structures of anthracene, para-terphenyl and triphenylene.

It is usually used as an intermediate compound for the manufacturing of dyes or used as a diluent for wood protection products, an insecticide, or a fungicide. Anthracene is also an organic crystallized photo-conductor used in electrophotography. Like anthracene, para-terphenyl also has three benzene rings while these rings are connected by C–C σ bond. Its molecular structure is non-planar with the ring in the middle rotated by 36.5° . It is in solid state at room temperature and melts at 212°C . Para-terphenyl is usually used as a laser dye or a sunscreen ingredient. Triphenylene is a fully benzenoid PAH with 4 fused benzene rings forming a planar structure. It melts at temperature of 198°C and could be used in optics and electronics.

The open circuit voltage of the LiSES based on the three PAH species mentioned above was measured with metallic lithium as its counter electrode in half-cell experiment where 1M LiPF_6 solution with 1:1 EC:EMC solvent was used as electrolyte and ceramic membrane was used as separator. The open circuit voltage is determined by the lithium chemical potential difference between the half-cell electrode and the reference electrode with equation

$$OCV = \frac{\mu_{hc} - \mu_{ref}}{zF}, \quad (4.1)$$

where z indicates the charge transferred for the cell reaction and F is the Faraday's constant. As mentioned above, for a LiSES half-cell with lithium metal as reference electrode, lithium atoms lose 1 electron while anthracene molecule

receive 1 electron during cell reaction. Hence, z was determined to be 1 for anthracene based LiSES. The lithium chemical potential difference is the free energy change of electrode materials with lithium content [12, 13] and the open circuit voltage could be written as a function of free energy change of the cell reaction (Nernst equation)

$$OCV = -\frac{\Delta G}{zF} = -\frac{\Delta H - T\Delta S}{zF}. \quad (4.2)$$

In the equation, ΔH is the enthalpy change of the cell reaction and ΔS is the entropy change. The entropy term determines how the OCV of the LiSES vary with temperature change as shown in Figure 4.2 while the enthalpy term indicates the OCV of the system at temperature of 0 K which is indeed the internal energy change of the system and could be obtained as the binding energy between lithium atoms and PAH molecules through first principle calculation using DFT.

The open circuit voltage was measured for 0.1 M solution with various Li-PAH. It was noticed that for all tested solutions, the OCV decreases with temperature. From equation 4.2, it could be concluded that entropy of the system decreases when lithium is added to the solution. The binding of lithium atoms to PAH molecules reduces the degree of freedom of the system and results in a negative entropy change.

Panel a of the figure presented the OCV against temperature for anthracene based LiSES. At temperature of 25 °C, the open circuit voltage of the solutions was measured to be 937.0 mV for 0.5:1 Li-anthracene ratio, 903.9 mV for 1:1 Li-anthracene ratio and 897.7 mV for 2:1 Li-anthracene ratio. Within the temperature range of 11 °C to 26 °C, the LiSES with 0.5:1 Li-anthracene ratio has the highest open circuit, followed by LiSES with 1:1 Li-anthracene ratio and the solution with 2:1 Li-ratio has the lowest OCV. One reason for the reduction of OCV when Li-anthracene increases is that the entropy of the system decreases more when more lithium was added to the solution due degree of freedom lost caused by binding of lithium atoms to anthracene molecules. This would result

FIGURE 4.2: OCV against temperature for anthracene, p-terphenyl and triphenylene based LISES.

in a reduction in free energy change, hence a decrease in the open circuit voltage. The value of ΔS could be determined as the slope of OCV against temperature according to equation 4.2.

The entropy change of anthracene based LiSES was found to be -1.38×10^{-3} eV/K when Li-anthracene ratio is 0.5, -1.42×10^{-3} eV/K when Li-anthracene ratio is 1.0 and -1.78×10^{-3} eV/K when Li-anthracene ratio is 2.0. These values are around 1 order of magnitude higher than that of solid state Li_xC_6 and Li_xCoO_2 [14, 15]. Indeed, this phenomenon is very general for PAH based LiSES. Among various species of PAH including biphenyl, naphthalene[8, 9], anthracene, para-terphenyl and triphenylene, the anthracene based LiSES has the lowest ΔS .

From equation 4.2, the enthalpy change (ΔH) of the LiSES during cell reaction could also be obtained. For anthracene based Lises, the enthalpy change was determined to be -1.347 eV, -1.328 eV and -1.428 eV for Li-anthracene ratio of 0.5, 1.0 and 2.0 respectively. These values would be compared with the internal energy change in subsequent sections.

Panel b and c of the figure presented the OCV of p-terphenyl and triphenylene based Lises respectively. The OCV of the solutions based on anthracene, p-terphenyl and triphenylene was close to each other with anthracene based Lises having a slightly larger OCV. Similar to the anthracene case, the entropy reduction becomes more significant when more lithium is added into the solutions because binding of more lithium atoms to the molecules would reduce the degree of freedom of the system further. For the case of p-terphenyl based LiSES, ΔS was measured to be $-1.74 \times 10^{-3} \text{eV/K}$ when Li-terphenyl ratio was set to be 0.5:1. When the ratio increases to 1:1, ΔS is enlarged to $-2.10 \times 10^{-3} \text{eV/K}$. The value was further enlarged to $-2.74 \times 10^{-3} \text{eV/K}$ and $-3.03 \times 10^{-3} \text{eV/K}$ when Li-terphenyl ratio increase to 2:1 and 2.4:1. For the case of triphenylene, the entropy change was $-1.63 \times 10^{-3} \text{eV/K}$, $-2.02 \times 10^{-3} \text{eV/K}$, $-2.48 \times 10^{-3} \text{eV/K}$, $-2.89 \times 10^{-3} \text{eV/K}$ and $-3.25 \times 10^{-3} \text{eV/K}$ for Lises with 0.5:1, 1:1, 2:1, 3:1 and

4:1 Li-triphenylene ratio. The enthalpy change, which describe the internal energy change of the system was also obtained for the solutions. ΔH was measured to be -1.293 eV, -1.289 eV, -1.539 eV and -1.479 eV for the 4 types of p-terphenyl based LiSESs. For triphenylene based LiSESs, the enthalpy change was measured to be -1.40 eV, -1.42 eV, -1.48 eV, -1.58 eV and -1.64 eV.

Conductivity is another important property for the PAH based LiSES. Many studies have demonstrated the dependence of the conductivity of lithium electrolyte on solvents species and their properties and amount of lithium added to the solution[16, 17]. For our LiSES system, this dependence is not exceptional.

The conductivity of the 0.1 M LiSES based on anthracene, p-terphenyl and triphenylene was measured at various temperatures for various Li-PAH ratios. The results were presented in Figure 4.3. Panel a shows the temperature dependence of conductivity for anthracene based LiSES; panel b shows the temperature dependence of conductivity of p-terphenyl based LiSES and panel c shows that for triphenylene based LiSES.

From the Figure, it was noticed that the conductivity of all the PAH based LiSESs exhibit metal-like behaviour - the conductivity of the solution decreases as temperature rises. It was also noticed that the conductivity of the LiSES first goes up as the Li-PAH ratio increases and then goes down. For the LiSES based on anthracene and p-terphenyl, the maximum conductivity was achieved when Li-PAH ratio was set to be 1.0:1, while for triphenylene, the maximum was achieved at 2.0:1 ratio. The conduction of the solutions could be attributed to ion transport and electron transport. The ion transport increases with temperature as the thermal motion of the ions become more violent while electron transport decreases with temperature. The negative slope suggests that electron transport would be the dominant conducting process. The magnitude of the slope indicates the relative weight of two carrier transport processes. A flatter slope means the electron transport was suppressed and ion transport become more significant.

FIGURE 4.3: Conductivity against temperature for LiSES based on anthracene, p-terphenyl and triphenylene with different Li-PAH ratios.

A closer look at the figure reveals that the conductivity of the LiSES based on anthracene, p-terphenyl and triphenylene are comparable to each other. At a temperature of 20 °C, the conductivity of the anthracene based LiSES was determined to be 226.0 $\mu\text{S}/\text{cm}$ for 0.5:1 Li-anthracene ratio, 547.0 $\mu\text{S}/\text{cm}$ for 1.0:1 Li-anthracene ratio and 229.0 $\mu\text{S}/\text{cm}$ for 2.0:1 Li-anthracene ratio. For the p-terphenyl based LiSES, the maximum conductivity is around 700 $\mu\text{S}/\text{cm}$ and the minimum is around 60 $\mu\text{S}/\text{cm}$. While for the triphenylene case, the maximum conductivity is around 600 $\mu\text{S}/\text{cm}$ and the minimum is about 20 $\mu\text{S}/\text{cm}$. Compared with the conductivity of liquid metal which is in order of $10^5 \text{ S}/\text{cm}$ [18–22], the conductivity of the three types of LiSES tested is much lower. The conductivity of 0.1 M NaCl solution was measured to be 9.9 mS/cm[23] which is also about 10 times higher than the conductivity of LiSESs. The small conductivity of the solutions implies that the conducting mechanism of the LiSES might be complicated. It is limited by the formation of lithium cations and PAH anion which are resulted from dissociation of lithium cation from the lithium bounded PAH molecules in the solutions.

4.2 Lithium Anthracene Interactions

In the anthracene based lithium solvated electron solutions, anthracene molecules act as electron acceptors to bind with lithium atoms and form various adducts according to the lithium-anthracene ratio. A gas phase anthracene molecule has weak electron affinity of 0.2 eV. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was presented in Figure 4.4.

The HOMO of anthracene molecule is the 46th excited state of the electron with energy of -5.50 eV and LUMO is the 47th excited state of the electron energy of -1.52 eV. The HOMO-LUMO gap of anthracene is determined to be 3.98 eV. For the HOMO of anthracene, the electron is located near the three carbon atoms of the mid-ring on the long edge of molecule or two carbon atoms of the side-ring on the long edge. While for the LUMO of anthracene, the electron locates near

FIGURE 4.4: The molecular orbital of gas phase anthracene molecule with iso-value=0.0200. The HOMO is the 46th excited state of the electron with energy of -5.50 eV and LUMO is the 47th excited state of the electron with energy of -1.52 eV. The HOMO-LUMO gap of anthracene is 3.98 eV.

2 carbon atoms on the short edge of the side-ring or around the other 4 carbon atoms of the side-ring or around the carbon atom of the mid-ring on the long edge.

In the half cell experiment measurement of open circuit voltage of anthracene based LiSES, metallic lithium was used as the counter electrode. On the lithium electrode side, lithium lose its 2s electron and is oxidized into Li^+ :

while on the LiSES electrode side, anthracene molecules receive electrons and absorb Li^+ from the electrolyte (1M LiPF_6 solution in 1:1 EC:EMC solvent):

The whole cell reaction could be treated as a process of lithium atoms binding to anthracene molecule to form Li-anthracene adducts as illustrated in Figure 4.5.

FIGURE 4.5: Optimized geometrical structures of adducts between lithium atoms and anthracene molecule. Lithium atoms were positioned at different location of each type of adduct.

The lithium atoms in the optimized binding structures are positively charged, indicating that the 2s electron of lithium atom is transferred to the benzene rings of anthracene when lithium atoms bind to the molecule. The adducts exhibit different configurations when lithium atoms are positioned at different location. With one lithium atom binding to the anthracene molecule, the atom would stay exactly above the center of the benzene ring if it is positioned above the mid-ring of the molecule. The distance between the lithium atom and the ring is 1.75 Å. While the lithium atom would slightly deviate to the edge of the ring if it is positioned above the side-ring of the anthracene molecule and the distance between lithium atom and the ring is 1.81 Å, which is slightly larger than the distance when lithium atom positioned above the mid-ring. Various

binding structures possess different stability which is characterized by its binding energy. Also, the stability varies for the two types of binding configurations which is characterized by the average binding energy per lithium atom of the system. And the average binding energy is determined by

$$E_b = (E_{system} - E_{anthracene} - n * E_{Li})/n. \quad (4.5)$$

With 1 lithium atom binding to an anthracene molecule, the binding energy of the two structures was determined to be 1.00 eV and 1.04 eV respectively. The structure with lithium atom above the mid-ring of the molecule is more stable, which is consistent the more intensive charge transfer in the system and closer distance between lithium atom and benzene ring and the fact that the mid-ring of anthracene molecule is more reactive than the other two[24]. It means the a2 type configuration would be the dominant specie in the solution where Li-anthracene ratio is 1:1. Considering the existence of THF solvent in experiment, the solvent effect was computed using M06 functional with 6-31g (d,p) basis set. SMD model developed by Marenich[25] was used in the computation. The binding energy of the a2 configuration in THF solvent phase was determined to be -1.363 eV with the solvent stabilization effect being 0.323 eV for anthracene molecules binding with one lithium atom.

When another lithium atom is added to the system, the anthracene molecule becomes non-planar. The molecules would undergo deformation due to its interaction with lithium atoms. When lithium atoms are positioned at the two side-rings of anthracene molecule (b3 and b4 configurations in Figure 4.5), the structures have average binding energy of -1.16 eV when lithium atoms are located above and below the benzene rings of the molecule and -1.14 eV when lithium atoms are located on the same side of the molecule. When one lithium atom is positioned at the mid-ring and the other at the side-ring (b1 and b2 configurations in Figure 4.5), the structures have average binding energy of -1.29

eV for b1 configuration and -1.19 eV for b2 configuration. It is noticed that the structures with lithium atoms on the same side of anthracene molecule are less stable with higher energy, due to the repulsive reaction between lithium atoms. Structures with lithium atoms at the two side-rings are also less stable because the mid-ring is more reactive than the side-rings. It is also noticed that the system exhibits much larger non-planarity when the site above the mid-ring is occupied by lithium atom and this large extent of bending might be related to the higher stability of the systems. The dominant specie in the solution with 2:1 Li-anthracene ratio would be the one with b1 configuration.

The average binding energy of the system is 0.2 eV lower than the value reported by Ishikawa. et al[26]. The difference is mainly caused by different functional used during computation. Ishikawa used Lee-Yang-Parr correlation functional (B3LYP) while in this work, M06 functional developed by Zhao and Truhlar in 2008[27] was used. "B3LYP" functional does consider Van der Waals force of the molecules, while "M06" functional has taken this effect into consideration. Compared with "B3LYP" functional, DFT simulations using "M06" functional are closer to the actual interactions of the system and give more accurate results. The Van der Waals force effect in our calculations resulted in lower binding energy. Again, the solvent effect was also examined for the most stable adduct with 2 lithium atoms and the binding energy in THF solvent phase was determined to be -1.521 eV. The system was stabilized by 0.231 eV when dissolved in THF. A comparison between the average binding energy of the structures with 1 lithium atom and 2 lithium atoms shows that the binding energy decreases when the second lithium atom is added.

The HOMO and LUMO of the most energetically stable structures were presented in Figure 4.6. With only 1 lithium atom, the HOMO energy of the adduct is determined to be -3.22 eV and the LUMO energy is -1.41 eV with the HOMO-LUMO gap being 1.81 eV. The gap is much smaller than that of anthracene, indicating that the material become more conductive when lithium atoms bind

FIGURE 4.6: Molecular orbitals of the most energetically stable Li-anthracene adducts with one lithium atom and two lithium atoms binding to single anthracene molecule. HOMO and LUMO are provided.

to the molecule. When the second lithium atom is added to the system, the HOMO of the system is lowered by 0.12 eV and the LUMO is increased by 0.16 eV with the gap enlarged to 2.09 eV. The larger band gap suggests a lower conductivity for the material with 2:1 Li-anthracene ratio. When comparing the molecular orbital of the adducts and anthracene, it was found that the HOMO of $\text{Li}_1(\text{anthracene})$ and $\text{Li}_2(\text{anthracene})$ could be treated as a combination of the LUMO of anthracene and distorted 2p orbitals of lithium. While for both $\text{Li}_1(\text{anthracene})$ and $\text{Li}_2(\text{anthracene})$, their LUMO is localized around the lithium atom and exhibit a s orbital shape.

A comparison between the value of ΔH measured from experiment and the binding energy obtained from DFT computation was shown Figure 4.7. For the case with 0.5:1 Li-anthracene ratio, there would be excess anthracene molecules in the solution. Considering that the LiSES used in experiment is very dilute (0.1 M), the anthracene molecules would be well separated after dissolving in THF solvent. It is reasonable to assume that the lithium atom binds to 1 anthracene molecule and the other anthracene molecule stays far away from the lithium atom, which

FIGURE 4.7: A comparison between the value of ΔH measured from experiment and the binding energy obtained from DFT computation for anthracene based Lises.

indeed exists as free molecules in THF solvent. This would lead to same binding mechanism as 1:1 Li-anthracene Lises with a binding energy of -1.363 eV.

The ΔH obtained from theoretical calculation was found to agree very well with the experimental results. There is a discrepancy of 0.016 eV for 0.5:1 Li-anthracene ratio Lises, 0.035 eV for 1:1 Li-anthracene ratio Lises and 0.093 eV for 2:1 Li-anthracene Lises. There could be several reasons for the discrepancy. From theoretical estimation side, the enthalpy change was treated as the internal energy change of the system where the volume effect was ignored. Also, DFT simulation with M06 functional may over or lower estimate the internal energy change. From experimental measurement side, there exist measurement uncertainties. Another important reason is that the electrolyte might interact with the lithium metal reference electrode during experiment. It has been reported that LiPF_6 in 1:1 EC:EMC solvent would slowly decompose into LiF and PF_5 through reaction[16, 28–30].

The PF_5 would be hydrolysed into HF and POF_3 if there exists water in the solution through reaction

Both products are highly reactive with the electrode. PF_5 could also form adduct with the solvent and trigger a series of subsequent reactions. These hidden processes occurred during experimental measurement were not captured in the theoretical calculation.

4.3 Lithium P-terphenyl Interactions

Similar to the anthracene case, in p-terphenyl based LISES, p-terphenyl molecules are electron acceptors which receive the 2s electron of lithium atoms and bind with the atoms to form various adducts in the solutions.

FIGURE 4.8: Optimized geometrical structures of Li-terphenyl adducts. Different positioning of lithium atoms was considered for 1:1 and 2:1 Li-terphenyl ratio.

Figure 4.8 presented the optimized geometrical structures of the adducts formed by lithium and p-terphenyl with different lithium positioning. With 1 lithium atom binding to p-terphenyl molecule, the atom would possibly be located at three positions, above the benzene ring in the middle, above the ring at two sides or above the σ bond which connects 2 benzene rings. When lithium atom is positioned above the ring in the middle the 2 σ bonds slightly bend towards the atom and the structure has a binding energy of -0.637 eV. When lithium atom is positioned above the ring at two sides, the ring with lithium atom above would rotate to the same plane as the ring in the middle and the σ bond bends upwards. The benzene ring at the other side seems to be not affected by the interaction between the lithium atom and p-terphenyl molecule. The binding energy of the structure was determined to be -0.528 eV. When positioned above the σ bond, the lithium atom would trigger larger σ bond bending with its binding energy being -0.482 eV. An energy analysis reveals that the site above the benzene ring in the middle is more favoured by lithium atom. Adding a second lithium atom to the system would rotate the benzene rings further towards the plane of the ring in the middle. The average binding energy for the three types of adducts were determined to be -0.815 eV for b1 structure, -0.812 for b2 structure and -0.649 for b3 structure. Lithium atoms prefer to be located at two sides of the molecule to avoid repulsive interactions between lithium atoms. Taking into consideration of the THF solvent, the binding energy of the most stable structure with 1 lithium atom bounded was stabilized to -1.258 eV and the binding energy of the most stable structure with 2 lithium atoms bounded was determined to be -1.495 eV in THF solvent phase.

The molecular orbitals of the p-terphenyl molecule and Li-terphenyl adducts were obtained. For p-terphenyl molecule, its HOMO is well separated among the 3 rings, while for its LUMO, the electron cloud was distributed over the C–C σ bonds. The HOMO energy level is determined to be -6.046 eV and the LUMO energy level is -0.901 eV with a gap of 5.146 eV. For Li-terphenyl adducts,

FIGURE 4.9: HOMO and LUMO of para-terphenyl and Li-terphenyl adducts in gas phase. Isovalue = 0.0200.

the HOMO of $\text{Li}_1(\text{p-terphenyl})_1$ and $\text{Li}_2(\text{p-terphenyl})_1$ resemble the LUMO of p-terphenyl molecule except that the electron density is slightly shifted to the sites where lithium atoms are located. Unlike the case of anthracene, the 2p orbital of lithium atom does not appear in the HOMO of the adducts. The LUMO of $\text{Li}_1(\text{p-terphenyl})_1$ is similar the that of anthracene case where the electron density is localized around the lithium atom and expresses as a s orbital shape. The LUMO of $\text{Li}_2(\text{p-terphenyl})_1$ is a bit different. The electron density locates around the 2 lithium atoms separately. The HOMO energy level of $\text{Li}_1(\text{p-terphenyl})_1$ is -2.939 eV and the LUMO energy level is -1.246 eV with a gap of 1.693 eV. When the second lithium atom is added to the system, the HOMO energy level becomes -2.732 eV and the LUMO becomes -1.298 eV with its gap narrowed down to 1.434 eV.

A comparison between the ΔH obtained from experiment and binding energy

FIGURE 4.10: A comparison between the value of ΔH measured from experiment and the binding energy obtained from DFT computation for p-terphenyl based Lises.

between lithium atoms and p-terphenyl molecules in THF solvent phase was made. Again, the theoretical value of the enthalpy change for 0.5:1 Li-terphenyl ratio was taken as the binding energy of 1 lithium atom to 1 p-terphenyl molecule. The difference between experimental value and theoretical was found to be 0.035 eV, 0.031 eV and 0.118 eV for 0.5, 1.0 and 2.0 Li-terphenyl ratio respectively. Generally, they agree quite well with the discrepancy being less than 8%. Similar to the anthracene case, the discrepancy could be due to complicated reactions ongoing in the electrolyte during measurement of OCV of the Lises.

4.4 Lithium Triphenylene Interactions

The optimized geometrical structures with most energetically favoured lithium positioning were presented in Figure 4.11. It shows that the triphenylene molecule becomes intensively distorted when more lithium atoms bind to the molecule. The benzene ring in the center of the molecule seems to be much less reactive than the other 3 rings and lithium atoms always prefer to be located at the site above or below the benzene rings outside. The structure with 4 lithium atoms exhibits

FIGURE 4.11: Optimized geometrical structures of Li-triphenylene adducts with Li-triphenylene ratio of 1:1, 2:1, 3:1 and 4:1. The lithium positioning of the structures are the most energetically favoured ones.

interesting properties. The 3 lithium atoms initially positioned above the 3 outside rings seem to aggregate. There exists a competition between the repulsive interaction between lithium atoms and deformation of triphenylene molecule. The binding energy was determined to be -0.52 eV for $\text{Li}_1(\text{triphenylene})_1$, -0.67 eV for $\text{Li}_2(\text{triphenylene})_1$, -1.03 eV for $\text{Li}_3(\text{triphenylene})_1$ and -0.94 eV for $\text{Li}_4(\text{triphenylene})_1$ in gas phase. The THF solvent stabilization effect for the 4 types of adducts was determined to be 0.78 eV for the adduct with 1 lithium atom, 0.66 eV for the adduct with 2 lithium atoms, 0.53 eV for the adduct with 3 lithium atoms and 0.62 eV for the one with 4 lithium atoms. A comparison between the internal energy change of the system in solvent phase and experimentally measured enthalpy change shows that they are consistent with each other.

The molecular orbitals of triphenylene molecule and Li-triphenylene adducts were

FIGURE 4.12: The molecule orbitals of triphenylene molecule and $\text{Li}_n(\text{triphenylene})_1$ ($n=1-4$). The HOMO and LUMO were presented with iso-value = 0.0200.

presented. For triphenylene molecule, a symmetric HOMO and LUMO were expected because of the symmetry of the molecule. Surprisingly, it exhibits asymmetric HOMO and LUMO. A closer examination on the molecular structure of triphenylene reveals that the bond lengths and charge distribution of the 3 benzene ring are not exactly the same. The bond length differs by around 0.0002 Å and the charge differs by 0.001 e. These small differences seem to be negligible, but they might account for the asymmetry of the HOMO and LUMO of triphenylene molecule. The molecule has a HOMO-LUMO gap of 6.03 eV which is the largest among anthracene, p-terphenyl and triphenylene.

For the adducts formed by lithium atoms and triphenylene molecule, the HOMO

of $\text{Li}_1(\text{triphenylene})_1$ and $\text{Li}_2(\text{triphenylene})_1$ was found to be a combination of the LUMO of triphenylene molecule and pi orbital of lithium atoms with electron density slightly shifted to the site where lithium atoms locate. For the LUMO of the 2 adducts, electron density locates around a lithium atom. Similar to case of anthracene and p-terphenyl, it expresses as a s orbital. When the 3rd and 4th lithium atom is added to the system, the HOMO and LUMO become very different. The electron density of the HOMO of the 2 adducts become highly localized around the lithium atom and looks like a distorted s orbital. While for the LUMO, the electron density spread out to the carbon atoms. Apparently, adding lithium atom to the system would localize the electron density of HOMO around the lithium atom while it delocalizes the electron density of the LUMO of the system.

4.5 Adduct Dissociation

To understand the metallic behaviour of the conductivity of the solutions and relatively low level of conductivity, the dissociation of lithium cations from the Li-PAH (anthracene, p-terphenyl and triphenylene) adducts was investigated. In the solutions, the adducts would be dissociated into lithium cations and PAH^- via the reversible process

Lithium cation dissociates from the adducts while at the same time, it also rebinds to $\text{Li}_{x-1}(\text{PAH})$ to recover the adducts structures. The system reaches a dynamic equilibrium when

$$k_f * [\text{Li}_x(\text{PAH})]_{eq} = k_r * [\text{Li}^+]_{eq} * [[\text{Li}_{x-1}(\text{PAH})]^-]_{eq}, \quad (4.9)$$

where k_f is the rate constant of the dissociation process and k_r is the rate constant of the association process. The brackets represent the activity of the corresponding particles. The equilibrium distribution of each component is correlated with the free energy change of the process. The free energy of the process consists of entropy change and enthalpy change. Generally, the dissociation of lithium cation would increase the degree of freedom of the system, resulting in an increase in entropy. The enthalpy term is obtained as the internal energy change from DFT calculations as

$$E_d = (E_{Li^+} + E_{[Li_{x-1}(PAH)]^-}) - E_{Li_x(PAH)}. \quad (4.10)$$

The values of the internal energy change during the dissociation process in THF solvent phase were presented in Table 4.1. It was noticed that for all types of adducts, the internal energy change of dissociation has positive values. The dissociation reaction is not favoured by enthalpy of the system and thus it is an entropy driving process. It is very likely that most of the Li-PAH adducts in the solution would remain associated due to the large enthalpy increase. Only a very small part of the adducts would dissociate into Li^+ and $[Li_{x-1}(PAH)]^-$. This explains the small conductivity of the solutions.

A closer look at Table 4.1 reveals that the total energy of $[Li_{x-1}(PAH)]^-$ is higher than the total energy of $[Li_{x-1}(PAH)]$ in THF solvent. It indicates that $[Li_{x-1}(PAH)]^-$ in the solution is not energetically stable and the extra electron of the system would not be confined by $[Li_{x-1}(PAH)]$. Instead, it would be highly delocalized and exists as solvated electron in the solutions.

The resulted lithium cations would be solvated by THF molecules with the first solvation shell illustrated in Figure 4. The lithium cation would interact with the oxygen atom in the THF molecules. The Li-Oxygen bond length was found to be 1.798 Å when one THF molecule is coordinated with the lithium cation and it slightly increases when the number of coordinated THF molecules increases. The attractive interaction between lithium cation and dipole of THF molecules drives

TABLE 4.1: The internal energy change from molecular calculation when lithium cation is dissociated from the Li-PAH adducts in THF solvent phase. Data were provided for anthracene, p-terphenyl and triphenylene cases. Energy in unit of eV.

Adduct formula	Energy	- charged	Dissociation
anthracene	-14670.36	-14670.04	-
Li ₁ (anthracene)	-14875.39	-14874.75	3.59
Li ₂ (anthracene)	-15080.75	-	4.24
p-terphenyl	-18880.40	-18879.56	-
Li ₁ (terphenyl)	-19085.09	-19084.09	3.77
Li ₂ (terphenyl)	-19289.97	-	4.12
triphenylene	-18847.94	-18847.26	-
Li ₁ (triphenylene)	-19052.13	-19052.09	3.91
Li ₂ (triphenylene)	-19256.63	-19256.80	2.79
Li ₃ (triphenylene)	-19462.05	-19461.16	3.50
Li ₄ (triphenylene)	-19666.38	-	3.47

* The energy of Li⁺ in THF solvent phase was -201.76 eV

the THF molecules closer to the lithium cation while the repulsive interaction between the two THF molecules offsets this driving effect. The geometries of the binding systems are planar and symmetric when the number of coordinated THF molecule vary from 1 to 3. The magnitude of the average binding energy per THF molecule decreases with increasing coordinated molecules for both gas phase and solution phase. It suggests a weaker interaction between lithium cation and the molecules and is consistent with the increasing Li-Oxygen bond length. In solvent phase, the magnitude of the total binding energy increase with number of THF molecules coordinated indicating an exothermic and spontaneous coordination of THF molecules up to number of 3, while the decreasing average binding energy indicates that coordination of additional THF molecule to the system becomes more difficult as number of coordinated THF molecule increases.

Adding a 4th THF molecule would break the symmetry of the system. The resulted geometry of the system was found to be a slightly distorted Li(THF)₃⁺ with a THF molecule nearby. The distance between the lithium cation and the fourth THF molecule was determined to be 4.45 Å, which is much larger than

FIGURE 4.13: The optimized geometries of Li-THF binding complexes. The number of THF molecules varies from 1 to 4 and the Li-Oxygen distances and Oxygen-Li-Oxygen angles are provided.

the distance between the cation and the other three molecules. Binding of a 4th THF molecule to the system is not favoured.

When exposed to external electric field, these solvated lithium cations would transport through the solution in the direction of the field where the schematic representation is described by Figure 3.1. The drift motion of lithium cations gives rise to ionic conduction for the solutions. In LISEs, there exists lithium cations and solvated electrons resulted from Li^+ dissociation. The ion transport is the minor conducting process compared with electron transport.

The electron transport in the solutions would account for the the metal-like behaviour of conductivity of the LISEs based on anthracene, p-terphenyl and triphenylene. In the solutions, electrons are scattered by the particles like THF molecules and lithium cations and other species. The process resembles that of liquid metal[31–33] where the effects of the particles could be treated as an effective potential center. The conductivity resulted from electron scattering would

be

$$\sigma = \frac{ne^2l}{mv}; \quad l = \frac{V}{NA}. \quad (4.11)$$

with l being mean free path of the electron and A being the effective scattering cross section of each scattering center. V is the total volume and N refers to the total number of scattering center in volume V . In the solutions, the interactions between electrons and particles were mainly electrostatic interactions. For example, electrons interact with the dipole moment of THF molecule or ions. With proper potential expression, the scattering cross section area could be solved with the method introduced in chapter 3. While it has to be noticed that the particles in the solutions undergo violent thermal motion. Hence, the potential center would not be static.

FIGURE 4.14: The correlation between conductivity and dissociation energy of Li-PAH adducts for LiSES based on anthracene, p-terphenyl and triphenylene. Values of the conductivity were taken at 22 °C.

The conduction contributed from scattering of the solvated electrons was mainly limited by the low electron density because of the positive internal energy change of the dissociation process. A correlation between the dissociation energy of the adducts and conductivity of the corresponding solutions was obtained. The

conductivity of the solutions was found to be linearly decrease with the dissociation energy of corresponding Li-PAH adducts. In general, higher dissociation energy implies that the dissociation process is very likely to be more difficult and that the corresponding amount of lithium cations and electrons would be lower. Hence, the conductivity becomes lower with higher dissociation energy. The slopes of conductivity against dissociation energy for the LiSES based on anthracene, p-terphenyl and triphenylene were very close, indicating the same conducting mechanism for them.

4.6 Conclusion

We studied the OCV, entropy change, enthalpy change and conductivity of the corresponding LiSESs based on the three types of PAH and modelled the interactions of lithium atoms with anthracene, p-terphenyl and triphenylene monomers during cell reaction.

The OCV of the Lises based on anthracene, p-terphenyl and triphenylene decrease with temperature, indicating an entropy decrease during cell reaction. The decrease of entropy is due to lost of degree of freedom when lithium atoms bind to the PAH molecules. When more lithium is added to the solutions, entropy of the system decreases further. Enthalpy change of the system could be treated as the internal energy change and obtained from first principle calculation. Among the three types of PAH, anthracene based Lises has the highest OCV and p-terphenyl based Lises has the lowest. It should be noticed that lithium metal was used as reference electrode during the half cell experiment. This means lower OCV correspond to lower standard reduction potential which is good for anode materials. The conductivity of the solutions based on different PAH species was found to be comparable to each other. The conductivity was relatively small and decreases with temperature which behaves like metals. It was also found to first increase with Li-PAH ratio and then decrease. A comparison between the properties of Lises based on anthracene, p-terphenyl and triphenylene suggests

p-terphenyl would have advantages over anthracene and triphenylene. Since the conductivity of the solutions is small and it would be easy to add additives like lithium salt to the liquid-state solutions to improve conductivity, the importance of OCV would override conductivity of the solutions when considering the optimal condition for LISES to be anode material. Among all the solutions studied, p-terphenyl based LISES with 2.4 Li-terphenyl ratio would be the best option.

The interaction between lithium atoms and PAH molecule was modelled with DFT calculation. The electronic structure reveals that HOMO of Li-PAH adducts could be treated as a combination of the LUMO of the PAH molecules and the pi orbital of lithium atoms. The LUMO electron density generally locates around the lithium atoms and exhibits a s orbital shape. Adding more lithium atoms to the system would gradually localize the HOMO electron density around the lithium atoms while delocalizing the LUMO electron density. An energy analysis of the adducts shows that the binding energy between lithium atoms and anthracene, p-terphenyl and triphenylene monomer is consistent with the enthalpy change measured from experiment. Which indicates that our model is suitable to describe the cell reaction. The conductivity of the LISES was understood by investigating the dissociation of lithium cations from the Li-PAH adducts and transport of the resulted carriers. The dissociation energy was found to be of positive value, indicating that only a small part of the Li-PAH adducts was dissociated into lithium cations and solvated electrons. The relatively small conductivity is limited by the small amount of carriers in the solutions. The conductivity of the solutions was found to decrease linearly with the dissociation energy of corresponding Li-PAH adducts and the slopes are close for anthracene, p-terphenyl and triphenylene based LISES.

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Chapter 5

Lithium Interaction with Anthracene, P-terphenyl and Triphenylene Beyond Monomers

In more concentrated LISES based on PAH, the PAH molecules would not be well separated by the solvent molecules and aggregate as small clusters. Or one considers depositing lithium to PAH solids. In these cases, lithium atoms do not interact with single PAH molecule. Instead, they interact with the entire cluster. Lithium deposited graphite is a good example for such kind of interactions. In this chapter, we investigated the interaction between lithium atoms and small anthracene, p-terphenyl, and triphenylene clusters formed by two or three molecules.

5.1 Lithium Interaction with Anthracene Clusters

In the previous chapter, we have investigated the interaction between lithium atoms and anthracene monomers. In highly concentrated lithium solvated electron solutions based on anthracene or one consider depositing lithium to anthracene crystals, the anthracene molecules would aggregate as clusters[50–52]. Figure 6.1 presented the molecular structures of the clusters formed by two and three anthracene molecules. The clusters were found to have a rigid layered structures with the separation between each layer being 3.90 Å which is larger than the 3.35 Å layer separation of graphite[53, 54]. It was noticed that the carbon atoms on the common edge of the rings were positively charged while other carbon atoms were negatively charged. With planar structure, the anthracene molecules in the cluster were exactly on top of each other. Repulsive interactions between these charged carbon atoms lead to the unusually large separation between layers. The binding energy of the two clusters were determined to be -0.19 eV and -0.35 eV respectively. The relatively small binding energy is consistent with the large separation between anthracene layers. While the negative sign of binding energy demonstrated that the formation of clusters in concentrated THF solutions of anthracene is spontaneous.

FIGURE 5.1: Optimized geometries of clusters formed by two and three anthracene molecules.

Lithium atoms interact with (anthracene)₂ cluster and form lithium deposited structures with the optimized structures presented in Figure 5.2. The lithium atoms were positioned at different sites and it turned out that the lithium atoms prefers to locate between the space enclosed by two anthracene molecules, forming sandwich-like structures. The most stable structures with lowest energy were shown in the first column of the figure. Lithium atoms would first fill up the space between the layers. Only when the sites between the two anthracene molecules were fully occupied, lithium atoms start to appear outside the layers. The separation between two anthracene molecules were determined to be around 3.60 Å to 3.70 Å, which is smaller than the separation of pure (anthracene)₂ cluster and larger than the 3.71 Å separation of lithium deposited graphite (LiC₆)[55–59]. The interaction between lithium atoms and anthracene molecules attracts the anthracene molecules closer. For each lithium bounded dimeric structure, the separation between 2 molecules is slightly larger at the lithium site. Compared with the case where lithium atoms interact with anthracene monomers, the distortion of the molecules is much less due to anthracene-anthracene interactions.

The average binding energy between lithium atoms and (anthracene)₂ clusters with lithium atom number vary from 1 to 4 were obtained as

$$E_b = (E_{Li_x(anthracene)_2} - xE_{Li} - E_{(anthracene)_2})/x \quad (5.1)$$

and presented in Figure 5.3. The lowest binding energy for the most energetically stable structures were coloured in red. With 1 lithium atom deposited, the lowest binding energy was determined to be -2.049 eV when the atom reside at the site between to side rings of anthracene molecules. It was 0.12 eV lower than the case where lithium atom locates at the site between the center rings. This is different to the case of anthracene monomer where lithium atoms prefers to reside above the center ring of the molecule. When the lithium atom resides outside the layers, the energy of the system is even higher with binding energy of -1.876 eV. When two lithium atoms were deposited, the binding energy generally become lower

FIGURE 5.2: Optimized geometries of lithium doped (anthracene)₂ clusters for 1 to 4 lithium atoms. The most energetically stable binding alternatives were listed in the first column.

with stronger binding strength between lithium atoms and (anthracene)₂ cluster. The most favoured binding sites were the two sites between the side rings of the anthracene molecules. Its binding energy were -2.224 eV. With three lithium atoms, the sites between the anthracene layers would be fully occupied and the average binding energy were increased to -1.914 eV. The 4th lithium atom would locate outside the anthracene layers and it prefers to reside above the center ring of the molecule. It was noticed that there is a big jump in the binding energy when the 4th lithium atom is deposited to the system. The reason for this big jump is that the 4th lithium atom could only interact with one anthracene molecule because the other one is too far to trigger significant interactions. Hence the overall interaction strength was reduced.

It has to be noticed that these lithium bounded structures could be formed

FIGURE 5.3: Binding strength between lithium atoms and (anthracene)₂ clusters. Red dots represent the most stable binding structures with corresponding lithium number.

through various ways. In solid crystals, the formation is triggered through binding of lithium atoms to the anthracene clusters. For instance, Li₂(anthracene)₂ is formed via:

In concentrated solutions, the process would be more complicate. Li₂(anthracene)₂ can be formed through the above reaction and

Reaction (5.2) indicates that anthracene clusters were preformed in the solution. Its reaction energy characterizes the binding strength between lithium atoms and anthracene clusters. Reaction (5.3) illustrated the binding of an extra lithium atom to existing lithium-anthracene clusters. The reaction energy was determined

FIGURE 5.4: Optimize geometries of Li-(anthracene)₃ clusters. Red boxes indicate most energetically stable structures among the alternatives.

to be -2.40 eV. The third reaction describes how tendency of cluster formation in the solutions. Its reaction energy was determined to be -2.56 eV.

When a slightly larger anthracene cluster with three molecules in the cluster is considered, lithium atoms bind to the clusters in a similar way. The optimized geometries of the most stable alternatives with various lithium number were presented in Figure 5.4. The red boxes indicate the most energetically stable structures among the alternatives. The separation between the layers of (Anthracene)₃ was 3.90 Å, which is the same as the cluster with two anthracene molecules. Deposition of lithium atoms lowers the separation. The lithium atoms prefer to reside between the layers until the sites are fully occupied.

The average binding energy per lithium atom with the (anthracene)₃ cluster was obtained. The red dots in the figure represent the lowest binding energy among the alternatives considered. The lowest binding energy was found to be -2.24 eV when coordinated lithium number is 3. The binding energy become lower when lithium number increase from 1 to 3 and then gradually increases when

more lithium atoms were added to the system. When the sites between the three layers were fully occupied by 6 lithium atoms, an extra lithium atom would greatly increase the binding energy from -2.09 eV to -1.92 eV. When compared with the case where lithium atoms bind with (anthracene)₂ clusters, the binding strength was found to be at the same level. For both cases, the binding first becomes stronger and then becomes weaker when more lithium atoms were deposited to the system. The strongest binding was found to be with 1:1 lithium-anthracene ratio for them. The lithium atoms would first reside at the sites between anthracene layers and occupancy of sites outside the layers was accompanied with a big jump in the reaction energy. These similarities indicate that in anthracene solid, lithium atoms interact with anthracene molecules in basic unit of (anthracene)₂ cluster.

To investigate the solvent effect of THF, SMD model was used and Li(THF)_n was studied. It was found that the solvent effect does not affect geometrical structures of the binding complexes. With THF solvent, the structures were stabilized by the solvation energy which vary from 0.24 eV to 0.45 eV for Li_n(anthracene)₃. The same phenomenon for p-terphenyl and triphenylene case was also observed. The Li(THF)_n complexes have the same geometrical structures with Li(THF)_n⁺ presented in Figure 4.13 in chapter 4. The optimal number of THF molecules on the first solvation shell was determined to be 3.

5.2 Lithium Interaction with P-terphenyl Clusters

The interactions between lithium atoms and p-terphenyl clusters formed by two and three p-terphenyl molecules were investigated. The geometrical structures of the clusters was presented in Figure 5.6. Similar to the anthracene case, p-terphenyl molecules also form layer structures[60, 61]. The separation between the layers was found to be 3.63 Å for (p-terphenyl)₂ cluster and 3.59 Å for (p-terphenyl)₃ cluster, which is slightly narrower. The separation was smaller than

FIGURE 5.5: Binding strength between lithium atoms and (anthracene)₃ clusters. Red dots represent the most stable binding structures with corresponding lithium number.

FIGURE 5.6: Optimized geometrical structures of (p-terphenyl)₂ and (p-terphenyl)₃ clusters.

anthracene case because the effect of repulsive interactions was offset by molecular rotation. The reaction energy of forming (p-terphenyl)₂ and (p-terphenyl)₃ clusters was determined to be 0.50 eV and 0.99 eV respectively. The formation energy of (p-terphenyl)₃ was about twice of the formation energy of (p-terphenyl)₂, which is expected since the p-terphenyl molecule in the center interact with two molecules.

The interaction between lithium atoms and (p-terphenyl)₂, (p-terphenyl)₃ clusters

FIGURE 5.7: Optimized geometries of most energetically stable lithium bounded (p-terphenyl)₂ and (p-terphenyl)₃ clusters.

were studied. The optimized geometries of the lithium bounded structures were obtained. Figure 5.7 presented the molecular structures of the most energetically stable alternatives for various positioning of lithium atoms.

For both cases, the existence of lithium atoms would rotate the benzene rings at two sides of the molecules around the C-C σ bond. Also, the bond was slight bent due to interaction with lithium atoms. The separation between the layers was slightly enlarged when lithium atoms were deposited into to the system. Similar to the case where lithium atoms interact with anthracene clusters, lithium atoms also prefer to reside between the p-terphenyl molecule layers to form sandwich-like

structures until the sites are fully occupied. An interesting phenomenon is that, the maximum number of lithium atoms between each two p-terphenyl layer was found to be 4. For anthracene case, the lithium atoms between anthracene layers would only bind to the benzene rings of the molecules. While for p-terphenyl case, lithium atom could reside near the C-C σ bond. With 4 lithium atoms between two p-terphenyl layers, 2 lithium atoms would bind to the benzene rings at the two sides and the other 2 would locate near the σ bond. The fifth lithium atom would not bind to the benzene ring at the center due to large repulsive interactions between lithium atoms. It would appear outside the layers as shown in panel a of Figure 5.7. It was noticed that for the (p-terphenyl)₃ cluster case, the p-terphenyl molecules were slightly sheared when number of lithium atoms was larger than 5.

The binding energy between lithium atoms and (p-terphenyl)₂, (p-terphenyl)₃ clusters was obtained and presented in Figure 5.8. For (p-terphenyl)₂ case, the number of lithium atoms deposited varies from 1 to 5. For each binding lithium number, various possible geometrical configurations were investigated. The red dots in the figure represent the most stable alternatives with lowest binding energies. Similar to the case where lithium atoms interact with p-terphenyl monomers, the center ring of the molecule was most preferred by lithium atoms. With 1 lithium atom, the binding energy of the most stable structure was determined to be -1.401 eV. When a second lithium atom is added to the system, the average binding energy was lowered to -1.623 eV. The interaction between each lithium atom and p-terphenyl molecules become stronger. The average binding energy was at its minimum with a value of -1.744 eV when there are 3 lithium atoms in the system. Each atom occupies a site between the benzene rings of the molecules. When number of lithium atoms increases to 4, the binding energy rise to -1.671 eV due to the repulsive interactions between the lithium atoms inside the layer space. The fifth lithium atom would increase the binding energy further to -1.502 eV. The large increase is expected since the configuration of the system

FIGURE 5.8: Binding energy between lithium atoms and a): $(p\text{-terphenyl})_2$; b): $(p\text{-terphenyl})_3$ clusters. Dots in red represent the lowest binding energy for the most stable alternatives among various lithium positioning.

become different with the lithium atom located outside layer enveloped by the $p\text{-terphenyl}$ molecules. For lithium atoms between the layer, they interact with both molecules. When it falls outside, only the interaction with the molecule close to the lithium atom would account.

For (p-terphenyl)₃ case, the number of lithium atoms varies from 2 to 8. Similar to the (p-terphenyl)₂ case, binding energy between lithium atoms and the cluster first decreases and then increases with a minimum binding energy of -1.762 eV when 5 lithium atoms were deposited into the system. The Li-terphenyl ratio 5:3 was close the ratio 3:2 where binding energy between lithium atoms and (p-terphenyl)₂ cluster was at its minimum. The binding strength between lithium atoms and (p-terphenyl)₂, (p-terphenyl)₃ clusters was found to be similar. The common characteristics indicate the (p-terphenyl)₂ to be the basic unit when p-terphenyl molecules aggregate and form clusters.

5.3 Lithium Interaction with Triphenylene Clusters

For triphenylene, the clusters with two and three triphenylene molecules were shown in Figure 5.9. Again the clusters exhibit layered structures, while there exist large displacement of 1.91 Å between layers[62, 63]. This large displacement is due to the charge distribution of the triphenylene molecules. The carbon atoms on the benzene ring at the center have positive charge while carbon atoms on the other benzene rings have negative charge.

FIGURE 5.9: Optimized geometries of (triphenylene)₂ and (triphenylene)₃ clusters.

The electrostatic repulsion between the carbons atoms drives the triphenylene molecules so that the energy of the system is minimized when the repulsion and attraction between the molecules are balanced. The vertical separation between

each layer is determined to be 3.39 Å. The small separation was due to displacement between layers and planarity change of triphenylene molecules. The formation energy of (triphenylene)₂ cluster was found to be -0.5 eV and that of (triphenylene)₃ cluster was -1.02 eV, which is about twice of the former.

FIGURE 5.10: Optimized geometries of lithium deposited (triphenylene)₂ and (triphenylene)₃ clusters.

When lithium atoms were deposited into the systems, the displacement between triphenylene layers was offset by the interactions between lithium atoms and triphenylene molecules. Similar to the case of anthracene and p-terphenyl clusters, lithium atoms prefer to reside at the sites between the triphenylene layers. It was noticed that lithium atoms do not bind to the benzene ring at the center of the molecules. When any lithium atoms were positioned at the site between the center rings, first principle calculation would end up with non-converge energy for the system. This is due to the charge distribution of triphenylene molecules.

Repulsive interactions between lithium atoms and positive charge on the benzene ring at the center of the molecules prohibits binding of lithium to the ring[64–67]. Another interesting phenomenon is the aggregation of lithium atoms in the $\text{Li}_8(\text{triphenylene})_2$ structure. Similar aggregation has also been seen in the structure of $\text{Li}_4(\text{triphenylene})$. When three lithium atoms locate on the same side of a triphenylene molecule, the molecule would be largely distorted and drives the lithium atoms closer to each other.

The binding strength between lithium atoms and $(\text{triphenylene})_2$, $(\text{triphenylene})_3$ clusters was obtained. For each number of deposited lithium atoms, various lithium positioning was considered and the red dots in the figure represent the binding strength of the most energetically stable alternatives. For the cluster with 2 triphenylene molecules, structures with 1, 2, 4, 6 and 8 lithium atoms were studied. When 1 lithium atom is bounded to the cluster, the binding energy was significantly lower with value of -1.295 eV when it is positioned between the triphenylene molecules. The binding energy was at its minimum value of -1.471 eV when there are 2 lithium atoms in the system. This is quite different from the monomer case where minimum binding energy is reached at Li-triphenylene ratio of 3:1. The binding energy increases with lithium number when more lithium atoms were deposited to the $(\text{triphenylene})_2$ cluster, indicating a weaker binding between lithium atoms and the cluster.

For the cluster with 3 triphenylene molecules, the binding strength also increase first and then decrease. While the strongest binding strength was reached at lithium number of 6, which corresponds to Li-triphenylene ratio of 3:1. Lithium bounded $(\text{triphenylene})_2$ and $(\text{triphenylene})_3$ clusters are very similar in the way lithium atoms bind to the clusters while very different in the binding strength behaviour.

FIGURE 5.11: Binding energy between lithium atoms and a): (triphenylene)₂; b): (triphenylene)₃ clusters. Dots in red represent the lowest binding energy for the most stable alternatives among various lithium positioning.

5.4 Conclusion

The interactions between lithium atoms and anthracene, p-terphenyl, triphenylene clusters were investigated. In solids or highly concentrated THF solution of these polyaromatic hydrocarbons, the PAH molecules form clusters and the clusters were found to have rigid layered structures. When lithium was deposited

into the systems, lithium atoms would reside at the sites between the PAH molecule layers, forming sandwich-like structures. For the case of anthracene and p-terphenyl, clusters with 2 molecules and clusters with 3 molecules have very similar behaviour in both geometries and binding strength. For anthracene clusters, the maximum number of lithium atoms between 2 anthracene layers was 3 where each atom bind to a benzene ring of the molecules. The binding strength between lithium atoms and (anthracene)₂, (anthracene)₃ clusters was similar and around twice that of anthracene monomer. The strongest binding was found to be at Li-anthracene ratio of 1:1 for clusters with 2 and 3 molecules. For p-terphenyl clusters, the maximum number of lithium atoms between 2 p-terphenyl layers was 4 with 2 atoms residing near the C-C σ bond. Similar to the case of anthracene, the binding strength between lithium atoms and p-terphenyl clusters of 2 and 3 molecules was similar and around twice that of p-terphenyl monomer. Binding strength was strongest at Li-terphenyl ratio of 3:2. The consistent behaviour of the clusters with 2 and 3 molecules indicates that (anthracene)₂ and (p-terphenyl)₂ are the basic units in their solids. For triphenylene clusters, there exists large displacement between layers due to charge distribution of the molecule. Lithium atoms prefer to reside between the layers but do not bind to the benzene at the center due to repulsive interaction caused by positive charge on the ring. The binding strength between lithium atoms and (triphenylene)₂, (triphenylene)₃ clusters behaves differently. Generally, binding was stronger for (triphenylene)₃ clusters. Strongest binding was found at 1:1 Li-triphenylene ratio for (triphenylene)₂ and 2:1 for (triphenylene)₃. The investigation predicts the behavior of the systems when adding lithium to concentrated THF solution of anthracene, p-terphenyl and triphenylene or depositing lithium atoms to corresponding solids.

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Chapter 6

Lithium Interaction with Nitrogen Substituted Biphenyl, Naphthalene and Anthracene Monomers

Phenylpyridine has similar molecular structure as biphenyl where one of the carbon atoms is replaced by a nitrogen atom. The properties of 3 types of phenylpyridine isomers were studied. We further extend the idea to naphthalene and anthracene. We replaced one of the carbon atoms as nitrogen atom and investigated the molecular properties of the nitrogen heterocycles. The properties of these nitrogen heterocycles were compared with corresponding polyaromatic hydrocarbons and the positioning effect of the nitrogen atom was analyzed.

6.1 Lithium Interaction with Phenylpyridine

The molecular structures of three types of phenylpyridine isomers were presented in Figure 6.1. According to the positioning of the nitrogen atom, the three types of isomers were labelled as 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine and the properties of the isomers differ from each other[1–7].

FIGURE 6.1: The molecular structures of 3 phenylpyridine isomers, 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine.

The phenylpyridine has similar molecular structure as biphenyl with one of the carbon atoms replaced as nitrogen atom. It was noticed that the non-planarity of the 2 rings for phenylpyridine isomers differs from each other. 3-phenylpyridine has largest non-planarity which is similar to that of biphenyl. The non-planarity of 2-phenylpyridine is slightly smaller while 4-phenylpyridine has a almost planar molecular structure.

The molecular orbitals and contour diagrams of the phenylpyridine isomers were obtained and compared with that of biphenyl molecule. For biphenyl molecule, the molecular orbitals and corresponding contour diagrams exhibit perfect symmetry[8, 9] while the symmetry was broken for phenylpyridine isomers due to the existence of nitrogen atom. The electron density of the HOMO of phenylpyridine isomers was shifted to the ring with nitrogen atom. This shift is especially significant for 3-phenylpyridine. The LUMO of 2-phenylpyridine and 3-phenylpyridine was similar to that of biphenyl with reorganization of electron density on the ring with nitrogen atom. The LUMO of 4-phenylpyridine is quite different. The electron density was significantly biased between the two ring with much higher electron

density on the ring with nitrogen atom. Also, the electron tend not to appear on the σ bond connecting the 2 rings.

FIGURE 6.2: The HOMO and LUMO of biphenyl, 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine and their corresponding contour diagrams. Isovalue=0.0200.

Similar to polyaromatic hydrocarbons such as biphenyl, anthracene and p-terphenyl, phenylpyridine could also be dissolved in THF solvent[10, 11]. Adding metallic lithium to the solution would achieve phenylpyridine based LISES. The solutions exhibit similar open circuit voltage and conductivity behaviour as those LISES based on PAH as shown in Figure 6.3 and Figure 6.4.

The molar ratio between phenylpyridine and THF was 1:10.4 and the corresponding open circuit voltage of the LISES based on the phenylpyridine isomers

FIGURE 6.3: The open circuit voltage of Lises based on 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine against temperature.

decreases with temperature, indicating a negative entropy change for the cell reaction during OCV measurement with the specific values presented in Table 6.1. The OCV of the solutions is of similar magnitude to the Lises based on anthracene and para-terphenyl with same concentration. It was noticed that the OCV of the solutions based on 3-phenylpyridine and 4-phenylpyridine with Li-phenylpyridine ratio 1:1 were very close at the tested temperature range. For 3-phenylpyridine based Lises, an increase in the Li-phenylpyridine ratio would lead to a significant decrease in its OCV. Also, the solution based on 3-phenylpyridine has higher OCV than the solution based on 2-phenylpyridine.

According to Table 6.1, among the Lises tested, 4-phenylpyridine based Lises with 1:1 Li-phenylpyridine ratio has the largest entropy change with $-113 \text{ JK}^{-1}\text{mol}^{-1}$. The entropy change for 3-phenylpyridine based Lises with 1:1 Li-phenylpyridine ratio and 2-phenylpyridine based Lises with 2:1 Li-phenylpyridine ratio was slightly smaller, $-108 \text{ JK}^{-1}\text{mol}^{-1}$ and $-111 \text{ JK}^{-1}\text{mol}^{-1}$ respectively. While ΔS of 3-phenylpyridine based Lises with 2:1 Li-phenylpyridine ratio was much lower with $-59 \text{ JK}^{-1}\text{mol}^{-1}$.

TABLE 6.1: The entropy and enthalpy change of phenylpyridine based LISES and entropy change of other PAH based LISES as well as solid-state $\text{Li}_x\text{CoO}_2/\text{Li}$, $\text{Li}_x\text{C}_6/\text{Li}$ [12, 13] half cell.

Type of LISES	ΔS ($\text{J K}^{-1}\text{mol}^{-1}$)	ΔH (kJ/mol)
$\text{Li}_1(\text{biphenyl})(\text{THF})_{10.4}$	-467	-
$\text{Li}_1(\text{naphthalene})(\text{THF})_{10.4}$	-290	-
$\text{Li}_1(3\text{phpy})(\text{THF})_{10.4}$	-108	-116.0
$\text{Li}_2(3\text{phpy})(\text{THF})_{10.4}$	-59	-39.2
$\text{Li}_1(4\text{phpy})(\text{THF})_{10.4}$	-113	-117.7
$\text{Li}_2(2\text{phpy})(\text{THF})_{10.4}$	-111	-90.9
$\text{Li}_x\text{CoO}_2/\text{Li}$ ($0 < x < 1$)	$-70 < \Delta S < 20$	-
$\text{Li}_x\text{C}_6/\text{Li}$ ($0 < x < 1$)	$-20 < \Delta S < 62$	-

It was noticed that the entropy change of the phenylpyridine based LISES was significantly lower than the entropy change of biphenyl and naphthalene based LISES[11, 14]. The values were more close to ΔS of solid-state $\text{Li}_x\text{CoO}_2/\text{Li}$ ($0 < x < 1$) half cell[13]. As for the enthalpy change which corresponds to the internal energy change during cell reaction, the LISES based on 3-phenylpyridine and 4-phenylpyridine with 1:1 Li-phenylpyridine ratio has very close ΔH , which is consistent with the close OCV values for the two types of LISES. ΔH of 2-phenylpyridine based with 2:1 Li-phenylpyridine ratio was -90.9 kJ/mol, around 30 kJ/mol lower than the previous two LISES, which led to a significant lower OCV for the solution. The enthalpy change of the last type of LISES was much lower. With a much lower entropy, its OCV was comparable to the OCV of 2-phenylpyridine based LISES. As mentioned, the enthalpy change of the solutions during cell reaction describes the internal energy change of the system, and the cell interaction could be treated as a binding process of lithium atoms to phenylpyridine molecules through molecular modelling, thus the values would be compared to the binding energy obtained from the molecular model at later part of this chapter.

According to Figure 6.4, the conductivity of the solutions generally exhibit metallic behaviour except for the solution based on 2-phenylpyridine with 2:1 Li-PAH

FIGURE 6.4: (a). Conductivity of the Lises based on 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine against temperature. (b). Conductivity of biphenyl based Lises against temperature for comparison[11].

ratio, whose conductivity demonstrated a more complicated correlation with temperature. It first decrease with temperature until the temperature hit the 283 K limit and then increase with temperature when the temperature increase further, forming a "V" shape curve. This phenomenon suggests that the metallic conduction of the solution is dominated by the electron transport between the adducts during collisions in the solution. It was also noticed that the conductivity of the Lises phenylpyridine isomers was much lower than that of the biphenyl based

LISES[11]. At the temperature of 285 K, the conductivity of the phenylpyridine based LISES varies in the range of 100 $\mu\text{S}/\text{cm}$ to 1450 $\mu\text{S}/\text{cm}$ while the conductivity of biphenyl based LISES was determined to be 11500 $\mu\text{S}/\text{cm}$ for 1:1 Li-PAH ratio and 7800 $\mu\text{S}/\text{cm}$. The slope of the conductivity against temperature for phenylpyridine was also much smaller than the slope for biphenyl. This is because the electrons of the Li-phenylpyridine adducts are more localized than Li-biphenyl adducts. Compared with biphenyl, phenylpyridine has stronger electron affinity and the 2s electrons of lithium atoms were confined by the phenylpyridine molecules, resulting in a reduction in the free electrons and hence a reduction in conductivity and slope. This explanation would be illustrated by molecular modelling subsequently.

Among the solutions based on phenylpyridine isomers, 4-phenylpyridine with 1:1 Li-PAH ratio has the highest conductivity, followed by 3-phenylpyridine with 1:1 Li-PAH ratio. The conductivity of 2-phenylpyridine is significantly lower than 3- and 4-phenylpyridine. It was also notice that higher conductivity generally comes with larger slope, which means metallic conduction still plays an important role in the conducting mechanism.

TABLE 6.2: Conductivity of biphenyl and phenylpyridine based LISES. The value of conductivity provided in the table was at 285 K.

Type of LISES	Conductivity ($\mu\text{S}/\text{cm}$)	σ (μ/cm) versus T
$\text{Li}_1(\text{biphenyl})(\text{THF})_{10.4}$	11500	$-94.1\text{T} + 39203$
$\text{Li}_2(\text{biphenyl})(\text{THF})_{10.4}$	7800	$-67.6\text{T} + 27664$
$\text{Li}_1(2\text{phpy})(\text{THF})_{10.4}$	100	$-0.58\text{T} + 270$
$\text{Li}_2(2\text{phpy})(\text{THF})_{10.4}$	160	$+0.28\text{T} + 75$
$\text{Li}_1(3\text{phpy})(\text{THF})_{10.4}$	1120	$-9.99\text{T} + 4070$
$\text{Li}_2(3\text{phpy})(\text{THF})_{10.4}$	900	$-0.63\text{T} + 820$
$\text{Li}_1(4\text{phpy})(\text{THF})_{10.4}$	1450	$-14.6\text{T} + 5762$

In the solutions, lithium atoms interact with phenylpyridine molecules and form Li-phenylpyridine adducts. The interaction process could be modelled as a binding process of lithium atoms to phenylpyridine molecules through DFT calculation. The first principle calculation was performed using M06 functional with

basis set of 6-31g(d,p). The optimized geometries of the binding structures between lithium atoms and phenylpyridine isomers were presented in Figure 6.5.

FIGURE 6.5: Optimized geometries of binding structures between lithium atoms and phenylpyridines isomers. Structures of Li-biphenyl adducts were provided for comparison.

From the optimized geometries, it could be noticed that the lithium atom would locate near the nitrogen atom when positioned above the ring with nitrogen atom. Also, the ring exhibits much larger distortion than the case when lithium atom was positioned above the other ring. The energy profile was presented in Table 6.3.

TABLE 6.3: Energy profile of Li-phenylpyridine and Li-biphenyl adducts. Energy in unit of eV.

LISES	HOMO	LUMO	Gap	Binding	Dissociation
Li ₁ (biphenyl)	-2.74	-1.49	4.23	-0.47	2.89
Li ₂ (biphenyl)	-2.54	-1.01	3.55	-0.75	3.01
Li ₁ (2phpy)	-4.59	-1.41	3.18	-1.28	4.45
Li ₂ (2phpy)	-2.42	-1.06	1.36	-0.85	4.27
Li ₁ (3phpy)	-3.97	-1.09	2.87	-1.36	3.52
Li ₂ (3phpy)	-2.20	-0.91	1.29	-0.90	3.83
Li ₁ (4phpy)	-3.88	-1.32	2.56	-1.41	3.39
Li ₂ (4phpy)	-1.82	-1.26	0.56	-0.80	3.78

For 2-phenylpyridine, when the lithium atom is positioned above the ring without nitrogen atom, the binding energy between lithium atom and 2-phenylpyridine molecule is determined to be -1.07 eV, which is 0.41 eV higher than the binding energy of the system with lithium atom above the ring with nitrogen atom. When the lithium atom is positioned above the σ bond, the binding energy is found to be -1.42 eV, which is also slightly higher than -1.48 eV presented in the table. For the 3-phenylpyridine and 4-phenylpyridine system, similar results were observed. Lithium atom would preferably locate above the ring with nitrogen atom and biased to the nitrogen atom site because nitrogen atom has larger electron affinity than carbon atoms. When a second lithium is added to the system, the binding energy becomes higher, especially for the case of 4-phenylpyridine case. The energy of the system is only lowered by 0.19 eV, and the adduct has a very narrow HOMO-LUMO gap of 0.56 eV, indicating that the Li₂(4-phenylpyridine) system is not so favored. These properties may explain synthesis failure of the 4-phenylpyridine based LISES with 2:1 Li-PAH ratio. The enthalpy change of Li₁(3-phenylpyridine), Li₁(4-phenylpyridine) and Li₂(phenylpyridine) was -1.20 eV, -1.22 eV and -0.94 eV respectively. The internal energy change of the system determined from DFT calculation agrees with the value quite well. A comparison between Li-biphenyl and Li-phenylpyridine interaction reveals that the binding between lithium atoms and phenylpyridine molecules is much stronger than the binding between lithium atoms and biphenyl molecule. The HOMO-LUMO gap

of the phenylpyridine systems is also lower.

The conductivity of the solutions involves dissociation of lithium cation from the adducts and electron delocalization of the PAH anions. An investigation on the electron affinity of the molecules suggests that the three phenylpyridine isomers have electron affinity of 0.47 eV, 0.49 eV and 0.45 eV for 2-, 3- and 4-phenylpyridine molecule, which is lower than 0.63 eV for biphenyl molecule. The positive value of electron affinity implies that, both biphenyl and phenylpyridine molecules do not tend to confine an extra electron. Hence the electron of the PHA anion would be highly delocalized, while the delocalization is more significant for biphenyl molecule. This would partly explain the larger conductivity of biphenyl based LISES than phenylpyridine based LISES. The dissociation energy of Li-biphenyl adducts was found to be much smaller than that of Li-phenylpyridine adducts, implying that in biphenyl based solutions, the resulted lithium cation and PAH anion concentration would be higher. Hence the amount of free elec-

FIGURE 6.6: Molecular orbitals of binding structures between lithium atom and phenylpyridine isomers. Isovalue=0.0200.

tron in the solution would also be higher, which is consistent with the higher conductivity of the solution. Among phenylpyridine based LISES, it was also noticed that the solutions with higher conductivity also have smaller dissociation energy, which provides evidence for the conducting mechanism of PAH based LISES illustrated in previous chapter.

The molecular orbitals of the Li-phenylpyridine adducts were presented in Figure 6.6. The HOMO of the systems indicate that the 2s electron of lithium would be dominantly localized near the nitrogen with higher electron density at the site. When the second lithium atom is added, the electron density is largely shifted to benzene ring without nitrogen atom. Similar to all other Li-PAH binding structures, the electron of LUMO was located near the lithium atom, exhibiting a s orbital shape for all three phenylpyridine isomers with Li-PAH ratio of 1:1 and 2:1. With 2 lithium atoms in the system, the LUMO was near the lithium atom above the benzene ring without nitrogen atom because the interaction of lithium atom with carbon is weaker than with nitrogen. The HOMO of $\text{Li}_2(4\text{-phenylpyridine})$ is special. The charge density is localized near the lithium atom above the ring with nitrogen atom, indicating that the 2s electron of the lithium would not be transferred to the molecule. It is consistent with the very small binding energy and narrow HOMO-LUMO gap of the structure.

6.2 Lithium Interaction with Nitrogen Substituted Naphthalene and Anthracene

From the study on the properties of phenylpyridine based LISES and modelling of Li-phenylpyridine interaction, the effect of lithium atom on the system was observed. We further extent our investigation to other nitrogen substituted PAH, naphthalene and anthracene[15–17]. The binding properties between lithium atoms and nitrogen substituted naphthalene and anthracene molecules were studied and compared with that of original naphthalene and anthracene molecules. From the comparisons of the binding properties, we predicted the properties of

the LISES based on nitrogen substituted naphthalene and anthracene and how their enthalpy change, conductivity would compare with the corresponding original PAH based LISES.

FIGURE 6.7: The molecular structures of nitrogen substituted naphthalene and anthracene with different nitrogen positioning.

According to the position of nitrogen atom, nitrogen substituted naphthalene 2 isomers with nitrogen atom at site 2 and 3. The nitrogen atom might not locate at site 1 since the carbon atom at site 1 is not reactive. The energy profile shows that 2-N substituted naphthalene has lower energy level than 3-N substituted naphthalene while the energy level of the molecule is much higher than both when the nitrogen atom locates at site 1. The 2-N substituted is also named quinoline, which is the commonly seen nitrogen substituted naphthalene. The nitrogen substituted anthracene has 3 isomers with nitrogen atom located at site 1, site 3 and site 4. The energy profile of the molecules demonstrates that the isomer with nitrogen atom at site 1 has the lowest energy level, followed by site 3. It implies that the carbon atom on the center ring is more reactive the atom at site 3 is more reactive than the atom at site 4, which is consistent with our previous results.

The optimized geometries of the binding structures between lithium atoms and nitrogen substituted naphthalene and anthracene were presented in Figure 6.8 and Figure 6.9. When 1 lithium atom is added to the 2-N substituted naphthalene molecule, the adduct has three possible structures. The first and second

FIGURE 6.8: Optimized geometries of the binding structures between lithium atoms and nitrogen substituted naphthalene molecules. The geometries of binding structures between lithium atoms and naphthalene molecule were provided for comparison.

structures have their lithium atom above the ring with nitrogen atom and the third has its lithium atom above the benzene ring. The three structures have binding energy of -1.21 eV, -1.61 eV and -1.17 eV respectively, indicating that the structure in the middle is the most stable one and lithium atom interacts stronger with nitrogen atom than with carbon atom. When a second lithium atom is added to the system, the average binding energy becomes 0.99 eV, which is much higher than -1.61 eV due to weaker interaction between lithium atom and carbon atom. For 3-N substituted naphthalene, similar phenomenon was observed. The binding energy of the first structure was determined to be -1.27 eV, higher than that of the second structure. The binding energy of the structure with 2 lithium atoms was -0.94 eV. It was noticed that the binding energy between

lithium atom and 2-N substituted naphthalene molecule is lower than that of 3-N substituted naphthalene. Both have lower binding energy than Li-naphthalene adducts. The lower binding energy implies that the LISES based on nitrogen substituted naphthalene might have lower enthalpy change than LISES based on naphthalene. The dissociation energy of adduct between lithium and 2-N substituted naphthalene was determined to be 3.66 eV and 3.92 eV 1 lithium atom and 2 lithium atoms added. The dissociation energy of the lithium bounded 3-N substituted naphthalene was a bit higher, 3.78 eV and 4.15 eV. Both are significantly higher than that for naphthalene. The dissociation energy might suggests a much lower conductivity for the LISES based on nitrogen substituted naphthalene. Also, 2-N substituted naphthalene based solutions are likely to have higher conductivity than 3-N substituted naphthalene based solutions.

When 1 lithium atom binds with the nitrogen substituted anthracene molecule, there exists a competition effect on the positioning of lithium atom. On one hand, the nitrogen atom has higher tendency to bind with the lithium atom than carbon atoms, on the other hand, the center ring is more reactive than the other two rings. This competition could be seen from the binding energy of the 3-N and 4-N substituted anthracene. For 4-N substituted anthracene, the binding energy of the second structure is -1.41 eV, which is slightly higher than the binding energy of the first structure, -1.37 eV. The lithium atom would prefer to be located above the center ring instead of the site near the nitrogen atom. While for 3-N substituted anthracene, the binding energy of the first structure is -1.62 eV, much lower than that of the second structure, -1.39 eV. The lithium atom prefers to be located near the nitrogen atom. This difference is consistent with the fact that site 3 is more reactive with site 4. For 1-N substituted anthracene, as expected, the structure with lithium atom near the nitrogen atom is the most stable one with binding energy of -1.60 eV. It is also noticed that the molecule is largely distorted due to the interaction between lithium and nitrogen atom, especially for 1-N substituted anthracene molecule. The molecule is bent by an

FIGURE 6.9: Optimized geometries of binding structures between lithium atoms and nitrogen substituted anthracene isomers. The geometries of Li-anthracene adducts were provided for comparison.

angle of 32° . When a second lithium atom is added to the systems, the binding energy become -0.99 eV, -1.05 eV and -1.09 eV for 4-N, 3-N and 1-N substituted anthracene. With 1 lithium atom, the binding energy of nitrogen substituted anthracene is lower than that of anthracene, suggesting a lower enthalpy change for the corresponding LISES. While with 2 lithium atoms, the binding energy becomes higher than that of anthracene. It implies that the enthalpy change of the solutions is likely to be higher than the enthalpy change of anthracene based LISES.

Similar to the case of nitrogen substituted naphthalene, we also investigated the dissociation energy of the adducts as a method to predict how the conductivity of the corresponding LISES would compare with the LISES based on anthracene. For 4-N substituted anthracene, the dissociation energy of the adduct was determined to be 4.07 eV with 1 lithium atom in the system and 4.42 eV with 2 lithium atoms in the system. The dissociation energy of 3-N substituted anthracene adducts was 4.23 eV and 4.54 eV while that of the 1-N substituted anthracene adducts was 4.29 eV and 4.65 eV for 1 and 2 lithium atoms in the system. These dissociation energies are all higher than that of Li-anthracene adducts, meaning that it would be more difficult to form lithium cations and anthracene anions in the solutions. It indicates that the solutions based on nitrogen substituted anthracene are likely to have lower conductivity than the LISES based on anthracene.

6.3 Conclusion

The investigation on phenypyridine suggests that the existence of nitrogen atom in the PAH makes it easier for lithium atoms to bind to the PAH molecules, resulting in more significant enthalpy change in the system. It also localizes the electron density around the nitrogen and leads to less significant entropy change. The LISES based on the nitrogen substituted PAH have a tendency to have higher OCV. In the mean while, it makes it more difficult for the lithium cations to be dissociated from the adducts due to high electron affinity of nitrogen atom, which hurt the conductivity of the solution. Our theoretical molecular modelling of the nitrogen substituted naphthalene and anthracene approves increase in dissociation energy and binding strength caused by the nitrogen atom. According to the OCV analysis and conduction analysis of the solutions in previous chapter, the corresponding LISESs are likely to have higher OCV and lower conductivity.

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Chapter 7

Summary and Future Work

The thesis focuses on the interactions between lithium atoms and various types of PAH in LISES. The interactions between lithium atoms and PAH monomers is correlated with the OCV, enthalpy change and conductivity of the solutions. The interactions between lithium atoms and clusters of PAH molecules were studied to describe the systems when depositing lithium into corresponding PAH solids or highly concentrated LISESs. The effect of nitrogen atom was investigated by comparing the properties of biphenyl based and phenylpyridine based LISES and their binding properties. Predictions were made for nitrogen substituted naphthalene and anthracene based on their electronic structures. This chapter provides an overall discussion on the research work and addresses the future work which could be carried out following this project.

7.1 Summary

The interactions between lithium atoms and anthracene, p-terphenyl, triphenylene monomers were investigated and correlated to the OCV and conductivity profile of the corresponding LISES. The electronic structures of the Li-PAH adducts shows that its HOMO is a combination of the LUMO of PAH molecules and pi orbital of lithium atom while the LUMO exhibits s shape orbital around the lithium atom. It suggests when the adducts captures an electron, it would fill up the 2s orbital of the lithium atom in the adducts. The lithium atom positioning around the PAH molecule greatly affects the its binding energy, hence the stability of the system. The binding energy calculated from molecular modelling generally agrees with the enthalpy change measured from experiment. The binding of lithium atoms resulted in the degree of freedom reduction in the system, hence a entropy decrease and negatively temperature dependence of the OCV of corresponding LISES. The dissociation of lithium cations from Li-PAH adducts determines the concentration of free carriers in the solutions and account for the conductivity behaviour.

The interactions between lithium atoms and clusters of anthracene, p-terphenyl, triphenylene molecules were studied to predict the behaviour of the systems when depositing lithium into corresponding PAH solids or highly concentrated LISESs. The clusters were found to have rigid layered structures. Lithium atoms would prefer to reside at the sites between the layers when deposited into the systems. For the case of anthracene and p-terphenyl, clusters with 2 and 3 molecules behave similarly both in the way lithium atoms bind to the systems and the binding strength. For triphenylene, there exists large displacement between layers. Lithium atoms bind to clusters with 2 and 3 triphenylene molecules in similar way while the binding strength behaves differently.

The nitrogen effect was investigated by comparing the properties of biphenyl

based and phenylpyridine based LISES and their molecular properties. The nitrogen atom enhanced the binding interaction between lithium atoms and PAH molecules, leading to more intensive enthalpy change in the system and the LISESs tend to have higher OCV than that without nitrogen. At the same time, the dissociation energy of lithium cation from the adducts is enlarged due to high electron affinity of nitrogen atom, which results in a reduction in the lithium cation and free electron density in the solutions. The conductivity of phenylpyridine based LISES is significant lower than that of biphenyl based LISES. From molecular modelling on the electronic structures of nitrogen substituted naphthalene and anthracene, the same effect was observed.

Overall, our investigation show LISES could be a good anode material with a few issues to be settled and we have found the tool and practical way to solve the problems. Molecular modelling could be used to predict the properties of LISES based on different PAH species. The standard reduction potential of LISES could be further improved by increasing lithium loading of PAH molecules. The conductivity of the solution could be improved by adding additives like lithium salt to the solutions since this is easy to do for a liquid-state solution. Another way out is to use PAH substituted by elements with lower electron affinity. Our investigation on the effect of nitrogen atom shows higher electron affinity would reduce the conductivity of the solutions. Vice versa, lower electron affinity could be expected to increase conductivity. These would be tested in our future work.

7.2 Future Work

This project investigated the interaction between lithium atoms and PAH monomers and clusters of PAH molecules as well as the properties of the LISES based on these PAH. The study suggests that for PAH based LISES to be promising anode materials for rechargeable lithium batteries, several concerns should be addressed, the issue with OCV of the material[1, 2], the lithium capacity and the conductivity of the solutions.

7.2.1 Increase of Lithium Loading

The OCV used in this thesis refers to the OCV against metallic lithium where lithium metal is used as the counter electrode during OCV measurement[3]. For the cell formed by lithium metal, PAH based LISES, electrolyte with LiPF_6 solute in 1:1 EC/EMC solvent and ceramic separator, lithium metal acted as the anode and was oxidized into lithium cation, while the LISES acted as the cathode and receives electrons. The standard reduction potential of the solution is thus

$$E_{LISES,red} = E_{Li,red} + OCV. \quad (7.1)$$

The expression clarifies that an increase in the OCV of the solutions would lead to an increase in its reduction potential while good anode materials requires low reduction potential (more negative)[4–6], hence low OCV. The investigation shows that higher Li-PAH ratio would reduce the OCV of the solution. Lithium loading plays an important role. An immediate idea to improve the performance of the PAH based LISES is to make the solutions over lithium-saturated so that they could be stronger reducing agents. The term "over lithium-saturated" refers to the Li-PAH ratio exceeds the limit using natural mixing method. It would be interesting to study the properties of the over lithium-saturated solutions. Such kind of solutions are likely to adopt the properties of metallic lithium and they might be expected to solve the problem of low conductivity of the materials and improve energy capacity as well.

Another approach to increase lithium loading of the system is to consider the potential of polymers[7–10]. From computational point of view, it would be interesting to look at how the binding energy change with number of lithium atoms bounded to the polymer until it reaches the maximum capacity and how lithium atoms locate themselves and affect the electronic structure of the systems. From experimental point of view, LISES made from polymers might exhibit more fantastic properties than small PAH molecules.

7.2.2 Quantitative Modelling of Conductivity

In this thesis, we have briefly analysed conductivity and electron transport in the PAH based LISEs and have found promising correlation between the electronic structures of Li-PAH adducts and conductivity. However, a complete model which formulates the conductivity as the parameters of the solutions is still missing.

With the assistance of molecular modelling on the interactions between lithium atoms and PAH molecules in the solution, the formation of solvated lithium cations and solvated electrons was illustrated. Ionic transport involves the change of relative permittivity and viscosity of the solutions when lithium is added to the solutions. The explicit modelling of electron transport in the solution would require a lot of work. The effective potential of the particles, especially solvent molecules has to be proposed to describe the scattering of solvated electrons, which would require deeper investigation on the molecular properties of the system. The motion of the scattering center also has to be handled. The potential should account for the coulomb effect, vibrational effect, Van der Waals effect and other possible interactions in the system. Future work could be done to build up a quantitative model so the conductivity of similar systems could be predicted based on some basic characteristics of the systems.

7.2.3 Lower Electron Affinity of PAH

Our investigation on the effect of nitrogen atom show higher electron affinity would reduce conductivity of the solutions. It would be reasonable to expect that lower electron affinity of PAH would increase the conductivity. Instead of nitrogen atoms, we could replace the carbon atoms in PAH molecules by elements with lower electron affinity such as phosphate and boron. The low electron affinity would reduce dissociation energy of corresponding Li-PAH adducts in the solution. This would dramatically increase the amount of solvated electrons and increase conductivity of the solutions.

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