IDENTIFICATION OF BATTERY PRODUCTS AND INTERMEDIATES THROUGH NMR SPECTROSCOPY

BY

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DISSERTATION

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Abstract

This dissertation focuses on identification of products and intermediates formed in the lithium-oxygen, lithium-sulfur, and lithium-ion battery systems. Interest in the species formed in cycled batteries is motivated by incomplete knowledge of the discharge mechanisms and products formed, where knowledge of these species can allow the design of more efficient batteries with greater specific energy density. The greater interest in batteries with high energy storage capabilities is motivated by the current social and economic goal of creating a sustainable energy future that is powered by renewable energy sources and energy storage devices.

The first section focuses on identification of species formed in lithium-oxygen (Li-O₂) batteries. Discharged lithium–O₂ battery cathodes are investigated with different catalysts present including Pd, α-MnO₂ and CuO, and containing two different electrolyte solvents, 1:1 ethylene carbonate/dimethyl carbonate (EC/DMC) and tetraethylene glycol dimethyl ether (TEGDME). Solid-state ⁶Li magic angle spinning (MAS) NMR spectroscopy is used to identify lithium products that are formed in the cathodes and differences between products formed with different catalysts and solvents present. Significant differences in the products formed in Li–O₂ cathodes with the two different solvents, EC/DMC and TEGDME, are described. Due to the small chemical shift range of lithium, the exact speciation is difficult to obtain from ⁶Li MAS NMR data alone. Fitting of the ⁶Li NMR peaks with tested Li-oxide powder standards indicates that Li–O₂ cathodes discharged in EC/DMC produce primarily Li₂CO₃ as a lithium product and those discharged in TEGDME produce primarily Li₂O₂. Solution 2-D correlation ¹H–¹³C NMR spectroscopy techniques allow for determination of side-products produced in Li–O₂ cathodes, which are presented.
The second section focuses on identification of products and intermediates formed in lithium-sulfur (Li-S) battery cathodes using solid-state $^{6}$Li and $^{33}$S MAS NMR spectroscopy. Cathodes are stopped and measured *ex-situ* at three different potentials during battery discharge to obtain chemical shifts and T$_2$ relaxation times of the products formed, which are discussed. The chemical shifts in the spectra of both $^{6}$Li and $^{33}$S NMR demonstrate that long-chain, soluble lithium polysulfide species formed at the beginning of discharge are indistinguishable from each other (similar chemical shifts), while short-chain, insoluble polysulfide species that form at the end of discharge (presumably Li$_2$S$_2$ and Li$_2$S) have a different chemical shift, thus distinguishing them from the soluble long-chain products. Spin-spin T$_2$ relaxation measurements of discharged cathodes are also presented, which demonstrate that T$_2$ relaxation rates form two groupings and support previous conclusions that long-chain polysulfide species are converted to shorter chain species during discharge. Through the complementary techniques of 1-D $^{6}$Li and $^{33}$S solid-state MAS NMR spectroscopy, solution $^{7}$Li and $^{1}$H NMR spectroscopy, and T$_2$ measurements, structural information about the discharge products of Li-S batteries is obtained and discussed.

The final section focuses on identification of compounds formed in the secondary electrolyte interphase (SEI) layer of lithium-ion (Li-ion) battery anodes using solid-state NMR spectroscopy matrix assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectrometry (MS). Solid-state $^{7}$Li and $^{13}$C MAS NMR spectra of cycled Li-ion anodes demonstrate SEI compound formation that occurs upon lithiation of Li-ion anodes and changes that occur in the SEI compounds upon de-lithiation of the anodes. Solid-state $^{13}$C DPMAS NMR shows changes in organic peaks associated with the solvent compounds (ethylene carbonate and dimethyl carbonate, EC/DMC) upon battery cycling, which are due to formation and subsequent changes in SEI compounds. Solid-state $^{13}$C NMR spin-lattice (T$_1$) relaxation rate measurements
of lithiated Li-ion anodes and standard polyethylene oxide (PEO) powders and MALDI-TOF mass spectrometry results indicate that large molecular-weight polymers are formed in the SEI layers of discharged anodes. MALDI-TOF MS and NMR spectroscopy results additionally both indicate that greater amounts of different products are present in de-lithiated anodes compared with lithiated anodes.
Dedicated to my family,

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CHAPTER 1

Introduction

Introduction to Battery Systems

1.1 Goals for Energy in the Future: Sustainable, Renewable Sources

Worldwide energy sustainability is currently a major area of focus for scientists, political figures and society as a whole. If current trends for increased use and demand for energy continue as they have for the past several decades, the demand for current sources of energy will not be met in the long-term by the limited supply of the primary, non-renewable energy resources used today, which are fossil fuels. Fossil fuels are considered non-renewable due to the millions of years required to create fresh supplies of this source and the much faster time-scale that they are depleted. Current primary energy sources will therefore not be able to meet future demands. Additional problems with current energy sources such as harmful side-effects on health and the environment as well as increased demand make it evident that drastic changes in energy production are necessary. A major goal of society is therefore to transition to using nuclear and renewable sources of electrical power including solar, water, biomass, wind, etc. as replacements for use of fossil fuels.\(^1\) Plans are underway in the U.S. to develop a completely electrified road transportation system. These goals are all unified under the overarching theme of creating a sustainable energy future.

A transition to renewable energy sources is largely driven by a constant rise in demand for energy. This increase in demand is due to overall population growth as well as increased use of power in countries with developing economies. Today the estimated total power consumption worldwide is 14TW and this number is projected to triple by the year 2050.\(^2,3\) The world
primary energy consumption grew by 2.3% in 2013. Hydroelectric and renewable energy sources grew by 6.7 and 2.2%, respectively.\textsuperscript{4} The increase in primary energy consumption is below average (for the third year in a row); however it indicates a continued increase in demand. It has been estimated that the world demand for energy will increase by a total of 41% between the years 2012 and 2035 at a rate of 1.5% per annum.\textsuperscript{4} These high increases in demand for power must be met in the future in a sustainable way.

Fossil fuels currently account for the world’s largest source for energy, which come in the form of oil (petroleum), natural gas, and coal. Energy sources from fossil fuels are predicted to each account for approximately 27% of total energy use by 2035 (or 81% total for fossil fuels) while renewable energy sources are expected to increase to nearly 20% of total energy use. There are several problems with the continued use of fossil fuels as the primary energy source worldwide including finite supply, politics, safety concerns, energy efficiency, and public opinion.

The issue of finite supply of natural fossil fuel resources has drawn much attention to the topic of creating sustainable energy in recent years. Petroleum (oil) and natural gas are formed from the anaerobic decomposition of organic materials in a process that takes millions of years, forming kerogen and hydrocarbons (liquid and gaseous). Kerogen is found in sedimentary rocks that are referred to as oil shales, which can be processed into liquid hydrocarbons. In the late 19\textsuperscript{th} century shale oil accounted for the largest source of fossil fuels worldwide. When liquid petroleum (crude oil) was discovered in the Middle East in the mid-20\textsuperscript{th} century, the market for petroleum shifted to this less expensive source and most of the shale oil industries were forced to stop production. However, in response to sharp rises in petroleum price from the Middle East the early 21\textsuperscript{st} century, shale oil processing has resumed in several countries (including the U.S.).\textsuperscript{5}
It has been estimated that advances in technology will allow fossil fuel use (specifically oil and gas) to meet the increasing demands for energy until the year 2050 with current prices. However, unknown factors such as the ability to recover oil and gas from new frontiers (i.e. the Arctic or deep water) due to climate, depth, pressure, remoteness, geological concerns, as well as uncertainty associated with the use of shale oil create uncertainty with regard to predictions for the extent of future fossil fuel use. Relatively low prices of oil and gas compared to renewables will likely allow them to remain competitive until at least 2050.

Another issue with continued use of fossil fuels as a major energy source is the environmental impact of fossil fuel use to the environment, which directly impacts the health of humans as well as all other species. The combustion of fossil fuels creates the harmful greenhouse gas carbon dioxide ($\text{CO}_2$), which accounts for 40% of total emissions. Greenhouse gases including $\text{CO}_2$, methane ($\text{CH}_3$), water vapor ($\text{H}_2\text{O}$), nitrous oxide ($\text{N}_2\text{O}$), and ozone ($\text{O}_3$) accumulate in the atmosphere and absorb and emit ever-increasing amounts of radiation from the earth and sun, causing a global warming effect (i.e. a rise in surface temperature) over time. Calculations predict that rises in temperature due to this greenhouse gas effect will ultimately create an atmosphere that will render life unsustainable due to extreme climate and weather changes. A current major goal that is outlined by the International Energy Agency is to limit the world’s temperature increase to 2°C by 2050.

Lastly, political factors play a large role in the goal to transition to renewable energy sources. International relations with countries that supply fossil fuels influence the availability of these resources to the U.S. Rights to geological locations where resources may be found are also a major concern. Increased prices in petroleum import from areas such as the Middle East additionally provide motivation for a transition to economical energy production. Oil production
in the U.S. and other non-Middle East locations are possible sources as well as nuclear energy and renewable energy sources from sunlight, water, wind, and biomass.

1.2 Energy Storage Devices as a Major Component of the Future Energy Solution

The most promising option to achieve the goal of a sustainable energy future is to transition from a system where energy is produced mainly by combustion of fossil fuels to one where use of fossil fuels is greatly reduced and the majority of energy is produced through renewable sources. An important difference in energy derived from renewable sources as opposed to fossil fuel sources that must be accounted for during a transition between them is that renewable sources intrinsically only produce energy intermittently. Therefore, for renewable sources to be feasible for use to power the U.S. electrical grid, etc., energy storage devices will be important to store energy during periods of low energy demand and release energy during periods of high energy demand when renewable sources are not able to meet power demands. Storage devices including batteries, fuel cells, capacitors, etc. will therefore likely play highly important roles in the sustainable energy solution.

Since petroleum is used in most automobiles today, which produces large amounts of CO$_2$ emissions that contribute to global warming, automotive transportation is one of the most important areas to transition to a renewable energy system. A great effort is currently underway to develop hybrid electrical vehicles (EVs) and plug-in hybrid vehicles.$^6$ The ultimate goal is to develop fully electrified vehicles that will allow for a fully electrified road transportation system.$^2$ The main problem in developing a complete electrification of automobiles is the inadequate storage capacity of current batteries, such as the lithium-ion battery. There are many
battery chemistries that offer higher specific energy density than the Li-ion battery that are currently being extensively researched. Some of the more promising new battery systems include the lithium-oxygen, lithium-sulfur, magnesium, and lithium-zinc batteries among numerous others. Since new energy storage devices will have to compete with modern automobiles that are powered by gasoline, a target range of 500 miles (800 km) per charge has been initiated by IBM for research pursuits. This target range is equivalent to a capacity of about 125 kWh with an average use of 250 Wh/mile.¹

Aside from automotive applications, energy storage devices will be required for use in other applications such as in portable electronic devices (cellular phones, laptop computers, electronic reading devices), remote sensors, and robotic uses.² Energy storage devices with energy densities that exceed those of current Li-ion batteries are critical to the achievement of a sustainable energy future. Battery systems in particular may offer the most promise as the most feasible energy storage devices compared to fuel cells and capacitors since battery development is further along. In particular, Li-O₂, Li-S, and Li-ion battery systems offer great promise in terms of capacity and feasibility of development within the required timeframe as energy storage devices for a future sustainable energy system.

1.3 The Reversible Li-O₂ Battery

The lithium-air (Li-air or Li-O₂) battery was proposed in the late 1970’s by Abraham and Jiang for automobile applications.⁷ It has since gained a great deal of interest as a highly promising candidate for electric vehicles (EVs) since it can theoretically store significantly more energy than any other battery chemistry, including the ubiquitous lithium-ion battery.⁷,⁸ Rechargeable lithium-ion batteries currently consist of a positive intercalation compound (such
as LiCoO$_2$) and a graphite negative electrode. Energy storage is limited by the intercalation capacity of the positive electrode and it is estimated that research efforts to improve Li-ion energy storage will only improve energy density by a factor of two.$^9$

A new approach to battery chemistry has been introduced through Li-O$_2$ battery chemistry, where no intercalation material is required and oxygen from the air is used directly as the cathode active material. The use of oxygen from the air as the cathode active material coupled with the low weight of lithium metal allows Li-O$_2$ batteries to be extremely lightweight. The theoretical specific energy of the Li-O$_2$ system has been estimated to be 11,140-18,000 Wh/kg by different sources.$^{10-12}$ Currently, Li-ion batteries can store approximately 160 Wh/kg and have a theoretical specific energy of 900 Wh/kg.$^{10}$ The Li-O$_2$ system is relatively new and is still under development. With its intrinsically high energy density, this technology is a promising candidate to resolve energy storage problems.

The Li-O$_2$ battery cell consists of a metal lithium anode, a porous carbon cathode with an interspersed catalyst and a non-aqueous electrolyte. During discharge, Li$^+$ ions migrate to the carbon cathode where they are reduced to form the reversible lithium peroxide product (Li$_2$O$_2$). Side-products such as lithiated oxide species also form during discharge. It has been proposed that the electrochemical discharge reaction to form the desired, reversible Li$_2$O$_2$ product at the cathode is a two-electron oxidation reaction with an operating voltage of 2.96 V vs. Li/Li$^+$.\textsuperscript{7}

\textit{Discharge mechanism (forward process, reversible)}:

\[ 2(\text{Li}^+ + e^-) + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2(\text{solid}) \]

Additional major discharge products that are proposed in previous reports include Li$_2$O, Li$_2$CO$_3$ and LiOH.$^{13,14}$ During the charge the newly-formed lithium oxide species are reduced to the
original reactants. Recently it has been proposed that side-reactions may occur that irreversibly produce Li$_2$O and LiO$_2$ species.$^{15}$

The theoretical, desirable charge mechanism of the Li-O$_2$ battery is the reverse of the discharge process. During charge, an external power supply causes electrons to travel from the cathode to the anode and the reversible Li$_2$O$_2$ product is broken down into the reactants, Li$^+$ and O$_2$. The Li$^+$ ions then migrate to the anode, where they deposit onto the Li metal surface, and the O$_2$ travels through the carbon cathode pores into the surrounding atmosphere.

*Charge mechanism (forward process, reversible):*

\[
\text{Li}_2\text{O}_2\text{ (solid)} \leftrightarrow 2(\text{Li}^+ + \text{e}^-) + \text{O}_2
\]

There are several problems with the operation of Li-O$_2$ batteries that must be overcome for them to be feasible for practical use. The basic operating principles of Li-O$_2$ batteries are not yet fully understood, thus fully-optimized Li-O$_2$ systems have not been accomplished. Li-O$_2$ systems have only achieved a small fraction of the theoretical specific energy and also have limited rechargeability.$^{10}$ It has recently been demonstrated that organic carbonate-based electrolytes decompose during cycling, producing undesirable species such as Li$_2$CO$_3$, HCO$_2$Li, CH$_3$CO$_2$Li and also CO$_2$.$^{16}$ The roles of electrolyte interaction with discharge products and in the reversible electrochemistry of the battery are not well-understood. However, it has been suggested that ionic liquids may be a suitable alternative to carbonate and ether-based electrolytes.

An additional problem with the Li-O$_2$ reversible battery system involves the large over-potentials associated with both the discharge and charge reactions.$^{2,17}$ The Li-O$_2$ battery field today is largely influenced by disagreement concerning what discharge products are formed,
mechanisms of charge and discharge reactions, the mechanism and extent of carbonate-based electrolyte decomposition, and the role of different catalysts on formation of different discharge products.

1.4 The Lithium-Sulfur Battery

The lithium-sulfur (Li-S) battery was introduced in the 1960’s, but has recently become an area of intense research and interest due to its very high theoretical capacity compared to the Li-ion battery (approximately five times larger than commercially available LIB’s), which is close to the Li-O₂ battery at 2,567 Wh kg⁻¹ (1,672 mAh/g). Other major advantages of the Li-S battery include the large availability of sulfur, which is the cathode active material, corresponding low cost, the relatively light weights of lithium and sulfur, as well as the negligible environmental impact of sulfur. This battery chemistry offers great promise as a next-generation energy storage device capable of reaching future goals of high specific energy density and with wide availability.

The Li-S battery typically consists of a lithium metal anode, a cathode composed of sulfur supported on carbon, and an organic carbonate or ether electrolyte solvent. The discharge reaction is the thermodynamically favorable process for the Li-S battery chemistry. During discharge of the cell, current flows from the anode to the cathode while lithium ions (Li⁺) migrate from the lithium metal anode, through a porous separator (usually polypropylene) to the cathode, where they react with elemental sulfur (ring-structured S₈) to form polysulfide species through a two-electron reduction process. The reduction of S₈ by lithium breaks the elemental sulfur ring, resulting in long chains of lithium polysulfide species (Li₂Sₓ, 1 < x < 8) with lithium
at the terminal ends. The first lithium polysulfide species that form are long in sulfur chain-length. As the battery is discharged to lower potentials, the polysulfide species become reduced to shorter chain lengths, forming $\text{Li}_2\text{S}_8$, $\text{Li}_2\text{S}_6$, $\text{Li}_2\text{S}_4$, $\text{Li}_2\text{S}_3$ (radical), and $\text{Li}_2\text{S}_2$ intermediate species. These lithium polysulfide intermediate species are soluble in the Li-S battery electrolyte solution. At the very end of discharge the final product, $\text{Li}_2\text{S}$, is formed as a solid deposit on the cathode surface. The final products $\text{Li}_2\text{S}$ and $\text{Li}_2\text{S}_2$ are both reported to be insoluble in the Li-S battery electrolyte system.

*Discharge mechanism:*

$$\text{Li}^+ + \text{S}_8 \rightarrow \text{Li}_2\text{S}_x (2 < x < 8) \rightarrow \text{Li}_2\text{S}$$

At the beginning of discharge the open circuit potential (OCP) of the cell, which is proportional to the difference in electrochemical potentials of the anode and cathode ($\mu_a$ and $\mu_c$, respectively) is nominally at ca. 3.6-4.1 V vs. Li/Li$^+$. As the battery species undergo reductive discharge reactions, the potential of the cathode decreases. The Li-S battery system is typically cut off at a potential of 1.5 V vs. Li/Li$^+$. The overall discharge voltage of the battery is approximately 2.1 V vs. Li/Li$^+$. This working voltage for the cell is low compared to the voltage obtained from the Li-ion battery (ca. 4.0 V), however, this deficiency in working voltage is offset by the extremely high specific energy densities that the Li-S battery is capable of achieving.$^{20}$

The charging reaction of the Li-S battery occurs when an external power supply causes electrical current to flow from the cathode to the anode. During the charge reaction, the cathode surface becomes an oxidative environment and short-chain lithium polysulfide species are oxidized back to lithium ions and sulfur. This process is essentially the reverse reaction of the discharge reaction.
Charge mechanism:

\[ \text{Li}_2\text{S} + \text{Li}_2\text{S}_x (2 < x < 8) \rightarrow \text{Li}^+ + \text{S}_8 \]

While the Li-S battery offers many advantages as a promising candidate as a next-generation clean energy storage device, there are several challenges that must be addressed for this battery system to become feasible for future use. The first problem is that sulfur and the lithium polysulfide discharge products, particularly the solid discharge end-products Li$_2$S and Li$_2$S$_2$, are insulating. These insulating species increase the overall resistance in the battery, which leads to a polarization that decreases its energy efficiency. An additional problem that results from the insulating nature of the sulfur species is that Li$_2$S and Li$_2$S$_2$ tend to form insulating layers on the cathode surface, which prevents reduction from occurring in the areas of the cathode containing these layers and ultimately leads to a decrease in the amount of active material that is utilized and poor re-chargeability of the cell.

Another major challenge in the Li-S battery system is that lithium polysulfide species (most notably Li$_2$S$_4$ and Li$_2$S$_8$) may react with or dissolve into the organic solvent system (typically 1,3-dioxolane and tetraethylene glycol dimethyl ether, TEGDME). Firstly, this leads to irreversible capacity fade of the sulfur cathode.\textsuperscript{21} This solubility of the lithium polysulfide species in the electrolyte system also allows the polysulfides to dissolve into solution and migrate to the lithium anode, where they are reduced, which leads to self-discharge of the battery and capacity fading. This problem of lithium polysulfide species migrating between the cathode and anode is referred to as the polysulfide “shuttle mechanism”. To prevent the polysulfide shuttling effect, efforts have been made to encapsulate sulfur in the cathode using conductive carbon,\textsuperscript{22} graphene oxide,\textsuperscript{23} and conductive polymers.\textsuperscript{24}
An additional challenge is associated with large increases in volume that occur in the cathode during battery discharge. Sulfur has been shown to expand by approximately 79% during reduction from elemental sulfur (S$_8$) to Li$_2$S due to intake of lithium. This large expansion of the sulfur causes parts of the sulfur to lose contact with the conductive carbon substrate or the current collector. As larger amounts of sulfur lose electrical contact with the cathode, the cell suffers from increased capacity fading.$^{25}$ Approaches have been taken to solve this problem by encapsulating the sulfur active material into core-shell structures and ensuring that the capsule is only partially filled with sulfur active material. This approach is referred to as yolk-shell nanoarchitecture. Using this yolk-shell method, sulfur expansion fills the void space in the capsule and does not cause cracking or breaking of the encapsulating shell.$^{25}$ Previous reports have used materials such as TiO$_2$, metal sulfides (i.e. SnS),$^{26}$ polyaniline,$^{27}$ and carbon$^{28}$ as yolk-shell structures to solve this volume expansion problem.

Another challenge is the selection of an ideal electrolyte solvent system for the Li-S battery. Fortunately, the operating voltages of the battery are within the electrochemical window of most organic electrolyte battery solvents.$^{29}$ Ether solvents are often used due to the high solubility of sulfur species into these types of systems, which allows for efficient reactions between Li$^+$ and sulfur. Unfortunately, ether-based solvents also result in the lithium polysulfide shuttle phenomenon due to the high solubility of the polysulfide species, which ultimately results in capacity loss. Carbonate solvents are not commonly used because they have been demonstrated to react with long-chain (Li$_2$S$_x$, $4 < x < 8$) lithium polysulfide species, which results in incomplete reduction of elemental sulfur.$^{30}$ Solvent systems such as ionic liquids and solid-state electrolytes have also been tested, however they result in slow Li$^+$ transport kinetics due to the high viscosity and nature of solid-state materials, respectively.$^{20,31}$
The typical discharge curve (potential versus capacity, mAh g\(^{-1}\)) for the Li-S battery results in three characteristic voltage plateau regions. However, the shape of this discharge curve remains largely not well-understood. It is highly important to understand the reaction chemistry of this battery in order to make improvements to the overall chemistry, capacity, discharge voltage, etc. Recently, much research and effort has focused on assigning which lithium polysulfide species are formed in each of the three plateau regions.\(^ {32}\) It is crucial to understand the exact discharge and charge mechanisms in order to design a Li-S battery that will overcome the problems addressed here and that will be a feasible energy storage system in the future.

1.5 The Reversible Lithium-Ion Battery

The lithium-ion (Li-ion) battery was first commercialized by Sony in 1991 and played a pivotal role in the development of portable electronic devices. Li-ion batteries are now ubiquitous in consumer portable electronic devices and are found in cellular phones, laptop computers, electronic reading devices, gaming devices, etc. This battery accomplishes these technological feats due to its high operating voltage of 3.6 V vs. Li/Li\(^+\) (for the cathode and 0 V vs Li/Li\(^+\) for the anode) coupled with its reasonable cycling capacity (ca. 240 Wh kg\(^{-1}\) currently achievable, 900 Wh kg\(^{-1}\) theoretical).\(^ {33}\) The energy output of a battery is a function of the product of its operating voltage and capacity. Higher energy density batteries therefore utilize materials with high operating potentials and high capacities.\(^ {34}\)

The three major components of the battery include the negative electrode (anode), electrolyte, and positive electrode (cathode). The anode is typically composed of carbon and the most commonly employed anode material is graphite. The original design for the Li-ion battery
utilized Li metal as the anode, however the development of intercalated graphite (LiC₃ₓ, 6 < x < 18) as an anode material led to major improvements in the safety of the battery. Intercalation materials are layered structures in two dimensions or porous networks in three dimensions that allow lithium ions (Li⁺) to insert between the layers and build electrical charge. High energy density anode intercalation materials are desirable, which allow for the insertion of the largest possible number of lithium ions. Many current Li-ion storage devices contain graphite as the anode material; however silicon anodes have been developed recently and continue to be investigated as a desirable alternative to carbon.

Cathode materials for the Li-ion battery are generally composed of transition metal oxides including layered oxide (i.e. lithium cobalt oxide, LiCoO₂), polyanion (i.e. lithium iron phosphate, LiFePO₄), or spinel (i.e. lithium manganese oxide, LiMn₂O₄) structures. Lithium cobalt oxide has been effective and the most commonly used cathode material, however due to problems with degradation upon overcharging and its lower natural abundance and accompanying high costs compared to other transition metals (such as nickel, manganese, and iron), research into different cathode materials is ongoing. Nickel-based cathode materials (such as LiNiO₂) have been investigated due to due lower costs and the higher volumetric specific capacity of these materials (870-970 mAh cm⁻³) compared to those of LiCoO₂ (808 mAh cm⁻³). Safety problems associated with the nickel-based cathode materials have been mitigated through doping with aluminum and cobalt. Vanadium oxide materials (such as V₂O₅ and LiV₃O₈) have also been investigated due to the high capacity of these materials. The vanadium oxide cathodes typically exhibit lower voltages of < 3 V vs. Li/Li⁺ compared to other materials tested, however.
Liquid electrolyte salts typically used in Li-ion batteries include lithium hexafluorophosphate (LiPF₆), tetrafluoroborate (LiBF₆), and perchlorate (LiClO₄). The electrolyte solvent is typically an organic carbonate such as ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). Together, the anode, cathode, and electrolyte make up the Li-ion battery cell.

The charge mechanism of the Li-ion battery occurs when an external power supply causes movement of current from the cathode to the anode. During this process, lithium ions are removed from the cathode (i.e. LiCoO₂) in a process that is referred to as de-intercalation (also de-lithiation or de-insertion). When lithium is removed, the cathode transition metal oxide is oxidized to higher valence states. During lithium insertion and de-insertion, the cathode material often undergoes compositional and phase changes that can lead to structural changes. High structural stability is an important characteristic for Li-ion battery cathode materials. The Li ions migrate from the cathode to the anode through the electrolyte where they intercalate (or insert) into the graphitic anode material. The graphite undergoes structural changes as the Li ions are inserted between graphene layers, from low Li density states (such as LiC₁₈) to higher Li-dense structures (such as LiC₁₂ and LiC₆). This process is referred to as lithiation (also insertion or intercalation).

Charge mechanism:

\[ C_6 + xLi + xe^- \rightarrow Li_xC_6 \]  
\[ \text{anode} \]

\[ \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + xLi + xe^- \]  
\[ \text{cathode} \]

Discharge of the Li-ion battery is the thermodynamically favorable process. During discharge, electrons travel from the anode to the cathode and lithium ions (Li⁺) are removed from
the anode (a de-intercalation process). Upon removal of the Li ions, the graphitic anode (of structure \( \text{LiC}_x, \ 6 < x < 18 \)) undergoes reverse structural changes (with respect to the charge process) from the most highly Li-dense structure (\( \text{LiC}_6 \)) to lower Li-dense states (such as \( \text{LiC}_{12} \) and \( \text{LiC}_{18} \)). Lithium ions then migrate from the anode to the cathode, where the cathode transition metal oxide is reduced to lower valence states.

\textit{Discharge mechanism:}

\[
\text{C}_6\text{Li}_x \rightarrow \text{C}_6 + x\text{Li} + xe^- \quad \text{(anode)}
\]

\[
\text{Li}_{1-x}\text{CoO}_2 + x\text{Li} + xe^- \rightarrow \text{LiCoO}_2 \quad \text{(cathode)}
\]

The lithium-ion battery is a promising candidate for use in future applications such as storage of renewable energy and electric vehicles due to the current success of the battery operation. The Li-ion battery is commercially available and has been proven to work. Other leading candidates such as the Li-O\(_2\) and Li-S batteries are still in the research and development stages and working systems with competitive capacities have not yet been realized. The specific capacity of the Li-ion battery must be increased by two or three-fold to reach goals for applications in electric vehicles and storing power for the grid. Intense research on this battery system for many years gives the Li-ion battery technology an advantage over competing battery chemistries, and it is possible that Li-ion batteries will continue to be the battery system of choice well into the future.

While the Li-ion battery offers many advantages over other battery chemistries, there are several challenges associated with this system. The primary challenge is similar to solvent problems associated with the Li-O\(_2\) battery where the organic solvents decompose into undesirable side-products. Organic carbonate solvents in Li-ion batteries undergo reduction at
the anode surface during the first charge (and in subsequent cycling) to form a solid electrolyte interphase (SEI) layer on the electrode. The SEI layer is composed of solvent and electrolyte decomposition products that are difficult to characterize spectroscopically and have not been fully identified. It is known that the SEI layer consists of both conductive and non-conductive regions, where thin, non-conductive regions form a protective passivation layer on the anode surface and can be advantageous for the battery. Advantages of the SEI include protection of the anode material from degradation during cycling and prevention of further decomposition of the electrolyte by blocking electron conductivity while allowing Li ion transport through the layer.\textsuperscript{33} The SEI passivation layer is therefore an important component for optimal battery operation. However, the SEI becomes problematic if the SEI film grows thick enough to prevent transport of Li ions through its layers. The SEI layer has been reported to be anywhere between several to tens or hundreds of Å in thickness.\textsuperscript{45} It is an important goal to understand the composition of the SEI passivation film in order to construct battery systems with optimal SEI properties (conductivity and Li-ion transport properties), which is currently an area of intense research and focus.

Models of the SEI have been formulated by several groups, which generally suggest that it is composed of inorganic species close to the graphite (including LiF and Li$_2$CO$_3$), with a porous organic or polymeric region close to the electrolyte.\textsuperscript{45-49} Crystals of LiF have been additionally been reported as found throughout the SEI layer.\textsuperscript{45,47}

There is currently no consensus on the species that compose the SEI layer due to limitations in sampling methodology such as inability to measure the battery components \textit{in-situ}, and additionally due to differences in types of electrode and electrolyte materials used in different research laboratories. Major components of the SEI that have been proposed include
Li$_2$CO$_3$, LiF, Li$_2$O, LiOH, Li$_2$C$_2$O$_4$, HCOLi, polycarbonates, ROLi, Li ethylene carbonate ((CH$_2$OCO$_2$Li)$_2$), and ROCO$_2$Li. Many different techniques have been implemented to identify the compounds formed in the SEI layer. A non-exhaustive list of the most common techniques used includes: X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge spectroscopy (XANES), Fourier transform infrared spectroscopy (FTIR), attenuated total reflection infrared spectroscopy, electrochemical methods (cyclic voltammetry), Raman spectroscopy, Auger electron spectroscopy (AES), atomic adsorption spectroscopy (AAS), temperature-programmed decomposition mass spectrography (TPD-MS), ion chromatography (IC), TOF SIMS and MALDI-TOF mass spectrometry, and scanning electron microscopy (SEM).

While the Li-ion system offers many advantages for future high-capacity applications, there are several disadvantages that must be overcome for the implementation of this battery to be feasible. First, the practical specific energy (Wh kg$^{-1}$) must be increased by two or three times that of current Li-ion systems. New and improved cathode materials with greater Li storage capacity and higher valence states will likely offer solutions to this first challenge. Secondly, the cycle life of the battery must be improved and cycling stability must be achieved for long-term battery use. Additionally, safety is a concern in all batteries containing inorganic lithium species, and the system must be optimized for user safety. Lastly, the secondary electrolyte interphase (SEI) layer must be characterized and a system must be optimized for its advantageous contributions to the operation of the battery.
1.6 Introduction to Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is an extremely powerful analytical method that may be employed to determine molecular structure, conformation, and dynamics. Solid-state NMR spectroscopy involves the study of heterogeneous, solid compounds and yields unique quantitative information that is unattainable in solution-state methods. Specifically, solid-state NMR can be used to determine quantitative information about chemical shift anisotropy, dipolar and quadrupolar couplings, and intra- as well as inter-nuclear bond distances and angles. This technique has developed rapidly over the past thirty years owing to sizable interest in the chemistry community in studying solid samples. Solid-state NMR spectroscopy has become an accessible method for many researchers with a vast array of experiments that may be used on a broad range of samples. Problems of poor spectral resolution due to anisotropic interactions within heterogeneous samples have been surmounted and resolution comparable to that found for solution-state samples is now routinely achievable. The use of solid-state NMR spectroscopy is expanding into many fields of chemistry due to the wealth of information it can provide and the increasing number of experiments that are being made available in NMR software packages that do not require detailed knowledge about pulse sequence theory for general users.\textsuperscript{60}

1.7 The Quantum Mechanical Basis of NMR Spectroscopy

The technique of NMR spectroscopy is based on the physical phenomenon of nuclear magnetic resonance, which occurs in nuclei that have the quantum mechanical property of
nuclear spin. The quantum mechanical spin of the nucleons (protons and neutrons) describes the magnetic angular momentum of the nucleus. Protons and neutrons consist of the subatomic particles quarks and gluons, which each have the properties of charge and spin. The neutron consists of two quarks with charge $-e/3$ and one quark with charge $+2e/3$, resulting in a net charge of zero and spin $1/2$. The proton consists of two quarks of $+2e/3$ charge and one quark with charge $-e/3$, yielding a net positive charge of $+1e$ and spin $1/2$. The magnetic properties of nuclei arise from the fact that nuclei have charge, and it follows from the Lorentz law that if the nucleus moves in a loop it will produce a magnetic field. Therefore, nuclei may possess a magnetic moment, which allows them to be probed using NMR spectroscopy.

Within the nucleus, protons and neutrons form spin pairs as described by quantum mechanics, which sum together to produce the total magnetic moment of the nucleus. If the number of protons and neutrons are even, the nuclear magnetic moment is zero. Nuclei with zero net magnetic moment are unobservable using NMR spectroscopy. If the number of protons and neutrons are odd, the sum of the spins of unpaired nucleons equals the total nuclear magnetic moment. The total spin angular momentum, $I$, can therefore occur only in increments of $1/2$ ($I = 1/2, 1, 3/2, 5/2, 7/2$, and $9/2$). In the nuclear shell model, the nucleus is described in terms of $I$, the magnitude of the spin angular momentum, $L$, the direction of the spin angular momentum, $m_p$, and the spin magnetic moment, $\mu_m$. The magnetic moment is defined in the following equation,

$$\mu_m = \gamma \frac{e}{2m_p} I$$

where $\gamma$ is the gyromagnetic ratio of the nucleus. The gyromagnetic ratio is unique for every nucleus and is the ratio of the magnetic moment to the angular momentum, usually given in units
of rad s\(^{-1}\) T\(^{-1}\). The spin angular momentum is a vector and may be described using its magnitude and direction according to the following equation.

\[ L = \hbar \sqrt{I(I + 1)} \]

The projection of the spin angular momentum vector may occur only as discrete values, \(m\).

\[ m = -I, -I + 1, -I + 2, \ldots + I \]

Nuclei with nonzero nuclear magnetic moments (i.e. that have nonzero nuclear spin) may be probed with NMR spectroscopy. Nuclei of nonzero spin consist of \(2I+1\) degenerate energy levels without the presence of an external magnetic field. However, when nuclei of nonzero spin are placed in an external magnetic field, these energy levels are no longer degenerate and each level has an energy described by,

\[ E = -\mu \cdot B_0 \]

where \(B_0\) is the external magnetic field strength (assumed to be along the \(z\)-direction of a Cartesian coordinate axis). In the absence of an external magnetic field the magnetic dipoles of nuclei are randomly oriented and distributed, thus, the sum of the net magnetization of the nuclei is zero. In the presence of a magnetic field, the magnetic dipoles have discrete energy levels for the spin angular momentum and have a nonzero net magnetization.

The presence of an external magnetic field causes magnetic dipole moments of nuclei to precess about the axis of the applied external magnetic field. The angular frequency of this precession is called the Larmor frequency. The Larmor frequency is proportional to the magnetic field strength and the gyromagnetic ratio of the nucleus, as described by
\[ \omega_L = \gamma B_0 \]

Different nuclei in the periodic table have different gyromagnetic ratios and they therefore precess at different frequencies under the influence of the same magnetic field. \(^{61}\)

In the case of a spin \( I = 1/2 \) nucleus, application of an external magnetic field will result in two energy levels, \( m_p = \pm 1/2 \). The magnetic moments of the nuclei will align either with or against the external magnetic field. The lowest energy state occurs when the nucleus is aligned in the direction of the external magnetic field, where \( m_p = -1/2 \) (often denoted as \( \beta \)). This lower energy level will be more populated than the higher energy level, \( m_p = +1/2 \) (denoted as \( \alpha \)), causing a net magnetization of the nuclei in the direction of \( B_0 \). The energy difference (\( \Delta E \)) between these spin energy levels is given by,

\[ \Delta E = E_\alpha - E_\beta = \gamma \mu_mB_0 \]

Since \( \Delta E = h\nu \), the frequency of the electromagnetic wave corresponding to the difference in energy levels between spin states is generally on the order of radiofrequency waves (tens to hundreds of MHz or \( 10^7-10^8 \) Hz). Therefore, the energy separations come into resonance when the radiation frequency satisfies the resonance condition,

\[ h\nu = \gamma \mu_0B_0 \]

When the resonance condition is met, strong coupling between electron spins and radiation occurs as well as strong absorption to excite spins to transition from the \( \beta \) to \( \alpha \) energy level. \(^{61}\) Thermal collisions (at similar energy levels, on the order of hundreds of MHz) can additionally be energetic enough to excite nuclei into higher spin states.
The above resonance condition is met for nuclear spins when the radiation frequency equals the Larmor frequency of the nucleus \( (\nu = \nu_L) \). This is called nuclear magnetic resonance (NMR), and occurs because the Larmor frequency is equal to,

\[
\nu_L = \gamma \frac{h B_0}{h}
\]

The distribution of nuclei in the different spin states (i.e. \( \beta \) and \( \alpha \) or upper and lower) can be described by the Boltzmann distribution,

\[
\frac{N_{\text{upper}}}{N_{\text{lower}}} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{h\nu}{kT}}
\]

Where \( N_{\text{upper}} \) and \( N_{\text{lower}} \) are the number of nuclei in the upper and lower spin states, \( \Delta E \) is the energy difference between spin levels, \( k \) is the Boltzmann constant \( (1.3805 \times 10^{-23} \text{ J/K}) \), \( T \) is the temperature (in K), \( h \) is the Planck constant, and \( \nu \) is the frequency of the electromagnetic wave that corresponds to the energy of \( \Delta E \).

Transitions between the nuclear magnetic spin energy levels may occur according to the selection rule,

\[
\Delta m = \pm 1
\]

Therefore, nuclei with spin \( I = 1/2 \) have two spin energy levels and one allowed transition (from \( +1/2 \) to \( -1/2 \)). Nuclei with spin \( I > 1/2 \) have multiple allowed transitions. For example, a nucleus with spin \( I = 5/2 \) will have six spin energy levels \( (2I+1) \) and therefore five allowed transitions. The transition from \( +1/2 \) to \( -1/2 \) is called the central transition and is the most commonly observed and studied transition. Transitions to or from any other spin levels are called satellite transitions.\(^{60}\)
NMR spectroscopy therefore involves the study of nuclei that contain the property of spin magnetization through the application of radio frequency waves that meet the nuclear resonance condition (at the Larmor frequency of the nucleus) and the absorption of this radiation through spin state transitions. The resultant absorption spectrum yields a wealth of information about the dynamics and structure of molecules. NMR is extremely useful as a tool to probe atomic, molecular, and even tertiary structure and dynamics.

1.8 Experimental Methods in NMR Spectroscopy

In a typical NMR spectroscopy experiment, a radio frequency (RF) wave is pulsed into the sample of interest in order to investigate nuclear and electronic properties of the molecules within the sample. The RF frequency ($\omega_{RF}$) is chosen such that it is equal to the Larmor frequency ($\omega_{L}$) of the nucleus to be studied. Since different nuclei precess at different Larmor frequencies in the same magnetic field, the application of an RF pulse allows for selective study of nuclei.

Upon the application of the RF pulse (along the y-axis of a Cartesian coordinate system), the net magnetization of the selected nuclei (i.e. with $\omega_{L} = \omega_{RF}$) is transferred from the direction of the external magnetic field ($B_0$, defined as the z-axis) in the direction of the x-axis (clockwise), perpendicularly to the axis of the applied RF pulse (the y-axis). This pulse is called the transmitter frequency. The length of time that the RF pulse is applied determines the angle of rotation of the net magnetization of the nuclear spins. Typically, the amount of time needed to apply a pulse to flip the net spin at a desired angle (i.e. to $90^\circ$ or $180^\circ$) is experimentally determined by arraying different pulse periods.
Nuclear spins of the same type of isotope (for example $^{13}\text{C}$ or $^1\text{H}$) do not all precess at the exact same frequency (i.e. the Larmor frequency), which is the phenomenon that ultimately allows for structural information of molecules to be obtained. Nuclear spins precess at slightly different frequencies due to shielding from the surrounding electronic environment, other magnetic dipole moments, the presence of unpaired electrons in nearby molecules (paramagnetic compounds), etc. In an atom placed in an external magnetic field, the electrons orbiting the nucleus generate a magnetic moment that opposes $B_0$ and effectively shields the nucleus from the full strength of $B_0$. The magnetic field strength experienced at the nucleus is the effective field strength, $B_{\text{eff}}$. The strength of the opposing magnetic field generated by the electron cloud of the atom depends on the electronic properties of the molecule at that particular nucleus.

A reference compound is always used in NMR spectroscopy that is chosen based on its surrounding electronic environment. Nuclei in the sample under study that are in close proximity to more electronegative atoms than that of the reference compound will experience less shielding from surrounding electrons. Conversely, nuclei close to less electronegative atoms will experience a greater density of surrounding electrons and therefore greater shielding from $B_0$. These shielding and de-shielding effects from the electronic environment of nuclei cause some nuclei to precess at higher frequencies than the Larmor frequency, when nuclei are de-shielded and experience a larger effective magnetic field ($B_{\text{eff}}$), and some to precess at lower frequencies than $\omega_L$, when nuclei are more shielded and experience a smaller effective magnetic field. Changes in the precession frequency of different nuclei due to different electronic environments are called chemical shifts.

Chemical shift ($\delta$) is typically normalized for the strength of the applied magnetic field ($B_0$) and is reported in units of part per million (ppm). Chemical shift is defined as,
where $X$ is the observed nucleus and $v_0$ is the nuclear resonance frequency. Normalization of the chemical shift with respect to the applied magnetic field allows chemical shift values for compounds to be universal (i.e. remain the same for all magnetic field strengths). NMR spectra are typically reported with chemical shift as the $x$-axis, with frequency and $\delta$ increasing from right to left.

In most NMR instruments, a receiver coil is located inside the probe in the $xy$ plane with respect to the sample and $B_0$. When the net magnetization of the nuclear spins is transferred to the $xy$ plane, the precessing spins generate a magnetic moment in the $xy$ plane that induces a flow of current through the loops of the receiver coil. This generates a detectable signal that consists of a mixture of frequencies generated by the spin-flipped precessing nuclei, which are on the order of tens to hundreds of MHz (similar to the applied RF pulse). The frequencies of oscillation in this signal arise from the precession rates of the individual nuclei in the sample as they precess around the $x$ or $y$ axis (along the same axis as the detection coil; however the location of signal detection is actually moved throughout the experiment). After the RF pulse has been applied and the net magnetization of the nuclear spins has flipped (at angle $\theta$), the net spin magnetization will return to the direction of $B_0$ (the $z$-axis). During this process, the spin angular momentum of individual nuclei returns from the excited to the ground state, which is called nuclear relaxation.
1.9 Spin Relaxation in NMR Spectroscopy: $T_1$ and $T_2$ Relaxation

There are two different components to nuclear relaxation, denoted $T_1$ and $T_2$, which are each caused by different physical processes. Spin-lattice ($T_1$) relaxation is the period of time required for the nuclear net magnetization to re-establish thermodynamic equilibrium with the surroundings (the lattice) after an RF pulse has been applied. Spin-lattice relaxation time measurements are typically measured for the return of the net magnetization to the direction of $B_0$ (the z-axis) over a 90° angle. This exponential process is described by,

$$M_z(t) = M_{z,eq}(1 - e^{-t/T_1})$$

for the case when $M_z(0) = 0$, where $M_z(t)$ is the nuclear net magnetization along the z-axis (a vector) after time $t$. The $T_1$ relaxation time can therefore be approximated as the time required for the net magnetization vector to return to 63% (or $(1 - 1/e)$) of its initial value (along the z-axis). Vibrational and rotational motion of nuclei within a lattice structure creates a magnetic field called the lattice field. Energy can therefore be exchanged and shared between nuclei that have different magnetic spin energy states. When an RF pulse is applied to a sample, the energy from the pulse dissipates quickly over time as the energy is transferred and shared between nuclei, causing increased vibrational and rotational energy in the surrounding nuclei and an increase in temperature as thermal equilibrium is reached. The spin-lattice ($T_1$) relaxation time depends upon the gyromagnetic ratio of the nucleus ($\gamma$) and the mobility of the surrounding lattice. When the mobility of surrounding atoms is higher, there is more vibrational and rotational energy in surrounding molecules and this increased energy and temperature promotes more transitions to occur between nuclear energy levels (so long as the thermal energy is on the order of the difference between energy levels). Nuclei experience the most efficient relaxation at the Larmor frequency of the nucleus.\textsuperscript{62} Different types of samples therefore return to thermal
equilibrium at different $T_1$ relaxation times, based on the mobility (or rigidness), size of molecules, and temperature of the system.

Spin-spin ($T_2$) relaxation is the period of time required for the transverse component of the net magnetization ($M_{xy}$) to return to equilibrium. After an RF pulse has been applied to a system of nuclear spins, nuclei with different resonant (precession) frequencies de-cohere at different rates in the transverse ($xy$) plane. In addition to this transverse magnetic phase decoherence due to precession frequency (due to shielding effects by surrounding electrons), interactions of the net magnetization in the transverse plane ($M_{xy}$) with local magnetic field inhomogeneities cause another source of decoherence (in the $xy$ plane). The latter type of transverse net magnetization decoherence consists of a slow or non-varying component and a varying component that is not reversible. The non-reversible component of the phase decoherence is caused by short and random processes such as collisions and diffusion that cause inhomogeneous decay of the net magnetization. Spin-spin ($T_2$) relaxation occurs through a separate mechanism than loss of net magnetization on the transverse plane by $T_1$ relaxation. The processes that cause $T_1$ and $T_2$ relaxation are distinct and the decay behavior of both processes should be considered separately. Spin-spin ($T_2$) relaxation is the rate of de-phasing that occurs within a collection of nuclear spins as they interact with one another.

The exponential decay of the net magnetization in the transverse plane is described by,

$$M_{xy}(t) = M_{xy}(0)e^{-t/T_2}$$

where $M_{xy}(t)$ is the nuclear net magnetization in the transverse plane after time $t$. The $T_2$ relaxation time can therefore be approximated as the period of time required for the net magnetization to return to 37% (or $1/e$) of its initial value.
Spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation rates have been correlated with molecular motion in BPP theory. In the $T_1$ curve there are three major regions of correlation: 1) the fast region where molecules tumble and traverse quickly, 2) the intermediate region, and 3) the slow region where molecular motion is more constrained. This plot of $T_1$ relaxation time versus correlation time (molecular motion) is V-shaped. The reason for this shape is that spin-lattice ($T_1$) relaxation is dependent on the nuclear gyromagnetic ratio (and therefore Larmor frequency, $\omega_L$) and the mobility of the surrounding lattice. Optimal $T_1$ relaxation occurs when the Larmor frequency of the nucleus is equal to the average surrounding molecular correlation time (reorientation rate), which occurs in region 2. When surrounding vibrational and rotational energies (and correlation time) of molecules is high, thermal (vibrational and rotational) energy transfer to the surrounding molecules and the rate of reaching thermal equilibrium are inefficient (average correlation times are high compared to $\omega_L$). As molecular motion decreases and becomes closer to $\omega_L$, as in region 1, transfer of thermal energy becomes more efficient and $T_1$ relaxation rate decreases. After the most efficient region of thermal equilibration has been passed (region 2) and molecular motion further decreases to below that of $\omega_L$, as in region 3, thermal transfer of energy again becomes inefficient and $T_1$ increases with increasing correlation time in this last region.
Figure 1.1: Spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation rate versus molecular correlation time. Reprinted with permission.

The $T_2$ curve follows a straight-forward inverse relationship with molecular correlation time according to BPP theory. Spin-spin ($T_2$) relaxation occurs by all frequencies of motion, not only frequencies near the Larmor frequency as is the case for $T_1$ relaxation. Therefore, as molecular motion decreases (i.e. correlation time increases) the efficiency of $T_2$ relaxation increases and $T_2$ relaxation time decreases.

1.10 The Free Induction Decay (FID)

The resultant signal that is produced during an NMR experiment consists of a mixture of frequencies due to the different precessions of nuclear spins in the transverse plane. This signal collectively decreases in an exponential decay that is dictated by transverse (or spin-spin, $T_2$)
relaxation mechanisms and is called the free induction decay (FID). The $y$-component of the net spin magnetization decays as,

$$M_y(t) = M_0 \cos(2\pi v_L t) e^{-t/T_2}$$

where $t$ is time, $M_0$ is the spin magnetization before the applied pulse, $v_L$ is the Larmor frequency, and $T_2$ is the transverse (or spin-spin) relaxation time. An approximation of $T_2$ relaxation time may be determined by the rate of the FID signal ($T_2^*$, the apparent $T_2$ relaxation period). The resulting detected FID signal (a mixture of RF frequencies) is lowered in frequency by subtracting the carrier frequency (usually the same as the transmitter frequency) so that it may be digitized. A mathematical operation called a Fourier Transform (FT) is then applied to the FID signal, which converts the signal from the time domain to the frequency domain, resulting in a spectrum of peaks at the oscillation frequencies of nuclear spins in different electronic environments. NMR spectroscopic signals are typically reported as intensity versus chemical shift (in ppm) spectra so that detailed information about molecular structure, dynamics, etc. can be obtained from the frequency at which peaks occur.

1.11 The Spin Hamiltonian

In quantum mechanics, wavefunctions are used to describe a nuclear spin or system of spins. Wavefunctions contain all of the information that is needed to calculate any property of a molecule. Any observable (such as position, energy, magnetization, etc.) may be computed using the appropriate operator on the wavefunction. In NMR spectroscopy, wavefunctions are highly important to understand and may be used to calculate precise information about a spin system. For example, the energy levels of a molecule, the quadrupolar coupling, or the way in
which the net spin magnetization evolves over time may all be calculated through knowledge of the wavefunctions.

The wavefunction of a molecule is generally a mixed state or a superposition of states. Quantum mechanics allows one to calculate all of the possible energy states that a spin may be found in upon measurement. However, a confusing result from quantum mechanics is that the spin need not only exist in one energy state at a time, but that it will be measured in one of the possible energy levels. When the spin is not being measured, it exists as a superposition (a mixture) of different energy levels. These mixed states from nuclear spins have long lifetimes compared to mixed states arising from molecular vibrational and electronic energy levels (such as in IR and UV spectroscopy). This is due to the fact that the energy levels are perturbed frequently by molecular collisions. Nuclei are located far inside molecules and are not disturbed to the same extent by these collisions. The superposition of energy levels is therefore important in the study of NMR spectroscopy, whereas it is not needed to explain UV or IR spectra.64

When a wavefunction is acted upon by an operator, the result is a set of Eigenfunctions and Eigenvalues. An Eigenfunction is the original function that was acted upon by the operator, which remains unchanged after the operation. The Eigenvalue is the corresponding constant that is multiplied to the Eigenfunction after an operator has acted upon a wavefunction. This general relationship can be described by,

$$(\text{Operator}) \text{ acts on (Eigenfunction)} = (\text{Eigenvalue}) \times (\text{Eigenfunction})$$

An example of the type of operation that yields an Eigenvalue and an Eigenfunction is the following where the operator, $d/dx$, acts upon an Eigenfunction to yield the same function (the Eigenfunction) times a constant (the Eigenvalue),
\[ \frac{d}{dx} \exp(AX) = A \times \exp(AX) \]

One of the most important operators in the study of NMR spectroscopy is that which represents the observable energy, the Hamiltonian operator \((\hat{H})\). The hat is generally used to denote an operator. The Hamiltonian operator results in the energy levels (Eigenvalues) and associated wavefunctions (Eigenfunctions) of a spin system. For a nuclear spin that is placed in an external magnetic field \((B_0)\) that is oriented along the \(z\)-axis, the Hamiltonian that describes the interaction between the spin and \(B_0\) is,

\[ \hat{H}_{\text{spin}} = -\gamma B_0 \hat{I}_z \]

where \(\hat{I}_z\) is the spin angular momentum operator along the \(z\)-axis. The operator \(\hat{I}_z\) has \((2I + 1)\) Eigenfunctions, as described by the quantum numbers \(I\) and \(m\) described previously \((m\) can take values between \(-I\) and \(+I\) in integer increments). The corresponding energies for the interaction between a nucleus and a magnetic moment \((\mu)\) are given by

\[ E_{m_I} = -\mu_z B_0 = -\gamma \hbar B_0 m_I \]

For a spin \(I = 1/2\) nucleus, the two resultant wavefunctions for application of the \(\hat{I}_z\) operator are,

\[ \psi_{+1/2} \text{ and } \psi_{-1/2} \]

Since a single spin may exist in a superposition of energy states, its wavefunction \((\psi)\) must be written as a linear combination of Hamiltonian Eigenfunctions. For a spin \(I = 1/2\) nucleus, the wavefunction can therefore be written as,

\[ \psi = c_{+1/2} \psi_{+1/2} + c_{-1/2} \psi_{-1/2} \]
where the coefficients $c_{+1/2}$ and $c_{-1/2}$ are numbers that yield the observable magnetization from one nuclear spin. The -1/2 and +1/2 spin states are often denoted as $\alpha$ and $\beta$, respectively (i.e. $\psi_{-1/2} = \psi_\alpha$).^64

To determine the wavefunction of a given nuclear spin system, it must be solved for using the appropriate Schrödinger equation. For a system with interactions that do not vary with time, the time-independent Schrödinger equation is used.

$$\hat{H}\psi = E\psi$$

The most complete description of a spin system that varies with time is the time-dependent Schrödinger equation.

$$\hat{H}(t)\psi(t) = i\hbar \frac{\partial \psi(t)}{\partial t}$$

The time-dependent Schrödinger equation (a linear partial differential equation) is a mathematical system used to predict the behavior of wavefunctions. It is applied in many different situations in quantum mechanics and the Hamiltonian operator takes on different forms depending upon the application. Usually the wavefunction of a system is determined by accounting for the kinetic and potential energies of a system in the Hamiltonian operator and solving for the wavefunction.

The total nuclear wavefunction contains both a spin and space component, as described by,

$$\psi = \psi_{spin}\psi_{space}$$
These two parts of the wavefunction must be treated separately and are largely uncoupled.\textsuperscript{60}

1.12 The NMR Hamiltonian and Coupling Interactions

The full Hamiltonian (energy operator) that is relevant for NMR spectroscopy can be written as follows,

\[ \hat{H}_{\text{NMR}} = \hat{H}_Z + \hat{H}_J + \hat{H}_{\text{CS}} + \hat{H}_{\text{DD}} + \hat{H}_Q + \hat{H}_{e,n} \]

where \( \hat{H}_Z \) represents the Zeeman interaction, \( \hat{H}_J \) represents J-coupling, \( \hat{H}_{\text{CS}} \) represents the chemical shift interaction (CSA), \( \hat{H}_{\text{DD}} \) represents both homo- and heteronuclear dipolar interactions, \( \hat{H}_Q \) represents quadrupolar interactions, and \( \hat{H}_{e,n} \) represents electron-nuclear interactions (sometimes denoted \( \hat{H}_{\text{II}}, \hat{H}_{\text{SS}}, \) and \( \hat{H}_{\text{IS}} \))\textsuperscript{65}.

The Zeeman term describes the interaction between the nuclear spin magnetic moment and the external applied magnetic field. As described in previous sections, the application of \( B_0 \) results in splitting of the degenerate ground state spin energy level into multiple spin energy levels (Zeeman splitting). The Zeeman interaction is the largest interaction experienced by an atomic nucleus in NMR spectroscopy and is on the order of tens to hundreds of MHz (radio frequency). The Zeeman Hamiltonian is often denoted as,

\[ \hat{H}_Z = -\hat{\mu} \cdot B_0 \]

where \( \hat{\mu} \) is the nuclear magnetic moment operator. The nuclear spin operator is denoted as,

\[ \hat{\mu} = \gamma \hbar \hat{I} \]

By combining these equations for \( B_0 \) along the z-axis, the Zeeman Hamiltonian becomes,
The eigenvalues of the Zeeman Hamiltonian $\hat{H}_z$ are the energies of the different possible spin states for the system.

$$E_{l,m} = -\gamma \hbar B_0 m$$

where $l$ and $m$ are the nuclear spin quantum numbers.

The scalar coupling constant, $J$, describes the interaction between the local field of one nucleus on the resonance frequency of a nearby (three bond-distances or less) nucleus. This interaction results in the splitting of peaks into smaller, individual lines called the spectral fine structure. This interaction is on the order of Hz and is commonly referred to as spin-spin or J-coupling. The J-coupling is proportional to the scalar product of the two interacting spins ($E \propto I_1 \cdot I_2$), and independent of the strength of $B_0$. J-coupling can be described by,

$$B_{nuc} = -\frac{\gamma \hbar \mu_0}{4\pi R^3} (1 - 3\cos^2 \theta)m_l$$

where $B_{nuc}$ is the $z$-component of a magnetic field generated by a nucleus with spin projection $m_l$, $R$ is the distance between the spins, and $\theta$ is the angle between the $z$-axis and the vector of the spin projection of a nucleus. As molecules freely and rapidly tumble in solution, the angle $\theta$ passes through all possible values, resulting in the $1-3\cos^2 \theta$ term averaging to zero. The J-coupling interaction is large in solution-state samples and aids in structural determination of molecules. However, this interaction is very small compared to more dominant interactions in the solid-state and is not usually observed in solid-state NMR.
Chemical shift anisotropy (CSA) describes the dependence of chemical shift on molecular orientation with respect to $B_0$. The interaction of the electronic shielding ($\sigma$) of a molecule with the external magnetic field ($B_0$) has orientation dependence. The total observed chemical shift shielding is the sum of three contributions: local, neighbor, and solvent shielding. The local shielding contribution consists of diamagnetic and paramagnetic contributions. The shielding contribution from neighboring molecules (or groups of atoms) has the approximate dependence,

$$\sigma_{\text{neighbor}} \propto (\chi_\parallel - \chi_\perp) \left( \frac{1 - 3 \cos^2 \theta}{r^3} \right)$$

where $\chi_\parallel$ and $\chi_\perp$ are the components of the magnetic susceptibility of a group of atoms, parallel and perpendicular to its axis of symmetry, respectively, $\theta$ is the angle from the axis of symmetry of a group of atoms to the vector connecting the neighboring atom, and $r$ is the distance between the atom and its neighboring group of atoms.\(^6\)\(^1\) Chemical shift interactions are on the order of KHz ($10^3$ Hz). In solid-state NMR chemical shift anisotropy results in very broad NMR peaks, which are averaged out in solution-state NMR to one sharp, isotropic peak due to rapid molecular tumbling.

Dipole-dipole interactions (dipolar coupling) are caused by the interaction of nuclear spin magnetic moments between two or more spins. This interaction can be classically compared to the interaction between two bar magnets. Each of the nuclear spins acts as a small bar magnet as it creates a local magnetic field that affects and interacts with surrounding spins. The dipolar Hamiltonian can be expressed in Cartesian tensor form for dipolar coupling between two spins $I$ and $S$ where spin $S$ is the source of the magnetic field felt at spin $I$ as,
\[ \hat{H}_{DD} = -2\mathbf{I} \cdot \mathbf{D} \cdot \hat{S} \]

where \( \mathbf{D} \) is the dipole-coupling tensor (with principal values \(-d/2, -d/2, +d\)), which describes the way the magnetic field varies with the direction of the spins \( I-S \) vector, and \( d \) is the dipolar coupling constant. The value of \( d \) (in units of rad s\(^{-1}\)) is expressed as,

\[ d = \hbar \left( \frac{\mu_0}{4\pi} \right) \frac{1}{r^3} \gamma_I \gamma_S \]

where \( r \) is the internuclear distance between the spins.\(^6\)

There are two different possible types of dipolar coupling, which include homonuclear and heteronuclear coupling. Homonuclear dipolar coupling involves spins (\( I \) and \( S \)) of the same species. The homonuclear dipolar Hamiltonian may be written concisely (often denoted as the secular or truncated form) as,

\[ \hat{H}_{DD}^{\text{homo}} = -d \cdot \frac{1}{2} \left( 3\cos^2\theta - 1 \right) [3\hat{I}_z \hat{S}_z - \hat{I} \cdot \hat{S}] \]

Heteronuclear dipolar coupling involves two spins (\( I \) and \( S \)) of two different species. The heteronuclear dipolar Hamiltonian can be written as,

\[ \hat{H}_{DD}^{\text{hetero}} = -d (3\cos^2\theta - 1) \hat{I}_z \hat{S}_z \]

In general, dipolar interactions are on the order of kHz \((10^3)\) Hz, similarly to chemical shift interactions.

Quadrupolar nuclei are defined as nuclei with spin \( I > 1/2 \), which have a non-spherically symmetric electric field distribution. Quadrupolar interactions are on the order of MHz \((10^6)\) Hz and are the second largest interaction experienced by nuclei in NMR spectroscopy. Generally,
quadrupolar coupling involves the interaction between the electric field at the nucleus and external electric field gradients. Quadrupolar coupling is explained in greater detail in the next section.

The electron-neutron nuclear Hamiltonian term, often referred to as hyperfine interaction, is due to interactions between the nuclear magnetic moment with the magnetic moment of electrons in the surrounding environment. When electronic spin is exchanged rapidly due to motions in conduction electrons (commonly in metals), NMR signals are shifted by the average hyperfine interactions. The observed shift is due to the local magnetic field produced at a nucleus by the magnetization of conduction electrons in or surrounding the nucleus. This interaction is often referred to as the Knight shift.

\[
\hat{H}_{KS} = -\sum_{i}^{N} \gamma_{i} \cdot \hat{I}_{i} \cdot \vec{R}_{i} \cdot \vec{B}
\]

where \(\hat{I}_{i}\) is a vector of nuclear angular momentum operators, \(\vec{R}_{i}\) is a second-rank tensor operator for the relative chemical shift \(K\), \(\vec{B}\) is a magnetic induction field, and the sum is taken for an ensemble of \(N\) spins for the \(i^{th}\) spin. The hyperfine interaction is composed of an isotropic part (the Fermi-contact contribution) and an anisotropic part (spin-dipole contribution). The isotropic Fermi-contact contribution only occurs for electrons in \(s\)-orbitals since they can have non-zero electron density at the nucleus and is described by,

\[
A = -\frac{2}{3} \mu_{0} \langle \mu_{n} \cdot \mu_{e} \rangle |\psi(0)|^{2}
\]

where \(A\) is the energy of the interaction, \(\mu_{n}\) is the nuclear magnetic moment, \(\mu_{e}\) is the electron magnetic dipole moment, and \(\psi(0)\) is the electron wavefunction at the nucleus.
The total spin Hamiltonian for solution-state NMR can be reduced to include only the largest interactions in this state. In solution-state, only the first two terms of the total NMR Hamiltonian are required to interpret spectra. The solution NMR Hamiltonian can therefore be written as,

\[ \hat{H}_{\text{Solution}} \approx \hat{H}_Z + \hat{H}_J \]

which summarizes the largest interactions present in solution NMR spectroscopy, Zeeman and J-coupling.

The solid-state NMR Hamiltonian can be similarly reduced to depict the largest interactions that occur in the solid state. The reduced solid-state NMR Hamiltonian is given by,

\[ \hat{H}_{\text{Solid}} = \hat{H}_Z + \hat{H}_Q + \hat{H}_{DD} + \hat{H}_{CS} \]

The above equation is highly important for the interpretation of solid-state NMR spectra and shows that the Zeeman, quadrupolar, dipolar, and chemical shift terms are the most important to consider when interpreting such spectra.\textsuperscript{65}

1.13 Quadrupolar Coupling

The electrical charge distribution at the nucleus in nuclei with spin \( I = 1/2 \) is spherically symmetric. The result is that NMR line shapes are isotropic and relatively straightforward to interpret. However, nuclei with spin \( I > 1/2 \) are called quadrupolar nuclei. The charge distribution in a quadrupolar nucleus is not spherically symmetric, which means that these nuclei possess an electric quadrupole moment which will interact with an electric field gradient (EFG).
Figure 1.2: Nuclear charge distribution inside an (a) spin $I = \frac{1}{2}$ nucleus with spherically symmetric charge distribution and (b) a quadrupolar (spin $I > \frac{1}{2}$) nucleus with a non-spherical electric charge distribution, with the electric field gradient shown outside of the nucleus.

The electric quadrupole moment ($eQ$) describes any asymmetry of the electric charge distribution within the nucleus.

Figure 1.3: Asymmetry in the charge distribution of quadrupolar nuclei as described by the electric quadrupole moment, $eQ$. 
Quadrupolar nuclei generally yield more complicated line shapes than spin $I = 1/2$ nuclei. The quadrupolar interaction is generally the second largest interaction that occurs in solid-state NMR (the first is the Zeeman interaction). The quadrupolar interaction can generally be expressed as,

$$\hat{H}_Q = \frac{eQ}{2I(2I - 1)\hbar} \mathbf{V} \cdot \mathbf{l}$$

where $Q$ is the nuclear electric quadrupole moment and $V$ is the electric field gradient tensor.

Another method to treat the quadrupolar interaction is by using perturbation theory. Generally perturbations to the quadrupolar interaction are only required to the first and second order to gain a complete understanding of spectra involving a quadrupolar nucleus. For a powder under static conditions, the first-order quadrupolar interaction may be written as,

$$H_{Q}^{(1)} = N_Q \frac{1}{6} \sqrt{6} \{3l_z^2 - l(l + 1)\} V_{z,0}$$

For a static powder sample, the first-order quadrupolar interaction has the dependence,

$$H_{Q}^{(1)} = \sigma_Q \frac{8I(2I - 1)\hbar}{3e^2 qQ} = 3\cos^2\beta - 1 + \eta\sin^2\beta\cos2\alpha$$

where $\sigma_Q$ is the quadrupolar coupling, $\frac{e^2 qQ}{\hbar}$ is the quadrupolar coupling constant, $eq$ is $V_{zz}$, the largest component in the EFG tensor ($V$), and $\alpha$ and $\beta$ are the polar angles of $B_0$. The first-order quadrupolar interaction ($H_{Q}^{(1)}$) is independent of $\sigma_L$, the Larmor frequency. The angular dependency of this first-order quadrupolar interaction with respect to $B_0 (3\cos^2\beta - 1)$ means that if the sample (i.e. the rotor) is placed at $\beta = \arctan\sqrt{2}$ (approximately 54.74°) from the $z$-axis (the direction of $B_0$), this term is reduced to a value of zero and the first-order quadrupolar coupling is
essentially cancelled out as the rotor rotates one full period.\textsuperscript{61} Placing the rotor at this specific angle and spinning the rotor are common techniques employed in solid-state NMR spectroscopy and are discussed in the magic angle spinning (MAS) section.

The second-order quadrupolar interaction ($H_Q^{(2)}$) is given by

$$H_Q^{(2)} = -\frac{N_Q^2}{\omega_L^2} \left( \frac{1}{2} V_{2,-1} V_{2,1} (4I(I+1) - 8I_x^2 - 1) + \frac{1}{2} V_{2,-2} V_{2,2} (2I(I+1) - 2I_x^2 - 1) \right) I_x$$

where the terms $V_{2,k}$ are components of the EFG expressed as a spherical tensor of rank 2. $H_Q^{(2)}$ is inversely proportional to $\omega_L$ and therefore decreases as the Zeeman field strength (magnetic field, $B_0$) is increased.\textsuperscript{66}

\subsection*{1.14 Solid-State NMR Spectroscopy and Magic Angle Spinning (MAS)}

The practice and interpretation of solid-state NMR is different than solution-state NMR due to the different physical interactions that dominate these two types of spectroscopy. As described in the previous section, the major interactions that must be considered for solution NMR experiments are the Zeeman and J-coupling interactions. Other interactions such as dipolar (dipole-dipole, DD), chemical shift anisotropy (CSA), and quadrupolar interactions need not be considered in solution-state NMR because the fast tumbling and Brownian motion of the molecules averages these interactions to zero (over time).\textsuperscript{65} Solution NMR therefore typically yields isotropic, narrow peaks. However, in the solid-state the rotation and motion of molecules is highly restricted by surrounding molecules (the lattice). Thus the dipolar, CSA, and
quadrupolar interactions are not rotationally averaged to zero for solid-state molecules and these terms make significant contributions to solid-state NMR spectra in addition to the Zeeman interaction. In the solid-state, the Zeeman and quadrupolar interactions contribute most strongly to NMR spectra because these interactions are large. J-coupling interactions are not observed in solid-state NMR spectroscopy. Due to the strong dependence of molecular orientation in solid-state NMR (in the CSA, dipolar, and quadrupolar interactions), these spectra are typically extremely broad (ca. tens of Hz to hundreds of kHz).

Magic angle spinning (MAS) is a technique used in solid-state NMR spectroscopy to sharpen the otherwise extremely broad solid-state lines. The MAS technique was first observed and described by A. A. Bradbury and R. G. Eades in 1958 and independently by I. J. Lowe in 1959. Experimentally, this technique is employed by physically placing the solid-state sample rotor (device that holds the sample) at an angle of 54.74° to the external magnetic field ($B_0$) and spinning the rotor at high speeds (5-70 kHz) using air blown directly at flutes in the drive tip located at the base of the rotor. A scheme of magic angle spinning inside the external magnetic field is depicted in Figure 1.4, below.
Figure 1.4: Experimental placement of the sample rotor at 54.74° with respect to the external magnetic field ($B_0$) for the technique of magic angle spinning (MAS) labeled to indicate the drive tip and rotor body.

The angle required in the MAS technique, 54.74° with respect to $B_0$, precisely cancels terms in the time-dependent dipolar and first-order quadrupolar interactions and averages chemical shift anisotropy interactions to a non-zero value. These anisotropic interactions cause broad lines in solid-state NMR spectra and MAS results in sharper lines with observable fine structure that is similar to the resolution obtained from solution NMR spectroscopy. Specifically, the $(3\cos^2 - 1)$ terms in the aforementioned interactions cancel to zero when $\theta$ is equal to $\cos^{-1}(1/\sqrt{3})$, or 54.74°. Physically, this angle occurs when the rotor is placed along the diagonal vector connecting two opposite vertices of a cube. At this angle the sample has equal projections onto each of the three Cartesian axes ($x$, $y$, and $z$), and therefore experiences interactions along each of the axes equally. After one rotor period around the center of the MAS axis, the rotor has experienced an averaging of the time-dependent anisotropic interactions.
These interactions effectively average out to zero, which results in narrower, more isotropic peaks. Line shapes are not always entirely isotropic due to second-order quadrupolar effects, etc. that are not completely averaged out through MAS.

![Geometrical derivation of the magic angle spinning angle ($\theta_m$).](image)

\[ \cos^2 \theta_m = \frac{1}{3} \quad \rightarrow \quad \theta_m = 54.74^\circ \]

Figure 1.5: Geometrical derivation of the angle ($\theta_m$) employed in the magic angle spinning (MAS) solid-state NMR technique.

The solid-state MAS technique can be applied to a wide range of samples including polycrystalline, monocrystalline, and amorphous solids. If the sample is spun at rates that are smaller than the anisotropic interactions that occur within the sample, artifacts (i.e. peaks) will appear on both sides of the central transition (CT) peak with separations of the MAS spinning speed (in Hz). These satellite peaks are called spinning sidebands and can yield useful information about molecular structure and orientation. When the rate of MAS spinning ($\omega_r$) is
increased to greater frequencies than those of the anisotropic interactions, the spinning sidebands do not appear.\textsuperscript{69}

1.15 Nuclear Magnetic Resonance (NMR) Spectroscopy as an Analytical Technique to Identify Battery Products

Solid-state magic angle spinning (MAS) NMR spectroscopy has demonstrated in previous reports to be useful in determining information about products formed in batteries. The area in which NMR spectroscopy has been employed by far the most is in lithium-ion batteries. A plethora of information about intercalation structures, distances, rates, etc. can be determined using NMR spectroscopy, which makes NMR spectroscopy extremely conducive to the study of Li-ion anode and cathode materials and products. The most extensively studied nuclei with applications to batteries include lithium ($^{6,7}$Li),\textsuperscript{70-77} carbon ($^{13}$C),\textsuperscript{78} and hydrogen ($^{1}$H).

Lithium is one of the most useful nuclei to study in the identification of lithium battery products since Li is present in most of the species formed within the battery. The chemical shift range of diamagnetic lithium species is small (ca. 10 ppm) and yields a more crowded spectrum than typical solution-phase NMR spectra. The $^{7}$Li nucleus is quadrupolar with quantum spin $I = \frac{3}{2}$ and has a very high natural abundance of 92.5\% while $^{6}$Li has a much lower quadrupolar moment (the smallest of any quadrupolar nucleus) and has integer quantum spin of $I = 1$.\textsuperscript{79-81} NMR spectra of $^{7}$Li nuclei are typically dominated by quadrupolar interactions and dipolar coupling resulting in highly broadened line shapes. The NMR spectra of $^{6}$Li nuclei typically have better resolution and peak dispersion due to the small quadrupolar interaction; however its low relative abundance (7.59\%) results in much lower sensitivity.\textsuperscript{79,80,82} The central transitions
of lithium nuclei are not broadened by quadrupolar interaction to first order, however in many cases second-order quadrupolar effects must be accounted for.\textsuperscript{80}

Solid-state \textsuperscript{7,6}Li MAS NMR spectroscopy has also been successfully employed to identify Li-O\textsubscript{2} battery discharge products.\textsuperscript{81,83,84} Previous reports of identifying species formed in Li-O\textsubscript{2} batteries are conducted \textit{ex-situ}, where exposure to moisture in the air could alter the species that were observed. Solid-state \textsuperscript{7}Li MAS NMR spectroscopy has allowed the identification of peaks close to 0 ppm to be irreversible Li inside the solid electrolyte interphase (SEI) layer of Li-ion batteries.\textsuperscript{85} Peaks close to 50 ppm are identified as Li\textsuperscript{+} ions that are intercalated between graphene layers in Li-ion anodes upon lithiation of carbon anodes in several studies.\textsuperscript{86,87}

1.16 \textbf{Research Motivations and Goals}

The goals for the research presented in this dissertation are to expand upon the current knowledge of products and intermediates formed in several of the most promising battery chemistries for a sustainable energy future.

In the first chapter, discharge products and intermediates formed in lithium-oxygen (Li-O\textsubscript{2}) batteries are explored. A variety of cathode catalysts are investigated with the goal of promoting the two-electron reduction of di-oxygen to lithium peroxide (Li\textsubscript{2}O\textsubscript{2}). Products and intermediates formed in the battery are identified using solid-state and solution-state nuclear magnetic resonance (NMR) spectroscopy. It is evident that in addition to the desirable, reversible Li\textsubscript{2}O\textsubscript{2} product other side-products are formed during the discharge reaction. Species formed in Li-O\textsubscript{2} battery cathodes are studied with several different catalysts present, as well as containing two different solvents: an organic carbonate mixture (ethylene carbonate and dimethyl carbonate, EC/DMC) and an ether-based solvent (tetraethylene glycol dimethyl ether,
TEGDME). Determination of the species formed in Li-O$_2$ batteries will ultimately assist in the design of more efficient batteries with greater specific energy density. Insights into side-products formed in Li-O$_2$ batteries are described.

In the second chapter, the products and intermediates formed during discharge of the lithium-sulfur (Li-S) battery are identified using solid-state NMR spectroscopy. The Li-S battery is another highly promising system for future renewable energy storage as well as for applications in electric vehicles. The Li-S battery discharge curve (voltage versus capacity) yields three characteristic plateau regions where different lithium polysulfide species are putatively formed. Herein, Li-S battery cathodes are stopped at the ends of these three important potential plateaus during discharge and tested using NMR spectroscopy to identify species present. The predominant species formed with several different catalysts as well as in the two different solvent systems are reported, which give insight into the discharge mechanism with each solvent system. In addition to one-dimensional NMR spectra, spin-spin (T$_2$) relaxation measurements are obtained for species at each of the three potential regions, which yield information about the relative size and physical state of species present. Differentiation between soluble intermediate species and the insoluble final discharge product, Li$_2$S, is achieved and described.

In the third chapter, species formed in the secondary electrolyte interphase (SEI) of the Li-ion battery are identified using solid-state NMR spectroscopy and matrix assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectrometry (MS). The exact speciation of the SEI layer remains unknown, and efforts to elucidate species present are reported. Intercalation of lithium into the graphite anode material is confirmed with solid-state $^7$Li NMR, and changes in the structure of solvent compounds are observed upon lithiation and
de-lithiation using solid-state $^{13}$C NMR and reported. These changes in the chemical shifts of solvent peaks as well as the graphite peak are indicative of SEI formation. Spin-lattice ($T_1$) relaxation rate measurements are made of lithiated Li-ion anodes and standard polyethylene oxide (PEO) powders and are compared, which give insight into the size of species formed in the SEI layer. Lastly, MALDI-TOF MS results are described, which give evidence of polymer formation in the SEI layer.

1.17 References


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Chapter 2

Identification of Products Formed in Li-O$_2$ Batteries through $^6$Li, $^{13}$C and $^1$H NMR spectroscopy

2.1 Introduction

The non-aqueous lithium-air battery or Li-O$_2$ battery, first reported in 1996,$^1$ has been the focus of considerable attention because its putative specific energy (3,505 Wh kg$^{-1}$) is substantially larger than that found for Li-ion batteries and approaches the theoretical specific energy for gasoline/air engines (11,860 wh kg$^{-1}$). In Li-ion batteries the specific energy is limited by the positive electrode (150 mAh g$^{-1}$ or a theoretical specific energy of 387 wh kg$^{-1}$)$^3$, which is itself the subject of substantial attention. The gravimetric capacity of the Li-air battery comes at the expense of volumetric capacity, where the Li-air battery is only slightly better than Li-ion (3,436 Wh L$^{-1}$ for Li-O$_2$ vs. 1,015 Wh L$^{-1}$ for Li-ion). The low volumetric energy density of Li-O$_2$ batteries arises from the need to store excess Li in the anode, since Li metal has a relatively low density (0.534 g cm$^{-3}$)$^2$.

The discharge reaction for the Li-O$_2$ battery involves the two-electron reduction of O$_2$, which migrates into a porous carbon (nanoporous gold catalyst has also been used as a cathode material)$^4$ cathode, and reacts with Li$^+$ ions from the lithium metal anode to produce lithium oxide products. The desired product is lithium peroxide, Li$_2$O$_2$, which is a theoretically reversible product with a reaction formal potential of 2.96 V, shown in scheme 2.1.$^5, 6$
Scheme 2.1: Reaction mechanisms for theoretical reactions that occur during Li-O₂ battery discharge at the cathode where $E_{rev}$ is referenced vs. Li/Li⁺ (as are all potentials throughout this study).\(^5\)\(^-\)\(^10\)

Several studies indicate that Li₂O₂ is the major discharge product formed in Li-O₂ battery cathodes.\(^1\)\(^,\)\(^11\)\(^,\)\(^12\) Although Li₂O₂ is the full oxygen reduction product and forms preferentially, Li₂O (as depicted in Scheme 2.1, with $E_{rev} = 2.91$ V\(_{Li} \)) is the more desirable product because of its higher specific energy and energy density.\(^5\) Li₂O formation has been suggested to occur by two different mechanisms, as shown in Scheme 2.1 with $E_{rev} = 2.91$ and 2.87 V\(_{Li} \). However, recharge of a battery with a Li₂O product is problematic.\(^13\)\(^,\)\(^14\)

While Li-air batteries are in concept advantageous, several studies indicate that the carbonate solvents commonly used in these batteries decompose readily in Li-O₂ discharge systems to form Li₂CO₃.\(^15\)\(^-\)\(^17\) The search for a more robust solvent and electrolyte has led to a recent report suggesting that tetraethylene glycol dimethyl ether (TEGDME) and lithium triflate (LiCF₃SO₃) might result in a more robust battery exhibiting greater cycleability.\(^18\) However, other studies suggest that ethers (such as DME, diglyme, triglyme, TEGDME and 1,3-dioxolane)\(^2\) decompose during discharge to some extent as well, especially over the period of

\[
2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \leftrightarrow (\text{Li}_2\text{O}_2)_{\text{solid}} \quad E_{rev} = 2.96 \text{ V}
\]

\[
4\text{Li}^+ + 4\text{e}^- + \text{O}_2 \leftrightarrow 2(\text{Li}_2\text{O})_{\text{solid}} \quad E_{rev} = 2.91 \text{ V}
\]

\[
(\text{Li}_2\text{O}_2)_{\text{solid}} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow 2(\text{Li}_2\text{O})_{\text{solid}} \quad E_{rev} = 2.87 \text{ V}
\]
many cycles.\textsuperscript{19,20} Thus, one large area of active study is to find a suitable electrolyte (i.e. salt + solvent system) that does not decompose or react with Li-O\textsubscript{2} products during cycling.

Another area seeing attention examines possible catalysts to reduce the overpotentials found during both discharge and recharge in Li-O\textsubscript{2} batteries. Noble metals such as Au and Pt\textsuperscript{8,21} as well as an Fe/N/C composite\textsuperscript{22} and mixed oxides such as MnO\textsubscript{2}, bismuth and lead ruthenium oxides (pyrochlore oxides), spinel-based metal oxides on graphene (containing Ni, Co or Mn) and non-crystalline metal oxides on graphene\textsuperscript{23-31} have been suggested as possible components of Li-O\textsubscript{2} cathodes. In order to design more effective catalysts, electrolyte systems (i.e. the Li salt and solvent) and cathode materials, there must be a method in place to identify the discharge products that are formed so that the discharge/charge chemistry may be well-understood and the system may be optimized for Li\textsubscript{2}O\textsubscript{2} production.

NMR spectroscopy is extremely useful for the identification and structural determination of a wide variety of materials. Solid-state MAS NMR spectroscopy involves spinning the sample at an angle, $\theta_m$ (54.7°) with respect to the static magnetic field in order to mimic the free rotations of molecules in solution.\textsuperscript{32} This orientation averaging reduces the three main interactions (dipolar, chemical shift anisotropy and quadrupolar), which can lead to extensive broadening of NMR lines that would otherwise dominate the spectra, resulting in little or no information to be obtained. Thus, MAS allows for well-resolved spectra of solid-phase materials.\textsuperscript{32,33}

Lithium has two stable NMR-active isotopes, $^7$Li and $^6$Li, both of which are quadrupolar nuclei (spin $I > \frac{1}{2}$), with $I = 3/2$ and 1, respectively. $^7$Li is approximately 93% naturally abundant, while $^6$Li is only 7% naturally abundant. While the low natural abundance of $^6$Li is a
disadvantage for NMR studies, $^6\text{Li}$ has the advantage of a much smaller quadrupolar coupling constant (the smallest of all quadrupolar nuclei), providing spectra with narrow linewidths and high resolution in comparison with $^7\text{Li}$ spectra. The quadrupolar nature of the $^7\text{Li}$ nucleus complicates spectra and can cause line-splitting and asymmetric lineshapes. Additionally, lithium generally has a small chemical shift range (ca. 2-5 ppm), meaning that high resolution is important in order to obtain exact chemical shift information from Li NMR spectra. Therefore, the main advantage of $^6\text{Li}$ is that it behaves like a nucleus with $I = \frac{1}{2}$, resulting in well-resolved spectra containing accurate chemical shifts.

In this paper, both $^6\text{Li}$ solid-state magic angle spinning (MAS) and $^1\text{H}/^{13}\text{C}$ solution-state NMR spectroscopy are used to identify and structurally characterize the discharge products of Li-O$_2$ carbon cathodes. There are a number of reports using NMR to examine Li-O$_2$ discharge products including $^6\text{Li}$ MAS NMR spectroscopy of cathodes containing ethylene carbonate/propylene carbonate (EC/PC), $^7\text{Li}$ and $^{17}\text{O}$ NMR spectroscopy. However, developments in both catalysts and solvent systems necessitate a more in-depth examination of discharge products using NMR. In particular, we report an in-depth study of two different solvent systems, a carbonate (1:1 ethylene carbonate/dimethyl carbonate, EC/DMC) and TEGDME as well as comparisons between several different cathode catalysts. In particular, we seek to understand whether discharge of a Li-O$_2$ battery in a non-carbonate solvent can yield a Li$_2$O$_2$ signal in the $^6\text{Li}$ MAS NMR and to identify putative decomposition products occurring during this process.
2.2 Materials and Methods

Electrochemical measurements were performed using a modified \textsuperscript{39} Swagelok battery cell design (the Swagelok cell assembly is illustrated in Figure A-1 in Appendix A). \textsuperscript{40} The cell features stacked layers contained inside a Swagelok apparatus (nylon Swagelok tube fittings, 1/2” inner diameter, purchased from Chicago Fluid System Technologies) consisting of a hollow aluminum cathode plunger and solid stainless steel anode plunger. The layers consisted of Li metal foil, a glass fiber separator (Whatman GF/F, 150mm diameter), a carbon cathode with or without catalyst and a Ni mesh current collector. The carbon cathode was synthesized from a slurry containing carbon black (carbon Super C65, Timcal) 27 wt% + polyvinylidene fluoride (PVDF, Kynar 2801) 41 wt% + acetone (Sigma-Aldrich) + catalyst (if used) 32 wt%. For cathodes containing carbonate solvents (EC/DMC), propylene carbonate was added to the slurry, at 61.9 wt%. The slurry was cast onto a glass surface, smoothed with a Gardco adjustable micrometer film applicator (Microm II, 5 1/2” width), and allowed to dry for ca. 5 min. The resulting cathode sheet was removed from the glass, and 1.2 cm diameter circles were punched out of the material. For all NMR experiments, the cathodes were first washed twice in acetonitrile for 10 minutes, and then dried under vacuum for one hour.

Pd catalysts for the Li-O\textsubscript{2} cathodes were obtained from Fisher Scientific (specifications). \textgreek{a}-MnO\textsubscript{2} was synthesized as described previously. \textsuperscript{24} The electrolyte was 1 M LiClO\textsubscript{4} in 1:1 ethylene carbonate/dimethyl carbonate (EC/DMC, Sigma-Aldrich). The entire Swagelok apparatus was contained in a glass enclosure (illustrated in Figures A-1 and A-2, Appendix A) to allow for controlled O\textsubscript{2} flow. Cell assembly and disassembly was performed in an Ar-filled glove box (<0.5 ppm O\textsubscript{2}). Samples for NMR were obtained by combining three cathodes into well-sealed 4 mm or 3.2 mm Si\textsubscript{3}N\textsubscript{4} rotors.
Chronopotentiometry was performed using model 760C and 760D CHI instruments electrochemical workstations. Discharge currents were 0.3 mA which was 150 mA g\(^{-1}\) on a whole cathode basis (i.e. battery discharge current and capacity was calculated per weight of the whole cathode). Discharge was continued until a cell voltage of 2.2 V was obtained. Lithium peroxide (95%), lithium oxide (97%), lithium carbonate (ACS reagent, ≥99.0%) and lithium hydroxide (reagent grade, ≥98%) powders were purchased from Sigma-Aldrich.

The \(^{6,7}\)Li DPMAS and DPMAS Echo experiments were performed at both 7.1 T and 17.6 T on Varian Unity Inova 300 and Varian VNMRS 750 (Varian is now part of Agilent Technologies) spectrometers, respectively. The Varian Unity Inova 300 and Varian VNMRS 750 spectrometers were equipped with 4 mm Varian Chemagnetics APEX Double Resonance HX and Varian Narrow Bore Triple Resonance T3 MAS probes, respectively. The \(^{13}\)C CPMAS spectra were acquired at 11.7 T on a Varian VNMRS 500 wide-bore spectrometer, equipped with a 3.2 mm Wide Bore Triple Resonance T3 Balun HCN probe. All samples were packed in silicon nitride rotors and spun at MAS rates of 10-15 kHz. \(^{6,7}\)Li and \(^{13}\)C chemical shifts were referenced to 1 M LiCl solution and TMS, respectively, at 0 ppm.

The experimental parameters for \(^{6}\)Li MAS NMR are given in the figure captions, employing the following symbols: \(B_0\) (magnetic field strength), \(\nu_r\) (magic angle spinning rate), \(\nu_{rf}^X\) (rf magnetic field applied to X spins), \(\tau_{CP}\) (cross polarization time), \(d1\) (relaxation delay) and \(NT\) (number of transients).

The \(^1\)H-\(^{13}\)C one and two-dimensional solution NMR spectroscopy was performed on a Varian Inova 600MHz spectrometer (14.1T) equipped with a 5mm triple-resonance HCN probe with Z-gradient capability and a 5mm AutoX dual broadband probe with Z-gradient capability.
for direct $^{13}$C detection. All experiments were recorded at 23°C. All NMR samples were prepared via D$_2$O-extraction of cathode products in 5mm NMR tubes after washing cathodes twice with acetonitrile. The $^1$H and $^{13}$C chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm.$^{41}$

The 2D TOCSY experiments reveal isolated continuously coupled spin systems in a molecule. The $^1$H-$^{13}$C gHSQC (gradient Heteronuclear Single Quantum Coherence) data reveal one bond cross correlations between protons and carbons in a two dimensional format. The edited gradient-enhanced HSQC inverts the CH$_2$ signals, leaving those cross peaks negative and the CH and CH$_3$ cross peaks are positive (or vice versa). The $^1$H-$^{13}$C gHMBC (gradient Heteronuclear Multiple Bond Correlation) data reveal the long-range bond correlations between proton and carbon nuclei from two to four bonds. These spectra provide crucial data for identification of molecular structures in solution.$^{41}$

The experimental parameters for $^1$H/$^{13}$C solution NMR are given in the figure captions, employing the following symbols: $B_0$ (magnetic field strength), sw (spectral window in the $^1$H dimension), sw1 (spectral window in the $^{13}$C dimension), pw (pulse width), pw90 (90-degree pulse width), d1 (relaxation delay), nt (number of transients) and ni (number of transients on the $^{13}$C dimension).

2.3 Results

Discharge Curves

Typical discharge curves obtained from Li-O$_2$ battery systems containing cathodes made using carbon only, carbon + $\alpha$-MnO$_2$ (32 wt%), and carbon + Pd (32 wt%) are depicted in Figure
2.1. Prior to discharge, the cell voltages were 2.9 ± 0.1 V for the carbon-only system, 3.0 ± 0.2 V for the carbon + Pd system, and 3.3 ± 0.1 V for the carbon + α-MnO$_2$ system. The discharge curves in Figure 2.1 exhibit a sigmoidal shape, with the potential decreasing sharply upon initial discharge and then plateauing to a roughly steady discharge potential. Eventually, the cell potential drops sharply again until it reaches the cut-off potential of 2.2 V, which we used to mark the end of the discharge. This final potential was chosen as Li$_2$O$_2$ is said to be converted into Li$_2$O at potentials more negative than this value. (Zhang, Read, J. Power Sources, 195, 2010, 1235-1240)
Figure 2.1: Li-O₂ battery discharge curves for cathodes containing the different catalysts Pd, α-MnO₂ and carbon alone (a) at a discharge current of 0.3 mA (corresponding to ca. 157 mA g\textsubscript{whole cathode}⁻¹) in 1 M LiClO₄ in EC/DMC and (b) at a discharge current of 140 mA g⁻¹ in 0.3 M LiClO₄ in TEGDME.

Solid-state MAS $^6$Li NMR of discharged cathodes

In order to obtain insight into speciation at the Li air battery cathode, $^6$Li solid-state MAS NMR spectroscopy was employed to characterize discharged cathodes. Standards for
comparison are provided by four lithium oxide powders implicated as possible Li-O$_2$ discharge products. Spectra of the lithium oxide standard powders, collected at 17.6 T are shown in Figure 2.2. (A table with the chemical shifts of discharged cathodes acquired at 7.1 T is provided in Appendix A, showing similar chemical shifts, as expected).

Figure 2.2: $^6$Li solid-state MAS NMR spectra of four lithium oxide powders and a solution of 1 M LiClO$_4$ in 1:1 EC/DMC (solution electrolyte used in Li-O$_2$ cells). $B_0 = 17.6$ T (750 MHz), $v_t = 12$ kHz, $\text{pw}90_x = 2.5 \mu$s, DP echo = 83 $\mu$s (echo was rotor synchronized), $d1 = 600$ sec. and $NT = 32$. 

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The four different Li oxide powders, depicted in Figure 2.2, exhibit a range of different chemical shifts and linewidths. A previous study using $^6$Li MAS NMR spectroscopy has been conducted on Li-O$_2$ cathodes containing ethylene carbonate/propylene carbonate (EC/PC) and the results shown in Figure 2.2 agree well with the previously reported spectra.\textsuperscript{37} We note that the chemical shift for Li$_2$O$_2$ is slightly more positive than that reported previously\textsuperscript{37} and attribute this to different sample preparations and conditions (i.e. extent of exposure to air).

Solid-state $^6$Li MAS NMR spectra of discharged cathodes containing EC/DMC and 1 M LiClO$_4$ are shown in Figure 2.3a after discharge to a cut-off potential of 2.2 V. Three different cathode catalyst materials were investigated: one consisting of Super C65 carbon-only + PVDF + PC and two others containing additional Pd or α-MnO$_2$. 
Figure 2.3: $^6$Li solid-state MAS NMR spectra of discharged Li-O$_2$ cathodes containing carbon, α-MnO$_2$ and Pd catalysts in (a) 1 M LiClO$_4$ in EC/DMC and (b) 0.3 M LiClO$_4$ in TEGDME. $B_0$ = 17.6 T (750 MHz), $\nu_r$ = 12 kHz, pw90$_x$ = 2.5 $\mu$s, DP echo = 83 $\mu$s (echo was rotor synchronized), d1 = 300 or 600 sec. and NT = 128-512.

The $^6$Li NMR spectra obtained for the cathodes in EC/DMC (Figure 2.3a) each consist of a single peak with chemical shifts ranging between -0.04 and 0.10 ppm. Table A.1 (in Appendix A) provides chemical shifts and linewidths for all the samples examined here. These chemical shifts of cathodes in EC/DMC are grouped around the 0 ppm region, which is in contrast to the chemical shifts of cathodes containing TEGDME (Figure 2.3b) that are grouped together in a region further downfield, ranging between 0.24 and 0.62 ppm (i.e. at more positive chemical shifts). The spectra of cathodes containing TEGDME (Figure 2.3b) also each consist of a single
peak that are centered around $\delta = 0.38$ ppm. Therefore, cathodes discharged in the two different solvents (EC/DMC and TEGDME) result in NMR chemical shifts that are grouped in two distinct regions and can thus be distinguished with $^6$Li NMR spectroscopy.

Solution NMR from discharged cathodes

In order to investigate other discharge products that form upon decomposition of the two cathode solvents (i.e. by-products that form in addition to the dominant Li$_2$O$_2$ and Li$_2$CO$_3$ products), which has been reported previously$^{15,19}$ and contributes to the $^6$Li NMR line shapes (Figure 2.3), solution $^1$H/$^{13}$C NMR were collected from D$_2$O-extracted products formed in Li-O$_2$ cathodes. The different decomposition mechanisms that occur during discharge for each solvent system was realized and described previously$^{19}$, where it is suggested that by-product formation is initiated by combination of O$_2$ with electrons to form the superoxide radical, O$_2^\cdot$. This superoxide radical then readily reacts with carbonate solvents (including EC, DMC and PC)$^{15}$ as well as ether solvents (DME, TEGDME, etc.)$^{19}$ to produce by-products through multiple-step radical reactions and polymerization reactions.

The $^1$H NMR spectrum of products from carbon-only cathodes in EC/DMC is shown in Figure 2.4, and the proposed structures elucidated using two-dimensional (2D) NMR are annotated on the figure. Several different types of 2D correlation NMR spectroscopy techniques were conducted to obtain structural information about the product compounds, including HSQC (Heteronuclear Single Quantum Coherence), HMBC (Heteronuclear Multiple Bond Correlation), COSY (COrrrelation SpectroscopY) and TOCSY (TOtal COrrlation SpectroscopY). Representative 2D HMBC spectra for cathodes containing Pd and discharged in both EC/DMC
and TEGDME are depicted in Figure 2.5a and b. Only major products are evaluated here; minor products did not always yield cross-peaks that would confirm their identity.

Figure 2.4: $^1$H solution NMR spectrum of products extracted from carbon-only cathodes containing (a) EC/DMC and (b) TEGDME in D$_2$O. Chemical shifts are depicted above each peak. The inset depicts the lithium acetate peak that is located farther downfield. The spectra were collected on a spectrometer with $B_0 = 14.1$ T (600 MHz), $sw = 6134.5$ Hz, for a 60 degree
flip angle $\text{pw} = 4 \mu s$, $\text{at} = 4 \text{ sec.}$, $d1 = 2 \text{ sec.}$ and $NT = 32$. The spectra were processed with zero-filling to 64k data points and a line-broadening of 0.5 Hz.

Figure 2.5: HMBC ($^{1}H$-$^{13}C$) NMR spectra of discharged cathodes (140 mA g$^{-1}$ discharge current density) containing Pd catalyst in (a) 1 M LiClO$_4$ in EC/DMC and (b) 0.3 M LiClO$_4$ in TEGDME. The spectra were collected on a spectrometer with $B_0 = 14.1$ T (600 MHz), $\text{sw} =$
6134.5 Hz (proton dimension), $sw1 = 36199.1$ Hz ($^{13}$C dimension), $pw90 = 6 \mu s$, $pwx90 = 12.9 \mu s$, at 0.167 sec., $d1 = 1$ sec. and $NT = 160$ or 544, $ni = 256$. The spectrum was processed with a 90-degree shifted sine-bell square window function in VnmrJ 2.1B.

2.4 Discussion

Discharge Curves

The discharge curves obtained from Li-O$_2$ battery systems (including cathodes made using carbon only, carbon + $\alpha$-MnO$_2$ (32 wt%), and carbon + Pd (32 wt%), depicted in Figure 2.1), result in discharge voltage plateau values that are consistent with those previously reported for both carbon and $\alpha$-MnO$_2$ cathodes, however they differ from the 2.96 V expected for a system where the open circuit potential is defined by the Li-Li$_2$O$_2$ couple. In particular, the cell voltage of the carbon + $\alpha$-MnO$_2$ cathodes at 3.3 V is too high to be associated with Li$_2$O$_2$ alone and has been attributed previously to a mixed potential from intercalation of Li$^+$ ions into the catalyst particles.

We next consider other possible half-cell reactions that might change the open circuit potential (OCP). Among many possible candidates, the formal potentials for Li$_2$O$_2$ and Li$_2$O most closely match the discharge potentials observed for Li-O$_2$ cathodes. Interestingly, several calculations conducted for different reactions that produce Li$_2$CO$_3$ yielded widely varying formal potentials, ranging from 0.09 to 5.87 V, as depicted in Table 2.1. It is therefore possible that the open circuit voltage of Li-O$_2$ batteries may arise from a combination of two or more of these various reactions rather than from one reaction alone (i.e. a mixed potential), since the formal potentials of these reactions span the observed OCP values.
<table>
<thead>
<tr>
<th>Final Product</th>
<th>Reactants</th>
<th>$\Delta G_f^\circ$ (kJ mol$^{-1}$)</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O$_2$</td>
<td>--</td>
<td>-571.12</td>
<td>2.96</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>--</td>
<td>-561.91</td>
<td>2.91</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Li, O$_2$, CO$_2$</td>
<td>-1132.19</td>
<td>5.87</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Li$_2$O$<em>2$, C$</em>\text{(graphite)}$, O$_2$</td>
<td>-72.42</td>
<td>0.09</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Li$_2$O$_2$, CO$_2$</td>
<td>-3730.23</td>
<td>4.83</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Li$_2$O, CO$_2$</td>
<td>-237.77</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 2.1: Calculated Gibbs free energy ($\Delta G_f^\circ$) and formal potential ($E^\circ$) values for various Li-O$_2$ battery discharge products.

Interestingly, the shape of the discharge curves varied with the identity of the cathode catalyst. The cell voltage in the carbon-only system immediately drops to ca. 2.4 V, while the Pd system has a small shoulder at ca. 2.8 V before dropping after ca. 20% of discharge. The $\alpha$-MnO$_2$ – containing cathode exhibits behavior intermediate between these two cases.

The discharge curve exhibited in Figure 2.1 also shows that cathodes containing different catalysts result in different discharge capacities. The discharge capacity (mAh g$^{-1}$ whole cathode) is determined from the start time of the discharge up to the time at which the 1.5 V set ending potential is reached. The mass of the whole cathode includes the carbon black, the binder and plasticizer, and the catalyst itself if present. The lowest capacity system was that containing carbon alone which exhibits a capacity of ca. 200 mAh g$^{-1}$ whole cathode. Although discharge capacities are known to be strongly dependent on the discharge rate the capacities reported here are consistent with those reported previously on related systems. Both the $\alpha$-MnO$_2$ and Pd...
– containing cathodes yielded discharge capacities greater than that found for carbon alone, with increases on the order of 25%.

These results show that catalyst identity affects the discharge mechanism. The origin of this change could be one of several different causes including changes in reaction kinetics, pore structure of the cathode, identity of reaction intermediates and final products.\textsuperscript{11}

\textit{Solid-state MAS $^6$Li NMR of discharged cathodes}

$^6$Li solid-state MAS NMR spectroscopy of the four lithium oxide powders (tested as standards), depicted in Figure 2.2, demonstrates that each of the standards displays a unique chemical shift value. The range in chemical shifts is due to the shielding effect, in which de-shielded nuclei shift downfield (to higher chemical shifts) and shielded nuclei shift upfield (to lower chemical shifts). For example, the Li nucleus in Li$_2$O is de-shielded by the electronegative oxygen atom and is therefore located further downfield than the Li peak from Li$_2$CO$_3$, which is de-shielded to a lesser extent by the carbonate group. The observation of two $^6$Li peaks in the spectrum of LiOH is most likely due to the presence of both LiOH and the monohydrate form of LiOH (LiOH$\cdot$H$_2$O). Lithium hydroxide monohydrate, assigned to the peak at 0.22 ppm, is a compound known to form in the presence of water and has been shown previously to appear in $^6$Li MAS NMR spectra as a separate peak located in a similar position to LiOH.\textsuperscript{44}

The lithium powders, depicted in Figure 2.1, have similar linewidths with the exception of lithium peroxide. In solid-state NMR, several factors contribute to linewidth including molecular orientations and structural order (short and long-range). The broader linewidth of Li$_2$O$_2$ has been seen previously,\textsuperscript{37,38} and has been attributed to short-range order within the
powder and also to the two different charges present on the Li atoms, which slightly affect the chemical shift of each Li nucleus, as described for the Föppl structure of Li$_2$O$_2$. The Föppl structure of Li$_2$O$_2$ has been suggested to be the most likely structure for lithium peroxide thus far.\textsuperscript{45-49} The line broadening of the Li$_2$O$_2$ peak in Figure 2.2,\textsuperscript{38} is most likely due to the same underlying phenomenon as has been described previously,\textsuperscript{47} as well as short range order effects.\textsuperscript{47}

The chemical shifts of the discharged cathodes and lithium powders acquired at 7.1 T (not shown) and 17.6 T (Figure 2.3a) have similar values, consistent with the trend observed with the powders. Again, this is expected since the quadrupolar coupling constant of $^6$Li is very small and its behavior is much like that of a spin-1/2 nucleus. Sample handling and processing was also found to change the observed chemical shifts only slightly. For example, samples maintained in the glove box for two weeks following discharge exhibited chemical shifts slightly more negative than those whose spectra were collected immediately after discharge.

This trend of cathodes containing the two different solvents being grouped into certain chemical shift ranges is significant because it indicates that differences in products formed are mainly solvent-dependent rather than dependent upon the type or presence of different catalysts or other factors. Catalysts do cause slight variation in the chemical shift of discharged cathodes, but do not alter the identity of discharge products to the extent that different solvents do.

Comparing the $^6$Li NMR chemical shifts obtained from the cathodes containing EC/DMC solvent (depicted in Figure 2.3a) with the standards reported in Figure 2.2, it is clear that the standard with the closest chemical shift is Li$_2$CO$_3$. However, the chemical shifts of the discharged cathodes are not an exact match to the chemical shifts of any of the powder standards.
alone. This inexact match is attributed to discharge product heterogeneity as has been described previously.\textsuperscript{15,38} This heterogeneity means that there are products in addition to the dominant species that contribute to the line shape and chemical shift. In particular, by-products from solvent decomposition\textsuperscript{15,19} can add to the peak shape and cause the chemical shifts of the cathodes to be slightly different than that of the dominant discharge product. We suggest that the species with a chemical shift that is closest to the one peak observed, which is Li\textsubscript{2}CO\textsubscript{3} for the EC/DMC-containing solvent, is the dominant discharge product in this solvent. This conclusion is identical others utilizing both \textsuperscript{6}Li MAS NMR\textsuperscript{37} as well as other NMR\textsuperscript{38} and other spectroscopic techniques.\textsuperscript{15}

For cathodes discharged in TEGDME, the standard powder with the closest chemical shift to those of the discharged cathodes is that of Li\textsubscript{2}O\textsubscript{2}, and we suggest that this species is the dominant product formed upon discharge in the TEGDME solvent system. In previous studies, conducted on different ether-based solvents (including both linear and cyclic ethers such as tetraglyme, 1,3-dioxolane and 2-methyl-THF),\textsuperscript{19} Li\textsubscript{2}O\textsubscript{2} was determined to form in Li-O\textsubscript{2} cathodes. Interestingly, the Li\textsubscript{2}O\textsubscript{2} was found to form in the largest quantities during the first discharge. In subsequent cycles the electrolyte solvent was found to decompose to a greater extent until no Li\textsubscript{2}O\textsubscript{2} was detected (usually by the 5\textsuperscript{th} cycle).\textsuperscript{19} While subsequent cycles (i.e. after the first discharge) were not studied in this report, the result of finding Li\textsubscript{2}O\textsubscript{2} during the first discharge in an ether-based solvent is consistent with results obtained here.

Apart from chemical shift information, NMR peak linewidths can also provide information regarding products formed during discharge.\textsuperscript{38} In general, the linewidths obtained from discharged cathodes were about a factor of three greater than those found for the lithium powder standards (shown in Figure 2.2). This broadening is attributed to the lack of order in the
products of the discharged cathodes and the presence of a conductive carbon matrix, as described previously. However, comparing the linewidths of discharged cathodes in different solvents reveals general trends that can be discerned. (Figure 2.3) In particular, the NMR linewidths found from the EC/DMC discharged cathodes are narrower (1.21 ppm) relative to those found from TEGDME (1.77 ppm). The narrower linewidth is more closely associated with the Li$_2$CO$_3$ standard relative to the broader linewidth attendant Li$_2$O$_2$ formation. We conclude that Li$_2$CO$_3$ is the predominant discharge product in discharged Li-O$_2$ cathodes containing EC/DMC solvent, while Li$_2$O$_2$ is the predominant discharge product in cathodes containing TEGDME, as was suggested for other ether-based solvents. Interestingly, the presence of any of the tested catalysts does not seem to significantly change the identity of the major product, although subtle changes in the chemical shifts do suggest that additional material may be present.

Solution NMR from discharged cathodes

Analysis of the 2D NMR measurements reveals that cathodes discharged in the two solvents evaluated here (EC/DMC and TEGDME) exhibited both similarities and differences in discharge products. Products found to be present in both types of solvent include lithium formate (LiCO$_2$H, $^1$H $\delta = 8.28$ ppm), lithium acetate (LiCO$_2$CH$_3$, $^1$H $\delta = 1.74$) and lithium carbonate (Li$_2$CO$_3$). We note that there is also a small amount of acetonitrile ($^1$H $\delta = 1.90$ ppm) present in the $^1$H spectra, which is from the acetonitrile used to rinse the cathodes.

Compounds detected with $^1$H/$^{13}$C NMR that are exclusively in EC/DMC include products that result in the low-intensity multiplets in Figure 2.5a, which have been determined to be lithium ethylene glycol (LiOCH$_2$CH$_2$OLi, $^1$H $\delta = 3.50$ ppm), lithium propylene glycol
(LiOCH$_2$CH$_3$CH$_2$OLi, $^1$H $\delta$ = 3.71, 3.38, 3.28 and 0.98 ppm, connected by cross-peaks in HSQC and HMBC experiments to $^{13}$C peaks at 66.33 and 67.95 ppm), an asymmetric compound with chemical formula LiOCH$_2$CH$_2$OCO$_2$CH$_2$CH$_2$OCH$_3$ ($^1$H $\delta$ = 3.61, 3.53, 3.50, 3.37 and 3.18 ppm, with cross-peaks to a $^{13}$C peak at 181.91 ppm), and a compound with the chemical formula LiOCH$_2$OCO$_2$Li ($^1$H $\delta$ = 3.77 ppm), depicted in Table A.3a (in Appendix A).

In NMR spectra of products formed in cathodes with EC/DMC solvent, the very large peak associated with Li ethylene glycol has been previously reported to form through a reaction between the D$_2$O (NMR solvent) and the original product formed in Li-O$_2$ cathodes, Li ethyl dicarbonate (C$_2$H$_4$(OCO$_2$Li)$_2$). Thus, the presence of Li ethylene glycol indicates that these cathodes have formed large quantities of Li ethyl dicarbonate, which then went on to react with D$_2$O forming Li ethylene glycol. This intense peak dominates the spectra for cathodes in EC/DMC, as can be seen by the residual peaks (i.e. noise) with the same $^1$H chemical shift as this large peak. As a consequence, any compounds that are produced in only small quantities are not seen in the spectra with EC/DMC solvent due to the large peak dominating the spectrum. More cross-peaks due to minor species are present in the 2D NMR spectra of cathodes in TEGDME because it does not contain this large, dominating peak.

Compounds detected with $^1$H/$^{13}$C NMR that are exclusively in TEGDME include a long polymer with the chemical formula –[OCH$_2$OCO$_2$CH$_2$CH$_2$OCO$_2$CH$_2$OCO$_2$CH$_2$O]$_n$– ($^1$H $\delta$ = 3.78, 3.77 and 3.20 ppm with $^{13}$C peaks at 69.3, 69.1 and 177.9 ppm) and pure TEGDME ($^1$H $\delta$ = 3.53, 3.52, 3.46, 3.22 ppm), as depicted in Table A.3b (in Appendix A). Of course, TEGDME is expected in the NMR of cathodes discharged in TEGDME. Additionally, longer chains of –[OCH$_2$CH$_2$O]- and -[OCH$_2$COO]- have been previously reported forming in Li-O$_2$ cathodes in TEGDME due to esterification and polymerization reactions following nucleophilic attack of
radical superoxide and oxidative decomposition,\textsuperscript{15,19} which may be present here as well. It is therefore apparent that cathodes containing EC/DMC solvent produce a greater number of different types of discharge products than those containing TEGDME.

Interestingly, the presence of Pd in the cathodes does not affect the type or amount of discharge products formed to a great extent, as seen in comparisons of \textsuperscript{1}H NMR spectra with and without Pd in the two different solvent systems (as depicted in the Supplemental Information). There are only slight variations in the different product peak intensities. The solvent appears to play a much larger role in dictating the types of products produced than the presence of this catalyst.

In summary, the discharge products that were produced in both EC/DMC and TEGDME were Li formate, Li acetate and lithium carbonate. Major differences in products formed in cathodes containing the two solvents include the fact that cathodes containing EC/DMC exclusively produce large quantities of Li ethyl dicarbonate (seen as Li ethylene glycol in solution NMR spectra for samples in D\textsubscript{2}O), Li propylene glycol, LiOCH\textsubscript{2}OCO\textsubscript{2}Li, and LiOCH\textsubscript{2}CH\textsubscript{2}OCO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3}, while cathodes containing TEGDME exclusively produce the polymer –[OCH\textsubscript{2}OCO\textsubscript{2}CH\textsubscript{2}OOC\textsubscript{2}CH\textsubscript{2}OCO\textsubscript{2}CH\textsubscript{2}O]\textsubscript{n}– and additionally contain residual TEGDME. No residual EC/DMC peaks are seen in NMR spectra of cathodes in EC/DMC. Additionally, comparison of the \textsuperscript{1}H NMR spectra of cathodes discharged in EC/DMC solvent versus those discharged in TEGDME reveals that cathodes containing EC/DMC produced more solvent decomposition by-products.
2.5 Conclusions

$^6$Li MAS NMR spectroscopy has been demonstrated to be a useful tool for the identification of discharge products in Li-O$_2$ battery cathodes. Major differences in the chemical shifts of discharged cathodes in the two different solvents (EC/DMC and TEGDME) revealed that the primary discharge products of the two solvent systems are different (Li$_2$CO$_3$ and Li$_2$O$_2$, respectively), which agrees well with previous reports.$^{15,19,38}$ Linewidth considerations also indicated this same result. Additionally, minor changes in $^6$Li MAS NMR chemical shifts of discharged cathodes containing different catalysts (carbon with Pd or α-MnO$_2$) indicate that there are slight differences in the types or amounts of discharge products produced with different catalysts.

$^{13}$C MAS, $^1$H and $^{13}$C solution NMR spectroscopy confirmed that there are slight variations in the concentrations of different discharge products depending on the type of catalyst used. Additionally, 2D NMR experiments allowed for the identification of by-products formed in the discharged cathodes, theoretically from decomposition of the solvents. The presence of small amounts of these additional by-products account for the slight differences in $^6$Li NMR chemical shifts of discharged cathodes compared with lithium powder standards. All of the discharged cathodes containing the two different solvents (EC/DMC and TEGDME) were found to produce lithium formate, lithium acetate and lithium carbonate, and likely also produce CO$_2$ and H$_2$O as reported in previous studies.$^{15,19}$ Major differences in discharge products found for the two solvents are that cathodes containing EC/DMC produce Li ethyl dicarbonate (seen as Li ethylene glycol in solution NMR spectra of samples in D$_2$O, which is formed due to a reaction between the original Li ethyl dicarbonate and D$_2$O), lithium propylene glycol (LiOCH$_2$CH$_3$CH$_2$OLi), an asymmetric compound with chemical formula
LiOCH₂CH₂OCO₂CH₂CH₃OCH₃, and a compound with the chemical formula LiOCH₂OOC₂Li. Cathodes containing TEGDME exclusively produce a long polymer with the chemical formula – [OCH₂OOC₂CH₂OCH₃O]ₙ– and residual TEGDME is also observed in these samples.

Additionally, comparison of the \(^1\)H NMR spectra of cathodes discharged in EC/DMC versus those discharged in TEGDME reveals that cathodes containing EC/DMC produced more solvent decomposition by-products. Two-dimensional correlation NMR spectroscopy experiments (including HSQC, HMBC, COSY and TOSCY experiments) have been found to be a useful tool to investigate by-products formed by decomposition. \(^6\)Li MAS NMR and solution 2D NMR have been found to be highly useful, complementary techniques for the investigation of discharge products in Li-O₂ battery cathodes.

2.6 Acknowledgements

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CHAPTER 3
Identification of Products Formed in Li-S Batteries through solid-state $^6$Li NMR spectroscopy

3.1 Introduction

New energy storage devices and battery chemistries are needed to meet the increasing energy storage demands of the future, which must be suited to store power for electric vehicles, renewable energies, and the grid, due to the increasingly pressing need to sustain the environment.\(^1\) The now ubiquitous lithium-ion (Li-ion) battery revolutionized the battery industry when it was first commercialized by Sony in 1991 by demonstrating exceptionally high potential, high energy density, low self-discharge rate, and long cycle life.\(^2\) The Li-ion battery quickly dominated many portable electronic devices including phones, camcorders, laptop computers, among others.\(^2,3\) However, despite the many advantages of the Li-ion battery, there are many disadvantages. These include: safety concerns, scarcity of battery constituents such as Co, and insufficient capacity for demanding uses such as transportation.\(^2,6\)

One of the leading next-generation energy storage candidates to replace the Li-ion battery is the Li-S battery.\(^4\) The Li-S battery features several attractive advantages over other types of batteries. These advantages include: a substantially higher theoretical energy density relative to conventional insertion Li-ion cathodes (2600 Wh kg\(^{-1}\) versus 800 Wh kg\(^{-1}\), respectively),\(^7\) a high specific capacity of 1675 mAh g\(^{-1}\) (calculated based on sulfur),\(^4\) as well as the high natural abundance and low cost of sulfur, the cathode active material.\(^4,8\) The Li-S battery contains a lithium metal anode (negative electrode) and a mixed carbon/sulfur cathode (positive electrode).
During discharge, lithium ions travel from the anode, through a separator (Li-ion-selective) and on to the cathode where they react with elemental sulfur (S$_8$), cleaving S-S bonds in the eight-membered sulfur rings and forming lithium polysulfide products ($\text{Li}_2\text{S}_n$, where $n \leq 8$). Ultimately Li$_2$S is the desired discharge product, which is stored on the cathode as a solid deposit until the battery is recharged, whereupon the Li$_2$S reversibly re-forms longer chain lithium polysulfide species. The discharge curve consists of three characteristic plateau regions (shown in Figure 3.1), which indicate three different reaction processes that occur during discharge. Evidence for the presence of different polysulfide chain lengths at different potentials of the battery discharge is abundant in the literature.$^7,9,10$

Despite the major advantages that the Li-S battery offers and decades of research, a Li-S battery with longer cycle life and sufficient energy storage to meet future transportation requirements has not yet been realized.$^4$ Problems with the battery chemistry include: (1) low rechargeability, low discharge/charge rates$^{11}$ due to the insulating properties of elemental sulfur ($S_8$) and the solid discharge products Li$_2$S and Li$_2$S$_2$, (2) low cycle life due to the well-established lithium polysulfide shuttle mechanism whereby soluble polysulfide species migrate between the anode and cathode,$^{12}$ and (3) poor electrolyte solvent options.$^4$ The problem of lithium polysulfide dissolution has been partially resolved in previous reports through encapsulation of the sulfur active material at the cathode using various carbon hosts including mesoporous carbon spheres,$^{13-15}$ carbon nanofibers,$^{16-18}$ carbon fiber,$^{19}$ and graphene oxides,$^{20}$ and non-carbon hosts such as TiO$_2$ yolk-shell nanospheres.$^{21}$

However, incomplete knowledge of the discharge products formed during battery cycling and the Li/electrolyte interface inhibits efficient design of the Li-S cell chemistry. Understanding speciation in different potential regions as the battery is discharged will provide
insight into the discharge mechanism. The knowledge of the mechanism of various reactions will help in the design of cathodes which minimize polysulfide formation and promote the formation of Li$_2$S.

Prior studies have used various techniques to identify discharge products in Li-S battery cathodes including XRD, UV-vis spectroscopy, Raman spectroscopy, XPS, FTIR, EPR, and X-ray studies (XANES). Relatively little work attends to the investigation of Li-S batteries using nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy is a powerful technique to apply to batteries, as demonstrated by the many investigations into Li-ion systems by Li NMR. We are aware of only one other paper that investigated Li-S battery products through Li MAS NMR spectroscopy. This previous study utilized synthesized lithium polysulfide species as references for XANES S k-edge studies of Li-S battery products and characterized the prepared references (Li$_2$S, Li$_2$S$_2$, Li$_2$S$_6$, and a two-component model for Li$_2$S$_8$) using XRD and $^7$Li MAS NMR spectroscopy. This study concluded that only two distinct Li environments exist for Li$_2$S and Li$_2$S$_6$ (at 2.3 and 1.0 ppm, respectively). This previous investigation used a different isotope of lithium ($^7$Li) than our study ($^6$Li), however it is noteworthy that chemical shift values are nominally the same between the two isotopes.

In this paper, we use $^6$Li and $^{33}$S magic angle spinning (MAS) and solution $^7$Li and $^1$H NMR spectroscopy methods to examine discharge products from Li-S battery cathodes. In addition to chemical shift information, we find that relaxation times ($T_2$ in particular) provide a powerful analytical method to distinguish between lithium polysulfide products in the battery.
3.2 Materials and methods

Lithium-sulfur batteries were assembled inside a modified Swagelok tube fitting apparatus (nylon, ½” inner diameter, purchased from Chicago Fluid System Technologies) inside an argon-filled glove box (<2 ppm O₂). The battery components were layered inside the tube fittings, between two solid stainless steel cylinders that serve as electrical connections, in the following order: lithium metal foil (as the anode, 0.75 × 45 mm thickness, 99.9% trace metals basis, Sigma-Aldrich), Celgard 2400 (polypropylene separator), Whatman glass fiber, (GF/F, 150mm diameter, separator), and Li-S cathode slurry coated onto aluminum foil (Sigma-Aldrich). The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1:1 tetraethylene glycol dimethyl ether (TEGDME, ≥99%, Sigma-Aldrich)/1,3-dioxolane (DIOX or DOL, anhydrous, ~75 ppm BHT as inhibitor, Sigma-Aldrich).

The Li-S cathode slurry consists of carbon black (2.14 wt. %, Super P Li, Timcal), polyvinylidene fluoride (PVDF) (0.71 wt. %, Kynar 2801), sulfur (4.29 wt. %, Sigma-Aldrich) and 1-methyl-2-pyrrolidone (NMP) (92.86 wt. %, TCI). The slurry components were stirred for 12 hours, cast on to aluminum foil (Sigma-Aldrich) with a thickness of 12 μm using a Gardco adjustable micrometer film applicator (Microm II, 5 ½” width), then allowed to dry at 55°C for 24 h. The Li-S cathode slurry + aluminum foil was then cycled into a glove box and punched into 1”-diameter circles for use as cathodes.

Li-S battery discharge

Electrochemical discharge of the batteries was performed on model 760C and 760D CHI instruments electrochemical workstations using chronopotentiometry. Batteries were cycled at a rate of C/60 (by weight of the whole cathode) or C/2.6 (by weight of sulfur in cathode only) from
the open circuit potential (OCP) to the desired cut-off potentials of 2.15, 2.03, and 1.50 V (vs. Li/Li\(^+\)). All batteries were cycled and disassembled inside an argon-filled glove box (<2 ppm O\(_2\)).

\textit{\(^6\)Li NMR spectroscopy}

\(^6\)Li DPMAS (direct-polarization magic angle spinning) NMR spectroscopy, T\(_1\) and T\(_2\) experiments were performed on a 7.1 T Varian Unity Inova 300 (Varian is now part of Agilent Technologies) spectrometer, equipped with a 4 mm Varian Chemagnetics APEX Double Resonance HX probe. The cathode and powder samples were packed in silicon nitride rotors inside a glove box, sealed, then removed from the glove box and spun to 10 kHz inside the spectrometer. \(^6\)Li MAS NMR spectra were then acquired \textit{ex-situ} in sealed rotors for each of the cathodes discharged to the three characteristic plateau regions (i.e. at 2.15, 2.03, and 1.50 V). A \(^6\)Li MAS NMR spectrum was also acquired for dry Li\(_2\)S powder (dried under vacuum overnight on the Schlenk line). Electrolyte solution (1 M LiTFSI in 1:1 TEGDME/DIOX) was added to an un-cycled Li-S cathode and the cathode + electrolyte sample was packed into a solid-state NMR rotor to determine whether the carbon cathode caused any changes in the electrolyte salt (LiTFSI) environment that would alter its chemical shift. The solution electrolyte (1 M LiTFSI in 1:1 TEGDME/DIOX) was pipetted into a small glass NMR tube and NMR spectra were acquired in the same solid-state probe used for the cathode and powder samples. The \(^6\)Li chemical shifts were referenced to a 1 M LiCl solution at 0 ppm. T\(_2\) relaxation measurements were conducted using a Hahn-Echo pulse sequence. All \(^6\)Li MAS NMR experiments employed a magic angle spinning speed of 10 kHz. A recycle delay of 7200 s was used for all T\(_2\) relaxation
experiments. Additional experimental parameters for $^6$Li MAS NMR are given in the figure captions, employing the following symbols: $B_0$ (magnetic field strength), $\nu_r$ (magic angle spinning rate), $d_1$ (relaxation delay), $n_t$ (number of transients), and $lb$ (line broadening). $T_2$ relaxation times were determined through fitting to a mono-exponential equation in MestReNova (MNova) to determine $M_0$ (Equation 1) and by plotting the natural log of peak height versus $\tau$ in OriginPro 8.6. $T_2$ relaxation time is taken as the negative inverse of the slope and the error in $T_2$ is determined through residual analysis of the slope in the natural logarithm plot.

*Solution $^7$Li and $^1$H NMR spectroscopy*

Li-S battery cathodes that were discharged in the glove box were dried under vacuum in the glove box for 12 h. The cathodes were then soaked in 1:1 TEGDME/DIOX solvent for 1 h, during which time the solution would change color from clear to yellow-orange at the beginning of discharge (~2.15 V) or teal to dark green toward the end of discharge (~2.03-1.5 V). The solution was then transferred to a clean solution NMR tube. A small amount (0.2 mL) of deuterated acetonitrile (CD$_3$CN) was added to the first sample on a Schlenk line to obtain a solvent lock on the spectrometer, however all subsequent samples contained no deuterated solvent. Solution NMR measurements were referenced to a 1 M solution of LiCl (to 0 ppm) and performed on a 14.1 T spectrometer.

*Solid-state $^{33}$S MAS NMR spectroscopy*

Discharged Li-S battery cathodes and dry Li$_2$S powder were packed into 5-mm pencil solid-state rotors in a glove box and sealed. Rotors were transported to the Chemistry Department of the University of Akron for all $^{33}$S solid-state MAS NMR measurements. All experiments were performed on a 17.6 T (750 MHz for $^1$H) Agilent Direct-Drive 2 spectrometer,
which was equipped with a Varian/Chemagnetics T3 double-channel probe, optimized for observing $^{33}\text{S}$. All $^{33}\text{S}$ MAS NMR samples were spun to 11 kHz and the chemical shifts were referenced to -29.0 ppm with CaS powder. The $^{33}\text{S}$ MAS NMR parameters used were as follows: the calibrated 90-degree pulse was 9.5 μs (26 MHz) but a 20-degree pulse of 2.1 μs was used, the spectral width was 100 kHz, acquisition time (at) was 0.1 s, recycle delay was 3.0 s, zero filling (fn) was 65536, and number of transients (nt) was 12800 for the cathode discharged to 1.5 V and 4096 for the Li$_2$S powder. A $^1\text{H}$ decoupling field of 11.6 kHz was used. Additonally, backward linear prediction was applied to the first three points of both spectra using a linear coefficient of 32 and a basis set of 256 points. Additional experimental parameters for $^{33}\text{S}$ MAS NMR are given in the figure captions, employing the following symbols: nt (number of transients) and lb (line broadening).

3.3 Results

Figure 3.1 shows a typical discharge curve obtained from a Li-S battery$^9$. The discharge curve shown in Figure 3.1 is a typical result obtained from a Li-S battery discharged at a rate of C/2.6 (or 0.4C), with a typical capacity of approximately 930 mAh g$^{-1}$ whole cathode or 1550 mAh g$^{-1}$ sulfur. This capacity is similar to that reported previously by several groups, with capacities ranging from 800-1200 mAh g$^{-1}$ sulfur at equivalent discharge rates.$^{26}$ The Li-S battery discharge curve typically consists of three plateau regions (labeled in Figure 3.1): two main plateau regions (Reg. 1 and 3), and a smaller region (Reg. 2) that occurs just after Region 1 and appears as a small shoulder in the discharge curve. Region 1 is associated with $S_6^{2-}$ and $S_3^{2-}$ as evidenced by UV-vis spectroscopy conducted in previous studies$^9$. The second plateau region is less
distinguishable than regions 1 and 3, however it is associated with $S_4^{2-}$. Region 3 is associated with $S_3^{2-}$, $S_2^{2-}$, and $S^{2-}$.  

Figure 3.1: A Li-S battery discharge curve (chronopotentiometric) at a C/2.6 rate (C/60 for weight of whole cathode).

Of particular interest in this study was whether the components present in the cathodes discharged to each of the three regions of discharge observed in the discharge curve (Figure 3.1) could be identified using NMR spectroscopy. Figure 3.2 shows $^6$Li solid-state MAS NMR obtained from several different control samples. The LiTFSI powder, the solution electrolyte, which consists of 1 M LiTFSI in 1:1 TEGDME/DIOX, and the un-cycled cathode with solution electrolyte all exhibit a single peak that ranges from -1.46 to -1.22 ppm relative to LiCl. Shifts similar to these have previously been reported$^{36,37,38}$. $^6$Li NMR resonances that occur between ±10 ppm are attributed to lithium ions in diamagnetic environments, including battery
electrolyte solutions and the solid electrolyte interface (SEI) of lithium-ion batteries.\textsuperscript{36} Resonances from $^6$Li located in paramagnetic environments are shifted by as much as -500 to +3,000 ppm due to hyperfine interactions with paramagnetic materials. Metallic lithium has a $^6$Li chemical shift of 250 ppm due to interactions with electrons in the conduction band of the metal, referred to as Knight shift interactions.\textsuperscript{36}

Figure 3.2 also shows the $^6$Li MAS NMR obtained from a sample of dry Li$_2$S powder. In contrast to the other three spectra, the single peak seen here is at 2.40 ppm, located significantly downfield from the LiTFSI resonance. This downfield shift indicates that the lithium nucleus is more de-shielded than it is in the presence of the Cl$^-$ environment from the LiCl reference compound. Additionally, this chemical shift (2.40 ppm) for Li$_2$S is extremely close to that observed previously for Li$_2$O at 2.87 ppm\textsuperscript{39}. Li$_2$S and Li$_2$O exhibit similar chemical shifts because sulfur and oxygen have similar electron-withdrawing and bonding properties. The chemical shift of Li$_2$S is located slightly upfield from that of Li$_2$O since sulfur is less electronegative than oxygen and therefore has weaker electron-withdrawing properties, resulting in more shielded lithium nuclei in the Li$_2$S powder.
Figure 3.2: $^6$Li solid-state MAS NMR spectra of (a) electrolyte salt LiTFSI powder, (b) the solution electrolyte (1 M LiTFSI in 1:1 TEGDME/DIOX), (c) an uncycled cathode containing electrolyte solution, and (d) dry Li$_2$S powder. $B_0 = 7.1$ T, $\nu_r = 10$ kHz.

Figure 3.3 shows the MAS $^6$Li NMR spectra obtained from cathodes containing 1 M LiTFSI in 1:1 TEGDME/DIOX electrolyte discharged to 2.15, 2.03, and 2.00 V. These cathodes, discharged to regions 1 and 2 of the discharge curve, all exhibit very similar chemical shifts (-0.53, -0.29 and -0.76 ppm, respectively). These shifts are located downfield relative to the electrolyte standards shown in Fig 3.2, suggesting that the lithium products formed in the first two regions of battery discharge contain lithium nuclei that are more de-shielded than those
in the LiTFSI electrolyte salt. In other words, the lithium nuclei in the battery products formed in the first two potential regions are in a less electron-rich environment.

Figure 3.3 also shows the $^6$Li MAS NMR spectra obtained from a cathode discharged to 1.50 V. In contrast to the results obtained at the previous three discharge voltages, the discharge products in batteries discharged fully to 1.50 V exhibit two peaks at 2.32 and 0.12 ppm. The peak at 2.32 ppm has a chemical shift that is very similar to that found for Li$_2$S in Fig. 3.2 at 2.40 ppm. However, the peak at 0.12 ppm is not found in the standards reported above. The 0.12 ppm shift is similar to the 0.11 ppm shift found previously for Li$_2$CO$_3$, and it is possible that a small amount of carbon in the Li-S battery cathode is oxidized to Li$_2$CO$_3$ at the end of battery discharge$^{39}$. 
Figure 3.3: $^6\text{Li}$ solid-state MAS NMR spectra of Li-S battery cathodes discharged to (a) 2.15 V, (b) 2.03 V, (c) 2.00 V, and (d) 1.50 V. $B_0 = 7.1$ T, $\nu_r = 10$ kHz.

In order to provide further discrimination between discharge products, we measured the $T_2$ times associated with each peak. The $T_2$ decay time for each cathode was determined using the Hahn-echo pulse ($90^\circ$ and $180^\circ$ pulses) technique, where spectra were acquired for an arrayed set of times between the pulses ($\tau$). The resulting peak heights were then fit to the mono-exponential curve,

$$M_y(2\tau) = M_0 \exp(-2\tau/T_2)$$
where $M_y$ is the amplitude of the transverse magnetization (proportional to peak height), $M_0$ is the amplitude of the magnetization just before an applied pulse, and $\tau$ is the arrayed delay time between the two Hahn echo pulses. The resulting peak heights are plotted against $\tau$ and fit to the above mono-exponential fit (Equation 1) for each of the cathodes discharged to different potentials (2.15, 2.03 and 1.50 V). Cathodes discharged to different potentials exhibit different slopes in the plot of peak height versus $\tau$ values, where the cathode discharged to the furthest depth of discharge (1.50 V) results in the highest decay rate and the cathodes discharged to smaller depths of discharge (2.03 and 2.15 V) result in smaller decay rates.

Table 3.1 shows measured T$_2$ relaxation times for cathodes discharged to 2.15, 2.03 and 1.50 V and Li$_2$S powder using $^6$Li solid-state MAS NMR spectroscopy. The T$_2$ times for the products formed in the Li-S battery cathodes follow a trend where the T$_2$ time is smaller for the cathode discharged to a lower potential (i.e. discharged to a greater extent, to 1.50 V) and larger for the two cathodes discharged to a higher potential (i.e. 2.03 and 2.15 V). The T$_2$ time for the Li$_2$S powder does not exactly match that of any of the measured discharged cathodes, and is smaller than any T$_2$ values obtained for the cathodes.
<table>
<thead>
<tr>
<th></th>
<th>NMR chemical shift (ppm)</th>
<th>Measured T$_2$ (ms)</th>
<th>Error in T$_2$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode to 2.15 V</td>
<td>-0.78</td>
<td>49</td>
<td>± 5</td>
</tr>
<tr>
<td>Cathode to 2.03 V</td>
<td>-1.25</td>
<td>41</td>
<td>± 4</td>
</tr>
<tr>
<td>Cathode to 1.50 V</td>
<td>2.25</td>
<td>26.5</td>
<td>± 0.6</td>
</tr>
<tr>
<td>Li$_2$S powder</td>
<td>2.35</td>
<td>11.9</td>
<td>± 0.5</td>
</tr>
</tbody>
</table>

Table 3.1: Experimentally measured T$_2$ relaxation times for Li-S battery cathodes discharged to 2.15, 2.03, 1.50 V, and dry Li$_2$S powder through solid-state $^6$Li MAS NMR spectroscopy with standard error reported. $B_0 = 7.1$ T, $\nu_r = 10$ kHz.

Preliminary T$_1$ relaxation time measurements were found to require excessive measurement times (ca. 4 days per measurement) and were not continued.

Table 3.2 shows solution $^1$H and $^7$Li NMR spectroscopy data of products extracted from cathodes discharged to different potential regions and a standard electrolyte solution. The $^7$Li solution NMR chemical shifts for all products extracted from cathodes discharged to 2.40, 2.03 and 1.98 V were very similar, in the range of -1.27 to -1.35 ppm. The $^7$Li NMR chemical shift for solution LiTFSI is very different than that of the Li-S battery discharge products, similar to the results from solid state $^6$Li MAS NMR, at -2.39 ppm.
<table>
<thead>
<tr>
<th>Species</th>
<th>$^7$Li chemical shift (ppm)</th>
<th>$^1$H chemical shift (ppm)</th>
</tr>
</thead>
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<tr>
<td>2.40 V</td>
<td>-1.29</td>
<td>4.08, 3.86, 3.78, 3.60, 2.70,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.59, 2.35, 2.24, 2.12</td>
</tr>
<tr>
<td>2.03 V</td>
<td>-1.35</td>
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<td></td>
<td></td>
<td>2.39, 2.28, 2.16</td>
</tr>
<tr>
<td>1.98 V</td>
<td>-1.27</td>
<td>3.99, 3.78, 3.70, 3.52, 2.61,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.27, 2.16, 2.04</td>
</tr>
<tr>
<td>LiTFSI (in CH$_3$CN)</td>
<td>-2.39</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 3.2: Solution $^7$Li and $^1$H NMR data of products extracted from Li-S cathodes discharged to different potentials (2.40, 2.03 and 1.98 V) in non-deuterated acetonitrile, LiTFSI in CH$_3$CN, and aqueous 1 M LiCl. $B_0 = 14.1$ T.

Figure 3.4 shows the solid-state $^{33}$S MAS NMR spectra of cathode material removed from a Li-S battery discharged to 1.50 V and standard Li$_2$S powder, which resulted in clear, sharp $^{33}$S NMR peaks. The chemical shifts for the cathode discharged to 1.50 V and Li$_2$S powder are extremely similar (at -344.1 and -342.7 ppm, respectively). The $^{33}$S NMR peak for the cathode (discharged to 1.50 V) is broader and shifted slightly upfield compared to the NMR peak for Li$_2$S powder, which is extremely sharp and slightly downfield. The broadness of the $^{33}$S NMR peak for the discharged cathodes is attributed to the presence of different lithium polysulfide species that may not have all been converted to the final Li$_2$S product. Longer-chain
polysulfides such as Li$_2$S$_2$, Li$_2$S$_4$, Li$_2$S$_6$, etc. could still be present in the cathode in small amounts particularly since these measurements were conducted ex-situ and it is possible that chemical reactions (such as disproportionation reactions) may occur after the battery discharge is stopped and the cathode is no longer held at a certain potential.

Spectra obtained from cathodes discharged to other potentials, however, did not exhibit clear peaks and showed only rolling baselines. A rolling baseline, attributed to “acoustic ringing,” is a well-known phenomenon that occurs in NMR probes used at low frequencies$^{41,42}$. The baseline results from a physical resonance frequency inside the NMR probe causing a ring-down phenomenon to occur inside the probe, distorting the first few points in the NMR free induction decay (FID) and yielding a large, moving, rolling baseline in the resulting NMR spectra$^{41}$.

An additional complication in studying elemental sulfur or polysulfides is the breadth of the NMR peak which has been reported at ±500 ppm$^{43}$. In one particularly clear spectrum of elemental sulfur powder, we found a peak ranging from +800 to -700 ppm centered at around -50 ppm. This sulfur peak does appear in other spectra from discharged cathodes acquired as either a shoulder on a rolling baseline or a small peak, but the background noise is too large to conclusively determine whether or not this feature obtained for sulfur powder is real. Therefore, information about the soluble lithium polysulfide species was not obtained in the $^{33}$S MAS NMR studies.
Figure 3.4: Solid-state $^{33}\text{S}$ MAS NMR spectra of (a) a Li-S battery cathode discharged to 1.5 V and (b) dry Li$_2$S powder. $B_0 = 17.6$ T, $\nu_r = 11$ kHz, line broadening = 200 Hz.

3.4 Discussion

The discharge curve shown in Figure 3.1 exhibits the three characteristic plateau regions that are associated with three different reaction processes$^{9,24}$. The identity of these processes is still controversial and may include S-S bond cleavage by lithium ions, disproportionation reactions, and differing degrees of polysulfide, Li$_2$S$_2$, and Li$_2$S formation$^4$. In this work we use $^6\text{Li}$ and $^{33}\text{S}$ solid-state MAS NMR spectroscopy (with both 1-D and T$_2$ relaxation measurements)
to investigate the products formed in each of the three characteristic plateau regions in order to further elucidate the discharge reaction mechanisms.

The consistent $^6$Li NMR chemical shift observed for LiTFSI, regardless of differing chemical environments tested demonstrates that the electrolyte salt is insensitive to the surrounding chemical environments and additionally that the LiTFSI salt has a different chemical shift than the Li$_2$S powder (Figure 3.2). Powders of other chain lengths of lithium polysulfides are not available for use as standards. LiTFSI is not found in discharged cathodes, which means that solvent incorporation in the cathode (following addition of electrolyte) is minimal. This background study confirms that the LiTFSI salt, which is the only other source of lithium in the battery aside from the anode, does not interfere with identification of the final discharge products.

$^6$Li solid-state MAS NMR chemical shift measurements (Figure 3.3) of discharged Li-S cathodes and Li$_2$S powder demonstrate that cathodes discharged to 2.15, 2.03, and 2.00 V exhibit very similar chemical shifts. Because these different voltage plateaus are associated with terminal Li polysulfide species of different lengths, it is suggested that changes in the number of neighboring sulfur atoms do not affect the electronic environment of the terminal lithium atoms strongly enough to further de-shielded them. The slight variation in chemical shift observed may be a consequence of disproportionation reactions from the highly soluble polysulfides$^{4,9,24}$ continuing after battery discharge is terminated. Thus, products of these disproportionation reactions may contribute to the observed signals. There is likely a distribution of different lithium polysulfide species present in the Li-S battery at each potential throughout discharge due to mass transport and kinetic limitations, as well as on-going disproportionation reactions and the well-known polysulfide shuttle mechanism$^{4,7}$. This means that there are a number of lithium
polysulfide chain lengths present in each cathode contributing to the aggregate observed chemical shift.

Cathodes discharged to the final voltage of 1.50 V have the same $^6$Li MAS NMR chemical shift as Li$_2$S powder. The slight (0.08 ppm) difference between the chemical shifts of the cathode discharged to 1.50 V and the Li$_2$S powder may be due to small, additional contributions from other Li polysulfide species (such as solid Li$_2$S$_2$).

It is clear from the $^6$Li solid-state MAS NMR studies that chemical shift alone does not allow the different chain lengths of lithium polysulfide species other than Li$_2$S to be distinguished. $T_2$ (spin-spin or transverse) relaxation measurements were conducted as a complementary method to distinguish the different polysulfide chain lengths since it is known that $T_2$ relaxation is affected by molecular size and physical state$^{44}$. $T_2$ relaxation was chosen rather than $T_1$ (spin-lattice or longitudinal) relaxation because $T_2 \leq T_1$ for solid-state species and therefore the measurement time is shorter. $T_2$ relaxation is caused by de-coherence of the magnetization of the nuclei under observation in the transverse plane (i.e. the plane perpendicular to the direction of the applied external magnetic field), which is due only to inhomogeneous interactions of the surrounding environment with the excited-state nuclei.

Two different groupings of $T_2$ relaxation times were measured for Li-S cathodes discharged to the ends of the three potential regions, indicating $T_2$ relaxation measurements may be a useful tool to distinguish products formed during the Li-S battery discharge. While it appears from the measured $T_2$ relaxation times that the cathodes discharged to 2.03 and 2.15 V yield different $T_2$ relaxation times, the error associated with these measurements due to low signal-to-noise of the $^6$Li MAS NMR spectra indicates that the difference in $T_2$ relaxation times
determined for cathodes discharged to 2.03 and 2.15 V are not statistically significant. Further studies with $^6\text{Li}$-labeled samples or longer collection times would be needed to determine whether or not the $T_2$ relaxation times are distinguishable for cathodes discharged to smaller depths of discharge (i.e. 2.03 and 2.15 V).

The two groups of measured $T_2$ relaxation values follow a trend associated with the extent of cathode discharge, where the products in cathodes discharged to more negative potentials have smaller $T_2$ times. $T_2$ relaxation times are affected by several different factors, which are related to the correlation time ($\tau_c$, related to Brownian motion) of the species under investigation. These factors include: (1) molecular size, where smaller $T_2$ values generally indicate larger molecular size, (2) viscosity, where smaller $T_2$ relaxation times indicate higher viscosity (decreased molecular movement), and (3) temperature, where lower temperatures cause $T_2$ relaxation times to decrease. These parameters are related by the equation below (Equation 2), which is derived from the Stokes’ law with a spherical approximation.

$$\tau_c = \frac{4\pi\eta r^3}{3kT} \quad \text{(Equation 2)}$$

Where $\eta$ is viscosity of the solvent, $r$ is the radius of the molecule, $k$ is the Boltzmann constant, and $T$ is the temperature. In the present system, temperature is constant and thus cannot contribute to the observed $T_2$ relaxation time changes. Possible viscosity changes in the electrodes discharged to different potentials could be associated with changes in the Solid Electrolyte Interphase (SEI) that may occur at different degrees of discharge. Little is understood presently about the SEI formed on the cathode aside from insulating elemental sulfur and solid product deposits such as $\text{Li}_2\text{S}_2$ and $\text{Li}_2\text{S}$. The anode SEI is known to contain lithium
polysulfide species along with solvent degradation products where lithium polysulfide species (Li$_2$S$_n$) may react with the ether-based solvents (R-O-R) to form R-OLi and R-Li$_2$S$_n$ species.$^{46}$

The final possibility for changes in T$_2$ relaxation times with degree of discharge relates to the different molecular sizes of discharge products formed. In particular, at low discharge potentials, higher molecular weight polysulfides are present, while at high discharge potentials, Li$_2$S has been demonstrated previously to be the major product formed. We therefore assign differences in T$_2$ relaxation times at different depths of discharge to different sizes of lithium polysulfide products in the battery cathodes, where smaller polysulfides are found at lower potentials, consistent with prior results.$^9$

The solid Li$_2$S powder has a different T$_2$ relaxation time than that of the products formed in the fully discharged (1.50 V) cathode (11.9 and 26 ms, respectively, Table 3.1). The origin of the increased relaxation time is likely the presence of species in addition to Li$_2$S in the discharged cathode. In particular, the $^6$Li NMR spectrum of cathodes discharged to 1.50 V results in two peaks: one attributed to Li$_2$S and one attributed to an oxide species such as Li$_2$CO$_3$ (2.32 and 0.12 ppm, respectively). Additionally, the Li$_2$S powder is crystalline while the products formed in the fully discharged cathode may be amorphous or only have short-range crystalline order, the differences of which also contribute to chemical shift dispersion.$^{47}$

Like the $^6$Li MAS, solution $^7$Li NMR of electrolyte solution and extracted products from discharged Li-S battery cathodes (Table 3.2) also exhibits minimal chemical shift differences among cathodes discharged between 2.15 V and 2.00 V. Since chemical shift differences between $^6$Li and $^7$Li NMR spectra are not significant$^{35}$, chemical shifts between the two isotopes may be directly compared. Spectra obtained from solutions above cathodes discharged to 1.5 V
did not exhibit a signal attributable to the discharge product, likely a consequence of Li$_2$S insolubility. The $^1$H spectra acquired for all of the extracted products from discharged Li-S batteries have been attributed to the TEGDME/DIOX solvent present in the cathodes.

Solid-state $^{33}$S MAS NMR of cathodes discharged to 1.50 V and Li$_2$S powder (Figure 3.4) also suggests that the cathodes discharged to this potential contain mostly Li$_2$S. The increased width of the $^{33}$S NMR peak for the discharged cathode relative to that of Li$_2$S powder suggests again that the cathode likely contains a small amount of other lithium polysulfide species contributing to its line shape.

### 3.5 Conclusions

$^6$Li T$_2$ relaxation measurements show that the first two characteristic plateau regions present in Li-S battery discharge curves are associated with larger lithium polysulfide species (at 2.03 and 2.15 V) that react to form smaller lithium polysulfide species with further depth of discharge into the third plateau region (at 1.50 V). Additionally, both solid-state $^6$Li and $^{33}$S MAS NMR studies demonstrate that Li$_2$S is produced only at the end of the Li-S battery discharge in cathodes discharged to 1.50 V, along with small amounts of longer-chain lithium polysulfide species. $^6$Li, $^{33}$S MAS NMR, and $^6$Li T$_2$ relaxation measurements all resulted in two regions of product formation during discharge, where the first state of discharge occurs in the first two plateau regions and the second state of discharge occurs in the third plateau region. These studies indicate that NMR spectroscopy is a powerful tool to study differences between the solution and solid-state products (i.e. soluble long-chain Li polysulfide species and insoluble
Li$_2$S$_2$ and Li$_2$S, respectively). Additionally T$_2$ relaxation measurements may be useful to distinguish between Li polysulfide products in all three states of discharge with further studies.

3.6 Acknowledgements

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3.7 References


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CHAPTER 4

Identification of Li-ion battery SEI compounds through $^7$Li and $^{13}$C NMR spectroscopy and MALDI-TOF Mass Spectrometry

4.1 Introduction

A current major goal in society is to transition to a sustainable energy system with emphasis on electrical power that will reduce the use of fossil fuels, which produce the harmful greenhouse gas carbon dioxide (CO$_2$) and may not meet future energy demands.$^1$ A sustainable energy system will incorporate renewable energy sources (solar, nuclear, wind, etc.) as our electrical power supply and require the use of energy storage devices to harness energy from these sources intermittently.$^2$ The lithium-ion battery is the electrical storage technology that allows the use of portable electronic devices and is ubiquitous in the world today where it is frequently used in cell phones, hand-held reading devices, laptop computers, etc.$^3$ The Li-ion battery offers several advantages compared to newer battery technologies (such as lithium-oxygen (Li-O$_2$), lithium-sulfur (Li-S), lithium-zinc, etc.) including the long period of time that has been dedicated to its research and development, its current already-established status as highly functional, and its high potential for improvement in discharge capacity and cyclability. However, several challenges remain for improvement of this battery chemistry to reach the goal of use in fully electrified vehicles (EVs) over a range of 500 km. The current Li-ion battery discharge specific capacity must be improved by at least two to three times in order to compete with newer battery technologies, the battery currently suffers from capacity fading during long-term cycling, there are safety concerns due to the use of Li and the flammability of common
electrolyte solvents, and in order to be feasible for use in a clean-energy sustainable future, the battery components must be made of abundant, environmentally benign materials.⁴

A critical area of study for improvement in these batteries is the secondary electrolyte interphase (SEI). The SEI is a layer that forms predominantly on the anode of the battery during cycling that is composed of electrolyte decomposition compounds and acts as a protective layer.⁵ The SEI provides some advantageous contributions to the battery cyclability as well as several problems. The SEI layer prevents plating of Li ions on the carbon anode during fast charge, provides a protective layer that prevents corrosion of the anode surface, prevents solvent co-intercalation, and also inhibits further electrolyte decomposition by blocking electronic conductivity through the SEI layer while allowing Li ions to be transported through.⁶ However, insulating and thick sections of the SEI prevent electronic conductivity throughout the anode and Li⁺ ion transport to and from the anode, thereby contributing to capacity fading and decreased cycleability. Currently, much effort is directed towards characterizing and identifying the species that make up the SEI in order to gain further insight to its function and to prevent undesirable properties in future Li-ion batteries.⁴⁻⁸ A large number of studies conducted on the SEI using various spectroscopic techniques have demonstrated the diversity and complexity of the SEI compounds. Due in part to the vast number of different electrode and electrolyte systems that have been studied and also to the complex nature of the SEI, there is currently no consensus on the compounds that make it up. Major components of the SEI that have been proposed using a vast array of spectroscopic techniques include Li₂CO₃,⁹ LiF,¹⁰ Li₂O,¹¹ LiOH, Li₂C₂O₄,¹² HCOLi,¹³ polycarbonates,¹⁰,¹⁴ ROLi,¹⁵ Li ethylene carbonate ((CH₂OCO₂Li)₂),¹⁶ and ROCO₂Li.¹⁷
Recent work utilizing matrix assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectroscopy (MS) and electrochemical quartz crystal microbalance (EQCM) measurements on Au and Sn electrode surfaces after electrochemical cycling show the presence of fragmentation patterns with a large repeat spacing (ca. 150-170 m/z) that is attributed to the oligomer of a polymer. Electrodes were cycled between one and five cycles and compared to un-cycled electrodes, anode material (graphite) mixed with the electrolyte salt (LiClO$_4$) and solvent (1:1 ethylene carbonate/dimethyl carbonate, EC/DMC) and graphite alone. MALDI-TOF-MS is used because this technique can detect high molecular weight polymers (up to 3,000 m/z), which other ionization mass spectroscopy techniques are unable to detect. Other previous reports use thermal gravimetric mass spectrometry (TG-MS), time of flight (TOF) secondary ion mass spectroscopy (SIMS), and high resolution mass spectroscopy (HRMS) to examine SEI compounds. Formation of long-chain oligomer polymers are reported in several of these studies, and are additionally observed through the use of x-ray photoelectron spectroscopy, AFM, STM, gel permeation chromatography, and infrared (IR) spectroscopy.

In a previous study, EQCM measurements exhibit a large mass change of 90 µg cm$^{-2}$ after the first cycle of all four systems tested: Au in EC/DMC, Au in propylene carbonate (PC), Sn in EC/DMC, and Sn in PC. This initial mass increase is attributed to the formation of the SEI on the anode surface. Additional experiments using MALDI-TOF mass spectrometry indicate the presence of polymers due to a fragmentation pattern with a large repeat unit with a large spacing between each subunit (ca. 166 m/z for LiClO$_4$ and EC/DMC on textured Au), which is attributed to oligomer units of a large polymer that is formed in the SEI layer of Li-ion anodes. Calculations performed using DFT give insight into a possible mechanism for the formation of this SEI polymer. These calculations indicate that ring-opening of the ethylene
carbonate (EC) solvent molecule occurs via nucleophilic attack on one of the \( \text{CH}_2 \) carbons attached to the oxygen next to the carbonyl group by the \( \text{PF}_6^- \) salt anion.

A previous report utilizing solid-state \( ^{13}\text{C} \) NMR spectroscopy to investigate SEI compounds in Li-ion anodes observed various peaks in the region of 100-160 ppm. This report assigns these peaks to SEI compounds formed from nucleophilic attack of the carbonyl carbon on solvent carbonate compounds (EC and DMC) though an SN\(_2\) attack, breaking the double bond to oxygen and forming products that lack carbonyl groups.\(^{18}\) Previous work using solid-state \( ^7\text{Li} \) NMR to investigate the SEI layer indicate that lithium ions (\( \text{Li}^+ \)) that are intercalated into carbon anodes yield characteristic \( ^7\text{Li} \) peaks at approximately 50 ppm. It has additionally been suggested that a characteristically sharp \( ^7\text{Li} \) peak at approximately 0 ppm is either due to irreversible Li inside the SEI layer of carbon anodes or to an intermediate phase of lithium intercalated in graphite (of the structure \( \text{Li}_x\text{C} \)), while a broad peak centered at around 0 ppm is characteristic of solvent decomposition products that may also be present in the SEI layer.\(^{19\text{-}26}\)

Herein, we report the use of solid-state \( ^7\text{Li} \) and \( ^{13}\text{C} \) MAS NMR spectroscopy, MALDI-TOF mass spectrometry, and SEM and TEM imaging to further identify the species formed upon lithiation of Li-ion anodes and to determine the changes that occur in SEI compounds between lithiation and de-lithiation.

\textit{4.2 Materials and Methods}

\textit{Li-ion battery discharge and charge}

The graphite active material used in the Li-ion flow cells is a GS-2299 nano-graphite powder, which has a reported nominal BET surface area of 400 m\(^2\) g\(^{-1}\) and a broad particle size
distribution of 0.25-5.01 µm. Anode slurries are composed of the GS-2299 nano-graphite powder (11.2 wt.%) and electrolyte solution (1 M LiPF₆ in 1:1 EC/DMC, 88.8 wt.%) and were mixed in an Aquasonic 150T Ultrasonic Cleaner for 1h. The Li-ion batteries were set up and cycled in a Swagelok-type cell design, which is shown in Figure B.1 in Appendix B. The Swagelok battery stack includes three components: a lithium cathode, a glass microfiber separator soaked with liquid electrolyte consisting of 1 M LiPF₆ in a 1:1 molar ratio of ethylene carbonate/dimethyl carbonate, and an anode slurry confined in a notch on one side of the current collector. The anodes had an approximate mass of 0.02 g, corresponding to 0.002 g of graphite active material. All anodes were cycled at a rate of C/50 from 3.5 to 0.1 V vs. Li/Li⁺.

Solid-state $^7$Li and $^{13}$C MAS NMR spectroscopy

Solid-state $^7$Li and $^{13}$C DPMAS (direct-polarization magic angle spinning) NMR spectroscopy and $T_1$ relaxation time experiments were performed on a 7.1 T Varian Unity Inova 300 (Varian is now part of Agilent Technologies) spectrometer, equipped with a 4-mm Varian Chemagnetics APEX Double Resonance HX probe. All solid-state experiments employed magic angle spinning (MAS) at a 10 kHz rotor spinning speed. All anode samples were packed in silicon nitride rotors inside a glove box, sealed to avoid air exposure, then removed from the glove box and spun to 10 kHz inside the spectrometer.

The parameters for the solid-state $^7$Li DPMAS NMR experiments for the LiPF₆ salt and anodes are as follows: the calibrated 90° pulse was 1.8 µs, the spectral width was 70,000 Hz, the acquisition time was 100 ms, and the number of complex points was 7000. Parameters that are different for the sample of graphite mixed with LiPF₆ and EC/DMC are: the spectral width was
93,349 Hz, the acquisition time was 109 ms, the recycle delay was 600 s, and the number of complex points was 10192. The parameters for the solid-state $^{13}$C DPMAS NMR experiments are as follows: the calibrated 90° pulse was 2.45 µs, the spectral width was 50,000 Hz, the acquisition time was 20 ms, the recycle delay was 30 s, and the number of complex points was 1000. Additional experimental parameters for MAS NMR experiments are given in the figure captions, employing the following symbols: $B_0$ (magnetic field strength), $v_r$ (magic angle spinning rate), $d_1$ (relaxation delay), $lb$ (line broadening), and $nt$ (number of transients).

Solid-state $^{13}$C MAS spin-lattice ($T_1$) relaxation rate NMR measurements were conducted using a two-pulse inversion-recovery experiment (180° followed by a 90° pulse). The parameters for the $T_1$ relaxation rate experiments are as follows: the calibrated 90° pulse was 2.45 µs, the recycle delay was 50 s, the spectral width was 50,000 Hz, the acquisition time was 20 ms, and the number of complex points was 1,000. Additional experimental parameters for the $^{13}$C MAS $T_1$ relaxation rate NMR experiments are given in the table caption, employing the same symbols as described above.

**Solution NMR spectroscopy**

Solution experiments were performed on a 14.1 T Varian (Varian is now part of Agilent Technologies) NMR spectrometer. These experiments were performed using 5mm Varian $^1$H/$^{13}$C/$^{15}$N PFG X, Y, Z and 5mm Varian AutoTuneX $^1$H/X PFG Z, Z=$^{31}$P/$^{15}$N probes. Again, additional experimental parameters for MAS NMR experiments are given in the figure captions, employing the following symbols: $B_0$ (magnetic field strength), $v_r$ (magic angle spinning rate), $d_1$ (relaxation delay), $lb$ (line broadening), and $nt$ (number of transients).
**MALDI-TOF Mass spectrometry**

All samples were prepared in an Ar-filled glove box (O₂ ppm < 2). Anode samples were ground into powder form using a mortar and pestle. Samples were then supported with copper tape and approximately 200 µL of the MALDI matrix, 2,5-dihydroxybenzoic acid (DHB) was applied to the samples. Samples with matrix applied were dried overnight in the glove box. The MALDI samples were run on a Bruker Daltonics UltrafleXtreme MALDI-TOF/TOF instrument which incorporates MALDI-TOF and TOF/TOF technology. All samples experienced minimal air exposure (< 1 min.) before placement under vacuum in the mass spectrometer.

**TEM and SEM images**

TEM and SEM samples were prepared by suspending graphite anode samples (after cycling) in dry acetone (>99.8%, Acros Organics) followed by sonication. In order to reduce sample exposure to air, all steps were conducted in an Ar-filled glove box. For TEM imaging, one drop of the prepared suspension was dropped onto a Cu grid coated with carbon film. The Cu grid was left to dry, mounted onto a JOEL single-tilt TEM holder and then sealed in a zipper bag. The TEM holder was transferred inside the zipper bag and was not removed until just prior to introduction to the microscope. TEM images were acquired using a JOEL 2010F TEM instrument operated at 200kV. For SEM imaging, the prepared suspension (graphite in acetone) was dried and a small amount of the dry powder was applied to double-sided carbon tape on an SEM sample holder. SEM samples were acquired using a Zeiss Merlin HRSEM instrument operated with an acceleration voltage of 3 kV.
4.3 Results

Li-ion battery cycling curve and SEM/TEM images

The Li-ion anodes in this work are made up of high surface area graphite relative to other carbon materials used in typical battery systems in order to maximize the amount of SEI compounds formed on the anodes upon cycling. We note that most research aims to limit the amount of SEI material formed on cycled anodes and practical Li-ion battery systems utilize low surface area graphite to prevent large amounts of SEI from forming in the batteries.\(^{27}\)

Figure 4.1 shows a representative charge and discharge curve for the Li-ion flow battery. As the battery is charged (lithiated), the cell potential decreases from approximately 2.9 V to ca. 0.01 V vs. Li/Li\(^+\) with an apparent capacity of approximately 1,541 mAh g\(^{-1}\) due to SEI formation. The charge (lithiation) curve demonstrates a characteristic sharp decrease in potential followed by a plateau at approximately 1.0 V vs. Li/Li\(^+\), and then a gradual decrease in potential between 0.8 and 0.01 V vs. Li/Li\(^+\). The cell is discharged from 0.1 V to 3.0 V vs. Li/Li\(^+\). The first charge capacity (1,541 mAh g\(^{-1}\)) is significantly greater than the first discharge capacity (262 mAh g\(^{-1}\)). The charge curve is associated with Li ions intercalating into the graphite anode and forming SEI compounds. The discharge curve is associated with removal of Li ions from the graphite anode. Since the discharge capacity is 17\% of the charge capacity, this indicates the majority of the current passed during charging is associated with either irreversible SEI formation or irreversible Li intercalation.
Figure 4.1: A Li-ion flow cell charge and discharge curve (voltage versus time) for anodes lithiated between open circuit potential (ca. 2.9 V) and 0.1 V vs. Li/Li$^+$ and de-lithiated from 0.1 V to 3.0 V vs. Li/Li$^+$. 

Figure 4.2 shows representative SEM images obtained from the graphite anodes before and after lithiation. These images demonstrate an amorphous layer on top of the graphite particles that is attributed to the SEI layer, which consists of the electrolyte salt and solvent decomposition products.
Figure 4.2: SEM images of high surface-area graphite Li-ion battery anodes after full charge (lithiation).

Figure 4.3 shows TEM images of lithiated anodes, which clearly depict an amorphous region that is separate from the crystalline graphite region. This amorphous region is again attributed to SEI compound formation on the graphite anode surface after lithiation.
NMR studies

In order to obtain information regarding the nature of the SEI, we obtained solid-state magic angle spinning (MAS) NMR spectra of un-cycled, lithiated, and de-lithiated graphite anodes prior to and following SEI formation. Figure 4.4 shows stacked solid-state $^7$Li DPMAS NMR spectra of LiPF$_6$ powder (Fig. 4.4a), an un-cycled anode containing electrolyte solution (1 M LiPF$_6$ and EC/DMC, Fig. 4.4b), as well as lithiated (Fig. 4.4c) and de-lithiated (Fig. 4.4d) Li-ion anodes. All anodes studied contain the same high surface area graphite material and 1 M LiPF$_6$ electrolyte solution. The $^7$Li nucleus is quadrupolar, which means that it has a nonspherical charge distribution at the nucleus. Due to its quadrupolar nature, in addition to the central transition ($I = -1/2$ to $+1/2$) center peak that is commonly detected in NMR spectroscopy,
the spin angular momentum of $^7\text{Li}$ can undergo satellite transitions to $\pm 3/2$ spin energy levels. Therefore, solid-state MAS NMR spectra containing large enough quantities of $^7\text{Li}$ will yield quadrupolar satellite peaks at the frequency of MAS spinning (i.e. separated by 10 kHz).\textsuperscript{28-30} Thus, large amounts of $^7\text{Li}$ nuclei result in relatively large side (satellite transition) peaks.

The spectrum of LiPF$_6$ salt (Fig. 4.4a) exhibits one isotropic peak at -3.01 ppm (referenced to 1 M LiCl solution) with two small satellite peaks visible. The spectrum of graphite mixed with LiPF$_6$ and EC/DMC shows one isotropic peak at -5.14 ppm and one very narrow peak (a spike) at -1.12 ppm with six slightly larger satellite peaks. We attribute the sharp peak in Fig. 4.4b to free Li ions from the electrolyte salt, LiPF$_6$, which are dissolved in solution on the un-cycled anode since this peak has a very similar chemical shift to the LiPF$_6$ powder. The broad peak near 0 ppm indicates heterogeneity in the species in Fig. 4.3b, which likely arises from a reaction between the LiPF$_6$ salt and the carbonate solvents (EC and DMC). Solid-state $^7\text{Li}$ MAS NMR spectra were additionally obtained for several possible inorganic species that could be formed in the SEI layer, including Li$_2$CO$_3$, Li$_2$O, and Li$_2$O$_2$, which are shown in the Appendix B (Fig. B.2). Since these lithium powders all exhibit chemical shifts within the range of chemical shifts covered by the central peak in Figure 4.4b, it is possible that these species also contribute to this broad, central peak (Fig. 4.4b).

Previous reports studying compounds present in cycled Li-ion anodes also suggest that a broad peak centered at ca. 0 ppm indicates the presence of solvent decomposition and SEI compounds.\textsuperscript{25,26,29} Additionally, there were numerous peaks observed located downfield from the 0 ppm peak, attributed to different Li$_x$C phases of the lithiated graphite material.\textsuperscript{26}
The spectrum of the lithiated Li-ion anodes (Fig. 4.4c) exhibits one peak at -0.76 ppm with a shoulder up-field of the main peak (i.e. the peak contains larger area under the right side). This spectrum shows six large satellite peaks that are separated by ca. 10049 Hz. The broad -0.76 ppm peak is again attributed to heterogeneity of Li-containing species after lithiation of the anode, as has been previously discussed.\textsuperscript{25,26,29} The appearance of intense quadrupolar satellite peaks indicates differences in the chemical shift anisotropy of the Li nuclei in the two spectra (Fig. 4.4b and c).\textsuperscript{31}

The spectrum of the de-lithiated Li-ion anodes (Fig. 4.4d) also exhibits one peak at -0.78 ppm. This peak exhibits a reduced peak to sideband intensity ratio (Table 4.1) relative to the lithiated anode shown in Fig. 4.4c, which is consistent with decreased Li content in the material. The increased linewidth of the -0.78 ppm peak relative to those in Figures 4.4b and c again suggests greater heterogeneity experienced by the Li nuclei in the discharged electrode.
Figure 4.4: Solid-state $^7$Li DPMAS NMR spectra of (a) LiPF$_6$ electrolyte salt powder, (b) graphite mixed with LiPF$_6$ and EC/DMC (subsequently dried), (c) lithiated anodes, and (d) de-lithiated anodes. $B_0 = 7.1$ T, $v_r = 10$ kHz, $d1 = 600$ s, $lb = 20$, and $nt = 8$ (LiPF$_6$ salt), 124 (anodes), and 1012 (graphite + LiPF$_6$ + EC/DMC).
<table>
<thead>
<tr>
<th></th>
<th>Chemical shift (ppm)</th>
<th>Full-width of half-maximum (Hz)</th>
<th>Peak/sideband height ratio</th>
</tr>
</thead>
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<tr>
<td>(a) LiPF$_6$ salt</td>
<td>-3.01</td>
<td>795</td>
<td>25.3</td>
</tr>
<tr>
<td>(b) Graphite + LiPF$_6$ + EC/DMC</td>
<td>-1.12, -5.14</td>
<td>1090, 1583</td>
<td>15.9</td>
</tr>
<tr>
<td>(c) Lithiated anode</td>
<td>-0.76</td>
<td>1495</td>
<td>7.3</td>
</tr>
<tr>
<td>(d) De-lithiated anode</td>
<td>-0.78</td>
<td>1532</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of solid-state $^7$Li MAS NMR chemical shift, full-width at half-maximum, and peak/sideband ratio values.

The presence of substantial heterogeneity in the solid-state $^7$Li NMR of lithiated and de-lithiated anodes led us to evaluate the nature of putative SEI species formed during anode cycling. Solid-state $^{13}$C MAS NMR is used in this study to identify compounds formed in the SEI layer of anodes upon cycling. Obtaining high quality spectra or structural information from natural abundance solid-state $^{13}$C MAS NMR of graphite and graphite oxide is difficult due to the heterogeneous and non-crystalline nature of these materials.$^{32,33}$ Prior work utilized $^{13}$C-labeled solvents to examine the effects of aging and high temperature in accelerating solvent degradation and growth of SEI compounds.$^{18}$ A number of SEI products were found in the 85-150 ppm $^{13}$C chemical shift range and assigned to acetals, orthoesters, orthocarbonates, and fluorinated carbons or carboxy species.
The spectra shown in Figure 4.5 are typical of natural abundance $^{13}$C DP-MAS NMR spectra of graphite and graphite oxide materials. The stacked solid-state $^{13}$C DPMAS NMR spectra (Fig. 4.5) all contain a large, underlying peak that originates from the graphite material. Graphene has previously been demonstrated exhibit a peak in solid-state $^{13}$C MAS NMR at ca. 130 ppm (with substantial error induced by the large peak width). Additional features found in previous reports of natural abundance solid-state $^{13}$C NMR of graphene and graphene oxide include sp$^2$-bonded carbons (at 129.3 ppm) such as carbon-carbon (C=C), epoxide (C-OC), carbonyl, and carboxylic groups (C-OH) and sp$^3$-bonded carbons such as C-OH (69.6 ppm) and epoxide (59.7). These additional non-equivalent $^{13}$C sites contribute to the large width of the graphene peak.

To identify compounds formed upon lithiation and de-lithiation of Li-ion anodes, solid-state $^{13}$C DPMAS NMR was conducted on graphite powder, graphite mixed with 1:1 EC/DMC solvent, and graphite mixed with LiPF$_6$ and EC/DMC (Fig. 4.5a-c). The spectrum of graphite powder shows one very broad peak centered at 96.67 ppm and a total width of 12800 Hz. The spectrum of graphite mixed with 1:1 EC/DMC solvent shows one large peak in the C-OR (sp$^3$-bonded carbon and oxygen) $^{13}$C NMR spectral region at 57.66 ppm, another large peak in the C=O (sp$^2$-bonded carbon and oxygen) spectral region at 147.62 ppm, and a very large underlying peak centered at 115.53 ppm with an approximate total width of 8466 Hz. The spectrum of graphite mixed with LiPF$_6$ salt and EC/DMC electrolyte shows one large peak in the C-O (sp$^3$) $^{13}$C NMR spectral region at 59.88 ppm, another large peak in the C=O (sp$^2$) spectral region at 150.87 ppm, and a very large underlying peak centered at 116.34 ppm with an approximate total width of 8900 Hz. The spectrum of the lithiated anodes (Fig. 4.5d) shows a large peak in the C-O region at 65.03 ppm, a large peak in the C=O region at 156.75 ppm, and a very large
underlying peak centered at 129.44 ppm with a total width of ca. 12900 Hz. The spectrum of de-lithiated anodes (Fig. 4.5e) shows a small peak in the C-O region at 65.91 ppm, a very small peak in the C=O region at ca. 157.68 ppm, and the large underlying peak centered at 139.78 ppm with a total width of ca. 21600 Hz.

Interestingly, both the chemical shift and total width of the broad graphite peak changes in all four spectra shown in Figure 4.5. The chemical shift value of the approximate center of the graphite peak moves to more positive (i.e. less shielded) values upon addition of electrolyte and further upon lithiation and de-lithiation in Li-ion anodes. Graphite powder (Fig. 4.5a) has a large peak that is the most shielded (i.e. located up-field, more negative) out of all of the graphite peaks in Figure 4.5. The center of the graphite peak shifts to less shielded (i.e. more positive) chemical shift values in the order of: graphite powder, graphite mixed with 1:1 EC/DMC, graphite mixed with LiPF₆ and EC/DMC electrolyte, lithiated anodes, and de-lithiated anodes. This trend in chemical shift values could indicate that the local electronic environment of the graphite becomes less shielded as electrolyte is added to the graphite, then further as the anode is first lithiated, and is further de-shielded upon de-lithiation of the anodes.

In addition to a trend in peak chemical shift, there is additionally a trend in the width of the broad graphite peak in the solid-state $^{13}$C DPMAS NMR spectra in Figure 4.5. The graphite powder is the only sample in Figure 4.5 that did not contain electrolyte solvent and has an approximate width of 12800 Hz. The width of the broad graphite peak in the samples containing electrolyte solvent (Fig. 4.5b-e) increases in the following order: graphite mixed with EC/DMC, graphite mixed with LiPF₆ and EC/DMC, lithiated anodes, and de-lithiated anodes, where the latter has the largest width of ca. 21600 Hz. The width of graphite solid-state $^{13}$C NMR peaks has been discussed previously, and has been attributed to sample heterogeneity including bulk
magnetic susceptibility shifts, paramagnetic impurities or radicals (causing Fermi contact or Knight shifts), and structural heterogeneity, as well as currents generated by MAS spinning of the conductive, aromatic sample in high magnetic fields.\cite{34}

To elaborate further on reasons that graphite exhibits a characteristically broad solid-state $^{13}$C NMR peak (Fig. 4.5), the breadth can be due to high numbers of non-equivalent carbon sites in the graphite particles (i.e. within the graphene sheets, edges of the sheets, and particles of stacked graphene layers) and the presence of paramagnetic sites in the graphene layers of graphite. The chemical shift anisotropy seen in this peak is typical for linewidths of aromatic carbon compounds (ca. 150 ppm) as noted in previous reports.\cite{35,36} Defects within graphene and graphene oxide sheets affect the electronic and magnetic properties of the material.\cite{36} The presence of paramagnetic sites in materials is known to significantly increase the spin-lattice ($T_1$) relaxation rate of compounds. This is an electronic-nuclear interaction that is similar to the Knight shift that occurs from conduction electrons in metals interacting with nearby nuclei. We note that during $T_1$ relaxation measurements (Hahn-echo experiments) conducted in this study, the $\tau_{null}$ time for graphene was shorter than the shortest $T_1$ relaxation period ($\tau$) tested in the array of $T_1$ values for lithiated anodes, 0.001 s. This result indicates that the $T_1$ relaxation rate for graphene is shorter than 1.4 ms, since $T_1$ relaxation rate can be approximated by,

$$T_1 \approx \tau_{null} \times 1.44$$

This result demonstrates that the spin-lattice ($T_1$) relaxation rate of graphite is indeed extremely short, which contributes to the broadness of the graphite peak.

The reason that the graphite peak width increases upon lithiation and de-lithiation of the anodes (Fig. 4.5) could be due to addition of lithium ions (Li$^+$). Addition of paramagnetic ions to
the graphene sheets can cause paramagnetic charge-transfer complexes with the graphene plane and influence spin-lattice ($T_1$) relaxation times as has been demonstrated previously with Mn$^{2+}$ ions and graphite.$^{37}$ The charge-transfer between paramagnetic atoms and graphene has been demonstrated to shorten $^{13}$C spin-lattice $T_1$ relaxation times (at room temperature), which has been attributed to the additional available route for $T_1$ relaxation through the charge-transfer pathway.$^{36}$ It is possible that lithium ions (Li$^+$), which can be paramagnetic with an un-paired electron, may be adding to the graphite in a similar manner by causing increased densities of paramagnetic centers in anodes with intercalated lithium. This is likely the cause of the increased graphite peak width after lithiation of the anodes.

In the solid-state $^{13}$C DPMAS NMR spectrum of graphite mixed with 1:1 EC/DMC solvent (Fig. 4.5b), the major peaks present yield chemical shifts of 57.66, 115.53, and 147.62 ppm. Therefore, the peaks at 57.66 and 147.62 ppm in Fig. 4.5b are assigned to solvent (EC/DMC) peaks. We note that these peaks are slightly different than those previously reported for solution EC and DMC,$^{18}$ and attribute this shift to the graphitic environment used in this study. The broad peak at 115.53 ppm is assigned to the broad graphite feature.

The solid-state $^{13}$C DPMAS NMR spectrum of graphite mixed with the electrolyte solution (Fig. 4.5c), the major peaks present have chemical shifts of 59.88, 65.09, 116.34 (broad graphite peak), 146.14, 150.87, and 156.89 ppm. Peaks in the C-O (sp$^3$) and C=O (sp$^3$) that are similar to those found in Fig. 4.5b at 59.88 and 146.14 ppm likely originate from EC/DMC solvent that has undergone an environmental change after addition of the electrolyte salt, LiPF$_6$. However, large peaks that appear in this spectrum, at 65.09 and 150.87 ppm, do not originate from pure solvent compounds. This result indicates that the EC/DMC solvent species undergo a chemical change upon addition of the electrolyte salt (LiPF$_6$).
The major peaks in the $^{13}$C DPMAS NMR spectra of cycled anodes (Fig. 4.5d and e) at ca. 65 and 157 ppm are shifted significantly downfield from those in the C-O and C=O regions of graphite plus solvent and un-cycled anodes, where the chemical shifts of de-lithiated anodes are located further downfield than lithiated anodes. This result indicates that the species present in un-cycled anodes undergo chemical changes upon lithiation, and these species undergo even further chemical changes upon de-lithiation. We note that this result is different than a previous result utilizing $^{13}$C-labeled EC and DEC solvents, where intact carbonyl groups were not found in lithiated anodes.$^{18}$ The different products seen here likely are due to differences in experimental conditions and solvents used between the two studies.

An additional interesting result seen in Figure 4.5 is that both the solvent (EC/DMC) and SEI $^{13}$C NMR peaks are larger in intensity in lithiated anodes (Fig. 4.5d) than in de-lithiated anodes (Fig. 4.5e). This result suggests that there are less organic compounds present in de-lithiated anodes.

The results found from Figure 4.5 suggest that the SEI compounds consist of carbon centers that are more electronically shielded than those of EC and DMC. Previous reports of compounds that yield chemical shifts of ca. 150.9 ppm are typically of aromatic benzene rings connected directly to an oxygen atom.$^{38,39}$ Reports for compounds with chemical shifts of ca. 143.8 ppm are typically from a carbon atom directly bonded to a benzene ring or the sp$^2$ carbon in a benzene ring connected to an OH, COOH, C-C, or HC=CH group. The SEI peak at 59.88 ppm is likely an sp$^3$ carbon directly bonded to an OOC group and a methyl group, based on previous reports of compounds containing this structure exhibiting the same chemical shift.$^{39}$
Figure 4.5: Solid-state $^{13}$C DPMAS NMR spectra of (a) graphite, (b) graphite mixed with electrolyte solvent 1:1 EC/DMC, (c) graphite mixed with LiPF$_6$ electrolyte salt and EC/DMC solvent (subsequently dried), (d) lithiated anodes, and (e) de-lithiated anodes. $B_0 = 7.1$ T, $\nu_r = 10$ kHz, $d_1 = 30$ s, $lb = 20$, and $nt = 4868$ (Graphite + LiPF$_6$ + EC/DMC), 5000 (lithiated anodes), 6000 (graphite), and 8440 (de-lithiated anodes).
<table>
<thead>
<tr>
<th></th>
<th>C-O (sp³)</th>
<th>C=O (sp²)</th>
<th>Graphite</th>
<th>Full graphite peak width (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Graphite</td>
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<td>N/A</td>
<td>96.67</td>
<td>12800</td>
</tr>
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<td>(b) Graphite + EC/DMC</td>
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<td>147.62</td>
<td>115.53</td>
<td>8466</td>
</tr>
<tr>
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<td>150.87</td>
<td>116.34</td>
<td>8900</td>
</tr>
<tr>
<td>(d) Lithiated anode</td>
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<td>156.75</td>
<td>129.44</td>
<td>12900</td>
</tr>
<tr>
<td>(e) De-lithiated anode</td>
<td>65.91</td>
<td>157.68</td>
<td>139.78</td>
<td>21600</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of solid-state $^{13}$C MAS NMR chemical shift (ppm) values for three different regions, including the C-O sp³, C=O sp², and graphite regions, and the full peak width (Hz) of the graphite feature.

NMR of PEO polymer standards

In order to evaluate the origin of the broad peaks seen in the $^{13}$C MAS NMR of the lithiated and de-lithiated anodes, we compared these spectra with those obtained from polyethylene oxide (PEO). PEO is found in a number of different molecular weights which helps to evaluate the spectral response and compare it with that from the anode systems. PEO is routinely used as a synthetic electrolyte for polymer Li-ion batteries. Standard polyethylene oxide (PEO) polymer powders of two different molecular weights (100,000 and 600,000 Da)
were tested using solid-state $^{13}$C MAS NMR to compare to the $^{13}$C NMR spectra of anode graphite plus electrolyte, lithiated and de-lithiated anodes (Fig. 4.5b-d).

The solid-state $^{13}$C MAS NMR spectra of the two different molecular weight PEO polymers (Fig. 4.6a and b) are extremely similar with both spectra exhibiting one peak at ca. 70 ppm. Previous studies of solid-state $^{13}$C MAS NMR of PEO polymers indicate that a single, isotropic peak at 70 ppm results from the crystalline form of PEO.\textsuperscript{41} This result indicates that the peaks in Figure 4.6 are due to crystalline PEO with possible amorphous regions found in the slightly broadened area at the base of the sharp crystalline (70 ppm) peak.

![Figure 4.6: Solid-state $^{13}$C DPMAS NMR spectra of standard polyethylene oxide (PEO) powders of molecular weight (a) 100,000 and (b) 600,000. $B_0 = 7.1$ T, $\nu_T = 10$ kHz, $d1 = 30$ s, $lb = 20$, and $nt = 1148$ (100k MW) and 1096 (600k MW).]
It has been proposed previously that polymeric species form in the SEI layer of Li-ion anodes upon lithiation of the anodes.\cite{14, 42, 43} In order to evaluate the size of this polymer, we use T$_1$ relaxation rate measurements from the lithiated anodes and compare these with corresponding measurements from the PEO polymers. Spin-lattice (T$_1$) relaxation rates of compounds yield information about the relative size, motion, and viscosity of the species.

Solid-state $^{13}$C spin-lattice (T$_1$) and spin-spin (T$_2$) relaxation rates are reported for lithiated anodes, PEO powder standards, and PEO polymers mixed with graphite in Table 4.1. Since the solid-state $^{13}$C MAS NMR spectra compounds formed in lithiated anodes result in two main peak groupings, designated sp$^3$ (C-O) and sp$^2$ (C=O), the T$_1$ relaxation rates are measured and reported for both of these regions. The $^{13}$C MAS NMR spectra of PEO polymers each exhibit only one peak in the sp$^3$ C-O region.

The solid-state $^{13}$C spin-lattice (T$_1$) relaxation rates of the standard PEO polymers (molecular weights 100,000 and 600,000) indicate that the higher molecular-weight polymer has a more efficient T$_1$ relaxation rate (at 0.5 s) than the lower molecular-weight polymer (3 s). Spin-lattice relaxation rates are typically most efficient when vibrational and rotational energies of the lattice (i.e. surrounding molecules) are close to the Larmor frequency ($\omega_L$) of the observed nucleus. Higher efficiency of T$_1$ relaxation rate indicates that surrounding vibrational and rotational energies of molecules are similar to the energy supplied by the RF pulse during the NMR experiment. The energy from the RF pulse is dissipated quickly when nuclei transition from the excited spin state to the lower energy ground state, releasing energy equal to the energy of the RF pulse to the surrounding lattice. These results therefore indicate that the higher
molecular-weight PEO polymer has thermal energy that is close to that of the Larmor frequency of the $^{13}$C nucleus (75.5 MHz in a 7.1 T magnet), whereas the lower molecular-weight polymer has a higher average of thermal energy that is not as close to the frequency of the Larmor frequency, yielding less efficient $T_1$ relaxation. According to Bloembergen-Purcell-Pound (BPP) theory, which relates $T_1$ relaxation times to molecular correlation time, the PEO polymers are in the first region of the $T_1$ relaxation curve, where $T_1$ rate is indirectly proportional to correlation time.$^4$

The $T_1$ relaxation rate of the C-O region in the lithiated anodes is more efficient than that of the large molecular weight PEO polymer (600,000 MW). Since the $T_1$ relaxation rate of the larger molecular-weight PEO polymer tested is more efficient than the smaller PEO polymer, this indicates that with PEO polymers of the approximate size 100,000-600,000 Da in the anode environment (i.e. mixed with graphite), larger molecular-weight polymers yield more efficient $T_1$ relaxation rates. The measured $T_1$ relaxation rate of the compounds formed in the SEI layer (in the lithiated anodes) therefore indicates that the lithiated anodes likely contain a larger molecular-weight polymer than the 600,000 Da PEO polymer. It is known that paramagnetic sites in samples can cause more rapid $T_1$ relaxation that would be observed without their presence.$^{22}$ Graphite has been demonstrated in previous studies to yield $T_1$ relaxation times (ca. 110 s) that are much less efficient than those of graphene or graphene oxide (1.9 and 39.6 s, respectively) since it is aromatic and contains paramagnetic sites. This indicates that the influence of paramagnetic sites on the $T_1$ relaxation is quite reduced for graphite compared with graphene. Samples containing graphite will therefore experience more efficient $T_1$ relaxation rates due to the effect of paramagnetic centers, but will not experience as much of an effect as samples containing graphene. We therefore measured $T_1$ relaxation rates of the PEO polymers
mixed with the graphite used in the Li-ion battery anodes to determine whether or not the graphite present in the lithiated anode sample contains paramagnetic sites that induce faster $T_1$ relaxation rates in the SEI compounds than would be observed without graphite present.

The measured $T_1$ relaxation rates of PEO polymers mixed with graphite are indeed shorter than the $T_1$ relaxation rates measured for the PEO polymers alone. This indicates that the graphite present in the Li-ion anodes does in fact induce faster $T_1$ relaxation in nearby nuclei. The trend in $T_1$ relaxation rates measured for PEO polymers alone remains true for the polymers mixed with graphite, where the larger molecular-weight polymer yields a more efficient $T_1$ relaxation time than the smaller polymer. Additionally, the measured $T_1$ relaxation rate for compounds in the SEI layer of lithiated anodes (0.29 s) is more efficient than the $T_1$ rate of the 600,000 Da PEO polymer mixed with graphite. This indicates more conclusively that the SEI layer of lithiated anodes contains a larger molecular-weight polymer than the 600,000-Da PEO polymer since the $T_1$ rates are measured for samples that are all in the same graphitic environment.

The presence of large molecular weight polymers in the SEI layer of lithiated anodes is further evidence by the $^{13}$C spin-spin ($T_2$) relaxation rate measurements of lithiated anodes and the 100,000 molecular-weight PEO polymer. The $T_2$ relaxation rate measured for the 100,000 Da PEO polymer is significantly more efficient (i.e. shorter) than the measured $T_1$ relaxation rate for the C-O (ether sp$^3$) region of the polymer. The $T_2$ relaxation rate measured for the C-O region of lithiated anodes (ca. 0.4 ms) is also significantly lower than the $T_1$ relaxation rate for this region (0.29 s). $T_2$ relaxation rates that are significantly lower than $T_1$ relaxation rates for the same region are known to indicate large compounds. The $T_2$ relaxation rate measurement therefore indicates that the carbon nuclei in the C-O region that were tested in lithiated anodes
are connected to large compounds, which is further evidence that high molecular-weight polymers (larger than 600,000 Da) are formed in the SEI layer of the anodes upon lithiation.

\[
\begin{array}{|c|c|c|c|c|}
\hline
 & C-O (sp^3) & \text{Chemical shift (ppm)} \\
 & T_1 (s) & T_1 \text{ error (s)} & T_2 (ms) & \\
\hline
\text{Lithiated anodes} & 0.29 & 0.05 & 0.4 & 62.8 \\
\text{PEO} & 100,000 & 3 & 1 & 3.5 & 69.3 \\
 & 600,000 & 0.5 & 0.1 & -- & 69.6 \\
\text{PEO + graphite} & 100,000 & 0.8 & 0.3 & -- & 71.0 \\
 & 600,000 & 0.41 & 0.06 & -- & 71.1 \\
\hline
\end{array}
\]

Table 4.3: Measured solid-state $^{13}$C MAS NMR $T_1$ and $T_2$ values for standard PEO polymers (of molecular weight 100,000 and 600,000), with and without added graphite, and lithiated Li-ion anodes. $B_0 = 7.1$ T, $\nu_r = 10$ kHz, $d_1 = 50$ s, $lb = 20$, and $nt = x$ (100k MW) and $x$ (600k MW).

**MALDI-TOF mass spectrometry of Li-ion battery anodes**

Matrix assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectra (MS) of graphite, un-cycled anodes, lithiated anodes and de-lithiated anodes are depicted in Figure 4.7. In these spectrographs, peaks below 500 $m/z$ are associated with the matrix and to material associated with the solvent mixed with the matrix. The mass spectrum of graphite
only (Fig. 4.7a) contains a mass fragmentation pattern with one repeat unit of 24.1 \textit{m/z}, where each peak is a doublet (i.e. contains two peaks) at low mass ratios. The spacing between the doublet peaks has an average of 5.0 \textit{m/z}. The overall fragmentation pattern appears to increase sharply to a maximum intensity at ca. 900 \textit{m/z} and the intensity decreases over a broad range of \textit{m/z} toward higher mass numbers (i.e. it tails off). The 24 \textit{m/z} spacing is associated with C\textsubscript{2} clusters. Previous MALDI mass spectra of graphite also demonstrate carbon clusters, with parent peaks separated by 12 \textit{m/z} and the largest peaks separated by 48 \textit{m/z}, indicating desorption of C\textsuperscript{+} species during MALDI MS experiments.\textsuperscript{45}

The mass spectrum of the un-cycled anode, which is graphite mixed with electrolyte solution (graphite mixed with LiPF\textsubscript{6} in EC/DMC, Fig. 4.7b), consists of two fragmentation patterns. The first pattern consists of a large repeat unit with spacing ca. 174.0 \textit{m/z} and the second pattern contains a smaller repeat unit with a spacing average of 35.4 \textit{m/z}. Both of these patterns contain high intensities (i.e. many fragments of this mass) at low mass numbers, but decreases in intensity and are no longer present by ca. 2,400 \textit{m/z}. The first pattern of interest with a large repeat unit spacing (ca. 174.0 \textit{m/z}) is composed of isotropic, broad (ca. 120 \textit{m/z}) peaks that extend to approximately 2,000 \textit{m/z}. A pattern of this nature, with a large repeat unit spacing and broad peaks, is indicative of a polymer.\textsuperscript{46} This 174 \textit{m/z} spacing is similar to the spacing found upon cycling in a different electrolyte but same solvent (LiClO\textsubscript{4} in EC/DMC) on a textured gold electrode in a previous report.\textsuperscript{14} The large repeat unit spacing is therefore attributed to an oligomer of the original polymer formed in the graphite mixed with electrolyte. This result indicates that the electrolyte solution mixed with graphite readily forms this polymer without any prior cycling in a Li-ion battery.
Interestingly, the first few large repeat unit peaks of Figure 4.7b contain doublet peaks with a spacing of 35.4 m/z (the second pattern in Fig. 4.7b). This spacing is associated with the presence of a -C-OLi group (molecular weight 35 m/z). Previous reports indicate that ROLi species are formed in the SEI layer. The doublet spacing indicates the presence of [Oligomer + COLi + H]^+ and [Oligomer +H]^+, respectively.

The mass spectrum of lithiated anodes (Fig. 4.7c) contains two overlaid fragmentation patterns, where the first pattern with a large repeat unit has a slightly different spacing as the large repeat unit in Fig. 4.7b (graphite mixed with electrolyte) of ca. 167.5 m/z. The second fragmentation pattern in Fig. 4.7c has a smaller repeat unit with an average spacing of 24.9 m/z. We note that this small repeat unit spacing is similar to that found in graphite (24.1 m/z). However, the standard deviation for m/z values in the graphite sample is 0.4 m/z. The error for the spacing in Fig. 4.7c is 24.9 ± 0.1 m/z. Comparison of these two patterns demonstrates that the patterns differ in phase (i.e. are not aligned), indicating that these two patterns arise from different fragment species. Both of the overlaid patterns in Fig. 4.7c contain high intensities at low mass numbers, similarly to Fig. 4.7b, but decrease in intensity and are no longer present by ca. 1,800 m/z. Figure 4.7c additionally contains small peaks with an average spacing of 5.0 m/z, which are present up to mass ratios of approximately 800 m/z.

The large MALDI-TOF MS repeat unit in Figure 4.7c (ca. 167.5 m/z spacing) attributed to the oligomer unit of the same polymer found in the un-cycled anode (Fig. 4.7b) without the presence of a Li ion (due to the difference of ca. 7 m/z). This result indicates that the polymer formed upon addition of electrolyte salt (LiPF₆) to the solvent (EC/DMC) remains present in the
lithiated Li-ion anodes. The doublet peaks on the large oligomer in Figure 4.7b with spacing ca. 35.4 m/z also remains present at small mass ratios (< 1,000 m/z).

Fig. 4.7c shows the presence of an additional m/z spacing shown in the inset to Fig. 4.7. This new fragmentation pattern however, a major change in the MALDI-TOF mass spectra that occur between an un-cycled anode (i.e. graphite mixed with electrolyte) and the lithiated anode includes the addition of a new fragmentation pattern with small ca. 24.9 m/z spacing. Lithiation of the anode is an electrochemically-driven reduction event. Previous reports demonstrate that lithiation results in the formation of crystalline regions of small inorganic compounds such as LiF and lithium oxide (Li₂O).\textsuperscript{10,11,20} We propose that the small repeat unit pattern found in lithiated anode samples is crystalline regions of LiF, with the addition or subtraction of Li-F (26 m/z) units. This fragmentation pattern extends to high mass ratios (ca. 1,500 m/z), which makes sense for a large crystalline region of inorganic SEI compounds with differing amounts of small fragments over a ca. 1,000 m/z mass range.

The mass spectrum of de-lithiated anodes (Fig. 4.7d) appears to contain three overlaid fragmentation patterns. The first fragmentation pattern with the largest repeat unit has a spacing of ca. 165.6 m/z, which is extremely similar to the spacing of the large repeat unit in the spectrum of lithiated anodes (Fig. 4.7c). The second fragmentation pattern also has approximately the same average repeat unit spacing as the second pattern in Fig. 4.7c of 25.9 m/z. The third fragmentation pattern in Figure 4.7d (shown expanded in Fig. 4.7e, inset) is unique to the de-lithiated anodes with a repeat unit spacing average of 74.6 m/z, which extends to very high mass ratios (up to 4,000 m/z). The intensity of the first two fragmentation patterns in Figure 4.7d contain high intensities at low mass numbers that decrease exponentially and are no
longer present at ca. 1,500 m/z. The intensity of the third fragmentation (Fig. 4.7d) extends out to much higher mass ratios than the first two patterns, extending to 4,000 m/z (not shown).

Figure 4.7: Stacked MALDI-TOF mass spectra of (a) graphite only, (b) graphite mixed with electrolyte (LiPF₆ in EC/DMC), (c) lithiated anodes, (d) de-lithiated anodes, and (e) an expanded region of the lithiated anodes spectrum (600-1000 m/z) with representative bars indicating the fragmentation patterns averaged. The laser power is 62% for (a) and (b) and 55% for (c) and (d).
4.4 Discussion

The results presented in this paper address the nature of the SEI formed during lithiation of graphitic materials used in Li-ion batteries. Solid-state $^{13}$C MAS NMR spectra acquired in this work exhibit an interesting chemical shift trend for the C-O ($sp^3$) and C=O ($sp^2$ carbonyl) regions of species, where the chemical shifts of both regions shift downfield in the order of: graphite with EC/DMC, graphite with LiPF$_6$ and EC/DMC (an un-cycled anode), lithiated anodes, and de-lithiated anodes. Many previous reports demonstrate that addition of electrolyte salt (i.e. LiPF$_6$) to the Li-ion battery solvent (EC/DMC) results in a spontaneous reaction that produces SEI products. $^{47-50}$ The results presented in Figure 4.5 support the formation of some SEI species from addition of LiPF$_6$ to EC/DMC since addition of electrolyte salt results in the major peaks shifting significantly downfield relative to those measured on samples without electrolyte salt. Our solid-state $^{13}$C MAS NMR results additionally suggest that further chemical change of the SEI compounds occur upon lithiation and de-lithiation, since the two major peaks exhibited by lithiated and de-lithiated anodes (Fig. 4.5d and e) are shifted significantly downfield compared to those found in the un-cycled anode. This result supports previous reports that also indicate new SEI species are formed upon lithiation of Li-ion anodes. $^{47-50}$

The C-O and C=O peaks in lithiated and de-lithiated anodes (Fig. 4.5d and e) are attributed to products of solvent (EC/DMC) decomposition or polymerization formed from the electrolyte (LiPF$_6$ salt and EC/DMC) and Li$^+$ in the battery during cycling. These two major peaks both contain shoulders that are located up-field (i.e. at more negative chemical shifts). This result indicates that the same SEI compounds that were formed on graphite upon adding the electrolyte solution (LiPF$_6$ in EC/DMC) are also found in cycled Li-ion anodes.
Interestingly, both the solid-state $^{13}\text{C}$ and $^7\text{Li}$ MAS NMR data agree that fewer compounds are present in de-lithiated anodes compared to lithiated anodes. The meaning of this in the $^7\text{Li}$ NMR is that less lithium nuclei are present in de-lithiated anodes. However, the fact that there are also less $^{13}\text{C}$ species present in de-lithiated anodes indicates that there is a loss of both lithium and organic species upon de-lithiation. These lithium and organic species (and likely also lithium-organic species) comprise the SEI compounds, and this result may indicate that the SEI layer undergoes re-dissolution into the electrolyte. It is possible that some unaltered solvent (EC/DMC) is also incorporated into the SEI, which is then dissolved into the electrolyte system during de-lithiation of the anode.

Another highly interesting result from the NMR and MALDI-TOF mass spectrometry studies of graphite anodes is that both of these techniques indicate that a large polymeric species is formed in the SEI layer of real battery anodes. The measured $T_1$ and $T_2$ relaxation rates of compounds in lithiated anodes compared to those of polymers (in the same graphitic environment) indicate that a polymer is formed in lithiated anodes that is larger than 600,000 Da, which is the molecular weight of the highest molecular-weight PEO polymer tested. The MALDI-TOF mass spectra of un-cycled, lithiated, and de-lithiated anodes contain a large polymer oligomer repeat unit that is likely due to a polymer, with the addition or subtraction of a Li$^+$ ion.

The first two MALDI-TOF MS fragmentation patterns of de-lithiated anodes (Fig. 4.7d) have the same repeat unit spacing as the two patterns observed in lithiated anodes, with spacing of 165.6 and 25.9 $m/z$, respectively. These two fragmentation patterns are attributed to the same oligomer and inorganic crystalline regions as described for Figure 4.7c. The large oligomer spacing (ca. 166 $m/z$) is attributed to ring-opened ethylene carbonate polymeric species, which
we therefore also attribute to the large repeat spacing found in un-cycled, lithiated, and de-lithiated anodes in this work. The difference in the oligomer subunit size between the un-cycled anode and the lithiated and de-lithiated anodes of approximately 8 m/z is attributed to the loss of a lithium ion (Li⁺) and a proton (H⁺).

The new fragmentation pattern with a spacing of 74.6 m/z is unique to de-lithiated anodes. Based on previous reports concerning the nature of compounds in the SEI layer of Li-ion anodes, a proposed polymer that may be formed in the SEI upon cycling of Li-ion anodes with EC solvent is presented in Scheme 4.1, along with the Li ethylene dicarbonate compound ((CH₂OCO₂Li)₂) that has been proposed by several sources in the literature as well.¹⁶,¹⁷,¹⁵¹,¹⁵² We propose two possibilities of break-down products that could occur upon laser desorption ionization during the MALDI-TOF MS experiment (in positive ion mode) that could make up the 74.6 m/z repeat unit spacing found in de-lithiated anodes that originate from the polymer and Li ethylene dicarbonate compound, which are depicted in Scheme 4.1. The nature of the SEI polymer and de-composition products (found in de-lithiated Li-ion anodes) is therefore depicted in Scheme 4.1.
Scheme 4.1: Proposed break-down sites on the proposed Li-ion SEI EC-derived polymer and Li ethylene dicarbonate compound. The resulting oligomer sub-units may comprise the large repeat unit spacing (74.6 m/z) observed in positive-ion mode MALDI-TOF mass spectra of lithiated and de-lithiated anodes with respective masses shown below the structures.

The large oligomer repeat unit that is found in MALDI-TOF mass spectra of the graphite mixed with electrolyte (Fig. 4.7b), lithiated anodes (Fig. 4.7c), and de-lithiated anodes (Fig. 4.7d) is extremely similar. This result indicates that the same polymer is present in lithiated, de-lithiated, and un-cycled anodes plus or minus an additional lithium ion (Li$^+$), since there is a difference of ca. 6.5 m/z between Figure 4.7b and Figures 4.7c and d. This result additionally indicates that this polymer is initially formed from reactions of the electrolyte salt (LiPF$_6$) with
the electrolyte solvent (EC/DMC) and remains present in lithiated and de-lithiated anodes. We attribute this large oligomer repeat spacing (ca. 166 m/z) to the same oligomer that has been reported previously for a similar Li-ion electrolyte system (LiClO$_4$ in EC/DMC) and we note that this result supports the previous conclusion that the polymer formed by ring-opening of the carbonate solvent(s) by nucleophilic attack of the electrolyte salt at the open circuit potential (i.e. without prior cycling).\textsuperscript{14}

Another interesting aspect of the MALDI-TOF mass spectrometry results is that these spectra show both organic as well as inorganic components at once in the SEI layer of cycled anodes. Crystalline regions of LiF as well as organic polymers and lithium-organic decomposition products are all seen simultaneously in the MALDI-TOF mass spectra of lithiated and de-lithiated anodes. To our knowledge, no previous MS study of the SEI compounds in Li-ion batteries exhibits both inorganic and organic components at once.

Finally, the results from both NMR and MALDI-TOF mass spectrometry indicate that there are a larger number of different species formed upon de-lithiation of anodes compared to lithiated anodes. In particular the MS shows the presence of a greater number of fragmentation patterns in de-lithiated anodes compared to lithiated anodes while the NMR shows the broadening of both the solid-state $^7$Li and $^{13}$C NMR peaks of compounds in de-lithiated anodes compared to lithiated ones. We propose that the speciation of lithiated anodes consists of crystalline regions of LiF, possible contributions from other inorganic species such as Li$_2$O, Li$_2$O$_2$, and Li$_2$CO$_3$, in addition to large polymeric species formed from the addition of LiPF$_6$ to EC/DMC, as shown in Scheme 4.1. The speciation of the de-lithiated anodes consists of the same LiF and large polymeric species and similar possible contributions from other inorganic
species such as Li$_2$O, Li$_2$O$_2$, and Li$_2$CO$_3$ compared with lithiated anodes, in addition to oxidative decomposition products of the polymer and solvent such as those depicted in Scheme 4.1.

4.5 Conclusions

Solid-state $^7$Li and $^{13}$C MAS NMR spectra of Li-ion anodes indicate that the SEI compounds formed during lithiation and de-lithiation are associated with different chemical shifts, which further that the SEI compounds initially formed upon addition of the electrolyte salt (LiPF$_6$) to the solvent (EC/DMC) change upon lithiation and further upon de-lithiation of the anodes. Changes in the chemical shifts of C-O region of un-cycled anodes to more positive values in cycled anodes likely indicates that the terminal groups of species present change from C-O-C groups to C-O-H groups upon lithiation. Spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation measurements indicate that the SEI compounds likely contain long-chain polymeric species with a molecular weight larger than 600,000 Da. MALDI-TOF mass spectra give further evidence of polymer formation in the SEI layer of Li-ion anodes. The MALDI-TOF results indicate that a polymer species with a large subunit (oligomer, ca. 166 m/z) is formed upon addition of the electrolyte salt to the solvent, which remains present in lithiated and de-lithiated anodes. This polymer has been previously observed and this report confirms that the ring-opened ethylene carbonate polymer comprises a major constituent of the SEI layer on cycled Li-ion anodes. A major change that occurs in the lithiated anodes observed in the MALDI-TOF mass spectra includes the addition of inorganic crystalline regions of LiF, which also remain present in de-lithiated anodes. Further changes that occur upon de-lithiation of the anodes include the formation of a second, smaller fragmentation oligomer that is likely a polymeric Li ethylene dicarbonate species.
4.6 Acknowledgements

This work was supported as part of the Center for Electrical Energy Storage: Tailored Interfaces, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. We also acknowledge Kai Xiang (MIT) for his assistance taking TEM and SEM images.

4.7 References


(51) Aurbach, D.; Ein-Eli, Y.; Markovsky, B.; Zaban, A.; Luski, S.; Carmeli, Y.; Yamin, H. 


Appendix A

A.1 Experimental

The Swagelok cell assembly consists of stacked battery components (from anode to cathode side): lithium metal, glass fiber separator (Whatman, GF/F, 150mm diameter), carbon cathode, nickel mesh, stacked between a stainless steel ‘anode plunger’ and hollow aluminum ‘cathode plunger.’ This assembly is illustrated below (Figure A.1). The stacked battery components were held together with nylon Swagelok tube fittings (0.5” I.D.) with electrochemical connections made with alligator clips to the anode and cathode plungers (depicted in Figure A.2).

Figure A.1: Li-O₂ battery components stacked between anode and cathode plunger and held together with Swagelok tube fittings (the so-called Swagelok cell assembly).
Figure A.2: Swagelok cell assembly with electrochemical connections made from glass enclosure wires to anode and cathode plungers via black and red wires. The glass enclosure is disassembled (top of glass enclosure on left, bottom on right).

A.2 $^{13}C$ MAS NMR spectroscopy

In order to further evaluate the by-products that form from decomposition of cathode solvents, $^{13}C$ MAS NMR spectra of discharged Li-O$_2$ cathodes were collected, as depicted in the top portion of Figure A.3.
Figure A.3: Solid-state $^{13}$C MAS NMR spectra of discharged cathodes containing carbon with $\alpha$-MnO$_2$ and Pd catalysts in 1 M LiClO$_4$ in EC/DMC. $B_0 = 11.7$ T (500 MHz), $\nu_r$ (spinning speed) = 12 kHz, $\text{pw90}_x = 2.5$ $\mu$s, DP echo = 83 $\mu$s (echo was rotor synchronized), decoupling field = 61 kHz, d1 = 5 sec. (cathodes), 30 sec. (DMC) and 10 sec. (EC/DMC) and nt = 64-1024.

$^{13}$C MAS NMR spectra were collected for discharged Li-O$_2$ cathodes containing different catalysts ($\alpha$-MnO$_2$ and Pd) and carbon-only. We note that the relative intensity of the peaks vary depending on the type of catalyst present. Background peaks and peaks from PVDF binder (120.3 and 42.6 ppm) are present in all spectra of discharged cathodes. Spectra of the pure
solvents (DMC and 1:1 EC/DMC) were additionally collected (bottom of Figure A.3). The chemical shifts for solvent components were confirmed to be ethylene carbonate (EC) at about 65.3 ppm, dimethyl carbonate (DMC) at about 54.4 ppm, and the carbonyl group for both solvent compounds appears at about 156.4 ppm.

Comparison of the $^{13}$C MAS NMR spectra of discharged cathodes and pure solvents demonstrates that two product peaks are distinguishable from the background, solvents and PVDF binder in the spectra of discharged cathodes (top of Figure A.3), at 62.5 and 58.3 ppm. Additional comparison of the pure solvent and discharged cathode spectra indicates that products formed in the Li-O$_2$ cathodes contain carbonyl groups in the same chemical shift region as the carbonyl groups in the EC/DMC solvent since there is a considerable size increase in the carbonyl peak (at 156.4 ppm) in discharged cathode spectra compared to the pure solvent.

The $^{13}$C MAS NMR cathode discharge product peak at 62.5 ppm is associated with either Li ethylene dicarbonate (reported at 62.4 ppm) or Li ethylene glycol (reported at 62.96 ppm), based on reports in previous literature. Aurbach et al. originally proposed that Li ethylene dicarbonate ((CH$_2$OCO$_2$Li)$_2$) was a likely reduction product of EC on noble metals and lithium electrodes. The carbonyl group in Li ethylene carbonate was also reported to be at about 160 ppm. However, another study demonstrates that Li ethylene dicarbonate readily reacts with water to form an ethylene glycol compound, which has a $^{13}$C NMR chemical shift of 62.4 ppm. The peak at 58.3 ppm shown in Figure A.3 is a CH$_2$ carbon in another by-product caused by solvent decomposition.

Interestingly, peaks from EC (65.3 and 156.4 ppm) are present in all of the spectra of discharged cathodes while DMC peaks (54.4 and 156.4 ppm) are not present in any of the
discharged cathode spectra. The presence of EC but no DMC (from an initial 1:1 EC/DMC mixture) indicates that DMC has evaporated from the cathode sample.[10] We also note that the carbonyl peak from EC has shifted downfield relative to the pure EC/DMC spectrum. This shift is likely due to the absence of DMC as well as the formation of decomposition products.

A.3 Chemical shift and linewidth information for $^6$Li MAS NMR spectra of standards and discharged cathodes in the two different solvents.

Table A.1: Chemical shifts and linewidths from $^6$Li MAS NMR spectra of lithium oxide powder standards.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (ppm)</th>
<th>Linewidth (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O</td>
<td>2.87</td>
<td>--</td>
</tr>
<tr>
<td>LiOH</td>
<td>1.33, 0.22</td>
<td>--</td>
</tr>
<tr>
<td>Li$_2$O$_2$</td>
<td>0.33</td>
<td>1.45</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>0.11</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Table A.2: Chemical shifts and linewidths for $^6$Li MAS NMR spectra of discharged cathodes containing different catalysts in 1 M LiClO$_4$ in EC/DMC and 0.3 M LiClO$_4$ in TEGDME.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>EC/DMC solvent</th>
<th>TEGDME solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical Shift (ppm)</td>
<td>Linewidth (ppm)</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.03</td>
<td>1.40</td>
</tr>
<tr>
<td>Pd</td>
<td>0.10</td>
<td>1.02</td>
</tr>
<tr>
<td>$\alpha$-MnO$_2$</td>
<td>-0.04</td>
<td>1.21</td>
</tr>
<tr>
<td>CuO</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

A.4 Table of products present in cathodes containing the two different solvents

Table A.3: All products present in discharged cathodes containing solvent (a) EC/DMC and (b) TEGDME.

a. Carbonate (EC/DMC) electrolyte

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li formate</td>
<td>LiCO$_2$H</td>
</tr>
<tr>
<td>Li acetate</td>
<td>LiCO$_2$CH$_3$</td>
</tr>
<tr>
<td>Li ethyl dicarbonate</td>
<td>LiCO$_3$C$_2$H$_4$CO$_3$Li</td>
</tr>
<tr>
<td>(seen in NMR as ethylene glycol)</td>
<td>(LiOC$_2$H$_4$OLi)</td>
</tr>
<tr>
<td>Li propylene glycol</td>
<td>LiOCH$_2$OLiCH$_3$</td>
</tr>
<tr>
<td>Li ethyl 2-methoxy-, 1,1’-carbonate</td>
<td>LiOC$_2$H$_4$CO$_3$C$_2$H$_4$OCH$_3$</td>
</tr>
<tr>
<td>Li methyl 1-(lithium carbonate)</td>
<td>LiOCH$_2$CO$_3$Li</td>
</tr>
</tbody>
</table>
Table A.3: All products present in discharged cathodes containing solvent (a) EC/DMC and (b) TEGDME.

b. Ether (TEGDME) electrolyte

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li formate</td>
<td>LiCO₂H</td>
</tr>
<tr>
<td>Li acetate</td>
<td>LiCO₂CH₃</td>
</tr>
<tr>
<td>TEGDME</td>
<td>CH₃OC₂H₄OC₂H₄OC₂H₄OC₂H₄OCH₃</td>
</tr>
<tr>
<td>Polymer</td>
<td>(CH₃OCH₂CO₂C₂H₄CO₂C₂H₄CO₂C₂H₄CO₂C₂H₄CO₂⁻)ₙ</td>
</tr>
</tbody>
</table>
A.5 Comparisons of $^1$H NMR spectra with and without Pd in the two solvent systems

Figure A.4: $^1$H solution NMR spectra of products extracted from cathodes with and without Pd catalyst, in the two solvent systems. Specifically the cathodes were, (a) with Pd and (b) without Pd in EC/DMC, (c) with Pd and (d) without Pd in TEGDME. The spectra were collected on a spectrometer with $B_0 = 14.1$ T (600 MHz), $sw = 6134.5$ Hz, a 60-degree flip angle $pw = 4 \mu s$, at 4 sec., $d1 = 2$ sec. and $nt = 32$. The spectra were processed with zero-filling to 64k data points and a line-broadening of 0.5 Hz.
A.6 References


Appendix B

B.1 Experimental

Lithium-ion flow cells were assembled using a Swagelok-type cell design. The Swagelok cell components are shown in Figure B.1 (left) along with the stainless steel current collectors, containing a cavity for the graphite anode material. The assembled Swagelok cell is also depicted in Figure B.1 (right), with steel current collectors shown protruding from the top and bottom of the cell.

Figure B.1: Swagelok cell parts (left) and assembled Swagelok Li-ion flow cell (right).

B.2 Solid-state NMR

Figure B.2 shows solid-state $^7$Li MAS NMR of three standard lithium powders, including Li$_2$CO$_3$, Li$_2$O$_2$, and Li$_2$O, which have been shown in previous reports to be possible discharge products in Li-ion battery anodes. We note that these spectra were acquired at a higher magnetic field strength than the Li-ion anodes; however the chemical shift values are not dependent on
magnetic field strength and are the same between the two spectrometers. The only difference that occurs upon using this higher magnetic field strength and higher spinning speed is that the peaks become sharper (i.e. less broad). These powders exhibit unique chemical shifts, which indicates that it may be possible to distinguish these species in lithiated and de-lithiated Li-ion anodes. Since the cycled anode $^7$Li MAS NMR spectra consist of one, broad peak with a peak width that covers the range of all of the powders tested (Fig. B.2), the anode peaks likely consist of a heterogeneous mixture of lithium inorganic species (such as those tested, Li$_2$CO$_3$, Li$_2$O$_2$, and Li$_2$O) along with other solvent decomposition products, which together make up the SEI layer.

Figure B.2: Solid-state $^7$Li MAS NMR spectra of standard inorganic powders, (a) Li$_2$CO$_3$, (b) Li$_2$O$_2$, (c) LiOH, and (d) Li$_2$O. $B_0 = 17.6$ T (750 MHz), $\nu_r = 15$ kHz, $\text{pw90}_x = 8.0 \mu s$, $d1 = 60$ s, $lb = 20$, and $nt = 16$. 

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