NMR Studies of Electrochemical Energy Storage Materials

Jing Peng

The Graduate Center, City University of New York
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by

Jing Peng

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

________________________________________
Date                      Steve G. Greenbaum
Chair of Examining Committee

________________________________________
Date                      Brian R. Gibney
Executive Officer

Supervisory committee:

________________________________________
Charles Michael Drain

________________________________________
Lynn C Francesconi

________________________________________
Ruth E. Stark

THE CITY UNIVERSITY OF NEW YORK
ABSTRACT

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Jing Peng

Advisor: Steve Greenbaum

Electrochemical energy storage materials constitute essential elements in the development of sustainable energy technologies. They are crucial for improving the efficiency of energy storage devices to facilitate the use of renewable resources. The increasing human demands for energy and limitation of fossil fuel stimulates the continued development of energy storage materials. Better understanding of their working mechanisms and electrochemical properties from a view of chemistry is quite necessary for improving the energy storage technology. In this work, Nuclear Magnetic Resonance (NMR) has been used as a powerful tool to characterize the solvation behavior and diffusion ability of some commonly used electrolytes in the lithium batteries. A challenging nucleus $^{17}\text{O}$ has been successfully studied in glyme-based electrolytes and carbonate based electrolytes, which along with NMR diffusion measurements provides significant information about ion-ion and ion-solvent interaction. Besides these battery projects, another investigation of silicon-doped hydrogenate amorphous carbon materials has been accomplished by using NMR and Electron Paramagnetic Resonance (EPR) techniques. The structure revolution of this material induced by thermal treatment has been described in this work.
For my new born son, Weiyi Yu, for accompanying me in the last year of my Ph.D. study

You make me brave and confident.

You are the best gift for my graduation.
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Chapter 1. Introduction

The population of the world increases from 700 million at the beginning of the industrial revolution to 7.4 billion in today, and it is estimated to grow to 9 billion by 2050 [1]. The rapid increases in population and rising economic growth place strong demands on energy supply. Moreover, due to a series of concerns of present energy economy, including the finite supply of non-renewable fossil fuel, unstable oil market, climate change induced by carbon emissions, etc., there is very urgent demand for developing clean energy sources to satisfy human needs [2]. The developments of affordable, accessible and sustainable energy sources are essential for an energy revolution in the future. Nowadays, consider the utilization of some clean energy sources, such as biofuel, solar radiation, wind, waves. However, many of these systems are still in the research and development stage. One of the biggest challenges of bringing them into large scale application is that these sources are variable in time and diffuse in space [3]. Therefore, vast improvement in energy storage techniques is necessary for utilizing these sources. As is known, the most convenient form of energy storage is portable chemical energy, in particular batteries which store chemical energy and deliver it as electrical energy with a high conversion efficiency [3].

A battery is consists of one or more electrochemical cells. Each cell is composed of two half-cells, one half-cell includes a positive electrode—a cathode and electrolyte, the other half-cell includes the negative electrode—an anode and electrolyte. Electrolytes are media allow the ions to move between the electrodes, which are necessary for electronic current to flow out of the battery to perform work. Those two electrodes do not touch each other but they are electrically connected by the electrolyte. Some cells have the same electrolyte in two half-cells, while some
of them use different electrolytes for each cell, in which the separator allows ion to flow through but prevents the mixing of two electrolytes.

The two main categories of batteries are primary batteries and secondary batteries. The electrode materials of primary batteries are irreversibly changed during discharge. Secondary batteries are also called rechargeable batteries, which can be discharged and recharged multiple times.

1.1 Lithium-ion battery

Li-ion battery is a rechargeable battery occupying a very large portion of the portable battery market. With continuous development since the early 1990s, it has become very attractive in applications of portable entertainment, computing, telecommunication devices and more recently, electric vehicles/hybrid electric vehicles [4, 5]. Unlike traditional batteries which cannot provide adequate energy density and power density, Li-ion batteries, with advantages of high energy density [6, 7], design flexibility and lightweight design, and longer lifespan than comparable battery technologies [8, 9], have been occupying 23.5 billion U.S. dollars of worldwide sales portable batteries markets by 2015 [10]. Because improvements in capacity and lifetime are constantly being sought, Li-ion batteries receive most attention at both fundamental and applied levels.

The main advantages of Li-ion batteries are high energy density (up to 640 Wh/L), low self-discharge rate, long cycle life, high specific energy (240 Wh/Kg), and wide temperature range for operation [11]. The most important disadvantage is safety, which requires development of nonflammable electrolyte with either a larger window between its lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) or a constituent that can develop rapidly—a solid/electrolyte-interphase (SEI) layer to prevent plating of Lithium on a
carbon anode during a fast charge of the battery [3]. The performance criteria of the batteries, such as cell potential, capacity or energy density, are dependent on the materials that form the cathode and anode electrodes. The nature of the interfaces between the electrodes and electrolyte determines the cycle-life and lifetime of batteries, whereas the stability of the electrode materials and interfaces plays a crucial role in safety issues.

1.1.1 Cathode

In Li-ion batteries, the positive electrode materials are required to be air-stable Li-based intercalation compounds to facilitate the cell assembly. LiCoO$_2$ was the most widely used cathode in commercial Li-ion batteries [12], while Ni and Mn are increasingly used to substitute all or part of the Co since the LiCoO$_2$ could pollute the environment during the production process, overcharge thus causing potential safety hazard, and the cost of cobalt is high [13]. LiNiO$_2$ has similar crystal structure as LiCoO$_2$ and lower price, however, the synthesis of it is difficult and its structure, thermal and cycling stability is poor [14]. The LiMn$_2$O$_4$ has the advantage of low cost and ease of synthesis, but the capacity of the battery using it decays rapidly at higher temperatures [15]. LiFePO$_4$ with olivine structure has high theoretical capacity (170 mAh g$^{-1}$) and low cost, acceptable operating voltage (3.4V vs. Li+/Li), good cycling stability [16]. And its most important advantage is that it is non-toxic compared to other Co, Mn, and Ni composed cathode. To improve the electrical conductivity of LiFePO$_4$, Hu et al. [17] reported on carbon-coated LiFePO$_4$, surface modified with 2 wt% of the electrochemically exfoliated graphene layers, which is able to reach 208 mAh g$^{-1}$ in specific capacity. Some doped cathode materials, such as layered LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$, LiNi$_{0.5}$Mn$_{0.5}$O$_2$, spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and olivine LiMnP$_4$ and LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ have also been studied as cathode materials for Li-ion batteries [18]. There is still much ongoing research on cathode materials.
1.1.2 Anode

In the 1950s, scientists found the lithium metal was stable in some non-aqueous electrolytes, and then lithium metal started to attract the attention in the application of rechargeable battery area. However, it was realized that lithium rechargeable battery had some difficulties in the cycle life and safety. The investigation of lithium anode materials uncovered the presence of needlelike lithium crystal, also called lithium dendrite, forming during the charge-discharge cycles. The formation of lithium dendrite makes the lithium metal gradually become electronically isolated from the substrate; therefore, the energy density was reduced due to lithium loss. More seriously, the electrochemically inactive dendrite can penetrate the separator and cause internal short circuit. In fact, there was highly publicized incident of fire in 1989 in a lithium rechargeable battery, which ended the commercial prospects of lithium rechargeable battery with lithium metal anode. In 1991, Sony commercialized lithiated graphite as Li-ion battery anode materials thanks to its relatively high specific capacity, stable two-dimensional structure and low redox potential [19]. Graphitic carbon is still the anode material in many commercial grade Li-ion batteries, but there is a theoretical limit 372 mA hg$^{-1}$ in capacity of them. Alloy materials, such as Sn and Si, have also been studied as anode materials in Li-ion batteries because they may have much higher specific capacity (>500 mA hg$^{-1}$) [20]. Metals such as aluminum (993 mA hg$^{-1}$) for LiAl, tin (994 mA hg$^{-1}$) for Li$_2$Sn$_5$ and antimony (536 mA hg$^{-1}$) for Li$_3$Sb have much higher capacities than graphite [21]. By forming metal alloys, these materials are capable of store much larger amount of Lithium per gram than carbon can, but it also results in a large increase of volume in anode. Repeated charge/discharge cycles eventually cause the anode to physically crumble.
1.1.3 Electrolytes

The electrolyte, which commonly refers to a solution comprising the salts and solvents, constitutes the third key component of battery. The electrolyte solvents not only should provide high ionic conductivity of the electrolyte [3], but also should maintain a stable and safe operation environment during the charging-discharging process. For an ideal electrolyte, there are four requirements that should be satisfied as following:

(1) Having a wide range in potential between the oxidative and reductive decomposition;

(2) Because the ion in the battery needs to transfer between the cathode and anode and the self-discharge needs to be reduced to be minimum, the electrolyte should be a good ionic conductor and electronic insulator;

(3) Since electrolyte is a media between cathode and anode, the electrolyte should be inert to all materials that it is in contact with, like electrode, cell separators and cell packaging materials;

(4) The salt, solvent and/or additives of the electrolyte should be safe and environmentally friendly.

The electrolytes in Li-ion batteries usually are composed of a solution of one or more lithium salt in two or more solvent mixtures. In 1980s, ethers have attracted much attention because of their low viscosity and high ionic conductivity. The cycling efficiency of lithium in ether-based electrolytes has reached 97% in polymethoxy ethers [22] and dimethoxy propane [23], and 98% in diethyl ether [24]. Besides ether solvents, some mixtures of cyclic carbonates, such as ethylene carbonate (EC), linear dialkyl carbonates are used as solvent in commercial Li-ion battery. An ideal electrolyte salt should be able to completely dissolve and dissociate in the solvent media, and solvated ions should have high mobility. Lithium perchlorate (LiClO₄), Lithium hexafluorosenate (LiAsF₆), Lithium tetrafluoroborrate (LiBF₄), Lithium
hexafluorophosphate(LiPF₆) have been very popular electrolyte solutes. However, the chemical reactions between electrolytes solvents and solutes at temperature higher than 60°C still cause safety concerns. Recently, there are some new solvent, such as esters, sulfones, sulfoxides, nitriles, etc. developed to replace the carbonate-based components in commercial electrolytes to achieve certain improvements over the state-of-the-art. And also some phosphates, borates and imides are being investigated as new lithium salts [25, 26].

1.1.4 The mechanism of Li-ion battery

Figure 1.1 displays a schematic of a common In Li-ion battery, in which Li₁ₓCoO₂ (or Mn, Ni) is used as cathode and LixC₆ is used as anode. Li-ions move between two electrodes via the electrolyte during the charging and discharging and reduction and oxidation of transition metal Co(III) ⇌ Co(IV) in the cathode. During discharge, the active negative electrode material becomes oxidized (Li⁰ → Li⁺ + e⁻) during Li⁺ extraction and active positive electrode material upon Li⁺ insertion becomes reduced (Co(IV) + e⁻ → Co(III)). The opposite reactions take place during charging, as Figure 1.1 and 1.2.

**Figure 1.1** Basic operation mechanism and components of a Li-ion battery, where M = Mn, Co, Ni.
Figure 1.2 Electrode reactions in Li-ion cell, where x and y selected based on the molar capacities of the electrode materials of the lithium (x/y~3).

1.2 Sodium-ion battery

Sodium shares similar chemical properties with lithium including ionicity, electronegativity and electrochemical reactivity. Due to the limitation of lithium sources, and associates high cost the current Li-ion battery need to be replaced by a new generation of rechargeable battery in order to satisfy the global demand, especially for larger format batteries such as grid storage. Na-ion batteries have been gaining increasing attention due to its high abundance and low toxicity of sodium resources. Although, studies on sodium-ion batteries are still at germination stage, their comparable synthetic protocols and electrochemical performances indicate that the Na-ion batteries can be successfully developed based on previously applied approaches or methods in their lithium counterpart [20]. Unlike lithiated graphite that has been successfully used in Li-ion battery, the sodiation of graphite is a thermodynamically unfavorable process. Therefore alternative anode materials need to be developed. Unexpected behavior in electrochemical performance and reaction mechanism were observed because the thermodynamic and/or kinetic properties of sodium-ion batteries are influenced by the larger size and slightly different bonding characteristics of sodium ions [27, 28]. More work need to be done before the Na-ion batteries can be commercialized.
1.3 Introduction of this work

Nuclear Magnetic Resonance (NMR) is the main characterization method used in this work.
The next chapter will be the introduction of this technique. Then, four projects are described
respectively from chapter 3 to chapter 6. Chapter 3 is the study of the thermally induced
structural evolution of silicon-doped hydrogenated amorphous carbon materials. This work was
undertaken before my main research topic on batteries. Chapter 4 is on diffusion and $^{17}\text{O}$ NMR
studies of glyme-based electrolytes. In chapter 5, $^{17}\text{O}$, $^{23}\text{Na}$ and diffusion NMR experiments were
performed to study various carbonate binary solvent electrolytes with NaPF$_6$ salt. The last
chapter of this work is the study of solvation effects on BF$_4^-$ and PF$_6^-$ in carbonate electrolytes.

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Chapter 2. Basics of NMR

2.1 Principle of NMR

Nuclear Magnetic Resonance (NMR) is a sophisticated and powerful analytical technique that has been used to determine the structure and dynamics of materials. It was first reported by Bloch, Hansen, and Packard at Stanford and by Purcell, Torrey, and Pound at Harvard in 1946 [1]. Substances that can be studied with NMR must contain nuclei of non-zero spin. For example, the deuteron ($^2$H) is composed of one unpaired proton and one unpaired neutron, and therefore a nuclear spin of 1. Since the magnetic moment of a nucleus is proportional to its spin, all non-zero spin nuclei possess magnetic moments.

In a macroscopic sized laboratory sample, some fair fraction of Avogadro’s number of atoms containing non-zero spin nuclei must be present for NMR to be observed. In the absence of an external magnetic field the nuclear magnetic moments in the sample are randomly oriented. However once subjected to a non-zero external magnetic field these moments orient themselves either parallel or anti-parallel to the external field.

![Figure 2.1](image) Two schematic representations of nuclear spins [2].
Considering a single proton $^1\text{H}$, which has a nuclear spin of one-half, in the presence of a magnetic field, two spin states are possible: $m=1/2$ (spin-up, or $\alpha$ state) or $m=-1/2$ (spin-down, or $\beta$ state), as shown in Figure 2.2. The magnetic moment vectors of the protons align as a low energy states N-S-N-S and a higher energy states N-N-S-S.

![Figure 2.2 Magnetic moments for spin $\frac{1}{2}$.](image1)

Additionally, when a nuclear moment is placed in a magnetic field, it will precess around the direction of magnetic field as shown in Figure 2.3 below. The energy of a magnetic moment $\mu$ when in a magnetic field $B_0$ is given by:

$$E = -\mu B_0 \quad (2.1)$$

with $\mu$ related to spin angular momentum by:

$$\mu = \gamma I \quad (2.2)$$

and $\gamma$ is the gyromagnetic ratio.

![Figure 2.3 An example of nuclear spins precessing at the Larmor frequency around the z-axis.](image2)
Equation 2.1 and Eq. 2.2 show that the minimum energy occurs when $\mu$ and $B_0$ are parallel. Eq. 2.3 is obtained by combining eq. 2.1 and 2.2:

$$E = -\gamma I_z B_0 \quad (2.3)$$

Here $I_z$ is the spin angular momentum in the z-direction, which has the following quantization:

$$I_z = m\hbar \quad (2.4)$$

Where $m$, the magnetic quantum number, can only take the values $m= (-I, -I+1, \ldots, I-1, I)$ and $\hbar$ is the Planck’s constant $h$ divided by $2\pi$.

$$E = -m\gamma \hbar B_0 \quad (2.5)$$

So the energy difference between the $m$ and $m+1$ energy levels is:

$$\Delta E = \gamma \hbar B_0 \quad (2.6)$$

This energy gap is related to the applied magnetic field $B_0$ and can be represented by an energy level diagram. It’s shown that with stronger magnetic field a higher transition energy is required for a nuclear moment to “flip” between spin-up and spin-down states.

![Energy Level Diagram](image)

**Figure 2.4** Energy diagram of nucleus in magnetic field [2].

Nuclear spins precess about the magnetic field $B_0$ direction with Larmor frequency $\omega$, given by Eq. 2.7. The procession is clockwise for $\gamma>0$ or counterclockwise for $\gamma<0$.

$$\omega = -\gamma B_0 \quad (2.7)$$
In an NMR experiment, the signal is created by the emission of energy from the nuclear moment as it returns to equilibrium after an excitation pulse. The frequency of this energy lies within the radio frequency (rf) range, as dictated by the magnetic field strength according to equation (2.7). A nuclear spin in the low energy spin-up state flips to the higher energy spin-down state through the absorption of a rf photon. The rf energy as given by Eq. 2.8 is related to its associated frequency, ν, through Planck’s constant (\(h=6.626\times10^{-34} \text{ J s}\)).

\[ E = h\nu \quad (2.8) \]

Since the energy should be equal to the energy difference between the two spin states, the frequency can also be represented as:

\[ \nu = \frac{\gamma B_0}{2\pi} \quad (2.9) \]

So far, the behavior of a single \(I = \frac{1}{2}\) nucleus in a magnetic field was discussed. In that example the two possible orientations are up and down. However, in bulk macroscopic sized materials typically studied by NMR, the distribution of up-down spin states are subject to classic thermodynamics and follow Boltzmann statistics. The number of spins in the lower energy level, \(N^\alpha\), slightly outnumbers the upper level, \(N^\beta\) at at equilibrium.

\[ \frac{N^\alpha}{N^\beta} = e^{-\frac{E}{k_B T}} \quad (2.10) \]

Where \(E\) is the energy difference between two spin states; \(k_B\) is Boltzmann’s constant, 1.3805 \(\times10^{-23}\) J/K; and \(T\) is the temperature in Kelvin. As the temperature decreases, more spins populate lower energy states, and as the temperature increases, the ratio approaches unity (\(N^\alpha \approx N^\beta\)). Instead of referring to a single spin, the focus, considering a system of nuclear spins, is on the spin ensemble or bulk nuclear magnetization of the sample. NMR spectroscopy measures the nuclear magnetization perpendicular to the field, not magnetization along the field. Suppose that
the spin system is allowed to reach thermal equilibrium in a large magnetic field. Now more spins populate the lower energy levels and the relative population of the level is given generally by the Boltzmann distribution. The macroscopic net magnetization vector has an equilibrium value $M_0$ pointing along the z-axis aligning with the magnetic field $B_0$.

$$\frac{N_m}{N} \approx \frac{1}{2I + 1} \left( 1 + \frac{m\hbar\gamma B_0}{k_B T} \right)$$  \hspace{1cm} (2.11)

Where $N_m$ is the number of nuclei in the $m^{th}$ state, $N$ is the total number of spins, $k_B$ is the Boltzmann constant, and $I$ is spin angular momentum.

![Diagram of net magnetization vector $M_0$ pointing along the z-axis due to the applied magnetic field $B_0$ along the z-axis.](image)

**Figure 2.5** Diagram of net magnetization vector $M_0$ pointing along the z-axis due to the applied magnetic field $B_0$ along the z-axis.

As described before, on a macroscopic level, the large number of nuclear spins at equilibrium all precess around the magnetic field at nearly the same Larmor frequency $\omega$. The resultant sum over the ensemble of nuclear spins yields a bulk nuclear magnetization oriented along the direction of the $B_0$ field (z-axis). Due to the statistical randomness of local magnetic fields, there
is a cancellation of planar magnetization components and the coherent nuclear magnetization along the x and y directions are identically zero.

By applying an external radiofrequency (rf) pulse with an oscillating magnetic field $B_1$ perpendicular to the static field $B_0$, the polarized (equilibrated) bulk magnetization under these conditions, can be induced to “flip” with the effect of rotating $M_0$ away from its equilibrium direction. The angle of rotation depends on the strength of the magnetic field ($B_1$), the duration of pulse $\tau$ and gyromagnetic ratio $\gamma$ following Eq. 2.12:

$$\theta = \gamma \tau B_1$$

(2.12)

\[\text{Figure 2.6} \quad \text{The effect on the net magnetization by a } \pi/2 \text{ RF –} x \text{ pulse when } \gamma \text{ is positive.}\]

In Figure 2.6 a $\pi/2$ rf pulse is applied along the –$x$ direction for a time $\tau$. This pulse rotates the polarization of every spin in the sample by the same angle ($\pi/2$), so the entire nuclear magnetization of the sample is rotated by $\pi/2$. During the rf pulse, the spin polarization, which was along $z$-axis before the RF pulse, rotates about the $x$-axis away from the $z$-axis, until it aligns with the $y$-axis. The action of the $\pi/2$ rf pulse is to orient the nuclear magnetization at a direction
perpendicular to the static field. In NMR, the net magnetization perpendicular to the magnetic field is called transverse magnetization or simply a coherence. After the rf pulse, the coherence precesses about the new direction at the Larmor frequency.

In order to create the rf pulse and detect the coherence, typically the sample containing the spin system is fixed within a solenoid or coil. The coil has the proper inductance such that it is optimized for detection at the Larmor frequency. As we described above, at thermal equilibrium, the bulk magnetization vector is orientated along the static magnetic field and no NMR signal is produced at this point. By subjecting the system to a rf pulse produced by applying a high-power rf oscillating voltage to the coil, a coherence is generated that precesses in the xy-plane. The precessing coherence in turn induces an electric potential across the coil which can be detected by a phase sensitive receiver. This small oscillating voltage at the receiver input is called the NMR signal or free-induction decay (FID). After the NMR signal has been received it can be further amplified and filtered using conventional rf signal processing techniques.

In summary, the NMR technique is composed the following three steps:
1) Polarization of a specific nuclear spin system by applying a strong magnetic field;
2) Manipulation and conversion of populations into coherences using a rf pulses;
3) Detection of the FID signal using rf induction, amplification and signal processing.

2.2 Relaxation in NMR

2.2.1 Spin-lattice relaxation ($T_1$) and Spin-spin relaxation ($T_2$)

Spin-lattice relaxation, also called longitudinal relaxation, characterizes the processes that nuclear spins undergo as $M_z$ evolves towards thermodynamic equilibrium. The spin-lattice relaxation time constant ($T_1$) refers to the characteristic time for this process as the evolution profile tends to be exponential. Typically, NMR experiments are designed in such a way as to
utilize the magnetization equilibrium state. At thermal equilibrium, $M_z$ equals to $M_0$, while the $M_x$ and $M_y$ are zero. One method to study spin-lattice relaxation is to saturate the spin system, then monitor the recovery as the system evolves towards thermal equilibrium. The fully saturated spin system is characterized by $M_z = M_0 = 0$ (i.e. zero population difference between the spin states). The population difference will gradually return to its Boltzmann equilibrium, as $M_z$ increases until $M_z = M_0$ within a time characterized by $T_1$. The longitudinal magnetization $M_z$ as a function of the time $\tau$ for simple spin-lattice relaxation after saturation follows Eq. 2.13:

$$M_Z = M_0 \left(1 - e^{-\frac{\tau}{T_1}}\right) \quad (2.13)$$

The spin-lattice relaxation time $T_1$ depends largely on the nature of the interaction, the sample composition, the temperature and phase (solid, liquid or gas).

There is another somewhat separate process that describes the relaxation behavior of the transverse $M_x$ and $M_y$ components. This process is called spin-spin relaxation and it also has a characteristic time constant, the transverse relaxation time constant, $T_2$. Using the above example for the nuclear magnetization immediately after the $\pi/2$ rf pulse along the $-x$ axis, the $M_z$ component is zero and the transverse magnetization $M_y$ (coherence) is maximum. At this point, on a microscopic level, individual spins precess at or near the Larmor frequency, according to the local field distribution. However, on a macroscopic level, the resultant planar $M_x$ and $M_y$ components while precessing about the static magnetic field direction, begin to decay. This happens due to the fact that the distribution of precession frequencies causes dephasing of the coherence. After some time, the $M_{x,y}$ coherences will return to their thermal equilibrium values of zero. $T_2$ is the characteristic time for the decay of the coherences.

$$M_{xy} = M_{xy0} e^{-\frac{\tau}{T_2}} \quad (2.14)$$
Figure 2.7 The bulk magnetization behavior according to $T_1$ (left) and $T_2$ (right) measurements.

$T_2$ is always shorter or equal to $T_1$. In summary, the relaxation of $M_{xy}$ coherences is governed by $T_2$, whereas the relaxation of the longitudinal population $M_z$ is governed by $T_1$. The fundamental origins of spin-spin relaxation are the internal magnetic interactions that the nuclear spins experience, and the variation in external magnetic field strength $B_0$. In practice, $T_2$ is not actually measured in a standard experiment, due to the static magnetic field inhomogeneity. Instead, $T_2^*$ is actually the measured quantity. It is defined as the characteristic transverse relaxation time as influenced by intrinsic $T_2$ processes and inhomogeneous static magnetic field effects $T_2'$. The relationship between the $T_2$ and $T_2^*$ is the following:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'} \quad (2.15)$$

In modern superconducting magnet systems the external field inhomogeneity can be made very small such that $T_2 \approx T_2^*$.

2.2.2 Relaxation broadening

The NMR linewidth, often defined as the full-width at half-height (FWHH) of the resonance lineshape, is a primary factor when assessing the resolution and signal-to-noise ratio of spectra
In the simplest case of strictly homogeneous magnetic interactions, the NMR linewidth is governed by $T_2$ relaxation. Therefore, larger magnetic interactions lead to shorter $T_2$s and broader resonances. The width at half height is determined by following equation:

$$v_{1/2} = \frac{1}{\pi T_2}$$

(2.16)

Where $v_{1/2}$=width at half height.

In some cases, $T_1$ relaxation can influence NMR linewidths. This can be seen from the following uncertainty relation:

$$\Delta E \Delta t > \hbar$$

(2.17)

$$\frac{\hbar v_{1/2}}{2} T_1 > \frac{\hbar}{2\pi}$$

(2.18)

$$v_{1/2} > \frac{1}{\pi T_1}$$

(2.19)

$T_1$ lifetime broadening occurs for extremely short relaxation times often encountered when $T_1 \approx T_2$. This situation can arise for systems that are subject to large paramagnetic and/or quarpolar interactions.

### 2.3 NMR interactions

Understanding the interactions between nuclei and their surrounding physical environment is very crucial for obtaining structural and dynamical information for a given sample. The NMR interactions are treated as additive perturbations to the primary Zeeman magnetic interaction. The NMR Hamiltonian can be expressed as:

$$H = H_z + H_J + H_{CS} + H_{DD} + H_Q$$

(2.20)

Where $H_z$ is the Zeeman interaction, $H_J$ is the J coupling, $H_{CS}$ is the chemical shift coupling, $H_{DD}$ is the dipolar coupling, and $H_Q$ is the quadrupolar coupling. The Zeeman interaction is the largest interaction, and is on the order of $10^8$ Hz. The quadrupolar interaction is generally large, and in
some cases can rival or exceed the Zeeman energy, however for typical NMR analysis this interaction might be on the order of $10^6$ Hz or less. The remaining three interactions are relatively much smaller and typically are less than $10^3$ ppm for chemical shift and dipolar couplings, and about 0-100 Hz for J-coupling. In the liquid state, due to fast molecular reorientation, all perturbative interactions except J-coupling are averaged (effectively reduced) since there is fast molecular reorientation and narrower resonances result.

2.3.1 Zeeman interaction

Zeeman interaction is the interaction between spin $I$ and magnetic field $B_0$. In a magnetic field, the ground state of a nucleus will split into $2I+1$ non-degenerate energy levels. The energy difference between levels is proportional to the strength of the magnetic field. As mentioned above, the Zeeman interaction is large compared to the other terms in the Hamiltonian. The perturbative interactions are responsible for the spectral features that when analyzed provide the structural and dynamical information. As illustrated earlier, the Zeeman Hamiltonian is:

$$\hat{H}_{Zeeman} = -\gamma B_0 \hat{I}_z$$

(2.21)

Where $\hat{I}_z$ is the $z$-component of the angular momentum operator.

2.3.2 Chemical shift interaction

The chemical shift refers to the collection of phenomena specifically regarding the interactions of nuclear magnetic moments with the magnetic fields generated by surrounding electronic currents. In the literature, these “shift” interactions are associated with a large number of distinct situations that range from electronic currents generated by molecular orbitals to conduction bands in metals, and direct electron-nucleus contact interactions. Although there is a range of phenomena that cause “shift” interactions, they all give similar spectral features that more or less can be analyzed with the same formalism.
The chemical shift refers to the frequency difference of the resonance, relative to some reference (i.e. Larmor frequency). The local resonance field can be separated into two parts: 1) the external field $B_0$ and the local field produced by induced electronic currents, $B^{induced}$. The local currents are induced by the external field, and correspondingly their effect on the resonant frequency increases with the size of the external field $B_0$. The induced field ($B^{induced}$) can add to or subtract from the external magnetic field $B_0$.

$$B^{loc} = B_0 + B^{induced} \quad (2.22)$$

![Figure 2.8 The mechanism of the chemical shift [4]](image)

Even though the induced field is very small, it is large enough to change the spin precession frequency such that $\omega = \gamma B^{loc} = \gamma B_0 + \gamma B^{induced} = \omega_0 + \omega_{shift}$. In this case, the resonance is shifted from the Larmor frequency; however, in practice the shift is expressed relative to some convenient reference frequency, called a standard. In this way, NMR chemical shifts can be used empirically as markers for specific chemical environments [3].

The field-independent expression for the chemical shift is as follows:

$$\delta = \left( \frac{\omega^0 - \omega_{TMS}^0 \text{ (Hz)}}{\omega_{TMS}^0 \text{ (MHz)}} \right) \quad (2.23)$$

Note the numerator is in Hz, whereas the denominator is in MHz. Where $\omega^0$ is the resonance frequency of the nucleus under investigation, and $\omega_{TMS}^0$ is the resonance frequency of the
reference, for $^1$H, $^{13}$C and $^{29}$Si this is usually is tetramethylsilane (TMS). The main reason $\delta$ is used is that it is independent of $B_0$, that is, the NMR chemical shift is the same regardless of the spectrometer field strength. In NMR spectroscopy, according to Eqn. 2.23, the chemical shift of TMS is defined as 0 in units of parts per million (ppm).

The NMR shift interaction in the solid state is complicated by the fact that the resonance frequency is angularly dependent. The general treatment represents the shift interaction as a tensor quantity in the Hamiltonian. Since in a polycrystalline material, all orientations between the tensor principal axes and the external magnetic field are realized, there will be a distribution of NMR frequencies represented in the spectrum called a powder pattern. For the particular case of the chemical shift frequency distribution, the powder pattern is called the chemical shift anisotropy (CSA).

2.3.4 J-Coupling

The molecules and atoms that comprise isotropic liquids have random motions that completely average through-space magnetic dipolar couplings. Yet for liquid molecular compounds residual indirect couplings are observed. These are called $J$-couplings, or scalar couplings and arise from through-bond hyperfine electron-mediated magnetic interactions. Consider two nuclei A and B whose atoms are bonded via two paired electron spins. With $J$-coupling, nuclear spin polarizes the spin of an intervening electron, whereby the electron spin distribution becomes slightly shifted by the spin polarization. The energy levels of the neighboring nuclear spin B are in turn perturbed by the polarized electrons and are effectively lowered because of the perturbation. The magnitude of $J$-coupling is represented as a $J$-coupling constant in units of Hz, which provides information about the bonding distance and angles relating the coupling partners. This constant is independent of external field strength $B_0$, and due
to the mutuality of the interaction affects both coupled partners equally ($J_{AB} = J_{BA}$). The magnitude of $J$ decreases very rapidly as the number of intervening bonds increases, such that $J$-coupling is unobservable across more than three bonds.

### 2.3.5 Dipole-dipole Coupling

The magnetic dipole-dipole coupling is the pure through-space magnetic interaction between two magnetic moments. A magnetic spin generates a magnetic field in the surrounding space. Any nearby nuclear spin can interact with this magnetic field, thereby altering its precession in an NMR experiment. The classical mutual energy of interaction between two magnetic moments $\mu_j$ and $\mu_k$ is:

$$E = \frac{\mu_0}{4\pi} \left[ \frac{(\hat{\mu}_j \cdot \hat{\mu}_k)}{r_{jk}^3} - \frac{3(\hat{\mu}_j \cdot \vec{r}_{jk})(\hat{\mu}_k \cdot \vec{r}_{jk})}{r_{jk}^5} \right]$$

(2.24)

where $\mu_0$ is the permeability constant and the internuclear vector $r_{jk} = r_{jk} \mathbf{e}_{jk}$.

![Figure 2.9](image.png)

**Figure 2.9** The unit vector $e_{jk}$ used in the dipole-dipole coupling formula. The angle $\theta_{jk}$ between the vector joining the spins and the external magnetic field.
Using the spin operators $I_j$ and $I_k$, the magnetic dipolar Hamiltonian between two spins becomes:

$$\hat{H}_{jk} = b_{jk} \left[ (\hat{I}_j, \mathbf{e}_{jk})(\hat{I}_k, \mathbf{e}_{jk}) - \hat{I}_j, \hat{I}_k \right] \quad (2.25)$$

The magnitude of the interaction is the coupling constant $b_{jk}$ with units of rad/s.

$$b_{jk} = -\frac{\mu_0 \gamma_j \gamma_k \hbar}{4\pi r_{jk}^3} \quad (2.26)$$

Where $\gamma_j$ and $\gamma_k$ are gyromagnetic ratio of spin $j$ and $k$. Therefore, it can be seen that the dipole interaction provides a way for computing distances between nuclei.

In a macroscopic sized sample, there is a mutual dipolar interaction between all spins. Therefore the total magnetic dipole-dipole Hamiltonian is just the sum over pairs and can be expressed as follows:

$$\hat{H}_{DD} = \sum_k \sum_{j=1}^{k-1} \hat{H}_{jk} \quad (2.27)$$

In condensed matter systems, the effect of dipolar interactions on the NMR lineshape for most cases is homogeneous broadening of the line. The broadening is usually well approximated by a Lorentzian convolution function (i.e. liquids) or a Gaussian convolution function (i.e. solids). Often in the case of solids where the nuclear moments are more rigidly held in space, the broadening is severe enough to obscure valuable spectral information. In such situations it is common to observe powder patterns of large linewidths spanning many tens of kHz. Magic-angle spinning (MAS) is a powerful experimental method that can be employed to alleviate some of the broadening, and allows for a deeper analysis of NMR lineshapes. But to see how this works, it is instructive to regard the dipole Hamiltonian in terms of its angular dependence ($\theta_{jk}$,
see Figure 2.9). For the moment, just considering dipolar interactions between like spins 
\( (\gamma_j = \gamma_k) \) and the fact that the dipole energy is much less than the Zeeman energy, the dipolar Hamiltonian can be expressed in terms of the angle between the vector joining the center of spin 
pairs and the external magnetic field, \( \theta_{jk} \):

\[
\hat{H}_{DD} = \sum_k \sum_j b_{jk} \left( 3 \cos^2 \theta_{jk} - 1 \right) \left( 3 \hat{I}_{jz} \cdot \hat{I}_{kz} - \hat{I}_j \cdot \hat{I}_k \right)
\]  

(2.28)

Notice here the \( 3 \cos^2 \theta_{jk} - 1 \) dependence. It turns out that this factor can be reduced to 0 by 
orienting the internuclear spin vector \( r_{jk} \) to the “magic angle” = 54.74°.

\[
3 \cos^2 \theta_{jk} - 1 = 0
\]  

(2.29)

or

\[
\theta_{jk} = \cos^{-1} \left( \frac{1}{\sqrt{3}} \right) \approx 54.74°
\]  

(2.30)

However, the trick is to orient all \( r_{jk} \) vectors in the sample at this angle. This can be 
approached by rapidly spinning the sample (~ kHz), during the NMR measurement, about an 
axis that is oriented at 54.74° relative to the \( B_0 \) field direction. This technique will effectively 
average each \( r_{jk} \) vector orientation at the magic angle. The more rapid the spinning (at least at a 
rate greater than the broadening width), the more effective the reduction of the \( 3 \cos^2 \theta_{jk} - 1 \) factor 
is. It turns out that MAS also effectively reduces heteronuclear dipolar interactions, chemical 
shift anisotropy and 1st-order quadrupolar interactions, as all these interactions are angularly 
dependent and include \( 3 \cos^2 \theta - 1 \) factors in their Hamiltonians.

2.3.6 Electric Quadrupolar Interaction

Nuclei with spin higher than \( \frac{1}{2} \) have non-spherical proton charge distributions and thereby 
possess electric quadrupole moments. In solids where electric field gradients, generated by non-
spherical electron charge distributions, can be very large, the magnetic energy levels of quadrupolar nuclei can be significantly perturbed. As shown in Figure 2.10, the charge distribution of spin ½ nuclei is spherical, while the nuclei with \( I \) greater than ½, possessing non-spherical distributions, can interact with the surrounding electric field gradient (EFG). So it can be seen during an NMR experiment that this interaction will affect the nuclear precession.

![Figure 2.10](image)

**Figure 2.10** Nuclear charge distribution for spin ½ and quadrupolar nucleus. The quadrupole nucleus can interact electronically with the surrounding EFG, whereas the spin-1/2 nucleus cannot.

The nuclear electric quadrupole interaction is formally written from the potential energy, as the coupling of the nuclear quadrupole moment with the electric field gradient. The EFG is a tensor quantity represented as:

\[
V = \begin{pmatrix}
V_{xx} & V_{xy} & V_{xz} \\
V_{yx} & V_{yy} & V_{yz} \\
V_{zx} & V_{zy} & V_{zz}
\end{pmatrix}
\]  

(2.31)
and therefore the quadrupole interaction is orientationally dependent. The full nuclear quadrupole Hamiltonian for an arbitrary orientation of the EFG tensor is given by the following equation:

$$H_Q(\theta) = \frac{eQ}{2I(2I-1)\hbar} \hat{I}.V(\theta)\hat{I} \quad (2.32)$$

where $I$ is the nuclear spin operator and $Q$ is the electric quadrupole moment of the nucleus. The Hamiltonian can be expressed within the principal axis system of the EFG:

$$H_Q = \frac{e^2qQ}{4I(2I-1)} \left[ 3l_z^2 - l(l+1) + \frac{1}{2} \eta(l_x^2 + l_y^2) \right] \quad (2.32)$$

where the asymmetry parameter is defined as $(V_{xx} - V_{yy})/V_{zz}$, $eq = V_{zz}$ and the raising and lowering angular momentum operators are $I_+$ and $I_-$, respectively.

The quadrupolar interaction can be large, and in such cases it is necessary to take higher terms in the perturbation expansion for the energy for an accurate computation for the energy:

$$H_Q = H_Q^{(1)} + H_Q^{(2)} + \cdots \quad (2.33)$$

where $H_Q^{(1)}$ and $H_Q^{(2)}$ are the first- and second-order quadrupolar Hamiltonian terms respectively.

The principal components of the electric field gradient tensor are $V_{XX}$, $V_{YY}$ and $V_{ZZ}$, and by Laplace’s equation their sum must be zero.

$$V_{XX} + V_{YY} + V_{ZZ} = 0 \quad (2.34)$$
The quadrupolar interaction in the extreme motional limit (i.e. in liquids) can also be evaluated in terms of the relaxation. A quadrupolar relaxation rate $R_Q$ can be defined as follows:

$$R_Q = \frac{1}{T_{1(Q)}} = \frac{3}{10} \pi^2 \frac{2I + 3}{I^2(I - 1)} \left( 1 + \frac{\eta^2}{3} \right) \left( \frac{e^2 Q q}{\hbar} \right)^2 \tau_c \quad (2.35)$$

where $\tau_c$ is the molecular correlation time (molecular or segmental rotation), and $T_{1(Q)}$ is the associated spin-lattice relaxation time. The relaxation of quadrupolar nuclei in liquids can be relatively fast, compared dipolar relaxation, and depends on the motionally averaged EFG. Although atomic and molecular motions in liquids can be isotropic, average EFGs about quadrupolar nuclei do not necessarily average to null. For $I > \frac{1}{2}$ nuclei, the quadrupolar coupling can be the primary source of linewidth broadening in the NMR spectrum [6].

2.4 Diffusion NMR

Diffusion can be considered as the most fundamental form of transport at the molecular level, which is the random thermal translational of molecules or ions. Or it can be thought as Brownian motion resulting from particles’ collision with the fast moving particles in the fluid where there is no driving force. Translational diffusion is necessary for a chemical reaction since the reacting species have to collide before the reaction can occur. The study of atomic, ionic and molecular
diffusion is of enormous importance for a great number of applications and theoretical considerations of modern sustainable energy technologies. The phenomenon of diffusion is intimately connected to the stochastic motion of molecules or ions at thermal equilibrium and is characterized by a single quantity, the self-diffusion coefficient.

Viscosity causes friction during the motion in a liquid. The mathematics of the diffusion process is related to Fick’s first and second law of diffusion, which postulates that the flux of particles across a given plane is proportional to the concentration gradient across the plane.

\[ J = -D \frac{\partial C(x, t)}{\partial x} \] (2.36)

where \( J \) is the flux, \( D \) is the diffusion coefficient for particles that are diffusion in the solvent, \( \frac{\partial C(x, t)}{\partial x} \) is the concentration gradient.

Fick’s second Law states that the change in the concentration over time is equal to the change in local diffusion flux.

\[ \frac{\partial C(x, t)}{\partial x} = -\frac{\partial J}{\partial x} \] (2.37)

In an isotropic system without thermal or concentration gradient, the average molecule displacement in all three directions is zero but the mean square displacement is non-zero and is given by

\[ D = \frac{<r^2>}{6t} \] (2.37)

In a two-component system, the diffusion force and the frictional force are equal since there are no external forces applied in it. By giving the Stokes-Einstein equation 2.38:

\[ D_M = \frac{k_B T}{f} \left( 1 + \frac{\partial (\ln(\gamma))}{\partial (\ln(c))} \right) (1 - \varnothing) \] (2.38)
Where $k_B$ is the Boltzmann’s constant (1.380622 J K$^{-1}$), $T$ is the absolute temperature (K), $f$ is the friction coefficient (kg s$^{-1}$), $\gamma$ is the activity coefficient, $c$ is concentration (M) and $\Phi$ is the volume fraction.

At infinite dilution, the second term in Eq. 2.38 in the first pair of parentheses approaches zero and Eq.2.38 can be simplified as Eq. 2.39:

$$D = \frac{k_B T}{f} \quad (2.39)$$

For the simple case of a spherical particle with an effective hydrodynamic radius $r_s$ (m) in a solvent of viscosity $\eta$ (Pa s), the $f$ is given by Eq. 2.40:

$$f = f_{sphere} = 6\pi \eta r_s \quad (2.40)$$

Where

$$b = \frac{6(1 + 2\eta/\beta r)}{(1 + 3\eta/\beta r)} \quad (2.41)$$

The parameter $\beta$ characterizes the friction between two components. So $b$ has lower limit of 4 while $\beta$ is very small and upper limit of 6 while $\beta$ is high where there are strong interactions between two components. Following the Stokes’ law, the relationship between $D$ and the molecular size of a spherical particle is given by Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi \eta r_s} \quad (2.42)$$

Based on Eq.2.42, it’s clear the diffusion of species are determined by the overall dimensions of the diffusing species and the viscosity of medium. The unit of diffusion is m$^2$s$^{-1}$. In a multicomponent system, each component has its distinct self-diffusion coefficient, $D_i$ (m$^2$s$^{-1}$). The range of self-diffusion coefficients varies over many orders of magnitude: e.g., from $\sim 10^{-20}$ m$^2$s$^{-1}$ for solids to $\sim 1$ m$^2$s$^{-1}$ for dilute gases [5], and typical self-diffusion coefficient in liquids at room temperature ranges from $10^{-9}$ m$^2$s$^{-1}$ as small molecules in low viscous solution to $10^{-12}$ m$^2$s$^{-1}$. 


as high polymers in solution. As shown in Eq. 2.42, the diffusion coefficient of species increases with temperature, but decreases with viscosity and radius of diffusing particle. In electrolytes system which we mainly studied, diffusion behavior of ions was characterized by performing measurement at various temperatures. Since the viscosity also strongly affects the diffusion coefficient, big differences of ion diffusion ability can be observed in electrolytes with different solvent compositions. The diffusion data can be used to evaluate the size of particles based on Eq. 2.42. However, this method (size determination) cannot be used in the case of particles with high charge density, such as Li⁺ in electrolytes, due to the varying degree of ionic solvation on Li⁺. However it is a very effective method to characterize the interaction between ions and molecules in the electrolytes.

Many investigations of diffusion phenomena have been reported, although the methods for measuring self-diffusion coefficients are limited. NMR diffusion measurements allow for non-destructive quantitative measurements of self-diffusion coefficients of cations, anions and solvent molecules in electrolyte systems. At present, ex-situ measurement is relatively straightforward, and provides an unrivaled approach towards understanding the degree of ionic association and its variation with salt concentration and temperature for viable rechargeable battery and PEM fuel cell technologies. The ability to characterize the diffusivity, mobility and conductivity of charged species are of primary importance for the development of battery and fuel cell technologies. The solvation behavior of ions can be evaluated through diffusion measurements since the diffusion coefficient are quite sensitive to the binding and association phenomenon. Diffusion is also very meaningful for characterizing the ionic conductivity of an electrolyte containing anions and cations, and it can be determined by the Nernst-Einstein equation:
\[
\sigma = \frac{[C]F^2}{RT}(D_{cation} + D_{anion}) \quad (2.43)
\]

Where \( F \) is the Faraday constant (96485 Coulomb); \([C]\) is the concentration of electrolyte (mol cm\(^{-3}\)).

Most of the time, conductivity data calculated from NMR diffusion coefficients is larger than the ionic conductivity measured by electrochemical impedance spectroscopy. That’s because NMR usually overestimates the electrolyte conductivity for the reason that it not only observes the diffusion of charged ions, but also neutral ion pairs. So the comparison of calculated conductivity and measured one often provides information on ionic association degree in electrolytes.

The diffusion NMR measurement is achieved by combining radio-frequency pulses as used in routine NMR spectroscopy with magnetic field gradients. The magnetic field gradient can specifically be used to encode motional information along a dimension of length. In the case of a spatially homogeneous magnetic field, all spins of the same type will exhibit the same Larmor frequency \( \omega = \gamma B_0 \). However, when a magnetic field gradient is applied along the \( z \)-axis, the magnetic field at any position along the \( z \)-axis will have the specific value:

\[
B_z = B_0 + zg \quad (2.44)
\]

where \( g \) is the gradient strength (usually in G/cm), \( z \) is the position along the \( z \)-axis in the sample [6].

Therefore, the effective frequency of a nucleus precessing in this field is:

\[
\omega_{eff} = \omega_0 + z\gamma g \quad (2.45)
\]

Figure 2.15 shows the effective Larmor frequency of different spins in a sample:
Figure 2.1 The spin frequency in an inhomogeneous field which varies linearly in one direction.

The most basic experiment to measure diffusion is called spin echo sequence with pulse field gradient (PFG SE), as shown in Figure 2.1. Between the π/2 RF pulse and π RF pulse, a field gradient of length δ and strength g is applied, and the second gradient with same length and strength is applied after the π RF pulse. The time Δ between two gradient pulses is called the diffusion delay.

Figure 2.2 A schematic picture of spin echo sequence with pulse field gradient.
In a homogenous magnetic field, same type of spins precess at the same frequency $\omega$. After the first $z$-gradient applied following a $\pi/2$ pulse, the transverse magnetizations dephase with respect to the $z$-position in the sample according to the phase:

$$\varphi(z_1) = \varphi(0) + z_1 \gamma g \delta \quad (2.46)$$

where $z_1$ is the position of the spin. The gradient causes the spin in different positions in the same sample to precess at different frequency, thereby enhance the dephasing process. The position of spin is encoded by the first gradient. Variation of the coherence (signal) with time is therefore:

$$M_X(t) = S \frac{\sin\left(\frac{h_{\text{max}} \gamma g t}{2}\right)}{h_{\text{max}} \gamma g t} \quad (2.47)$$

where $h_{\text{max}}$ is the sample height. Herein, it is a way to evaluate nuclear diffusion (motion to another $z$) in terms of the encoded phase according to $z$-position. Between two gradient pulses, the nucleus is allowed to diffuse in a period of time $\Delta$. After the second pulse,

$$\varphi(z_2) = \varphi(0) + z_1 \gamma g \delta - z_2 \gamma g \delta = \varphi(0) + (z_1 - z_2) \gamma g \delta \quad (2.48)$$

If a second gradient pulse is applied after a refocusing RF pulse, which simply causes a change in the sign of the gradient, only in-phase transverse magnetizations will be refocused, i.e. only those associated with nuclear spins that have not moved significantly up or down along $z$ during the course of time. So the second gradient is used to decode the position. Due to diffusion, the magnetic contributions of those nuclei that have moved along $z$ axis cannot be refocused, thereby reducing the intensity of the resulting signal [7]. The more intense and the longer the magnetic field gradient pulse, the more spatially selective it is and the weaker the FID signal that can be collected. A profile of increased dephasing with gradient strength can be obtained by sequentially increasing the gradient strength, while keeping the time constant. By plotting the
intensity of NMR signal verse gradient strength, the self-diffusion coefficient $D$ can be obtained by using the following Stejskal-Tanner equation:

$$I = I_0 \cdot e^{-D(\gamma g \delta)^2 \left( \frac{\Delta - \delta}{3} \right)}$$  \hspace{1cm} (2.49)

where $I$ is the relative signal strength, $I_0$ is the signal in absence of the field gradient, $\gamma$ is gyromagnetic ratio of the studied nucleus, $g$ is the gradient strength, $\delta$ is the gradient pulse duration and $\Delta$ is the diffusion delay.

For some samples containing nuclei with extremely short $T_2$, most of the signal has disappeared by the time of echo. A stimulated pulse sequence (STE) was designed to take the advantage of comparably long $T_1$ in these systems. After the second $\pi/2$ in this sequence, the magnetization is along the $-z$ axis, and the $T_2$ relaxation doesn’t affect the signal decay.

![Figure 2.3](image)

**Figure 2.3** A schematic picture of stimulated echo sequence with pulse field gradient.

There are some other factors that need to be considered for choosing the parameters in diffusion NMR measurements. Firstly, it is of great importance to consider the relaxation time $T_1$ and $T_2$ of the nuclei under study. The diffusion delay time is determined by these two values in case the signal has vanished due to the short relaxation time if a too long $\Delta$ is used. PFG STE sequence should be used when $T_1 \gg T_2$. During the delay $T$, the spins only experience $T_1$
relaxation. In order to optimize PFG STE pulse sequence, the time when the spin experiences $T_2$ relaxation should be as short as possible. In many cases, the sequence allows use of rather long diffusion time. Secondly, the application of strong magnetic field gradients usually cause disturbance in the NMR spectrometer and cause eddy currents, therefore a certain limit on time intervals between RF pulses is needed. These two factors limit the accessible diffusion coefficients to be measured.

Even though the diffusion pulse sequence can be optimized by varying parameters such as gradient pulse duration $\delta$ and diffusion time $\Delta$, this technique still has some limitations. For nuclei with very short relaxation time, $T_1$ and $T_2$, the time $T$ between the second and third RF pulse has to be very short, which is problematic since the diffusion delay $\Delta$ has to be very short. In this circumstance, a strong gradient is needed in order to observe the diffusion in a short period. However, due to the properties of some nuclei and the instrumental limitation of gradient strength, the diffusion measurements for some materials are still not practical. For example, $^{17}$O diffusion measurement has been never reported. This is mostly because of low natural abundance (0.038%) of $^{17}$O, but also due to its extremely short relaxation time. The former induces weak signal/noise ratio, and the latter cause signal loss during the diffusion delay. For some quadrupolar nuclear, such as $^{23}$Na, which also have very short relaxation time, we are able to manage the diffusion measurement by using a strong gradient.

2.5 NMR pulse sequences

2.5.1 Spin echo pulse sequence

Spin echo pulse sequence is the one of the most commonly used sequences. Since relaxation and local magnetic field inhomogeneity cause spins throughout the sample to precess at different rates, the NMR signal decays after an initial excitation pulse. In many applications the spin echo
pulse sequence allows for recuperation of much of the homogeneous signal and removal of inhomogeneous dephasing by applying an 180° inversion pulse. Depending on the time delay (τ), the 180° inversion pulse inverts the cohenences such that the signal rephrases forming an echo signal.

![Spin echo pulse sequence](image)

**Figure 2.4** Schematic of spin echo pulse sequence

### 2.5.2 T₁ measurement pulse sequence

The inversion recovery pulse sequence was used to measure $T_1$. The sequence begins with a 180° pulse followed by a recovery period and 90° pulse. The initial 180° pulse inverts the nuclear magnetization along $-I_Z$ direction. The spins relax during the delay time $τ$ due to spin-lattice relaxation. After the recovery period, the 90° pulse creates the transverse magnetization coherences which are allowed to freely evolve (free induction decay or FID). The FID is acquired at this point, and its magnitude depends on the spin-lattice relaxation allowed to transpire during the recovery period. In an inversion recovery measurement, the $τ$ is always systematically varied, the profile of NMR signal magnitudes as a function of $τ$ is proportional to the recovered z-magnetization just before the 90° Pulse, as Eq. 2.13.
A saturation recovery pulse sequence also can be used to measure $T_1$. This sequence is particularly useful if $T_1$ is very long. It consists of a train of 90° pulses at relatively short repetition times followed by a recovery period ($\tau$) and a 90° pulse. A recovery profile can be obtained by systematically varying $\tau$.

Figure 2.5 Schematic of inversion recovery pulse sequence

Figure 2.6 Schematic of saturation recovery pulse sequence.

2.5.3 Diffusion NMR measurements

In this work, the diffusion NMR measurements were performed on most of electrolytes under study. Convection within the solution causes serious problem affecting the accuracy of diffusion measurement. The diffusion coefficient can be overestimated due to the convection currents induced by small temperature gradients along the z-axis which can’t be avoided even though reasonable time for thermal equilibration was allowed before the measurements. The smaller the viscosity of the solvent or the sample, the larger the velocity of the convective flow will be. Therefore, it’s necessary to optimize the design of probe to avoid heating from the bottom. Then,
a special sequence, Double-stimulated-echo (DSTE) sequence, was used to measure the self-diffusion coefficients in low viscosity liquids that are susceptible to convection effects. In this sequence, the convection effect from the first stimulated echo period is cancelled out during the second stimulated echo period, and the signal can be refocused if two gradients with length of $\delta$ for each are applied between two stimulated echo pulse sequences. The eddy current is reduced by using an additional longitudinal eddy-current delay $T_e$.

$$\delta$$ is the gradient strength; $\tau$ is pulse recovery delay; $T_e$ is the longitudinal eddy-current delay and the diffusion delay equals $T + 3\delta + 3\tau$.

**Bibliography**

Chapter 3. Solid State Magnetic Resonance Investigation of the Thermally Induced Structural Evolution of Silicon Oxide-Doped Hydrogenated Amorphous Carbon


3.1 Introduction

Amorphous materials are ubiquitous in nature and in synthetic systems [1]. In light of many unique mechanical, optical, magnetic, and electronic properties, they are attractive materials for current and emergent technologies, including photovoltaics, thin-film transistors, p-n diodes, light valves, spacecraft components, springs, biomedical implants, and energy-absorbing structures [1-4]. The structural characterization of amorphous solids constitutes a challenging materials science problem, since the lack of crystallinity in these materials hinders the use of diffraction methods, and the structures cannot be described by simple symmetry rules, nor do they form stable, well-defined low-energy configurations. Furthermore, while the chemical composition of these solids can be readily determined using standard analytical methods, such as energy dispersive spectroscopy or secondary ion mass spectroscopy, the investigation of the bonding configuration of the elements constituting the amorphous network is rather difficult due to the broad range of bond lengths and angles present. This inhibits the use of simple structural models, which are usually employed for investigating crystalline materials, for obtaining insights into the structure of amorphous solids.
Among the several amorphous materials that have been synthesized in the last decades, carbon-based materials have been used in a particularly wide range of technologically important applications thanks to their impressive properties, notably their high strength and strain to failure, ability to withstand harsh physical and chemical conditions, their ability to form smooth, continuous, ultra-thin, conformal coatings, as well as their outstanding tribological performance (i.e., low friction, wear, and adhesion) [5, 6]. The most well-known class of carbon-based materials for these applications is composed almost purely of amorphous carbon (a-C). Thin-film a-C materials containing some hydrogen are usually referred to as amorphous hydrogenated carbon (a-C:H), and are typically grown by chemical or physical vapor deposition. The highly non-equilibrium conditions in these deposition methods result in the presence of carbon atoms in different hybridization states (mainly \( sp^3 \) and \( sp^2 \), with a small fraction of \( sp \) [5, 7-10]. Depending on the growth method and precursors, hydrogen can be included in the disordered network with amounts ranging from less than 5 at.% to about 50 at.%. Hydrogen modification significantly affects the resulting physico-chemical properties, including optical gap, electrical resistivity, internal stresses, elastic moduli, strength, and tribological properties [9].

To achieve multifunctionality, as well as to boost existing properties or introduce new ones, the synthesis procedure of amorphous carbon-based materials can be tailored by introducing dopants or alloying elements [11]. Silicon oxide-doped hydrogenated amorphous carbon (a-C:H:Si:O), sometimes referred to as diamond-like nanocomposites (DLNs), are a particularly promising class of multicomponent carbon-based materials for several engineering applications because they may have a higher thermal stability compared to hydrogenated amorphous carbon. The composition of this material can vary, but it has been reported in some cases to be approximately \((CH_{0.15})_{0.7}(SiO_{0.3})_{0.3}\) [12]. As discussed later, the material in the present
investigation differs substantially from this. It is well known that a-C:H, upon heating above 150°C, undergoes degradation that starts with the out-diffusion of hydrogen and is followed by the conversion of $sp^3$ bonds to $sp^2$ at higher temperatures [13]. a-C:H:Si:O’s maintain very good tribological properties across a broader range of conditions and environments than a-C:H films. The structure of a-C:H:Si:Os films, although fully amorphous, has been proposed to consist of two interpenetrating, interbonded networks, one being a-C:H, and the other a silica glass (SiO$_x$) network [14]. Even though the interpretation of the two networks constituting a-C:H:Si:O, i.e., a-C:H and SiO$_x$, has been postulated to be complete [12, 15], no definitive model for the bulk structure(s) of a-C:H:Si:O has been adopted, nor has the thermally-induced evolution of its bulk structure been studied. This lack of knowledge inhibits developing a fundamental understanding of the mechanisms by which the excellent thermal stability and tribological performance of a-C:H:Si:O are achieved. To gain insights into the structure and composition of DLCs, some of the most powerful tools in the material characterization arsenal have been used, including Raman spectroscopy [9, 16-19], X-ray photoelectron spectroscopy (XPS) [13, 20, 21], near edge X-ray absorption fine structure (NEXAFS) spectroscopy [22-24], electron energy loss spectroscopy (EELS) [25], Fourier-transform infrared spectroscopy (FT-IR) [26], X-ray reflectivity (XRR) [25], forward recoil elastic scattering (FRES) [27], nuclear magnetic resonance (NMR) spectroscopy [27-41], and electron paramagnetic resonance (EPR) spectroscopy [42-46]. Among them, the most direct analytical techniques that allow for quantitative structural characterization of DLCs are NMR and EPR spectroscopies.

The power of solid state NMR spectroscopy for the determination of the bonding configuration of carbon in DLCs derives from the presence of two well-separated, resolvable peaks in $^{13}$C NMR spectra, as confirmed by *ab initio* calculations [47]. Pan et al. [39], Golzan et
al. [34] and Jäger et al. [36] effectively employed NMR spectroscopy for gaining insights into the carbon hybridization states in sputtered a-C and tetrahedral amorphous carbon (ta-C). Besides providing information about the carbon hybridization state, NMR can also be used for investigating the evolution of the local structure of ta-C upon annealing [28, 29]: for example, on the basis of the peak lineshape and width, Alam et al. concluded that the reordering of \( sp^2 \)- and \( sp^3 \)-bonded carbon atoms, rather than rehybridization from fourfold- to threefold-coordinated carbon, which is known to occur at much higher temperatures, is the mechanism leading to stress relaxation in ta-C upon annealing. The availability of high-power proton decoupling (HPDEC) and cross-polarization magic-angle spinning (CP-MAS) methods in NMR spectroscopy [27, 30-32, 37, 40, 41] and also EPR [43, 45] has enabled a thorough structural characterization of hydrogenated amorphous carbon (a-C:H) materials as well as DLC and Si-DLC films [27, 35, 44].

This present work is an effort to better understand the structure of as-deposited a-C:H:Si:O and its evolution upon annealing at moderate temperatures. Generally, the structural evolution of a-C:H occurs via: passivation of defects/mending of broken bonds, diffusion/effusion of hydrogen, carbon \( sp^3 \) to \( sp^2 \) conversion, and clustering and ordering of \( sp^2 \) hybridized carbon atoms. Some questions have been answered regarding the energetics of these processes [13, 48], but several questions remain concerning the interdependence of these phenomena on each other. This is the first report on the thermally-induced evolution (via annealing performed between 20\(^\circ\)C and 300\(^\circ\)C) of the structure of a-C:H:Si:O as ascertained through a combination of NMR and EPR. \(^1\)H, \(^{13}\)C, and \(^{29}\)Si NMR is used for the quantitative determination of the distributions of \( sp^3 \)- and \( sp^2 \)-bonded carbon, the concentration of hydrogen, and to some lesser extent the
bonding state of Si in the as-grown film. EPR spectroscopic analyses were carried out to investigate the number density of unpaired electron spins (dangling-bond defects).

3.2 Experimental

3.2.1 Preparation of a-C:H:Si:O film

Silicon oxide-doped hydrogenated amorphous carbon (a-C:H:Si:O) coatings were deposited on aluminum foils by Sulzer-Metco Inc. (Amherst, NY, USA) using a proprietary plasma-enhanced chemical vapor deposition (PECVD) process, whose details are described elsewhere [49-57]. Briefly, a plasma discharge was formed from a proprietary siloxane precursor by means of a hot filament, whose temperature ranged between 2073 K and 2273 K. During the deposition, a negative radio frequency (RF) bias voltage between -300 and -500 V was applied to the substrate. Although the substrate temperature was not deliberately increased during the deposition process, the near-surface region could increase due to ion impingement; the temperature rise is expected to be no more than 200 K above room temperature. The thickness of the a-C:H:Si:O coating was 2 µm. The chemical composition of the films was: [C] = 57±3 at.%; [O] = 3±1 at.%; [Si] = 6±1 at.%; [H] = 34±3 at.%, measured by Rutherford backscattering spectrometry (RBS) and hydrogen forward scattering (HFS) spectrometry (Evans Analytical Group, Sunnyvale, CA, USA). The film density, determined by X-ray reflectivity, was 1.8±0.1 g/cm³.

The a-C:H:Si:O films were removed from the substrate by dissolving the aluminum foil in a 25% v/v solution of hydrochloric acid (HCl, Fisher Scientific). Etching the aluminum substrate left flakes of a-C:H:Si:O films, which were then filtered from the solution, washed with distilled water (Fisher Scientific), and dried with nitrogen. The chemical etching of the aluminum
substrate did not affect the surface chemistry and structure of a-C:H:Si:O, as indicated by control XPS and NEXAFS experiments (not shown).

3.2.2 Annealing Experiments

The hydrogen concentration \((N_H)\), paramagnetic content \((N_S)\), and carbon \(sp^2\) and \(sp^3\) fractions were monitored stepwise by examining samples of as-prepared a-C:H:Si:O heated to 50°C and subsequently to 100°C in a nitrogen atmosphere for 14 h using a Büchi model B-580 glass oven. The oven enclosure was initially evacuated by rough pumping to ~ 88 kPa then backfilled with N\(_2\) gas at standard pressure prior to the heat treatments. Since the initial assumption was that the material contained an intrinsic proton concentration of ‘fixed’ hydrogen along with a more volatile hydrogen component (i.e., unbound molecular species), it was necessary to perform the EPR and NMR measurements after driving off any ambient water and superficial hydrocarbon impurities. To follow any further H\(_2\) effusion, the sample was subsequently annealed at 150°C, 200°C and 300°C for 14 h. EPR and NMR measurements were carried out under N\(_2\) gas and at room temperature after each heating period.

3.2.3 Characterization

3.2.3.1 Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR measurements were performed on a Bruker EMX electron paramagnetic resonance spectrometer operating at X-band (9.74 GHz continuous wave, field swept). Small amounts of a-C:H:Si:O (~1 mg) were placed at the bottom of quartz EPR tubes and measured at ambient lab temperature (~20°C). Spectra were acquired with 100 kHz field modulation, 0.25 mW microwave power, 3.00 Gauss modulation amplitude, 20.48 ms time constant, and 81.92 ms conversion time. The choice of modulation amplitude was guided by several considerations, mainly to obtain sufficient signal to noise in one scan without significantly distorting the EPR
lineshape. In cases where changes in linewidth were observed under annealing, spectra acquired with smaller modulation amplitude were checked but not found to differ substantially from the ones shown later. Under these experimental conditions EPR signals exhibited no saturation. In order to ascertain the unpaired spin density in a-C:H:Si:O from the EPR spectra, a calibration was made using 4-hydroxy-TEMPO (C$_9$H$_{18}$NO$_2$ 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl). TEMPO signal intensities (integrals of absorption spectra) were plotted versus number of radical TEMPO units, and the calibration (EPR signal intensity/spin) was obtained from the slope. Calibration samples were made using 0.02, 0.04, 0.06 ml aliquots of a freshly prepared 0.026 M TEMPO/toluene solution.

### 3.2.3.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

$^1$H NMR spectra were for the most part recorded at 300 MHz using a $^1$H-free static probe. A spin-echo pulse sequence ($\pi/2 - \tau - \pi - \tau - \text{acquire}$) was employed to record these data where: $\pi/2 = 4.75$ μs, $\tau = 15$ μs to 5 ms, with a recycle delay of 4 s. Spin-spin relaxation times ($T_2$) were extracted from these data, whereas a saturation-recovery sequence was used to obtain spin-lattice relaxation profiles ($T_1$). The absolute number of protons in the sample ($N_H$) was obtained through comparison with results from known quantities of standard materials, i.e., glycine or poly-methylmethacrylate, etc. The hydrogen content calibration ($^1$H NMR intensity per proton, $I_{\text{proton}}$) was determined by: 1) obtaining a set of static $^1$H spin-echo spectra with respect to (w.r.t.) pulse separation (i.e., $\tau = $ echo dephasing time in the CPMG method [58] for substances with a known hydrogen content; 2) integrating these spectra; 3) plotting the natural log of the integrals w.r.t. $\tau$ to get the intercept, $ln[I_c(\tau = 0)]$; and 4) using this $I_c(0)$ to obtain the NMR signal intensity per proton ($I_{\text{proton}} = I_c(0) \div \#$protons in reference). $N_H$ is therefore obtained by first measuring the sample echo signal $I(\tau)$. The absolute intensity, $I(0)$, which cannot be measured directly, is
extrapolated from a bi-exponential fitting function (eqn. 1, see below). The final value for $N_H$ is obtained by dividing $I(0)$ by the calibration and sample mass, $N_H = [I(0) ÷ (I_{proton} \times \text{mass})]$.  

$^{13}$C magic angle spinning (MAS) NMR measurements were carried out on a Varian Inova solid state NMR spectrometer operating near 125 MHz (11.8 T) using a 4.0 mm DOTY MAS probe and silicon nitride rotors. In order to minimize background $^{13}$C and $^1$H NMR signals, the probe was modified, as practical, by removal of flourinated plastics (PTFE, Teflon) and hydrogen-containing plastics, epoxies and fabrics. $^{13}$C chemical shifts are given relative to tetramethylsilane (TMS, (CH$_3$)$_4$Si), whose position is set to 0 ppm. $^{13}$C NMR data were collected using a spin-echo pulse sequence, where the pulse parameters were: $\pi/2 = 5$ µs, $\tau = 62.5$ µs (= 1/16 kHz for roto-synchronization). As a practical matter for acquiring spectra, shorter excitation pulses were used (i.e., 3 µs) to reduce the signal saturation limit and to improve the excitation bandwidth. Using these parameters, no significant differences in signal strength were observed with recycle delays greater than 7 s. $^{13}$C MAS NMR spectra of a-$\text{C:H:Si:O}$ samples are similar to those observed previously for amorphous hydrogenated carbon films [27, 29, 32, 41]. The isotropic chemical shift ranges are well known for the carbon $sp^2$ site (105 to 145 ppm) and $sp^3$ site (30 to 70 ppm), and their spectral components can be integrated to give the relative concentration of carbon hybridizations [27, 30, 32, 33, 37, 41]. $^{13}$C spin-lattice relaxation times ($T_1$) were measured using a saturation recovery method with echo detection: $[\pi/2]_n - \tau_{rec} - \pi/2 - \tau - \pi/2 - \text{acquire}$, where $n = 25$ was chosen for complete signal saturation and 10 ms $< \tau_{rec} < 10$ s. $^{13}$C CP-MAS can give insight into dipolar couplings between $^{13}$C nuclei and nearby protons. For these measurements a suitable Hartmann-Hahn match was obtained using a proton $\pi/2$-pulse of 4 µs and spinning speed of 8.5 kHz. A recycle delay of 3.5 s was sufficient to prevent signal saturation and about 13000 scans were accumulated for reasonable signal-to-noise. In order to
gauge the strength of the interactions, the contact time was varied between 500 μs and 6 ms. Two samples were studied by CP: unannealed (as-prepared) a-C:H:Si:O and a-C:H:Si:O annealed at 50°C for 14 h.

29Si NMR measurements were carried out at 60 MHz (7.1 T) using a Varian/Chemagnetics 3.2 mm MAS probe (zirconia rotors) with a spinning rate of 20 kHz. 29Si chemical shifts are also given relative to TMS (i.e., (CH₃)₄Si). Echos were collected using a spin-echo pulse sequence ($\pi/2-\tau-\pi-\tau$-acquire) with $\pi/2 = 4 \mu$s, $\tau = 50 \mu$s (= 1/20 kHz for rotosynchronization). Due to the very low signal strength (even upon acquiring data for about 18000 scans), no comprehensive 29Si spin-lattice relaxation measurements were performed. However, a recycle delay of 3.5 s appeared to be sufficient for the prevention of signal saturation. 29Si CP-MAS was performed on the as-prepared a-C:H:Si:O sample with a spinning rate of 7.4 kHz and 1H $\pi/2$ of 4 μs. For these CP experiments roughly 5100 scans were accumulated.

3.3 Results and discussion

3.3.1 EPR

The primary objectives of this study are to use isotropic shifts, spin counts and relaxation data to gain insights into the structural changes that occur within a-C:H:Si:O films due to lower-temperature annealing. Any structural picture must take account of $sp^2$ and $sp^3$ hybridized carbon, as well as hydrogen content and defects. Broken bond structural defects in a-C:H:Si:O materials are associated with unpaired electronic spins, which can be monitored by EPR. The right side of Figure 1 displays the EPR spectrum for a-C:H:Si:O. This and the other single-featured EPR spectra gathered after annealing were centered near $g = 2.0039$ with peak-to-antipeak linewidths of about 4 G to 4.5 G. The fact that the spectra are relatively narrow with no additional discernable features, suggests that the resonances are not indicative of strong
hyperfine interactions with protons or transition metal impurities. The powder pattern spectra do not display anisotropy, if at all present, most likely because of strong homogeneous paramagnetic dipolar distributions present in the material.

**Figure 3.1** EPR spectrum for the as-prepared a-C:H:Si:O sample (right), and the peak-to-antipeak linewidth (G) w.r.t. annealing temperature (left). The Voigt EPR line shape description is indicated by the bar insert, from 40:60 (G:L) to purely Lorentzian 0:100 (L).

Upon annealing, peak positions did not vary (within experimental uncertainty), although linewidths decreased by about 10% (left side of Figure 3.1). The lineshape, initially Voigt-like (convoluted by 40:60 Gaussian to Lorentzian contributions), became increasingly Lorentzian to almost 100% upon annealing at 200°C and 300°C. These empirical differences mark substantial changes within the defect distribution as the material evolves. For example, a non-uniform distribution resulting in clustering could be related to the Gaussian character of the lineshape through enhanced spin-spin coupling. The g-value, being very much toward the high end of the typical range associated with thin-film hydrogenated amorphous carbons, indicates the resonance is more likely the result of a distribution of unpaired electrons in primarily broken non-graphitic
carbon bond defects [9, 33, 45, 46]. Some amount of paramagnetic contribution from $\pi$-bond graphitic networks might also be present, considering the carbon $sp^2$ content of these films (Fig. 8) [43]. However, if present, the crystalline graphitic content must be very small due to the fact that EPR spectra of a-C:H:Si:O do not show any asymmetry or large distributions in $g$-values, which are characteristic of graphitic EPR powder patterns [44, 59].

The integrated EPR signal intensity ($2^{nd}$ integral of the derivative lineshape) is proportional to the number of detected unpaired spins. Therefore the sample spin density ($N_s$) can be computed (this can be obtained by comparing the integral with that of a standard sample containing a known number of spins (TEMPO calibration, see Experimental Section)). This analysis shows that the spin number density $N_s$ in a-C:H:Si:O progressively decreases upon annealing (Figure 3.2). For comparison, the $N_s$ data compiled by Barklie for carbon films fabricated by a variety of methods [42] show a relatively constant $N_s$ for annealing temperatures between 20$^\circ$C and 300$^\circ$C. On the other hand, the temperature dependence of $N_s$ data presented in Figure 3.2 appears to be closer to that of ta-C:H materials prepared by Conway et. al. [60, 61]. A possible mechanism for the decrease in $N_s$ in a-C materials upon annealing is the reduction of internal stresses and decrease in hydrogen content. These processes involve the scission of C-H bonds and passivation of defects, which results in an increased $sp^2$ content. However, this description does not completely account for the data presented here, which were gathered at lower annealing temperatures. Although a defect passivation mechanism (i.e., coalescence of carbon defects, atomic hydrogen recombination and/or capture at carbon defect sites) is likely responsible for the $N_s$ behavior, the required mechanism must not rely significantly on covalent bond breaking, carbon rehybridization and carbon $sp^2$ clustering for the following reasons: 1) the EPR signal is not consistent with a graphitic interpretation (although the carbon $sp^2$ content
increases slightly upon annealing at 200-300°C; 2) while \( N_s \) continues to decrease, the hydrogen content (\( N_H \)) decreases to a lower extent with increasing annealing temperature (Figure 3.4).

![Figure 3.2](image)

**Figure 3.2** \( N_s \) (unpaired spin density) in units of # unpaired electron magnetic moments (\( \mu_e \)) per gram of a-C:H:Si:O w.r.t. annealing temperature. The data in this figure have an uncertainty of about ±7%.

### 3.3.2 \(^1\)H NMR

Investigating the correlation between carbon hybridization, hydrogen content, structural defects, topological disorder (i.e., clustering of \( sp^2 \) carbons) and macroscopic behavior is of primary importance in characterizing a-C:H films [62]. Along these lines \(^1\)H NMR was employed to probe magnetic environments and motional dynamics for hydrogen in the material.

Room temperature static and MAS \(^1\)H spectra of the unannealed a-C:H:Si:O is displayed in Figure 3.3. The static lineshape reflects a large structural distribution of hydrogen sites containing both relatively narrow and broad components. The MAS lineshape displays a single isotropic peak (~0 ppm) flanked symmetrically by sidebands. Even though the proton chemical shift range is not large enough to provide resolution of specific hydrogen sites (CH, CH\(_2\) and
CH₃) even under MAS, dynamic information and absolute content can be obtained from these spectra.

Figure 3.3 (a) Static and (b) MAS ¹H NMR echo spectrum with τ = 35 µs for the as-prepared a-C:H:Si:O sample; the insert is the resonance linewidth w.r.t. annealing temperature for the static case. The linewidth data has an uncertainty of about ±5%.

After an initial dramatic decrease of about 1/2 in full-width at half maximum (FWHM) upon annealing beyond 50°C, the general lineshape for the most part decreases in intensity w.r.t. annealing temperature, whereas linewidths appear to increase only slightly upon annealing between 50°C and 300°C. Low temperature spectra (at -50°C, not shown) of the unannealed sample are roughly twice as broad, and therefore indicate the presence of mobile hydrogen-containing species at room temperature. The results indicate that initial annealing at 50°C gives substantial molecular effusion, in the form of ambient water, and/or simple hydrocarbons. Effusion of molecular hydrogen (and perhaps other hydrocarbons) is known to occur more prominently with annealing at much higher temperatures due to the recombination of atomic hydrogen by thermally activated structural changes [60, 61].
The observation of two very different time scales in the spin-echo results of Figure 3.4 leads to the bi-exponential proton relaxation formulation of Eqn. 3.1. It is from this analysis by which both characteristic spin-spin relaxation times $T'_2$, $T''_2$ (short and long resp.) and the weightings $f$ are determined (Table 3.1).

**Figure 3.4** Hydrogen heterogeneity is evident by the two recovery components in the $^1$H NMR echo intensity (logarithm) vs. $\tau$ (dephasing time) for the as-prepared a-C:H:Si:O sample. The two asymptotic rates, $1/T'_2$ and $1/T''_2$, are clearly apparent in the bi-exponential.
Table 3.1 $T_1$ (C), $T_2$ (C), $T_1$ (H), and $T_2$ (H) of annealed a-C:H:Si:O

<table>
<thead>
<tr>
<th>Annealing temp.</th>
<th>as-prep.</th>
<th>50°C</th>
<th>100°C</th>
<th>150°C</th>
<th>200°C</th>
<th>300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp^2$ $T_1$ (f)</td>
<td>0.95s (52%)</td>
<td>1.03s (59%)</td>
<td>1.11s (62%)</td>
<td>1.36s (62%)</td>
<td>1.42s (60%)</td>
<td>1.60s (67%)</td>
</tr>
<tr>
<td>$sp^2$ $T_2$ (f)</td>
<td>0.08s (48%)</td>
<td>0.04s (41%)</td>
<td>0.04s (38%)</td>
<td>0.09s (38%)</td>
<td>0.10s (40%)</td>
<td>0.12s (33%)</td>
</tr>
<tr>
<td>$sp^3$ $T_1$ (f)</td>
<td>0.90s (58%)</td>
<td>1.14s (59%)</td>
<td>1.15s (59%)</td>
<td>1.45s (64%)</td>
<td>1.50s (61%)</td>
<td>1.57s (65%)</td>
</tr>
<tr>
<td>$sp^3$ $T_2$ (f)</td>
<td>0.06s (42%)</td>
<td>0.06s (41%)</td>
<td>0.05s (41%)</td>
<td>0.04s (36%)</td>
<td>0.06s (39%)</td>
<td>0.07s (35%)</td>
</tr>
<tr>
<td>$^{13}$C $T_1$ (f)</td>
<td>0.023s (48%)</td>
<td>0.334s (18%)</td>
<td>0.353s (10%)</td>
<td>0.434s (10%)</td>
<td>0.410s (8%)</td>
<td>0.529s (8%)</td>
</tr>
<tr>
<td>$^{1}$H $T_1$ (f)</td>
<td>0.012s (52%)</td>
<td>0.013s (82%)</td>
<td>0.015s (90%)</td>
<td>0.016s (90%)</td>
<td>0.016s (92%)</td>
<td>0.017s (92%)</td>
</tr>
<tr>
<td>$^{1}$H $T_2$ (f)</td>
<td>0.99ms (3%)</td>
<td>0.96ms (8%)</td>
<td>1.08ms (6%)</td>
<td>0.94ms (8%)</td>
<td>1.16ms (11%)</td>
<td>0.86ms (10%)</td>
</tr>
</tbody>
</table>

*Results of bi-exponential expressions, Eqns. 3.1 and 3.2.

The majority of protons (≥ 90%) are characterized by very short spin-spin relaxation times near 15 μs, whereas the remaining 10% or less have $T_2 \sim 1$ ms. There are some interesting trends in the data. For instance, the fraction of short-$T_2$ protons decreases slightly upon annealing (unlike the $T_1$ data). This proton population experiences strong interactions with neighboring paramagnetic dangling-bond defects, yet their fraction will decrease as the paramagnetic content becomes less concentrated with annealing ($N_s$ data of Figure 3.2). There is hydrogen loss as well, and this can be monitored through $N_H$, which is obtained according to the procedure outlined
above from extrapolated \( I(0) \) values via Eqn. 3.1. The results for \( N_H \) are plotted in Figure 3.5 at each annealing temperature.

\[
I(\tau) = I(0) \left[ f e^{-\frac{\tau}{T_1'}} + (1 - f) e^{-\frac{\tau}{T_1''}} \right] \quad (3.1)
\]

![Figure 3.5](image)

**Figure 3.5** Total hydrogen concentration (\( N_H \) as measured via NMR) of a-C:H:Si:O samples w.r.t. annealing temperature (filled circles, ●). \( N_H \) is determined from the intercept of spin-echo data, via Eqn. 3.1). The data in this figure have an error of about \( \pm 10\% \) and the lines are guides for comparison. \( N' \) and \( N'' \) are the hydrogen concentrations derived respectively for the \((sp^2-sp^3)_{T_1'}\) and \((sp^2-sp^3)_{T_1''}\) carbon-silica groups (see discussion).

Additional insight can be gained through spin-lattice relaxation measurements \( (T_1) \). Previous \( T_1 \) analyses of a-C:H materials have used bi-exponential recovery profiles to evaluate proton magnetic relaxation [32, 41]. For this analysis of saturation recovery data, a bi-exponential formulation is used as well (Eqn. 2), where characteristic relaxation times \( T_1', T_1'' \) (short and long resp.) and the weightings \( f \) are determined accordingly (Figure 3.6, top).

\[
I(\tau) = I(\infty) \left[ f \left( 1 - e^{-\frac{\tau}{T_1'}} \right) + (1 - f) \left( 1 - e^{-\frac{\tau}{T_1''}} \right) \right] \quad (3.2)
\]
The reliance upon a bi-exponential magnetic relaxation recovery is not unique, as this approach has been consistently used in many magnetic resonance relaxation studies of sputtered and CVD a-C:H materials. Stretched-exponential schemes have been applied as well, although the formalism of its direct application to magnetization data is less grounded. It has been used nevertheless to account for the effect on relaxation due to very broad and heterogeneous distributions of paramagnetic spins [41, 63].

![Figure 3.6](image)

**Figure 3.6** $^1$H (top) and $^{13}$C (bottom) spin-lattice relaxation ($T_1$) profiles (signal strength, $I(\tau)$ vs. $\tau$) expressed in arbitrary units, for the 150°C annealed a-C:H:Si:O sample.

The solid curve is the bi-exponential “best-fit” obtained using Eqn. 3.2.

The fitting results given in Table 3.1 reveal that a large fraction of protons are characterized by short $T_1$ values (~10 ms). An apparent difference with the $T_2$ behavior is that the short-$T_1$ proton fraction *increases* with the sample annealing temperature. This is perhaps better understood considering the decreasing long-$T_1$ fraction, i.e. the result when more mobile long-$T_1$ protons leave due to effusion, defect passivation and consolidation of hydrogen-free domains. The presence of surface adsorbed molecular entities (*e.g.*, water) will tend to enhance the long-$T_1$
fraction; therefore, as these volatile species leave the material at 50°C - 100°C, the less volatile short-$T_1$ proton fraction increases. The as-prepared a-C:H:Si:O has a hydrogen concentration of about $1.9\times10^{22}$ g$^{-1}$; however, as the data reveal (considering the difference between the first values, $\Delta N_H \sim 0.3\times10^{22}$ g$^{-1}$), a significant portion of $N_H$ is due to the ambient water content. In other words, the change of the hydrogen content for temperatures less than about 100°C is largely associated with the desorption of water and other surface hydrogen-containing species. Also, due to hydrogen effusion there is a steady reduction of $N_H$ through anneals up to 200°C, after which the concentration appears to level off near $0.7\times10^{22}$ g$^{-1}$. These data are averaged over both short and long-$T_1$ populations, yet the proposed structure (see discussion below) allows for a separated analysis of these components, as $N_H$ can be decomposed into proton populations associated with $T'_1$ and $T''_1$, given as $N'$ and $N''$ in Figure 3.5. We next discuss the $^{13}$C relaxation and it will be seen that there are also two populations with distinct relaxation behavior. However it is important not to impute a simple one-to-one relationship between the $^1$H and $^{13}$C results because unlike for protons discussed above, there are no volatile effusing carbon species with increasing annealing temperature.

### 3.3.3 $^{13}$C NMR

The $^{13}$C MAS NMR spectrum in Figure 3.7 for the as-prepared a-C:H:Si:O reveals solid-state chemical shift anisotropy/distributions and magnetic dipolar interactions between $^{13}$C and surrounding spins. These dominant interactions account for the peak positions and side band patterns observed. Unlike some previous $^{13}$C results published in the literature, no significant variations in the spectra were observed using proton decoupling, although cross-polarization was observed. It is assumed that higher power decoupling can improve overall signal strength for hydrogen-containing amorphous carbon materials. Nevertheless, all data in this study were
obtained without proton decoupling. The well-established $^{13}$C chemical shifts for carbon hybridizations in a-C materials assign the peak at 140 ppm to $sp^2$ carbons and the more shielded peak at 56 ppm to $sp^3$ carbons. No variation of peak position was observed due to annealing. Integration of these spectral signatures gives the fractions of carbons in $sp^2$ and $sp^3$ environments, as shown in Table 3.2 and Figure 3.8 left. The results indicate that the $sp^2$ content starts at about 65% for the as-prepared material and slightly increases to just over 70% for the 300°C annealed sample.

**Figure 3.7** $^{13}$C MAS NMR spectra (scale relative to TMS) of the as-prepared (unannealed) a-C:H:Si:O sample. Top spectrum (a) is the spin-echo ($\tau = 35 \mu s$), middle spectrum (b) single-pulse (DP), and bottom spectrum (c) obtained using CP. Note the varied signal strengths within the dotted curve (see text). *denotes spinning sidebands.

Comparison of the spectra collected via spin-echo, direct polarization (DP) and $^1$H-$^{13}$C CP measurements (also shown in Figure 3.7) indicates the presence/absence of certain spectral features within the region bordered by the $sp^2$ and $sp^3$ peaks (~100 ppm). Among the three
methods, the echo provides the most accurate estimation of the $sp^2$ and $sp^3$ resonance intensities. However, it is noted that significant paramagnetic density is encountered for this sample ($\sim 10^{20} \mu$/gram) and undoubtedly some of the $^{13}$C NMR signal is rendered unobservable due to extremely short transverse magnetic relaxation, regardless of DP, CP or echo. This issue will be revisited below in light of the experimental results. The more attenuated signal intensity around 100 ppm observed in the DP spectrum suggests a very short spin-spin interaction for associated carbons (e.g., carbon $T_2 \leq 15 \mu$s, within the instrument deadtime after the pulse). In the CP spectrum, the almost complete absence of $^{13}$C signal in this region indicates zero correlation between the associated carbons and their closest protons. This $^{13}$C signal is largely composed of unprotonated and highly disordered $sp^2$ carbons characterized by very short $T_2$ s. A consistent assignment for this spectral component, made by Xu et al. near 105 ppm, is for disordered non-graphitic $sp^2$ carbons [41].
Table 3.2 Fraction of carbon atoms in $sp^2$ and $sp^3$ hybridization state together with the unpaired spin density ($N_s$) and the number of hydrogen atoms ($N_H$)

<table>
<thead>
<tr>
<th>Annealing temp.</th>
<th>$f_{sp^2}$</th>
<th>$f_{sp^2}/f_{sp^3}$</th>
<th>$N_s \times 10^{20}\text{g}^{-1}$</th>
<th>$N_H \times 10^{22}\text{g}^{-1}$</th>
<th>$z$</th>
<th>$\mu/e\times10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-prepared</td>
<td>0.658±0.050</td>
<td>1.92</td>
<td>1.95±0.13</td>
<td>1.90±0.19</td>
<td>0.52±0.04</td>
<td>5.3</td>
</tr>
<tr>
<td>50°C</td>
<td>0.662</td>
<td>1.99</td>
<td>1.80</td>
<td>1.57</td>
<td>0.43</td>
<td>4.9</td>
</tr>
<tr>
<td>100°C</td>
<td>0.665</td>
<td>2.01</td>
<td>1.68</td>
<td>1.43</td>
<td>0.39</td>
<td>4.6</td>
</tr>
<tr>
<td>150°C</td>
<td>0.667</td>
<td>2.00</td>
<td>1.61</td>
<td>1.05</td>
<td>0.28</td>
<td>4.4</td>
</tr>
<tr>
<td>200°C</td>
<td>0.685</td>
<td>2.17</td>
<td>1.01</td>
<td>0.74</td>
<td>0.20</td>
<td>2.7</td>
</tr>
<tr>
<td>300°C</td>
<td>0.727</td>
<td>2.66</td>
<td>0.53</td>
<td>0.66</td>
<td>0.18</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$f_{sp^3} = 1 - f_{sp^2}$

Additionally, the computed $z$ values (for the formula $(\text{SiO}_x)_y\text{-CH}_z$) and the number of unpaired electron spins per carbon ($\mu/e\times[C]$) are reported.

The ability of resolving $sp^2$ and $sp^3$ carbons in $^{13}$C MAS spectra allows for independent $T_1$ measurements, which thereby can provide further insights into the carbon environments. The results of a bi-exponential analysis (Eqn. 2) on the saturation-recovery data (e.g., bottom of Figure 3.6), as compiled in Table 3.1, show that the $^{13}$C spin-lattice relaxation does not discriminate unequivocally between $sp^2$ and $sp^3$ carbons. As the overall fraction of carbons characterized by $T_1'$ (~40-120 ms) decreases somewhat from the as-prepared value, $T_2''/T_1$ for the remaining majority of carbons (~60%) increases slightly. This is not surprising, since the $^{13}$C relaxation is enhanced by dangling-bond paramagnetic defects whose concentration ($N_s$) also decreases with annealing. Although there is no discernable contrast in the relaxation between $sp^2$ and $sp^3$ carbons, a different association can be made between separate carbon groups, due to the
very different relaxation characteristics that they exhibit. In this way, the data allows for the identification of two carbon groups characterized by short and long-$T_1$, namely $(sp^2-sp^3)_{T \cdot 1}$ and $(sp^2-sp^3)_{T \cdot \cdot 1}$. The results from Tables 3.1 and 3.2 can be used to monitor the fractions of carbon in these groups w.r.t. annealing (labeled $f'$ and $f''$ respectively), as compiled in Table 3.3.

**Table 3.3** Fraction of carbon atoms with long and short $T_1$

<table>
<thead>
<tr>
<th>Annealing temp.</th>
<th>$f'_{sp^2}$</th>
<th>$f'_{sp^3}$</th>
<th>$f''_{sp^2}$</th>
<th>$f''_{sp^3}$</th>
<th>$f'<em>{sp^2}/f'</em>{sp^3}$</th>
<th>$f''<em>{sp^2}/f''</em>{sp^3}$</th>
<th>$z'$</th>
<th>$z''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-prep.</td>
<td>0.316</td>
<td>0.144</td>
<td>0.342</td>
<td>0.198</td>
<td>2.2</td>
<td>1.7</td>
<td>0.46</td>
<td>0.59</td>
</tr>
<tr>
<td>50°C</td>
<td>0.271</td>
<td>0.139</td>
<td>0.391</td>
<td>0.199</td>
<td>2.0</td>
<td>2.0</td>
<td>0.41</td>
<td>0.86</td>
</tr>
<tr>
<td>100°C</td>
<td>0.253</td>
<td>0.137</td>
<td>0.412</td>
<td>0.199</td>
<td>1.8</td>
<td>2.1</td>
<td>0.39</td>
<td>0.90</td>
</tr>
<tr>
<td>150°C</td>
<td>0.253</td>
<td>0.120</td>
<td>0.414</td>
<td>0.213</td>
<td>2.1</td>
<td>1.9</td>
<td>0.37</td>
<td>0.68</td>
</tr>
<tr>
<td>200°C</td>
<td>0.274</td>
<td>0.123</td>
<td>0.411</td>
<td>0.192</td>
<td>2.2</td>
<td>2.1</td>
<td>0.40</td>
<td>0.46</td>
</tr>
<tr>
<td>300°C</td>
<td>0.240</td>
<td>0.096</td>
<td>0.487</td>
<td>0.177</td>
<td>2.5</td>
<td>2.7</td>
<td>0.34</td>
<td>0.49</td>
</tr>
</tbody>
</table>

$* f'_{sp^2} + f'_{sp^3} + f''_{sp^2} + f''_{sp^3} = 1$, $f''_{(sp^2-sp^3)_{T \cdot \cdot 1}} = 1 - f'_{(sp^2-sp^3)_{T \cdot 1}}$.

Figure 3.8 (right) shows through the ratio, $f''/f'$, how annealing enhances the $(sp^2-sp^3)_{T \cdot \cdot 1}$ content at the expense of the $(sp^2-sp^3)_{T \cdot 1}$ content. Some insight into the internal make-up of these carbon networks may be obtained by considering the effect of annealing on their respective $f_{sp^2}/f_{sp^3}$ ratios. As shown in Figure 3.9, there appears to be slight enhancement in the $sp^3$ content at the 300°C annealing temperature in $f''$ relative to $f'$. These data reveal an important aspect of the structural evolution within the material, and will be discussed below.
Figure 3.8 Left: The fractional components of carbon hybridized as $sp^2$ and $sp^3$ in a-C:H:Si:O samples w.r.t. annealing temperature. The lines are guides for comparison and the error bars represent an uncertainty of about ±4%. Right: The ratio of carbon groups characterized by short ($f' = f_{sp2}' + f_{sp3}'$) and long ($f'' = f_{sp2}'' + f_{sp3}''$) spin-lattice relaxation times (uncertainty of about ±6%).

The issue regarding the effect on the NMR by large paramagnetic concentrations, i.e., the $sp^2/sp^3$ evaluation, refers to signal wipeout which is typically encountered in paramagnetic systems, as electron-nuclear dipolar couplings can shorten $T_2$ to less than a few $\mu$s. Since the NMR signal decays at a rate proportional to $1/T_2$, significant spectral information can be lost within the instrument dead time, which is in the best of circumstances typically on the order of 10 $\mu$s or so. The problem could be exacerbated in the present case, as previously reported $^1$H and $^{13}$C $T_1$ values [32, 41] are generally longer than those reported here for a-C:H:Si:O films. This is believed to be an effect of larger dangling bond paramagnetic content in the a-C:H:Si:O material.

Concerning the proton counts, via spin-echo results analyzed with Eqn. 3.1, it is assumed that the linear extrapolation to the intercept, $I(0)$, gives a reasonably accurate measure of the proton magnetic moments, including the undetected $^1$H short-$T_2$ components. On the other hand, the
breakdown of protons into weightings according to Eqn. 3.2 is less reliable, since the saturation method becomes more difficult to implement for \( T_1 < 1 \times 10^{-4} \) s. Nevertheless, an important outcome from the \(^1\text{H} T_1\) analyses is that upon annealing, an increasingly large fraction of protons (up to over 90% at the higher annealing temperatures) are characterized by a fast-relaxation mechanism. \(^{13}\text{C}\) NMR signal intensities can also be adversely affected by large paramagnetic interactions [64]. For instance, Cho et al.[32] have reported signal losses of about 50% due to high paramagnetic content for a variety of sputtered a-C:H samples. It is therefore likely that not all \(^{13}\text{C}\) nuclei are represented in the a-C:H:Si:O spectra. As stated, the interpretation given here envisions the carbon group in terms of distinct relaxation subdivisions of similar \( f_{sp2}/f_{sp3} \) ratios (i.e. \( f_{sp2}/f_{sp3} \approx f_{sp2}/f_{sp3} \approx f_{sp2}/f_{sp3} \approx f_{sp2}/f_{sp3} \)), which includes any undetected (\( sp^2-sp^3 \)) factions with extremely short \( T_2 \) s. Since the relaxation does not discriminate between \( sp^2 \) and \( sp^3 \) carbons, even within the undetected factions, the quantitative \( sp^2/sp^3 \) analysis is not significantly affected by paramagnetic wipeout effects.
Figure 3.9 Ratio of the fraction of all $sp^2$ and $sp^3$ carbons: $fsp^2/fsp^3$ from integrated $^{13}$C spectra (top); $f^{'}sp^2/f^{'}sp^3$ from short-relaxation time data (center); and $f^{''}sp^2/f^{''}sp^3$ from long-relaxation time data (bottom). The center and bottom plots are generated using the $^{13}$C $T_1$ weightings ($f$) from table 3.1 and carbon hybridization weightings ($fsp^2$ and $fsp^3$) from Table 3.2, i.e., $f^{'}sp^2 = f \times fsp^2$. The lines are guides for comparison.

Magnetic dipolar interactions between nearby protons and $^{13}$C nuclei in $sp^2$ and $sp^3$ hybridizations can be probed individually by CP-MAS. Since the efficiency of the polarization transfer depends on the strength of the H-C coupling, the contact time can be varied to optimize the signal intensity [65]. Select CP-MAS experiments were performed on the as-prepared and 50°C annealed a-C:H:Si:O samples using a variety of contact times between 0.5 ms and 6.0 ms.
The results displayed in Figure 3.10 show that the signal strength of $sp^2$ carbons is maximized near 2 ms, whereas $sp^3$ carbons appear to have a maximum below 1 ms. In that the magnetic dipolar relaxation rate during CP varies inversely with the $^1H-^{13}C$ distance to the sixth power [66, 67], it is generally understood that the CP effect is more efficient at short dipolar interaction distances, i.e., for immobile protons within a van der Waals contact distance and for direct C-H bonds. In order to optimize CP for longer interaction distances (a few Å), for suitably long rotating frame relaxation times, the power and/or Hartmann-Hahn match duration (contact time) is usually adjusted gradually to larger values. In this way, an evaluation of the CP optimization profile can provide a qualitative assessment of the relative $^{13}C-^1H$ distances for $sp^2$ and $sp^3$ carbons [68]. The results shown in Figure 3.10 indicate that the observed $sp^3$ carbons with contact times less than 1 ms, can be characterized as having immobilized hydrogen atoms as close as a single bond length away, whereas $sp^2$ carbons with contact times greater than 2 ms may be better described as having neighboring hydrogen atoms further away, at distances of a few Å (two or three bond lengths). The greater affinity for hydrogen to be associated with $sp^3$ over $sp^2$ carbons can be partially addressed using purely statistical reasoning [69]; however, a full description requires consideration of nano-clustering and heterogeneous structural distributions. Unfortunately, CP doesn’t seem to provide much contrast specifically regarding the $f'$ and $f''$ content. Overall, these results are consistent with CP-MAS studies of a-C:H [27, 32, 41] and Si-amorphous carbon [35] materials.
Figure 3.10 Normalized $sp^2$ and $sp^3$ $^{13}$C peak intensities for the as-prepared material (●) and the 50°C annealed sample (★) as determined using the CP-MAS experiments as a function of the contact time.

3.3.4 $^{29}$Si NMR

Several conclusions about silicon sites can be inferred from the results. The analysis of $^{13}$C NMR results in PECVD grown a-C:H:Si films by Iseki et al. [35] shows that the resonance becomes more shielded with Si content, although those materials contain no oxygen. According to that trend, the $^{13}$C peak positions reported here at 140 ppm and 56 ppm for respectively $sp^2$ and $sp^3$ carbon, imply a low Si content for the a-C:H:Si:O material under investigation. This is in agreement with the outcomes of the chemical analysis of the as-deposited materials by Rutherford backscattering spectrometry (RBS). Based on the observed $^{29}$Si chemical shift (-11 ppm, Figure 3.11), the silicon site appears to be covalently situated within the carbon ($sp^2$-$sp^3$) group; quite possibly maintaining at least 3 carbon neighbors [35], and at most one hydrogen. For comparison, SiC is known to give shifts within the range of -14 to -25 ppm depending on the crystal environment about silicon atoms, and the cubic form gives a resonance near -18 ppm.
The data are not conclusive concerning the presence of Si-O bonds, as the resonance of the SiC₆O unit is expected to be near -6 ppm, and other oxycarbides (SiC₂O₂, SiCO₃, SiO₄) typically reside beyond -30 ppm [71]. Since the width of the MAS spectrum is about 90 ppm, the existence of some of these units cannot be categorically discounted. There is no strong evidence for the existence of larger silicon groupings, *i.e.*, SiSi₄₋ₙCₙ, as they generally give more shielded ²⁹Si resonances within -34 ppm to -136 ppm [72].

![Chemical shift (ppm)](image)

**Figure 3.11** ²⁹Si MAS NMR spectrum for the as-prepared a-C:H:Si:O sample.

Considering the ¹H-²⁹Si CP results summarized in Figure 3.12, an interpretation analogous to that of carbon can be made where the maximizing contact time of about 2.8 ms indicates that direct Si-H bonds are not abundant and of the ¹H-coupled silicon atoms, most are probably associated with an immobile proton at least two bond lengths away (*i.e.*, hydrogen bound to a neighboring carbon or oxygen atom).
3.3.5 Discussion

The NMR and EPR data presented here is now used to obtain a structural perspective of the PECVD grown a-C:H:Si:O film and how its structure evolves under moderate heating. The average number density of dangling-bonds, hydrogen content and carbon $sp^2/sp^3$ profile in as-prepared material appears to be typical for amorphous hydrogenated carbon materials; however, certain stand-out features are evident: 1) the heterogeneity in the hydrogen distribution; and/or 2) the dangling-bond distribution; and 3) the absence of graphitic $sp^2$ nanoclusters. The interpretation given here is of two silicon- and oxygen-infused ($sp^2$-$sp^3$) carbon groups with somewhat similar $sp^2/sp^3$ ratios, i.e., similar carbon composition within experimental uncertainty, yet very different in their respective defect and hydrogen contents. Since the identification is largely based on magnetic relaxation, there is some uncertainty in describing the overall structure this way. For instance, the long-range structure could be viewed as a random arrangement of large segregated silicon oxide-carbon ($sp^2$-$sp^3$) networks. On the other hand, the picture could be
that of a more integrated arrangement of smaller silicon oxide-doped $f'$ clusters within a matrix of silicon oxide-doped $f''$ content. This point will be discussed below.

Annealing has the effect of increasing $f_{sp2}$, and decreasing $f_{sp3}$, $N_S$ and $N_H$. Also, the main dynamical argument, which correlates both $^1$H and $^{13}$C spins with unpaired electron spins, is a normal interpretation of events where relaxation times expectedly tend to get longer as $N_S$ decreases. The thermally induced structural changes within the hydrogen population appear to occur along two fronts: 1) emission of more weakly bound hydrogen-containing species (between 20° and 100°C); and 2) thermally induced effusion of hydrogen (higher temperatures). Structural interpretation in terms of coexisting carbon groups shows that the $f''$ content increases with annealing, at the expense of the $f'$ content. Yet there might be small differences in the $sp^2/sp^3$ ratios between the two groups, which would indicate differences in the internal structural conversions (i.e., $sp^3 \rightarrow sp^2$) occurring with annealing. The structural role of Si and O are less clear. In spite of the low S/N in the $^{29}$Si spectra, the data is consistent with the interpretation of tetrahedral SiC$_3$H and SiC$_3$O- structural units comprising the bulk of silicon sites in the as-prepared material. It is assumed that these units do not change considerably during annealing up to 300°C. The discussion below considers the stoichiometry ($SiO_x$)$_y$-CH$_z$, the hydrogen content, the defect distributions and how the carbon structure evolves, as monitored through the experimentally determined values for $N_H$, $N_S$, $f_{sp2}$ and $f_{sp3}$.

First, the composition parameters ($x$, $y$, $z$) are computed and comparisons are made between the HFS and NMR data. If the $^{29}$Si spectrum center-of-gravity at -11 ppm can be treated as the result of a linear superposition of two structural units, say SiC$_3$O at -6 ppm and SiC at -18 ppm, then a crude estimation for the number of O per Si atoms can be obtained, namely $x = 7/12 \approx 0.58$. Upon comparison with the RBS values (see experimental section), one obtains $x = [O]/[Si]$
0.50±0.19, and it is clear that the selection of these particular silicon environments is reasonable. As mentioned above, in comparison with the lowest Si content DLC film ([Si]/[C] = 4/66 = 0.06) studied by Iseki et al. [35], the sp\(^2\) and sp\(^3\) \(^{13}\)C peak positions for a-C:H:Si:O imply a similarly low value for y. Indeed, the RBS values for [Si] and [C] given here show this: y = 0.11±0.02. Furthermore, using the HFS value for [H], one obtains z = [H]/[C] = 0.60±0.02. Now, using the RBS and HFS values for x, y, z and some algebraic analysis,

\[
N_H = \frac{z N_A}{12.01 g_{\text{mol}} + x y (16.09 g_{\text{mol}}) + y (28.09 g_{\text{mol}}) + z (1.01 g_{\text{mol}})}
\]  

where \(N_A\) is Avogadro’s number and the atomic weights of H, C, O and Si have been used, the average hydrogen concentration for the as-prepared material is computed: \(N_H = 2.19±0.03\times10^{22}\) g\(^{-1}\). In comparison, the NMR value, reflecting about a 10% uncertainty, is: \(N_H = 1.90±0.19\times10^{22}\) g\(^{-1}\), which is about 15% lower than the compositionally determined value. It is highly likely that the discrepancy is more related to the fact that HFS is a strong measure for surface hydrogen down to about 300 Å, whereas NMR in principle measures surface and bulk hydrogen. The average number of hydrogen atoms per carbon, determined using \(x\), \(y\) and the NMR value for \(N_H\), is therefore: \(z = 0.52±0.04\). These results show in another way how the hydrogen content, being a bit less concentrated within the bulk of the film, is heterogeneously distributed throughout the material. The computed \(z\) values for the specified annealings are compiled in Table 3.2.

To get a better sense of the defect content, a similar computation can be made for the number of unpaired electron spins per carbon (\(\mu_e/[C]\)):

\[
\frac{\mu_e}{[C]} = \left[12.01 \frac{g}{\text{mol}} + x y (16.09 \frac{g}{\text{mol}}) + y (28.09 \frac{g}{\text{mol}}) \right] \frac{N_S}{(N_A - N_H (1.01 g/mol))}
\]  

Application of Eqn. 3.4 to the as-prepared a-C:H:Si:O material, using the RBS values for \(x\) and \(y\), \(N_S = 1.95±0.13 \times10^{20}\) unpaired spins/gram and \(N_H = 1.90±0.19\times10^{22}\) protons/gram, one obtains: \(\mu_e/[C] = 5.35\times10^{-3}\), or about one broken bond defect per 187 carbon atoms. The results
for the 300°C annealed material yields, $\mu/[C] = 1.42 \times 10^{-3}$ or about one broken bond defect per 704 carbon atoms on average. Evidently, the defect distribution is heterogeneous as well, since separate relaxation regimes are observed in all $^1$H and $^{13}$C $T_1$ and $T_2$ measurements. Generally, it is understood that homogeneous magnetic dipole distributions yield classical single-exponential relaxation profiles. Related to this is the evolution of the EPR lineshape from a broader Voigt (60:40 Lorentzian:Gaussian) lineshape towards a purely Lorentzian lineshape upon annealing, where the number of dangling bond defects decreases with annealing temperature. The associated trend in the NMR is the emerging prominence of one component from the bi-exponential at higher annealing temperature (which is more pronounced as the short-$T_1$ component in the $^1$H data, but more subtle in the $^{13}$C data as the long-$T_1$ component). The simplest interpretation is that of defect annihilation within clusters, leaving behind smaller groups surrounded by large regions of more rarefied defect populations. Extensive low temperature EPR, $^1$H and $^{13}$C NMR relaxation measurements made by Blinc et al. [63] on a-C:H with roughly 35 at.% hydrogen prepared by CVD provide evidence of paramagnetic clustering. The phenomenon is probably more distinct in their work, since the reported EPR widths are somewhat larger (6G) while their paramagnetic density is lower ($2.5 \times 10^{19} \mu$/gram) than what is reported here for a-C:H:Si:O. The implied picture of a more clustered defect distribution, in the case of the as-prepared material, gives a defect-to-defect distance (within clusters) of less than about 4 or 5 C-C bond lengths. This distance increases as the defect population lowers such that for the 300°C annealed material a defect-to-defect distance of at most 7 or 8 C-C bond lengths is found.
It is reasonable to link the hydrogen distribution and the silicon oxide-doped carbon groups via the strong paramagnetic interactions that more or less govern relaxations in both. The proposed structure therefore is based on two assumptions:

1) the short-$T_1$ ($sp^2$-$sp^3$)$_{T_1}$ group ($f'$) is structurally associated with short-$T_1$ hydrogen atoms ($f_H$) and a greater density of paramagnetic defects; and likewise the long-$T_1$ ($sp^2$-$sp^3$)$_{T_1'}$ group ($f''$) is structurally associated with long-$T_1$ hydrogen atoms and a smaller density of paramagnetic defects;

2) the silicon and oxygen content is homogeneously distributed throughout both $f'$ and $f''$ and does not change with annealing.

The second assumption is another way of stating that the substantive compositional differences between $f'$ and $f''$ are solely due to their respective hydrogen and defect contents. This is corroborated by in situ XPS measurements performed under high vacuum conditions (subject of a separate publication), which demonstrated that upon annealing at temperatures above 200°C the composition of a-C:H:Si:O changed very slightly (variation of [C], [O], and [Si] between 25°C and 300°C less than 2 at.%). Furthermore, the similar behavior of their respective $sp^2/sp^3$ ratios (table III and Figure 3.9) shows that their carbon structures are similar. Considering only these, the following relation can be made,

$$(SiO_x)_yCH_z = f'(SiO_x)_yCH_{z'} + (1-f') (SiO_x)_yCH_{z''}$$

where $z'$ is the number of hydrogen atoms per carbon in the $f'$ content, and $z''$ is the number of hydrogen atoms per carbon in the $f''$ content. But also, the fraction of hydrogen atoms subject to short-$T_1$ relaxation can be used ($f_H$ from Table 3.1) to separate $z'$ from $z''$ through the following identifications:

$$z_fH = f'z' \quad \text{and} \quad z(1-f_H) = (1-f')z''$$
or \[ z' = \frac{f_H}{f'} \quad \text{and} \quad z'' = \frac{(1-f_H)}{(1-f')} \] (3.5)

The number of hydrogen atoms per carbon \((z)\), thereby obtained for the two silicon oxide-doped carbon groups are compiled in Table 3.3. These results can in turn be used with Eqn. 3.3 to obtain the respective concentrations of protons in the two groups, \(N'\) and \(N''\), which are plotted with the average hydrogen concentration \(N_H\) in Figure 3.5.

This last analysis shows the difference in hydrogen content between the two coexisting silicon oxide-doped carbon groups. As mentioned earlier, the first two sets of data points are adversely affected by the additional long-\(T_1\) fraction \((1 - f_H)\) from protons in spectator water molecules, and as a result \(N'\) and \(N''\) for the as-prepared and 50\(^\circ\)C data are lower and higher, respectively, than their projected values. The proposed structure does not consider the ambient water content, therefore after annealing at 100\(^\circ\)C a more reliable picture of the intrinsic hydrogen concentration emerges: a very high hydrogen concentration of around \(3\times10^{22}\) g\(^{-1}\) assigned to the \(f'\) content, and correspondingly, the \(f''\) content has a value below \(0.3\times10^{22}\) g\(^{-1}\). Under these considerations, the analysis indicates that the as-prepared material must have at least 90\% of its intrinsic hydrogen content bound within about 45\% of the silicon oxide-doped carbon matrix (i.e. the defect-laden silicon oxide-doped \(f'\) content).

While \(N_S\) and \(N_H\) generally decrease with annealing, it seems the two quantities are fairly independent. As pointed out earlier, each display a different behavior at the higher annealing temperatures, i.e., the rate of hydrogen loss appears to abate somewhat, whereas the defect content continues to fall. Nevertheless, it is interesting that the bulk of the hydrogen content is found within the same proximity of the defect clusters. This reflects on the manner in which the \(f'\) and \(f''\) contents are dispersed (see Figure 3.13). The \(f''\) contents comprises those parts of the
film where a much lower concentration of paramagnetic broken bond defects resides. This picture seems favored in consideration of the starkly separated components in the proton $T_2$ relaxation profiles, which imply highly segregated relaxation domains within the material. On the other hand, the $N_H$ value for the as-prepared material (based on HFS measurements of the film’s hydrogen content) is larger than the bulk NMR value, but is not as large as expected in consideration of the projected $N'$ value. Therefore, this scenario for the silicon oxide-doped $f'$ and $f''$ contents is probably more nuanced than that implied by the relaxation data.

![Illustration for the 20°C – 300°C ($f' \rightarrow f''$) structural evolution of a-C:H:Si:O](image)

**Legend:** C = ●, Si = ○, H = °, O = ○, and defect sites are indicated with dots.

### 3.4 Conclusion and summary

The a-C:H:Si:O silicon oxide-carbon network exhibits long-range structural disorder, and is understood in terms of its basic $sp^2:sp^3 \sim 65:35$ carbon constituents interspersed randomly with SiC$_{4-x}$O$_x$ entities (most populated by $x = 0$ and 1). The silicon oxide-carbon network, in a
structural sense, is viewed here as a stage for defect and hydrogen distributions. The relaxation data indicate two distinct networks ($f'$ and $f''$), as defined solely by their defect and hydrogen distributions. It follows for the as-prepared material that a significantly large amount of protons and dangling bond defects are concentrated to within about 45% of the a-C:Si:O matrix. The remaining 55% of the material has the same $sp^2:sp^3$ carbon content, is not graphitic, and has a significantly lower concentration of hydrogen and defects.

Upon thermal treatment, the structure evolves towards a more thermodynamically favorable state. The first step (with the lowest activation energy) involves hydrogen effusion and emission. Associated with this structural reorganization is a moderate level of defect reduction. This is not highly evident in the $sp^2$ and $sp^3$ singular specie trends, but is nicely summarized within the $f'$ and $f''$ data of Figure 3.8. The second step occurs during higher temperature annealing (150°C to 300°C), where hydrogen emission appears to lessen, as most of the more volatile atoms have left the material, and a marked increase in $sp^2$ content occurs, as well as a greater rate of defect annihilation. Although carbon $sp^3 \rightarrow sp^2$ conversion is known to occur at higher annealing temperatures (where the activation energy requirements are more likely met), the increased $sp^2$ signal will also include contributions from $sp^2$ entities formed as a result of defect passivation during annealing, e.g., $defect-sp^2 + H-sp^2 \rightarrow H^+ + sp^2-sp^2$. Carbon $defect-sp^2$ belong to a population of species that are very close to or are directly involved with paramagnetic defects, and as defects disappear the resonances of these nearby $^{13}$C nuclei become increasingly observable. The implication here is that these NMR results may provide at least qualitative information regarding lower energy conversion of defect carbon states to $sp^2$.

Even though no evidence for significant clustering and ordering of $sp^2$-bonded carbon appears in this work, as this has been reported for a-C:H materials at higher annealing
temperatures [13], XPS and NEXAFS data acquired while annealing a-C:H:Si:O under vacuum conditions, which will be the subject of a separate publication, indicate that two structural changes occur at elevated temperatures, namely clustering and ordering of $sp^2$ carbon and transformation of $sp^3$- to $sp^2$-hybridized carbon (through the scission of C-H, C-Si, and C-C bonds). While the present study provides clear evidence of the thermally-activated processes taking place in a-C:H:Si:O at low temperatures, additional experimental work at higher temperatures should be performed to elucidate other thermally-activated processes occurring in the bulk of this material, while enabling the comparison of NMR/EPR results with the outcomes of surface-sensitive analytical techniques (e.g., XPS and NEXAFS spectroscopy).

Bibliography


66. Abragam.

67. Noack.


Chapter 4. Diffusion and Natural abundance $^{17}$O NMR studies of glyme-based electrolyte


4.1 Introduction

The rechargeable lithium-air ($O_2$), lithium-ion, lithium-sulfur batteries are receiving a great deal of interest in battery domain. Since they were first described, a number of aspects of those batteries have been investigated. The electrolyte is recognized as one of the greatest challenges in rechargeable, nonaqueous battery technology with high specific energy [1]. Good capacity retention over long cycle life requires stable electrolyte solvents that are not consumed during the charge-discharge process [2]. The identification of solvents having long-term stability in the operating environment of the Li-air, Li-sulfur and Li-ion battery remains an elusive challenge [3]. To data, the typical electrolytes used in present lithium ion battery are composed of a mixture of organic carbonates, such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), etc, containing a suitable lithium salt [4]. However, there is very strong evidence that organic carbonate solvents react with the discharge components of Lithium battery to form decomposition products [5, 6]. This phenomenon leads to a great limitation in the lithium battery application. It is very important to investigate other suitable electrolyte solvents to replace organic carbonate.

Recently, studies of Freunberger [1] et, al. and McCloskey et, al. [7] have shown glymes are attractive substitutes for organic carbonate. Glyme-based electrolytes, with structure formulation $\text{CH}_3(\text{-OCH}_2\text{CH}_2\text{)}_n\text{OCH}_3$, are particularly promising as alternative solvents of aprotic electrolytes
to be used in the lithium battery due to their low cost and higher safety behavior [8]. An ideal solvent for Lithium battery should have the following capabilities: capable of operating with a lithium metal or graphite anode and lithium transition metal oxide cathode, stable to oxidation potentials in excess of 4.5 V verses Li/Li⁺, safe, of low cost, low volatility and relatively low viscosity. Glymes are one of few solvents that combine those behaviors. Moreover, their other properties, such as high solvation ability for salt dissociation, as well as high electron donation ability and relatively strong Lewis basicity due to the lone pair of oxygen atoms in their structures [9-12], greatly promote the research interests in glyme-based electrolytes. Our collaborators, Prof. Jusef Hassoum group, have investigated the thermal properties, ion conductivity, and lithium interface stability of the glyme-based electrolytes [13-15]. Since the mobility and interaction behavior between solvent molecule and cations, as well as ion dissociation degree play an important role in determining the cell performance and stability, a detailed study on these properties are necessary for designing a suitable electrolyte for lithium battery.

The glyme-lithium solvate behavior has been studied by using various characterization methods, like differential scanning calorimetry (DSC) [16, 17], X-ray diffraction [18, 19], Raman and infra-red spectroscopy [20]. Highly concentrated glyme-lithium salt solutions easily crystalize at room temperature[16] and form four, five or more coordinate Li⁺ cations by multiple anions and oxygens on ether chains[16-19, 21]. Huang and Frech [20] studied the dependence of ionic association on chain length in glyme-lithium triflate complexes. Their results indicate that the ‘free’ anion concentration increases in glyme solvent from 1, 2-dimethoxyethane (DME) to diethylene glycol dimethyl ether (DEGDME) and then remains constant until chain length reaches that of Tetraethylene glycol dimethyl ether (TEGDME). In
addition, the concentration of ion pairs in glymes increases while the concentration of larger aggregates decreases with the chain length.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful quantitative technique that has been used to characterize cation-solvent coordination and complex formulation of glyme-based electrolytes and carbonate electrolytes. $^{13}$C NMR were performed to elucidate the preferential solvation to Li$^+$ ions in three binary mixed organic solvent system and used the order of normalized coordination shift to represent the coordinating ability of each solvent [22]. Plewa-Marczewska [23] evaluated the formation of ion pairs of XCF$_3$SO$_3$ (X=Li$^+$, Na$^+$, K$^+$, N(n-Bu)$_4^+$ in low molecular weight glymes, including DME, DEGDME and triethylene glycol dimethyl ether (TREGDME), and found a significant dependence on the chain length by using $^{19}$F, $^{11}$B and $^7$Li NMR characterization.

$^{17}$O NMR characterization is very useful to study Li$^+$ ion solvation behavior since the lone pair of oxygen in electrolyte solvents, like carbonates or glymes, is directly responsible for coordinating with cations [21, 24]. Oxygen-17 is a quadrupolar nucleus with a spin of 5/2, which yields broad signals with the associated technical challenge of observing high resolution NMR spectra. Moreover, oxygen-17 has very low natural abundance of 0.038%. Most of previous $^{17}$O NMR investigations in the literature used enriched oxygen-17 sample in order to increase the signal/noise ratio, which is also not very practical since this enrichment tends to be costly. These challenges obstruct the application of oxygen-17 NMR studies on lithium solvation behavior resulting in few publications on oxygen-17 NMR characterization on lithium battery materials. Recently, natural abundance $^{17}$O NMR studies have attracted some attention in battery field and have been performed in some carbonate electrolytes. Bogle, et.al introduced natural abundance oxygen-17 characterization for the first time in EC/DMC binary solvents system, in which Li$^+$
ions were found to adopt preferential coordination with the carbonyl group of EC, although DMC still remains in or near the primary solvation shell [25]. The work of Deng using $^{17}$O NMR technique [26] indicates that the first solvation shell of Li$^+$ ion is composed of four oxygen atoms donated by solvent molecules of EC, PC, EMC and TFSI anions.

The first part of this work reports the self-diffusion coefficient of cation, anion and solvent molecules by performing $^7$Li, $^{19}$F and $^1$H NMR diffusion measurements on a series of glyme-based electrolytes with various ether chain length, beginning from the monomeric units DME, to Polyethylene glycol 500 dimethyl ether (PEG500, MW500) containing Lithium-Trifluoromethanesulfonate (LiTf); and the second part is a natural abundance oxygen-17 NMR study to probe the lithium ion solvation behavior of electrolytes based on a series of glyme solvents containing LiTf or Lithium-Bis(trifluoromethane)sulfonimide (LiTFSI). LiTf and LiTFSI are two widely studied salts used in lithium battery electrolytes due to their high dissociation constants in low dielectric media, as well as high solubility in nonaqueous solvents, resistance to oxidation, thermally stability, and insensitivity to ambient moisture [17, 27]. Although anions of these two salts have some similar properties, for example, they are both stabilized by strongly electron withdrawing groups-perfluorinated alkyls and the conjugated structures, and the formal negative charge in them are delocalized; compared with LiTf, the conductivity of LiTFSI is an order of magnitude higher [28, 29]. To better understand the behavior of these two different salts in glyme-based electrolytes, NMR techniques were performed to characterize the chemical shift and linewidth of oxygen-17 nucleus in both salt and solvents in the solutions.
4.2 Experimental

4.2.1 Preparation of glyme-based electrolytes

All reagents were purchased from Sigma Aldrich. Electrolyte solutions were prepared by dissolving 1 mol of LiTf or LiTFSI in 1 kg of solvents. The six solvents are DME, DEGDME, TREGDME, TEGDME, Polyethylene glycol 250 dimethyl ether (PEG250, MW250) and PEG500. Six neat solvents without salts as standards were also set aside for comparison. All solvents were dried under molecular sieves (5Å) for several days until the water content was under 10 ppm.

4.2.2 Characterization

4.2.2.1 Self-diffusion coefficient measurements

D$_2$O was used for shimming and field correction in diffusion measurements. It was placed in a 4 mm borosilicate tube which was inserted in a 5 mm NMR borosilicate tube containing the sample. All sample handling procedures were performed in an Ar-filled glovebox, and inserts and outer tubes were all sealed under Ar. The diffusion measurements were performed on LiTf series (DME, DEGDME, TEGDME, PEG250 and PEG500) acquired on a 400 SB Bruker Avance III spectrometer with a broadband probe. Measurements were performed on the LiTf series in DEGDME, TEGDME, PEG250 and PEG500 from 20°C to 70°C, while the DME were measured from 20°C to 60°C because of its lower boiling point. Self-diffusion coefficient $D$, was determined by fitting data according to Stejskal-Tanner equation 2.50.

Because of the relatively low viscosity of some samples, self-diffusion coefficient measurements were performed using double-stimulated-echo (DSTE) sequence which suppresses convection artifacts [30]. $^1$H NMR was used to measure the diffusion of the solvent, $^7$Li
measurements for diffusion of the cation and $^{19}$F measurements for diffusion of the anion. Table 4.1 listed resumed the parameters of diffusion coefficient measurements on each nuclei.

**Table 4.1 Parameters used in diffusion experiments**

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</table>

4.2.2.2 Natural abundance $^{17}$O NMR characterization

For $^{17}$O NMR characterization, the chemical shift reference dimethyl carbonate (DMC) was placed in a 4 mm borosilicate tube which was inserted into a 5 mm NMR borosilicate tube containing the electrolyte solution or neat solvent. This coaxial arrangement offers a reference spectrum while preventing contact between the reference and the sample. The $^{17}$O chemical shifts are expressed with respect to $^{17}$O in water (0 ppm), using DMC as a secondary reference (two resonances: 239.4 ppm for the carbonyl O, 90.5 ppm for the methoxy O). All sample handling procedures were performed in an Ar-filled glovebox, and inserts and outer tubes were all sealed under Ar. The $^{17}$O NMR experiments were acquired on a 400 SB Bruker Avance III spectrometer with a broadband probe working at $^{17}$O frequency of 54.25 MHz. All experiments were performed at 60°C in order to improve spectra resolution and each spectrum was averaged between 32k to 128k scans for good Signal/Noise ratio. However, we expect similar behavior at
room temperature based on conductivity measurements of glyme-based electrolytes reported elsewhere [13].

The average number of -(OCH\(_2\)CH\(_2\))- units (n) in PEG250 (M.W. 250 g/mol) and PEG500 (M.W. 500 g/mol) molecule, with formula CH\(_3\)(CH\(_2\)CH\(_2\)O\(_n\))OCH\(_3\), has been estimated as n \( \approx \) 4.6 and 10.3, respectively, by using Eq. 4.1:

\[
(2 + 2n) \times 12.011 \text{ g mol}^{-1} + (6 + 4n) \times 1.008 \text{ g mol}^{-1} + (n + 1) \times 15.999 \text{ g mol}^{-1} = M_{\text{ave}} \quad (4.1)
\]

Where \( M_{\text{ave}} \) is the average of molecular weight of PEG250 or PEG500.

\( (N(O)) \) to Li\(^+\)(\( N(\text{Li}^+) \)) molecular ratio in chain of solvent for both LiTf and LiTFSI electrolyte series has been calculated by using Eq.4.2:

\[
\frac{N(O)}{N(\text{Li}^+)} = \frac{1000 \text{ g} \times N(O)}{M_{\text{ave}} \times n_{\text{Li}^+}} \quad (4.2)
\]

Where the salt concentration is 1 mol/kg; \( n_{\text{Li}^+} \) is 1 mol; \( m_{\text{elec}} \) is 1 kg, and \( N(O) \) is n+1. \( N(\text{Oxygen in R-O-R'}) \) always equal to \( N(O) \)-2.

**4.3 Results and discussion**

**4.3.1 Diffusion results**

Diffusion measurements were used to carry out the mobility of species in the electrolytes. The signal intensity of NMR spectra with increasing gradient strength was plotted VS gradient strength as Figure 4.1.
Figure 4.1 $^1$H diffusion of LiTf in TEGDME.

Figure 4.2 Self-diffusion coefficient data of $^1$H, $^7$Li and $^{19}$F in all LiTf electrolytes.
Figure 4.2 presents self-diffusion coefficient data for solvent, Li$^+$ and F$^-$ respectively obtained by NMR measurement. These figures show the expected increase of the diffusion coefficient of various species in all electrolytes by increasing the temperature. By comparing the Li$^+$ diffusion data with other species in each electrolyte, Li$^+$, which is the smallest particle in the solution, is showing the lowest values of diffusion coefficient due to a high solvation degree in view of its high charge density.

The electrolyte conductivity ($\sigma$) is given by the Nernst-Einstein equation:

$$\sigma = \frac{[C]F^2}{RT}(D_{cation} + D_{anion})$$  \hspace{1cm} (4.3)

Where $F$ is the Faraday constant (96485 Coulomb);

$[C]$ is the concentration of electrolyte (mol cm$^{-3}$);

$R$ is the ideal-gas constant (9.314472 J K$^{-1}$ mol$^{-1}$);

$T$ is the temperature;

and $D_{cation}$ and $D_{anion}$ are the diffusion coefficient of the cation Li$^+$ and anion, Tf$^-$ respectively.
Figure 4.3 Conductivity data of selected LiTf electrolytes with respect to the temperature ((a) Directly Measured by our collaborators; (b) Predicted from the Nernst-Einstein equation with diffusion values.

Figure 4.3 shows the conductivity of the selected electrolytes with respect to the temperature, evidencing conductivity values suitable for application in lithium battery for all samples in the studied temperature range. Figure 4.3(a) displays the conductivity data measured by our collaborators, while the Figure 4.3(b) shows the predicted data calculated from using Nernst-Einstein equation using diffusion coefficient data. At room temperature, the measured conductivity data decrease from about 2*10^{-3} S cm^{-1} for DME and DEGDME to 7*10^{-4} S cm^{-1} for PEG500, while the predicted data decreases from about 6*10^{-2} S cm^{-1} to 6*10^{-4} S cm^{-1} as the glyme chain length increases. The reason for this big disagreement between the measured data and predicted data is due to ion association in these electrolytes. As is known, diffusion NMR overestimates the conductivity since this technique records the motion of all species containing the nuclear spin being observed, including charged ions and neutral ion pairs. The much higher predicted conductivity data compared to measured data indicates the high ion association in these electrolytes.
Ion transference number is the fraction of the total current carried in an electrolyte by a given ion. Differences in transference number arise from differences in charge carrier mobility. Lithium transference number has a key role in allowing the optimized behavior of the electrolyte in Li-based cell. This important parameter has been determined the self-diffusion coefficient as determined by NMR. Transference numbers describe directly the charge transport and accordingly the current transport of a specific ion. The cation transference number \( t^+ \), corresponding to the fraction of current carried out by the lithium ions, was calculated by using equation (4.4).

\[
t^+ = \frac{D_{Li^+}}{D_{Li^+} + D_{TFSI^-}} \tag{4.4}
\]

Ion transference number of LiTf series glyme-based electrolytes is reported in Figure 4.4. The figure shows a decrease of cation transference number as the glyme chain length increases. This decrease may due to the expected kinetic limits hindering the solvated-ions mobility by increasing the glyme-chain length \([31]\). It should be noted that \( t^+ \) may have limited meaning in electrolytes with such a high degree of ion association. The fact that the \( t^+ \) values are close to 0.5 suggests that a significant fraction of ions move as ion pairs.
**Figure 4.4** The comparison of Li\(^+\) transference number determined NMR at room T.

The self-diffusion activation energy can be estimated by plotting the \(-\ln D\) versus \(1/RT\):

\[
D = D_0 \exp\left(-\frac{E_a}{RT}\right)
\]

\[(4.5)\]

With

- \(D_0\) temperature-independent preexponential (m\(^2\)/s);
- \(E_a\) the activation energy (J mol\(^{-1}\));
- \(R\) the gas constant (8.3145 J mol\(^{-1}\) K\(^{-1}\));
- \(T\) the absolute temperature (K).

The activation energy is the slope of the linear fit.

Figure 4.5 shows the Arrhenius plot for the solvent \(^1\)H NMR data in the DME-based electrolyte. The good linear fit confirms the Arrhenius-like behavior of the diffusion process in this temperature range (20 to 60°C). The data plotted in Figure 4.6 were obtained by fitting as Figure 4.5.
Figure 4.5 Arrhenius plot of solvent diffusion ($^1$H NMR data) in DME-based electrolyte

Figure 4.6(a-c) shows the activation energy of cation, anion and solvent in selected electrolytes respectively. The $^7$Li (Figure 4.6b) and $^{19}$F (Figure 4.6c) self-diffusion activation energy are ascribed to the LiCF$_3$SO$_3$ salt ions moving with the selected solvent, while the $^1$H self-diffusion activation energy is associated to the ether-chain motion. Interestingly, for every Glyme solvent, all species show very similar $E_a$. The activation energy of every species increases with the solvent molecular chain length (and probably its viscosity). Lower activation energy is associated with more facile ionic motion in electrolytes, which also unfortunately implies the shorter chain ethers allow an easier pathway for polysulfide migration from the cathode to anode, and consequent direct reaction.
Figure 4.6 Activation energy of various species in selected LiTf electrolytes.

4.3.2 $^{17}$O NMR results

Diffusion NMR measurements provide information on the mobility of cation, anion and solvent within different glyme-based electrolytes. These results clearly evidence the influence of the solvent chain length on the species mobility. However, the diffusion NMR technique doesn’t provide sufficient information for describing how species interact with each other in solutions and how these interactions vary as the glyme chain length changes. $^{17}$O NMR is an ideal probe for characterizing the cation solvation behavior thanks to the direct interaction between the lone pair of oxygen in the solvent and the cation. In this study, we performed $^{17}$O NMR experiments on two series of glymes-based electrolytes with different salts to investigate the lithium solvation and ionic association behavior.
Figure 4.7 shows the $^{17}$O NMR spectra of 1.0 m LiTf solution and 1.0 m LiTFSI solution in DME, along with the corresponding neat DME solvent in the absence of lithium salt. The DMC reference shows two $^{17}$O resonances located at 239.4 ppm (carbonyl $^{17}$O, a$_1$) and 90.5 ppm (methoxy $^{17}$O, a$_2$) respectively, i.e., in convenient positions not overlapping the resonances of Tf$^-$, TFSI$^-$ and glyme solvents. The addition of LiTf salt and LiTFSI salt leads to further $^{17}$O resonances observed at around 156.3 ppm and 160 ppm, respectively, in the DME solutions. Methoxy $^{17}$O resonances of DME experience an upfield shift by adding the LiTf and LiTFSI salts, as will be discussed later. It is noteworthy that the relative signal intensities of $^{17}$O in DMC and glyme electrolytes directly depend on the amount of sample in the NMR reference tube and insert.

![Figure 4.7 $^{17}$O NMR spectra of DME electrolytes.](image)

$^{17}$O NMR experiments were performed on LiTf and LiTFSI electrolyte solutions with various glymes differing by chain length. Stacked $^{17}$O NMR spectra are displayed in Figure 4.8 (a) for LiTf series and Figure 4.8 (b) for LiTFSI series, respectively. The $^{17}$O resonances of glyme
oxygen are located between 0 ppm and -25 ppm. Besides DME, in which there is only one $^{17}$O nuclear environment, the $^{17}$O NMR spectra of longer chain glymes (DEGDME to PEG500) show two $^{17}$O resonances. The more positive resonance is the average $^{17}$O nuclear chemical shift of the oxygen located in the middle of the glyme chain, which is defined as $\text{R-}^{17}\text{O-R}'$ group, while the more negative chemical shift is associated with the terminal oxygen nucleus, i.e., $^{17}$O-CH$_3$. The linewidth of ether $^{17}$O increases from short chain glyme to long chain glyme, as indeed expected by the increase in molecular mass and hence viscosity, becoming particularly large in PEG500 electrolyte, complicating the ability to resolve the two $^{17}$O resonances. Line broadening of quadrupolar nuclei is particularly sensitive to viscosity effects. The interaction between salt and solvent is another source of glyme $^{17}$O NMR line broadening, due to the reduction of the solvent molecular mobility (again, the same phenomenon that leads to an increase of the macroscopic viscosity) [32]. The linewidth data are listed in Table 4.2.

![Figure 4.8 $^{17}$O NMR spectra of all electrolytes (a. LiTf series  b. LiTFSI series).](image)
Table 4.2 The $^{17}$O NMR Linewidth data of neat solvents and electrolytes

<table>
<thead>
<tr>
<th>Solvent name</th>
<th>Linewidth of $^{17}$O in R-O-R’ group(Hz)</th>
<th>Linewidth of $^{17}$O in O-CH$_3$ group(Hz)</th>
<th>Linewidth of $^{17}$O in LiTf (Hz)</th>
<th>Linewidth of $^{17}$O in LiTFSI (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>neat solvent</td>
<td>LiTf Elec.</td>
<td>LiTFSI Elec.</td>
<td>neat solvent</td>
</tr>
<tr>
<td>DME</td>
<td>2.1</td>
<td>3.0</td>
<td>3.2</td>
<td>4.1</td>
</tr>
<tr>
<td>DEGDME</td>
<td>4.8</td>
<td>7.4</td>
<td>7.7</td>
<td>2.9</td>
</tr>
<tr>
<td>TREGDME</td>
<td>6.8</td>
<td>11.8</td>
<td>12.1</td>
<td>3.9</td>
</tr>
<tr>
<td>TEGDME</td>
<td>8.4</td>
<td>13.9</td>
<td>17.1</td>
<td>4.6</td>
</tr>
<tr>
<td>PEG250</td>
<td>11.5</td>
<td>25.8</td>
<td>22.6</td>
<td>5.9</td>
</tr>
<tr>
<td>PEG500</td>
<td>22.6</td>
<td>45.3</td>
<td>33.9</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Figure 4.9 shows a detailed comparison of $^{17}$O resonance corresponding to the glyme oxygen of electrolytes prepared using each solvent with either LiTf or LiTFSI salts, along with that of the pure solvent, magnified in the low chemical shift region. In this expanded view, the line broadening by adding the Li salt in the glyme compared to neat solvent is clearly observed. The smallest solvent molecule (DME) and corresponding electrolytes show very clear, relatively sharp $^{17}$O resonances. Increasing the ether chain length from DEGDME to PEG500 leads to signal bordering, however neat solvents still show two distinguishable $^{17}$O resonances, even in the case of the glyme with largest molecular mass (PEG500). All $^{17}$O NMR resonance position data are listed in Table 4.3. The difference of $^{17}$O NMR chemical shift between each electrolyte and its corresponding pure solvent, plotted in Figure 4.10, may actually quantify the interaction between the solvent and the salt, that is most likely dominated by the Li$^+$ ions. However, the aforementioned broadness of $^{17}$O lines in PEG500 electrolyte solution leads to excessive uncertainty in determining its chemical shift and limits the data of Figure 4.10 to PEG250 glyme and shorter ones. The bar diagrams of Figure 4.10 reveal much larger signal shift of the R-O-R’ group compared to -O-CH$_3$ group by adding the LiTf and LiTFSI salts into the glyme solvents,
while the $^{17}$O chemical shifts of glymes exhibit a decreasing trend in both -O-CH$_3$ and R-O-R’ groups by increasing the chain length.

Figure 4.9 $^{17}$O NMR resonances of neat solvent and glymes in all electrolyte (a. solvent; b. LiTf electrolytes; c. LiTFSI electrolyte)
Table 4.3 The $^{17}$O NMR chemical shift of pure solvents and electrolytes

<table>
<thead>
<tr>
<th>Solvent name</th>
<th>Chemical shift of $^{17}$O in R-O-R’ group (Hz)</th>
<th>Chemical shift of $^{17}$O in O-CH$_3$ group (Hz)</th>
<th>Chemical shift of $^{17}$O in LiTf (Hz)</th>
<th>Chemical shift of $^{17}$O in LiTFSI (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec.</td>
<td>pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec.</td>
<td>pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec.</td>
<td>pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec. pure solvent LiTf Elec. LiTFSI Elec.</td>
</tr>
<tr>
<td>DME</td>
<td>-23.4 -24.3 -24.6 156.3 160.1</td>
<td>-23.4 -24.3 -24.6 156.3 160.1</td>
<td>-23.4 -24.3 -24.6 156.3 160.1</td>
<td>-23.4 -24.3 -24.6 156.3 160.1</td>
</tr>
<tr>
<td>DEGDME</td>
<td>-2.2 -3.6 -4.1 157.5 161.5</td>
<td>-2.2 -3.6 -4.1 157.5 161.5</td>
<td>-2.2 -3.6 -4.1 157.5 161.5</td>
<td>-2.2 -3.6 -4.1 157.5 161.5</td>
</tr>
<tr>
<td>TREGDME</td>
<td>-2.6 -3.6 -4.1 158.3 161.8</td>
<td>-2.6 -3.6 -4.1 158.3 161.8</td>
<td>-2.6 -3.6 -4.1 158.3 161.8</td>
<td>-2.6 -3.6 -4.1 158.3 161.8</td>
</tr>
<tr>
<td>TEGDME</td>
<td>-2.5 -3.3 -3.9 158.6 162.0</td>
<td>-2.5 -3.3 -3.9 158.6 162.0</td>
<td>-2.5 -3.3 -3.9 158.6 162.0</td>
<td>-2.5 -3.3 -3.9 158.6 162.0</td>
</tr>
<tr>
<td>PEG250</td>
<td>-2.7 -3.3 -3.9 159.0 162.5</td>
<td>-2.7 -3.3 -3.9 159.0 162.5</td>
<td>-2.7 -3.3 -3.9 159.0 162.5</td>
<td>-2.7 -3.3 -3.9 159.0 162.5</td>
</tr>
<tr>
<td>PEG500</td>
<td>-1.6 -1.8 0.5 159.6 162.5</td>
<td>-1.6 -1.8 0.5 159.6 162.5</td>
<td>-1.6 -1.8 0.5 159.6 162.5</td>
<td>-1.6 -1.8 0.5 159.6 162.5</td>
</tr>
</tbody>
</table>

Figure 4.10 Chemical shift difference of $^{17}$O resonance of glyme between Li salt solution and pure solvent ($\Delta \delta = \delta_{\text{electrolyte}} - \delta_{\text{solvent}}$)

Local electron density dominates the shielding of a specific nucleus. To investigate the behavior of oxygen nuclei a series of aliphatic ethers with variable chain length was studied by measuring the chemical shift of $^{17}$O nuclei and calculating the net (nuclear minus electronic) charges on the nucleus [33]. An evaluation of the atomic net charge $q_0$ of oxygen has been performed by increasing the electron-releasing ability of the substituents, thus enhancing the electron withdrawal of oxygen due to its electron enrichment [34-36]. Following the study of
Delseth and Kintzinger [37], Béraldin et al. [33] determined a linear correlation between $^{17}$O NMR chemical shift ($\delta_o$) and net charge variation ($\Delta q_o$) by performing an extensive geometry and exponent optimization for various ethers, such as dimethyl-, diethyl-, and di-isopropyl-ethers. The connection between $\Delta q_o$ and chemical shift $\delta_o$ is reported in Eq. 4.6:

$$\Delta q_o = -0.267 \Delta \delta_o \quad (4.6)$$

This result indicates that the increase in electronic charge at the oxygen atom leads to a downfield $^{17}$O NMR shift, which contradicts the commonly held view of upfield shift by electron density increase [6].

The $^{17}$O chemical shift of the glyme-based electrolytes studied herein moves upfield upon lithium salt addition, i.e., by decreasing the net charge of the oxygen due to the electron withdrawal effect of Li$^+$, thus in agreement with Eq. 4.3 [26]. Accordingly, the salt addition induces a larger chemical shift change on the downfield shifted, more polar and electron richer chain oxygen (R-O-R’) with respect to the terminal oxygen (-O-CH$_3$), since the former represents the preferred site for complexing Li$^+$ cations [25, 33]. Figure 4.10 also reveals decreasing trends of the $^{17}$O chemical shift of both in -O-CH$_3$ and in R-O-R’ group by increasing the ether chain length. Figure 4.11 reports the calculated $N_{(O)}$ to $N_{(Li^+)}$ molar ratio in the glyme-based electrolytes (see Eq.4.1), and exhibits a slightly increasing $N_{(O)}/N_{(Li^+)}$ by chain length increase. Hence, glycmes of longer chain have an increased number of oxygen atom per Li$^+$ ion, and a higher ratio of lithium ion preferential sites R-O-R’ to terminal -O-CH$_3$ sites. Consequently, the individual oxygens in R-O-R’ competing for Li$^+$ association experience a smaller change in chemical shift due to the presence of the salt in the longer glycmes. Accordingly, the increase of $N_{(O)}/N_{(Li^+)}$ ratio from DEGDME, TREGDME, TEGDME to PEG250 (Figure 4.11) changes the chemical shift of the corresponding electrolyte by -1.5, -1.0, -
0.8 and -0.6 ppm (LiTf series), and by -1.6, -1.5, -1.4 and -1.2 ppm (LiTFSI series), respectively (see Table 2). In summary, the lower ratio of lithium solvating R-O-R’ groups in the shorter chain glyme electrolyte (smaller $N(O)/N(Li^+)$ in Figure 4.11) induces a stronger shielding effect and corresponding ether chain oxygen chemical shift change. Furthermore, oxygens from both R-O-R’ and methoxy groups in LiTFSI series exhibit larger shifts than in LiTf series, as most likely ascribed to the higher dissociation degree of the LiTFSI salt. Indeed, TFSI$^-$ ions are less likely to be located in the first coordination shell of the Li$^+$ compared to Tf$^-$, thereby allowing a stronger interaction between Li$^+$ and oxygens from the glymes.

**Figure 4.11** Ratios of the number of Li$^+$ and oxygen in ether chain of selected electrolytes

The $^{17}$O chemical shifts of Tf$^-$ and TFSI$^-$ plotted as a function of glyme chain length in Figure 4.12, show a slightly increasing trend with respect to glyme chain length. This behavior can be explained by taking into account the electron density of the oxygen in the anion. Henderson et al. [16] reported that the exceptional cation solvation in the glymes, often results in poorly solvated or even naked active anions. In contrast, the NMR measurements reported in
Figure 4.12 indicate a change of anion environment from the observed downfield shift with increasing chain length. It has been reported that lithium cations preferentially interact with the SO$_3$ group rather than CF$_3$ group in LiTf containing electrolytes [38]. The positive Li$^+$ ions attract electrons from oxygen atoms in Tf$^-$ group, thereby inducing a downfield shift. Accordingly, the $^{17}$O NMR results of Figure 4.12 suggest enhanced Li-Tf association degree with chain length increase. This result is consistent with the literature data [20] suggesting ion pairs as the predominant species instead of ‘free’ ions and aggregates, and indicating an increase of ion pairs concentration with increasing the chain length in glymes with n=1~4. Similar increasing trend however to a somewhat smaller extent, except for the DME solution, is observed for the $^{17}$O chemical shift in TFSI. This weaker dependence suggests a higher dissociation degree for LiTFSI salt in glyme. It’s also possible that steric effect of the larger solvent molecules may influence the observed trends, as well as weaker but still present anion solvation effect. Perhaps variable salt concentration studies could shed additional light on this.

![Figure 4.12](image.png)

**Figure 4.12** The chemical shift of the anion in the different electrolytes
4.4 Conclusion and summary

Various glyme-based electrolytes differing by chain length as suitable electrolytes for lithium-sulfur cell have been studies by using diffusion NMR techniques. The results show that on the NMR timescale there is significant ion pairing. The conductivity of these electrolytes and their cation transference number in them decrease, and the activation energy of various species, including cation, anion and solvent increases as the glyme chain length increases.

The sensitivity of natural abundance $^{17}$O NMR technique for investigating the lithium ion solvation behavior was confirmed by comparing the chemical shift of the glyme oxygen in electrolytes with those of corresponding neat solvents. This unique method can directly observe the specific oxygen atom coordinating sites associated with the lithium ion solvation sheath, and probe the dependence of cation-solvent interaction on the glyme chain length. In general, our results suggest stronger interaction for the ether oxygens with higher electron density compared to terminal oxygens. In addition, the data indicate decreasing oxygen shielding effect on Li$^{+}$ by increasing chain length due to a more competition between the oxygen atoms for Li$^{+}$ solvation. The downfield shift of anion oxygen in the electrolytes suggests that longer chain length favors the association of cation and anion.

Bibliography


Chapter 5 Natural abundance $^{17}\text{O}$, $^{23}\text{Na}$ and Diffusion characterization of NaPF$_6$ in various carbonate binary solvents

5.1 Introduction

The development of energy storage and conversion devices has become extremely urgent in daily life because of the limitation of non-renewable fossil fuel and serious climate problems caused by carbon emissions [1]. Using renewable and cleaner energy sources, such as solar radiation, wind and waves, is essential for sustainable development of technology and human life. However, the utilization of them requires sufficient off-peak electricity storing and on-peak period releasing [2]. In another words, a powerful energy storage equipment is necessary to transfer these energy sources to efficient, stable and reliable electricity. Battery has assumed the role in transforming between chemical energy and electrical energy with high conversion efficiency. In the past few decades, Li-ion battery has been developed as a mature technology conquering the portable electronic storage market. However, as lithium resources continue to decline worldwide, the cost the of Li-ion battery for large formats such as electric vehicles is growing fast due to the concern of lithium supplies’ running out in the foreseeable future [3]. Therefore, the next generation of portable electronics will most likely be powered by something other than Li-ion batteries. Based on the similar chemical properties to lithium and high abundance of sodium-containing precursors, Na-ion battery is one potential candidate to compete and substitute Li-ion battery.

Ceder et al. [4] did some computational studies, which indicated Na-ion batteries can be competitive with Li-ion batteries in the aspect of voltage, stability and diffusion barriers of materials. Because sodium interaction chemistry is very similar to lithium, similar compounds of the widely studied positive electrode materials in Li-ion batteries can also be used in Na-ion
batteries [5]. Phosphate based materials with high thermal stability and high voltage have been reported as best candidates to be cathodic materials [6-8]. Although some anode materials, including carbon black, amorphous carbon and hard carbon, have been studied as anode materials in Na-ion battery [9-12], further studies are still needed to improve the performance of anode for making Na-ion batteries. Moreover, compared with Li-ion battery, Na-ion battery system has the advantage of using electrolyte systems with lower decomposition potential. Therefore, on the electrolytes sides, water based electrolytes can be used instead of organic ones to reduce the cost of Na-ion battery [5]. Solid polymer salt and aqueous salt solutions have been studied as possible electrolytes by many researchers. Gel polymer electrolytes possessing good mechanical properties of solids and excellent diffusion properties of liquids have been reported [13-15]. In addition, other lower cost sodium salts, such as Na$_2$SO$_4$, NaNO$_3$, NaOH, et al. could be used in aqueous electrolytes [5].

In this report, our collaborators from Army research lab prepared four binary electrolytes series using Sodium hexafluorophosphate (NaPF$_6$) salt. Several NMR characterization methods were performed on these electrolytes in our lab. Natural abundance $^{17}$O, $^{23}$Na NMR techniques were used as probes of solvent and cation respectively to characterize the ion-ion interactions and ion-solvent interactions in these electrolyte systems. Diffusion NMR measurements were also performed on all electrolytes to characterize the mobility of species in these electrolytes.

5.2 Experimental

5.2.1 Preparation of carbonate electrolytes

NaPF$_6$ was purchased from American Elements and stored in an argon-filled glovebox and used as received. Ethylene carbonate (EC), dimethyl ether (DME), ethylmethyl carbonate (EMC), propylene carbonate (PC) and fluoroethylene carbonate (FEC) were purchased from BASF. The
electrolytes were prepared by dissolving NaPF₆ in EC/DME, EC/EMC, EC/PC and EC/FEC mixtures at 1M concentration. Five different molar ratios for each binary solvent electrolyte, 100:0, 80:20, 50:50, 20:80 and 0:100 were prepared. Figure 5.1 displays the chemical structures of solvents we mentioned above.

![Chemical structures of solvents](Image)

**Figure 5.1** Chemical structures of solvents

### 5.2.2 Characterization

The NMR experiments were performed with a 400 SB Bruker Avance III spectrometer. The sample was placed in a 4 mm Teflon tube and inserted in a 5 mm NMR tube containing a deuterated lock reference.

For $^{17}$O experiments, the reference was DMSO-d₆ ($\delta = 14.89$ ppm with respect to $^{17}$O-enriched water which has $\delta = 0$ ppm). For $^{23}$Na experiments, the reference was a 1M NaCl in D₂O $\delta = 0$ ppm). The $^{17}$O and $^{23}$Na experiments were done at 60°C in order to improve the resolution (by reducing the quadrupolar broadening of $^{17}$O NMR) and for more convenient comparison with each other.

The NMR diffusion experiments for $^1$H and $^{19}$F nuclei were done using a double stimulated echo pulse sequence to suppress convection effects. Gradient strength was arrayed (32 values, linear increase, $g = 0$-45 G/cm) for each experiment. Gradient pulse duration was $\delta = 1.2$-2.5 ms and diffusion delay was $\Delta = 100$-200 ms. Since the relaxation time of $^{23}$Na is extremely short, $^{23}$Na NMR diffusion experiments were done on a 300MHz Varian Direct Drive spectrometer.
with a DOTY Z-gradient diffusion probe. Gradient strength was arrayed (32 values, linear increase, \( g = 0\text{-}1200 \text{ G/cm} \)) for each experiment. Gradient pulse duration was \( \delta = 1.5 \text{ ms} \) and diffusion delay was \( \Delta = 15 \text{ ms} \).

5.3 Results and discussion

5.3.1 \( ^{17} \text{O} \) NMR results

\( ^{17} \text{O} \) NMR characterization is a very useful method for observing the cation-solvent interaction since the lone pair of oxygen atom is responsible for coordinating with cation. Figure 5.2 shows the \( ^{17} \text{O} \) NMR spectra of EC/EMC 20/80 and EC/DME 20/80 with 1 M \( \text{NaPF}_6 \) which were accumulated for about 32k scans in a total of 3 hours for each sample. In order to observe the interaction between the salt and solvent, \( ^{17} \text{O} \) NMR were performed on each electrolyte and its corresponding salt-free solvent. Table 5.1 and Table 5.2 display the chemical shift data of electrolytes and solvents respectively, while Table 5.3 displays the chemical shift difference between electrolytes and solvents.

\[
\begin{array}{c}
\text{Figure 5.2: } ^{17} \text{O NMR spectra of EC/EMC 20/80 and EC/DME 20/80 with 1 M NaPF}_6 \\
\text{with chemical shifts at positions } 1, 2, 3, 4, 5, 6.
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Table 5.1 $^{17}\text{O}$ NMR chemical shift of electrolytes

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Table 5.3 $^{17}$O NMR chemical shift difference between electrolyte and neat solvents

\[(\Delta_{\text{ppm}}=\delta_{\text{electrolyte}}-\delta_{\text{neat solvent}})\]

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Figure 5.3 $^{17}$O NMR Chemical shift difference of four solvents

$^{17}$O NMR chemical shift difference, which is the $^{17}$O chemical shift of electrolyte subtracted from the $^{17}$O chemical shift of solvent are plotted in Figure 5.3. In EC/DME, the carbonyl oxygen of EC exhibits a large upfield shift about 4 ~ 6 ppm after adding the NaPF$_6$ salt, while the ether oxygen shows a constant downfield shift around 1 ppm, indicating the carbonyl oxygen dominates coordinate on with the cations. On the DME, the upfield shift on ether oxygen suggests there are also some interactions between DME and cations. However, these data do not provide sufficient information on solvent preference. In EC/EMC, EC/PC and EC/FEC system, in which the solvents are composed by two carbonates, $^{17}$O data of these three systems still indicate it’s the carbonyl oxygen, not ether oxygen that most strongly interacts with cations. In
EC/EMC system, the carbonyl oxygen of EC has a downfield shift as the EC content increases. That’s because the carbonyl oxygen has a stronger upfield shift at low EC content when all EC molecules are in the primary solvation shell of the cation. When the EC content increases, the cation solvation is saturated and EC molecules don’t coordinate with cation. So the measured average $^{17}$O NMR chemical shift moves to downfield as the EC content increases. This phenomenon provides strong evidence that the cation prefers coordinating with EC. Carbonyl $^{17}$O NMR chemical shift of EC and PC are almost same in this system because of their similar chemical structures, which means EC and PC are roughly equally likely to be in the solvation shell. There is an interesting phenomenon in that the ether oxygen 1 (labeled as Figure 5.1) of PC exhibits a downfield shift at low EC content and an upfield shift at high EC content. The reason for this can’t be explained by NMR results, so more data obtained from other characterization methods, such as electrospray ionization mass spectroscopy (ESI-MS) and Molecular dynamic simulation (MD) from our collaborators are needed. In EC/FEC system, FEC contains a strong electron withdrawing group, which dramatically reduces the electron density of carbonyl oxygen. In this case, the chemical shift change of carbonyl oxygen of FEC is smaller than EC because less electron density is available to the cation.

5.3.2 $^{23}$Na NMR results

$^{23}$Na NMR chemical shift of NaPF$_6$ solutions referenced to the shift value of 100% EC solvent are plotted in Figure 5.4. The $^{23}$Na data provides independence evidence EC and PC compete approximately equally for the cation solvation because $^{23}$Na chemical shift doesn’t change much in this system. In EC/DME system, $^{23}$Na has a downfield shift as the EC content decreases. This highly unusual behavior may be caused by different behavior of methoxy oxygens in the mixed solvent. In contrast to EC/DME system, EC/EMC and EC/FEC exhibit a
$^{23}$Na downfield shift as the EC content increases, which probably due to the solvation preference over EMC or FEC in these systems or stronger dissociation effect in higher EC content. However, the diffusion data doesn’t support the latter.

**Figure 5.4** Normalized $^{23}$Na NMR Chemical shift of NaPF₆ solutions reference to the shift value at 1M NaPF₆ in 100% EC solution
Table 5.4 $^{23}$Na NMR chemical shift

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<td>-9.9</td>
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5.3.3 Diffusion NMR

$^1$H, $^{23}$Na and $^{19}$F diffusion NMR experiments were performed to characterize the mobility of solvent, cation and anion respectively and to shed additional light on the chemical shift results. In most cases, $^1$H diffusion NMR is sufficient to characterize the mobility of both organic solvents in each binary system since the resonance of each solvent is well separated. However, as shown in Figure 5.5, some resonances of FEC overlap with EC, which yields to uncertainty in diffusion coefficient data obtained from $^1$H NMR diffusion measurements. In this particularly case, the diffusion coefficient of FEC has been measured by performing $^{19}$F NMR diffusion measurements on the solvents. All diffusion data are listed in Table 5.5. In order to eliminate the effect of viscosity as a variable (which will depend on salt content in addition to the solvent ratio), F and Na mobility is expressed here as the ratio between their respective diffusion
coefficient and the one of solvent 2 (Solvent 1 is EC, Solvent 2 is DME/EMC/PC/FEC). In EC/FEC electrolyte, the diffusion coefficient of solvent 2 is determined from the $^{19}$F diffusion behavior of FEC.

**Figure 5.5** $^1$H NMR spectra of 1M NaPF$_6$ in EC/FEC 80/20 electrolyte
Table 5.5 Diffusion data for NaPF$_6$ electrolytes at 60°C

<table>
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<th>Solvent ratio</th>
<th>D Solvent 1 (EC) (m$^2$/s)</th>
<th>D Solvent 2 (m$^2$/s)</th>
<th>D* Solvent 2 (m$^2$/s)</th>
<th>D Na (m$^2$/s)</th>
<th>D F (m$^2$/s)</th>
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</table>

*Solvent diffusion data measured by $^{19}$F NMR.
Figure 5.6 The relative mobility of Na and PF$_6^-$ in NaPF$_6$ electrolytes

Figure 5.6 displays the relative mobility of Na and F in four NaPF$_6$ electrolytes series, which provides some very interesting information. As shown in upper left of Figure 5.6, the Na diffusion data and F diffusion data decrease as the EC content decrease, that’s probably due to stronger ionic interactions in higher EMC content solvent. In EC/EMC system, F diffusion is slightly higher than Na diffusion and the two converge as the EC content decreases, which indicate the EMC solvent favors ion association. EC/PC system exhibits opposite behavior as EC/EMC in that the F data slightly diverge as the EC content decreases. It’s probably due to a lower ion association degree in higher PC content solvent. Na and F show a roughly constant
relative mobility in EC/FEC system in the low EC content solvent, which suggests a high degree of ion association.

5.4 Conclusions

A sensitive probe, $^{17}$O NMR, has been used to investigate the sodium ion solvation behavior in four binary carbonate electrolytes systems by measuring the chemical shift of oxygen in electrolytes. This technique demonstrates that carbonyl oxygen is primarily responsible for coordinating with cations rather than ether oxygen. By combining $^{23}$Na NMR and diffusion data with the $^{17}$O results, solvation preference on binary solvent electrolytes EMC, for example, $^{17}$O, $^{23}$Na and diffusion NMR data all show that EC and PC exhibit roughly equal solvation tendencies. To complete this project, we await more information from the MS and modeling results from our colleagues.

Bibliography


Chapter 6 Solvent effects on BF$_4^-$ and PF$_6^-$ anions in carbonate electrolytes

6.1 Introduction

Lithium ion batteries (LIBs) are in ever-increasing demand for their wide application in portable electronic devices area such as cell phones, notebook computers and Plug-in Hybrid Electric Vehicles (PHEV), *et al.* Ethylene carbonate (EC), dimethyl carbonate (DMC), methyl carbonate (EMC), dimethoxyethane (DME) and diethyl carbonate (DEC) and their binary mixtures are some popular solvents for LIBs electrolytes [1]. Lithium hexafluorophosphate (LiPF$_6$) was proposed as an electrolyte salt in the 1960s. It stood out above numerous electrolytes salts and was eventually commercialized. At present, LiPF$_6$ dissolved in carbonate mixtures, including cyclic carbonate, EC or PC, and linear carbonates, DMC, DEC or EMC, are the most widely used electrolytes for LIBs taking advantage of their high electrolytic conductivities, and good electrochemical stability [2]. Despite this, LiPF$_6$ still presents restrictions in applications because of its comparably high moisture sensitivity and low thermal instability. Compared with LiPF$_6$, a great interest in Lithium tetrafluoroborate (LiBF$_4$) has returned because it is relatively safe [3], less moisture-sensitive and more thermally stable at low temperature as an electrolyte salt for LIBs [2]. However, the small dissociation constant and the low ion conductivity of LiBF$_4$ are obstacles to their application in LIBs [4-6]. Achieving ideal Li-based electrolytes requires a better understanding of the fundamental aspects of ion dissociation and transport. Recently, the nature of Li$^+$-solvent interaction have been reported for LiPF$_6$ EC/DMC system using $^{17}$O NMR technique [7]. Ding’s studies concluded that cation-solvent interactions play a dominant role in determining the charge transport ability, but solvent effects on the anion influences the formation of cation-anion aggregates [1, 8, 9]. Therefore, the investigation of solvent effects on anions is important since the association, solvation and other processes determine the formation and states
of aggregates in the electrolytes, thereby influences the charge transfer ability and working mechanism of each battery component [10]. Some previous publications focused on studying the solvation behavior of cations in LiPF₆ electrolyte through chemical shift and diffusion analysis [7, 11]. Systematic studies on temperature dependence of self-diffusion coefficients of cations, anions and solvents have been reported for LiBF₄ and LiPF₆ salts in EC, PC, and DEC single solutions and EC/DEC binary solution system [12, 13]. To argument the anion solvation studies on LIBs electrolytes, in this work we present some NMR spectra and diffusion measurements on LiBF₄ and LiPF₆ EC/DMC electrolytes in an effort to better understand the ion dissociation and solvent interaction between particles in these electrolytes systems.

6.2 Experimental

6.2.1 Preparation of electrolyte

LiBF₄ (Ferro) and LiPF₆ (Morita Chemical Industries) were stored in an argon-filled glovebox (Vacuum Atmospheres Nexus One, < 1 ppm O₂, < 1 ppm H₂O). EC (BASF) and DMC (BASF) were dried over 3 Å molecular sieves and then stored in the argon-filled glovebox until needed. LiBF₄ and LiPF₆ were dissolved in EC and DMC binary mixture with mole ratio of 80/20, 50/50, 20/80 and 0/100. The LiBF₄ was prepared in two concentrations of 0.01 M and 1 M and the concentration of LiPF₆ varied from 0.01 M, 0.05 M, 0.5 M, 1.0 M to 1.2 M. Preparations were completed in a glove box under argon atmosphere.

6.2.2 NMR Characterization

The NMR experiments were done with a 400 SB Bruker Avance III spectrometer (9.4 T). The samples were sealed in NMR tubes in the glovebox in order to prevent moisture absorption and air exposure. To avoid any interaction between the electrolyte sample and the borosilicate glass made NMR tube and/or reference solution, each sample was placed in a 4 mm Teflon tube
and inserted in a 5 mm NMR tube containing a chemical shift reference in deuterated solvent. This set-up allows an optimal chemical shift referencing and an optimal adjustment of magnetic field homogeneity (i.e. shimming) using a $^2$D lock signal for each sample. The external reference solutions (set to 0 ppm) were CFCl$_3$ in CDCl$_3$ for $^{19}$F experiments and boric acid in D$_2$O for $^{11}$B experiments. All spectra were collected using direct pulse sequence, while spin-lattice relaxation times ($T_1$) and spin-spin relaxation times ($T_2$) of $^{11}$B were collected by using inversion recovery pulse sequence and Carr-Purcell-Meiboom-Gill (CPMG) sequence respectively.

The diffusion NMR experiments were done with the same spectrometer using a double-stimulated-echo sequence which suppresses convection artifacts [14] at 25°C. Gradient pulses, of rectangular shape with duration of gradient pulse $\delta = 1.2-4$ ms and gradient strength $g = 0$-45 G/cm, were applied with a separation of $\Delta=150$-400 ms. In present case, all measurements were performed by keeping the delays constant and varying the gradient strength. The diffusion coefficient $D$ is measured as the only fitting parameter by plotting the signal intensity $I$ using the Stejskal-Tanner equation [15, 16]. The diffusion of the EC and DMC molecules, cation and anion were measured using $^1$H, $^7$Li and $^{19}$F NMR operating at (400, 155.5 and 376.5) MHz respectively.

6.3 Results and discussion

6.3.1 BF$_4^-$ analysis

Boron has two naturally occurring NMR active isotope $^{10}$B (19.9% Natural abundance) with spin of 3 and $^{11}$B (80.1% Natural abundance) with spin of 3/2. The typical $^{19}$F NMR spectrum of BF$_4^-$ consists of two components representing fluorine nuclei bounding with $^{10}$B and $^{11}$B with relative signal intensity corresponding to the natural abundance of the isotopes. Figure 6.1 displays several selected $^{19}$F NMR spectrum of LiBF$_4$ in EC/DMC electrolytes. As is shown, the
resonance of $^{11}$B-bound F is located at lower chemical shift than $^{10}$B-bound F due to the difference in mass between the two isotopes.

**Figure 6.1** (a) Selected $^{19}$F NMR spectrum of LiBF$_4$ in EC/DMC electrolytes; (b) $^{19}$F NMR chemical shift of 0.01M and 1M LiBF$_4$ in EC/DMC electrolytes

Due to the $J$ coupling between the $^{19}$F and two boron nuclei, two resonances of BF$_4^-$ should be a septet for the $^{10}$B bound $^{19}$F and a quartet for the $^{11}$B bound $^{19}$F respectively. The $J$ coupling values are related to the gyromagnetic ratios of $^{11}$B and $^{10}$B ($J_{11B-^{19}F}/J_{10B-^{19}F} = 2.98$). However, since two isotopes of boron with spins greater than $\frac{1}{2}$ have quadrupolar moments which couple strongly with electric field gradient fluctuations, relaxation of the boron nucleus occurs and the line shapes of $^{19}$F resonances are strongly affected resulting in collapse of the $^{19}$F multiplets as shown in Figure 6.1(a). The chemical shift data of $^{19}$F NMR of LiBF$_4$ solutions are plotted in Figure 1 (b). The LiBF$_4$ in EC/DMC shows a chemical shift range of about 1.2 ppm for 0.01 M electrolyte and 0.9 ppm for 1 M electrolyte with the increasing content of DMC. The upfield shift with increasing DMC content of $^{19}$F chemical shift is caused by the solvent effect induced by the change of solvent dielectric constant (i.e. with decreasing EC/DMC ratio).
phenomenon is in agreement with the studies of Plakhotnyk et al. [17, 18], which confirmed that \(^{19}\text{F}\) chemical shift of BF\(_4^-\) in various solvents moves upfield as the solution dielectric constant decreases. The concentration dependence, with the \(^{19}\text{F}\) showing upfield shift about 1.3-1.7 ppm as the salt concentration increases from 0.01 M to 1 M for each specific solvent ratio, is induced by the interactions among electrolyte components which changes the electrical environment of fluorine nuclei [10, 17, 19-21]. Moreover, in the low polarity solvent system, the interparticle interaction not only includes the cation-anion aggregation, but also involves other particles, such as oligomeric ions, higher aggregates and solvent molecules [10].

A detailed \(^{19}\text{F}\) multiplet resonance can only be seen when there is no electric field gradient on the boron nucleus in which case the quadrupolar interaction between the boron nuclear electric quadrupolar moment and the local electrostatic field gradient is absent. Theoretically, in a solution with LiBF\(_4\) completely dissolved, BF\(_4^-\) ions are tetrahedral and the boron nuclei are in an environment which is electronically symmetric. However, unlike the predicted well resolved resonances, all \(^{19}\text{F}\) spectra of tested LiBF\(_4\) electrolytes are collapsed to varying degrees. Because of that, the apparent splitting of the \(^{19}\text{F}\) spectra does not correspond to the theoretical multiplicity and prevents their simulation and the evaluation of \(J_{\text{BF}^{11}}\) and \(J_{\text{BF}^{19}}\). However, the \(^{11}\text{B}\) spectrum displays the expected line shape (a quintet with 1:4:6:4:1 ratio from \(^{11}\text{B}\) coupling with four equivalent \(^{19}\text{F}\) nuclei) as shown in Figure 6.2. Hence the \(J_{\text{BF}^{11}}\) can be extracted from \(^{11}\text{B}\) spectra by fitting the line shape as pure-Lorentzian quintets. Figure 6.3(a) shows \(^{11}\text{B}\) NMR chemical shift data of LiBF\(_4\) electrolytes system. The increase of DMC content induced a downfield effect on boron nuclei with small chemical shift less than 0.3 ppm for both concentrations. The higher concentration electrolyte system shows an upfield shift due to the cation-anion aggregation.
Figure 6.2 $^{11}$B spectra of 0.01 M and 1 M LiBF$_4$ in EC/DMC

Figure 6.3 (a) $^{11}$B NMR chemical shift and $J_{11B-19F}$ values of 0.01 M and 1 M LiBF$_4$ in EC/DMC

The ions solvation of LiBF$_4$ salt dominates the nature of their ion electronic structures and mobility, thereby affect the $J$ coupling constant of the nuclei involved in the solvation process. The ions in these studied electrolytes, Li$^+$ and BF$_4^-$, have a nonnegligible interaction with EC/DMC solvents. In order to understand this phenomenon, the $J_{11B-19F}$ of LiBF$_4$ electrolyte
systems with respect to the DMC percentage are presented in Figure 6.3(b). The BF$_4^-$ show an anomalously small and negative $J_{^{11}B-^{19}F}$ coupling constant (BF$_4^-$: 0~8Hz) as Fig. 3(a). As is known, the $J$ coupling constant is determined by diverse factors including Fermi contact, paramagnetic, spin-orbital and dipolar. However, previous literature [22] have concluded that the Fermi contact mechanism is the main factor that determines the $J_{^{11}B-^{19}F}$ in BF$_4^-$ by using molecular orbital theory. A close balance between large terms of opposite sign in the atom-atom polarizability leads to an anomalously small size of $J$ coupling constant in BF$_4^-$ [23]. The concentration dependence of $J_{^{11}B-^{19}F}$ can be observed by comparing the $J$ coupling constant data between two set of LiBF$_4$ electrolytes with different molarity. The $J_{^{11}B-^{19}F}$ in 1 M LiBF$_4$ electrolytes have a range about -5.3 Hz varying between -1.9 Hz with EC/DMC 80:20 to -7.2 Hz with EC/DMC 0:100; while $J_{^{11}B-^{19}F}$ in 0.01 M LiBF$_4$ electrolytes have a range about -3.6 Hz varying between -0.6 Hz to -4.2 Hz. This result is consistent with the study of Mazitov [21], in which the data evidenced that the $J$ coupling constant increases with increasing salt concentration in various organic or H$_2$O solvent media. Moreover, the $J$ coupling constant of $^{11}$B-$^{19}$F is also strongly dependent on the composition of the solvent. Gillespie. R. J. et al. [20] have reported solvent effects on BF$_4^-$ in different organic solvents and water, which indicated $J_{^{11}B-^{19}F}$ is negative in organic solvent and it becomes more negative when the solvent polarity decreases. This phenomenon appears to be consistent with our results.

By using $J$ values extracted from $^{11}$B spectra, the $^{11}$B quadrupolar relaxation time can be obtained by fitting $^{19}$F line shape using the expression described by Bacon et al. as Eq. 6.1 [24].

\[
l(x) \propto \tau f(\eta, x) \quad (6.1)
\]
where \( f(\eta, x) = \frac{320+\eta^2(25x^2+17)+\eta^4(80x^4+56x^2+45)}{1024x^2+64\eta^2(36x^4-20x^2+25)+16\eta^4(96x^6-160x^4+110x^2+45)} + \eta^6(256x^6-1280x^6+1888x^4-720x^2+81) \)

\[ \eta = \frac{2\pi J}{\tau}, x = \frac{\omega_0-\omega}{2\pi J} \]

Here \( \tau \) is the quadrupolar relaxation time; \( J \) is the \( J \) coupling constant; \( \eta \) is the line shape and \( \omega \) is frequency of the \( ^{19}F \) multiplet.

The fitted \( \tau \) values and measured \( ^{11}B \) \( T_1 \) and \( T_2 \) data versus the DMC percentage are plotted in Figure 6.4. As shown in this figure, \( T_1 \) and \( T_2 \) values are very similar in two series of LiBF\(_4\) electrolytes. In low concentration electrolytes, the \( \tau \) values are much smaller than measured relaxation time at higher polarity solvent (high EC content); while they decrease and converge toward the measured relaxation time as the solvent polarity decreases. At high concentration, the fitted quadrupolar relaxation time \( \tau \) and the \( T_1 \) and \( T_2 \) values are almost same. Decreasing \( \tau \) values as DMC content increases in 0.01M LiBF\(_4\) electrolytes suggest that boron of BF\(_4^-\) ions gradually loses electronic symmetry as the polarity decreases, which provides significant evidence for stronger cation-anion aggregation in higher DMC content solvents [24]. In 1M LiBF\(_4\) electrolytes, quadrupolar interaction dominates the relaxation mechanisms (\( ie. \tau \approx T_1 \approx T_2 \)), evidencing a strong cation-anion interaction when the concentration is high.
Figure 6.4 (a) Quadrupolar relaxation time $\tau$ and (b) Measured relaxation time ($T_1$ and $T_2$) of 0.01M and 1M LiBF$_4$ in EC/DMC.

The diffusion coefficient data of cation, anion and solvents at 25°C for LiBF$_4$ electrolytes are listed in Table 6.1. Some interesting phenomena were observed from the diffusion behavior of them. In all electrolytes, $D_{DMC} > D_{EC} > D_{BF4} > D_{Li^+}$ throughout the whole EC/DMC range and both salt concentrations. However, the order of van der Waals radii of these molecules or ions are $r_{DMC}$ (0.310 nm) $> r_{EC}$ (0.258 nm) $> r_{BF4}$ (0.143 nm) $> r_{Li^+}$ (0.076 nm) [5, 25-27]. Although the van der Waals radius of DMC is obviously larger than EC, the smaller molecule EC diffuses slower than the bigger solvent molecules DMC. This was attributed to the fact that the orientation of oxygen lone pairs significantly increases the dipole moment on cyclic carbonates but partially cancels the polarity of linear carbonates, and this is the reason that Li$^+$ exhibits a strong solvent preference for cyclic carbonates (EC). Moreover, the Li$^+$, which is the smallest particle in the electrolytes, has the lowest diffusion coefficient. That’s due to its high charge density and the very high ratio of solvent molecules per cations. Li$^+$ ions are bonding with EC molecules through the ion-dipole interaction [7], hence reducing their diffusion mobility of EC and themselves [28].
The solution viscosity, which is mainly determined by EC and DMC composition and the salt concentration of electrolytes, plays a crucial role in determining the diffusion behavior of particles in electrolytes. In order to gain additional insight by removing this variable, BF$_4^-$, and Li$^+$ mobility data are expressed as $D/D_{DMC}$, as Figure 6.5(a). The constant ratio of Li$^+$ mobility suggests that the solvation sheath of Li$^+$ has been saturated by the EC solvent and associated BF$_4^-$ ions, resulting in no dramatic change in diffusion data with solvent ratio. Contrary to lithium, the relative mobility of BF$_4^-$ is very high for low DMC content. It progressively converges towards lithium numbers when the polarity of the system decreases. This feature indicates that decreasing polarity (i.e. increasing DMC content) favors cation-anion interaction and/or anion-solvent interaction. But comparing the two diffusion data sets of LiBF$_4$ EC/DMC electrolytes with different concentrations, Li$^+$ in 0.01M electrolytes maintain a constant ratio of 0.2 and BF$_4^-$ has a maximum mobility at 86% if the solvent mobility, while the Li$^+$ in 1 M electrolytes exhibit a higher ratio of 0.4 and BF$_4^-$ shows a diffusion ratio of less than 0.6. The closer mobility numbers for Li$^+$ and BF$_4^-$ in 1 M electrolytes suggests a higher degree of ionic association, which is confirmed by ESI-MS in which the naked BF$_4^-$ wasn’t observed [29]. As suggested by the relatively minor effect of quadrupolar relaxation on $^{19}$F line shape, the high mobility of fluorine for 0.01 M LiBF$_4$ in 80/20 EC/DMC suggests that the ions are well dissociated. Close examination of the Li/solvent diffusion ratio shows about a 20% decrease in going from 80% EC to pure DMC, although the anion/solvent diffusion decreases at a somewhat faster rate. The aggregation behavior can be seen more clearly according to the data as plotted in Figure 6.5(b). The ratios of anion diffusion to cation diffusion gradually decrease from four in 0.01 M solutions, while they are getting very close to one as the DMC content increases in 1 M solutions. These
diffusion data indicate that decreasing the polarity of mixture solvents and increasing salt concentration lead to ionic aggregation.

![Graph](image)

**Figure 6.5** Two representations of the mobility of cation and anion in LiBF₄ electrolytes: (a) \( \frac{D}{D_{DMC}} \); (b) \( \frac{D_{anion}}{D_{cation}} \)

### 6.3.2 PF₆⁻ analysis

\(^{19}\text{F}\) NMR experiments were performed on series of LiPF₆ electrolytes with five concentrations ranging from 0.01 M to 1.2M, with several solvent ratios (EC/DMC) of 80/20, 50/50, 20/80 and 0/100. \(^{19}\text{F}\) and \(^{31}\text{P}\) are both 100% natural abundance isotope with nuclear spin \(\frac{1}{2}\), therefore \(^{19}\text{F}\) NMR spectrum of LiPF₆ shows typical lineshape of a doublet characterized by a large \(J\) coupling between Fluorine and Phosphorus nuclei, as shown in Figure 6.6. The absence of additional fluorine resonance evidences the stability of LiPF₆ in EC/DMC solvents.
**Figure 6.6** $^{19}$F NMR spectrum of 0.5 M LiPF$_6$ in EC/DMC 20/80 (A closer view of PF$_6^-$ signal is presented in the insert.)

The $^{19}$F NMR chemical shift data of LiPF$_6$ solutions and $J$ coupling constant are plotted in Figure 6.7 along with the LiBF$_4$ data replotted from Figure 6.1. Compared with LiBF$_4$ in EC/DMC electrolytes, LiPF$_6$ salt with different concentrations in a spread of EC/DMC electrolytes shows a much smaller $^{19}$F chemical shift less than 0.3 ppm over all tested electrolytes as Figure 6.7(a). That is due to either a weaker interaction between the PF$_6^-$ anion and the solvent or between anion and cation. Despite the smaller range compared to LiBF$_4$, the $^{19}$F chemical shift of LiPF$_6$ electrolytes also follows the trend of upfield shift as the salt concentrations increases from 0.01 M to 1.2 M, which is similar behavior to the BF$_4^-$ system.
Figure 6.7 $^{19}$F NMR chemical shift (a) and $J$ coupling constant (b) of LiPF$_6$ electrolytes

As in Figure 6.7(b), LiPF$_6$ electrolytes show a much larger $J^{31P-19F}$ coupling constant of about 700 Hz but with the same decreasing trend as LiBF$_4$ electrolytes when the DMC content increases. A possible mechanism for decreasing $J$ coupling constants is that the interaction between Li$^+$ and PF$_6^-$ increases as the solvent polarity decreases, and the P-F bond distances slightly increase due to the a stronger pull from the positive ions (Li$^+$). This is also an evidence for increasing cation-anion aggregation in high DMC solvents.
Figure 6.8 Two representations of the mobility of cation and anion in LiPF$_6$ electrolytes: (a) $D/D_{DMC}$; (b) $D_{anion}/D_{cation}$

In LiPF$_6$ electrolytes, the order of diffusion of every species is similar to that in LiBF$_4$ electrolytes, $D_{Solvent} > D_{anion} > D_{cation}$. Li$^+$ shows a constant ratio around 0.4. At high content of DMC, Lithium and PF$_6^-$ have similar mobilities, which supports the presence of ionic aggregates. In 100% DMC electrolytes, the DMC molecules, without competition with EC molecules, are still polarized and forming solvation sheath around the high positive charged ion, Li$^+$ [7]. Since this solvation is weaker than EC solvation, the Lithium mobility in 100% DMC electrolyte is slightly higher than it in EC/DMC mixtures, even taking into account the lower viscosity of DMC. Contrary to LiBF$_4$ electrolytes, in which the salt concentration plays a crucial role in determining the mobility of cation and anion because of the presence of ionic clusters, Li$^+$ and PF$_6^-$ mobility data are very similar in two sets of LiPF$_6$ EC/DMC electrolytes with different concentrations. This difference between cation and anion mobility is comparably smaller than the one in 1M LiBF$_4$ EC/DMC electrolytes, which is due to the weaker ion pair formation ability of LiPF$_6$ with respect to LiBF$_4$. This in turn is attributed to greater charge delocalization around the larger ion, PF$_6^-$, compared to BF$_4^-$ [13]. Unlike the dissociation degree of LiBF$_4$ which
decreases dramatically with salt concentration, the concentration of LiPF₆ has very small effect on the degree of ion dissociation.

**Table 6.1** $D_{EC}$, $D_{DMC}$, $D_{Li^+}$, $D_{BF_4^-}$ and $D_{PF_6^-}$ in 0.01 M and 1 M LiBF₄ and LiPF₆ EC:DMC electrolytes (10⁻¹⁰ m².s⁻¹)

<table>
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<th>Name</th>
<th>EC:DMC</th>
<th>EC</th>
<th>DMC</th>
<th>Li⁺</th>
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<th>PF₆⁻</th>
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**6.4 Conclusion and summary**

The solvation behavior and cation ion interactions of LiBF₄ and LiPF₆ in various EC/DMC solvent mixtures were studied by $^{19}$F and $^{11}$B NMR technique spectroscopy as well as $^7$Li and $^{19}$F NMR diffusometry. All information obtained, including chemical shift data, line shape analysis, relaxation times and self-diffusion coefficient, give insight into the nature of ionic interactions in these electrolytes. Low solvent polarity favors the ion aggregations in both LiBF₄ and LiPF₆ electrolytes, evidencing from the decreasing $^{11}$B relaxation time and Li⁺, BF₄⁻ diffusion coefficients as the DMC content increases. The LiBF₄ system exhibits an extremely high
aggregation degree in the concentrated (1M) electrolyte. However, the concentration plays a negligible effect on LiPF₆ electrolytes as evidenced by the fact that mobility ratio of F and Li in 0.1 M and 0.01 M electrolyte systems are similar with the variation of DMC content. Although the chemical shift of PF₆⁻ shows a weak interaction between anions and solvent, the influences on the J coupling constants between P-F and B-F induced by the solvent also suggests the existence of anion solvation or anion-cation interaction.

Bibliography


