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Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries

Lisa Cirrincione

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Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries

by

Lisa Cirrincione

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries

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Lisa Cirrincione

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

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Abstract

Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries

by

Lisa Cirrincione

Advisor: Prof. Steve G. Greenbaum

In this thesis, Nuclear Magnetic Resonance (NMR) spectroscopic techniques are used to study lithium electrode and electrolyte materials for advanced rechargeable lithium ion batteries. Three projects are described in this thesis. The first involves $^{23}$Na and $^{37}$Al static and magic angle spinning NMR studies of NaAlH$_4$/C anode materials for advanced rechargeable batteries. The second project is a study of paramagnetic lithium transition-metal phosphate cathode materials for Li-ion batteries, where $^7$Li, and $^{31}$P single crystal NMR was used in order to obtain detailed information on the local electronic and magnetic environments. The third project investigates the dynamics and motional properties of PS-PEO (16-16)/LiTFSI, a solid electrolyte material, through pulse field gradient NMR.
“To see a World in a Grain of Sand
And a Heaven in a Wild Flower,
Hold Infinity in the palm of your hand
And Eternity in an hour”

-William Blake, Fragments from “Auguries of Innocence”

To my family
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Introduction

There is much concern over how much longer the world's consumption of gas and oil can continue as well as the associated impact on the environment. Alternative forms of energy are being looked at attentively. The renewable sources such as solar energy and wind energy are alternatives but require large energy storage systems for viable grid usage. At this point, green power technologies have not been universally realized as replacements for the current grid systems, yet much research is geared in this direction. To this end, batteries, fuel cells and capacitors are intensely studied and developed with the aim of further improving their properties and features. The main challenges facing battery system development are cost and the specifics concerning performance, i.e. the amount of usable energy density, power density (fast charging), cycle lifetime and robustness. There has been an explosion in battery research and development in the past 10 years, in all of the three basic components: cathodes, anodes and electrolytes.

Lithium-ion batteries employ lithium intercalation/insertion compounds such as LiCoO$_2$ and carbon (graphite) as the positive and negative electrode materials respectively. These batteries occupy a very large portion of the market due to their high specific energy, high energy density, low weight and design flexibility. However there are some disadvantages, like poor rate performance and a host of major safety issues including thermal runaway, the toxicity of cobalt, high reactivity of lithium and (liquid) electrolyte leakage. Attempts to address these and other issues have ushered in increased activity towards developing new electrode and electrolyte materials for the rechargeable battery market[13].
Chapter 1

1.1 Batteries

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy via electrochemical reaction. The battery itself consists of one or more individual cells that are connected in series and/or parallel to provide the required voltage and capacity. Each cell consists of a positive electrode (cathode) and a negative electrode (anode) separated by an electrolyte. The latter component contains a salt solution in a porous separator, which enable ion transfer between the two electrodes. Once these electrodes are connected through an external circuit a chemical reaction is triggered liberating electrons and enabling the current to flow through the circuit. The amount of electrical energy, expressed usually per unit of mass ($W \cdot h \cdot kg^{-1}$) that a battery is able to deliver is a function of the cell potential (V) and capacity ($A \cdot h \cdot kg^{-1}$), both of which are linked directly to the chemistry of the system [14].

There are two types of batteries: primary (non-rechargeable or recyclable) batteries and secondary (rechargeable) batteries. Primary batteries are convenient, low cost and lightweight for portable electronics. The most common types of primary batteries are zinc-carbon and alkaline. The power delivered by these devices comes from redox chemical reactions and is limited by the amount of convertible material initially present. Therefore, after being completely discharged once, these batteries are discarded or recycled. Due to their relatively short lifetimes, primary batteries must constantly be replenished, and therefore are not very convenient for many modern applications (i.e. computers, smart phones, etc.).
Unlike primary batteries, secondary or rechargeable batteries are storage devices for electric energy. These can be recharged electrically, after discharge, to their original condition by passing current through them in the opposite polarity to that of the discharge current. The secondary battery is defined by its ability to charge and discharge reversibly. The degree of reversibility, i.e. the transformation of chemical energy into electrical energy and back again to the chemical energy, is compromised by the chemical/physical degradation of the battery, a general consequence of increasing entropy with battery cycling. Attempts to limit the degradation impose very strict physico-chemical requirements on the component materials employed in these devices. Examples of rechargeable batteries are lead-acid batteries, nickel-cadmium, nickel-zinc, nickel-hydrogen, silver-oxide, zinc/alkaline/manganese dioxide, Na-ion and Li-ion batteries [13]. The work described in this thesis focuses on Li-ion electrode and electrolyte materials.

1.2 Lithium-ion Batteries (LIB).

Among the various types of rechargeable battery configurations, Lithium Ion Batteries (LIB) are the perhaps most common, as they comprise almost 63% of worldwide portable battery sales. The first lithium ion battery was introduced commercially by the Sony Corporation in 1991. Rechargeable LIBs involve a reversible insertion/extraction of lithium ions (the guest species) from a host matrix. The positive electrode (cathode) in a LIB is a metal oxide (e.g. Li$_{1-x}$CoO$_2$), which has a layered or a tunneled structure while the negative electrode (anode) is made by graphitic carbon materials that have a layered structure, usually graphite (e.g. Li$_x$C$_6$) or other graphitic carbon. During discharging/charging of the battery, Li-ions are transported between the two electrodes via the electrolyte. Chemical oxidation and reduction of the transition metal Co(III) $\leftrightarrow$ Co(IV) occurs in the cathode during cation insertion/deinsertion. For example, when the LIB discharges within a circuit, the active negative electrode material becomes oxidized (Li$^0$ $\rightarrow$ Li$^+$ + e$^-$) as Li$^+$ migrates into the electrolyte and the active positive electrode material upon Li$^+$...
insertion becomes reduced (Co(IV) + e⁻ → Co(III), Figures 1.1 and 1.2). The opposite takes place during charging.

**Figure 1.1** Schematic of the electrochemical processes in a Li-ion cell.
In Figure 1.2, $x$ and $y$ are chosen based on the molar capacities of the electrode materials. Generally $x$ is approximately 0.5 and $y$ is about 0.16, and $x/y \approx 3$. It is noted that while batteries can in principle use metallic lithium as the anode, LIBs are safer, offer longer cycle life, and are less chemically reactive than those that employ lithium metal as the negative electrode material. Li-ion batteries have several other advantages as well. For example they can exhibit relatively high specific energy (up to 240 Wh/kg) and energy density (up to 640 Wh/L), low self-discharge rate (2 to 8% per month) and a broad temperature range of operation (charged at 0 to 45 °C and discharged at -40 to 65 °C). Lithium cells can produce 1.5V to 4.2V depending on the design and the chemical composition. All these positive features make Li-ion batteries most commonly used for consumer electronics such as: cell phones, laptop computers, MP3 players, digital cameras, electric bikes. LIBs also have extensive military and aerospace applications. The big new market for Li-ion cells is electric vehicles.
Technological improvements of Li-ion batteries include addressing the degradation at high temperature when discharged below 2V and the prevention of venting and fires when overcharged [13].

1.3 Negative Electrode Materials

The choice for the negative electrode (anode) material considers the efficiency of insertion of large amounts of lithium rapidly and reversibly. In order to provide a large cell voltage, the anodic redox potential vs. Li must be much smaller than the cathodic potential. As a result of numerous chemical and physical modifications and improvements, carbon electrodes are well suited as anodes in LIBs [14]. Carbon-based materials, in particular graphite, have low cost, and universal availability. They are considered less hazardous and have very good electrochemical stability during cycling.

Many electrode materials used in Li-ion batteries are based on intercalation/deintercalation reactions. Some possible alternatives towards improving the specific capacities in LIBs involve details of the conversion mechanism. In this work are the results from NMR experiments conducted on various synthesized alanate/carbon systems, NaAlH$_4$/C. Besides preserving conductivity, the presence of carbon is beneficial toward preventing grain growth by limiting the large volumetric changes encountered during lithium intercalation/de-intercalation. In particular solid state NMR has been used to investigate the structural impact of mechanochemical treatments and address issues concerning the reversibility of the conversion process [15].
1.4 Positive Electrode Materials

Positive electrode (cathode) materials in commercially available LIBs utilize a lithiated transition metal oxide or lithiated transition metal phosphate as the active material. Feasible positive electrode materials must have low production costs, possess high lithium capacity, and be capable of incorporating large quantities of lithium without structural change. Also, good cathode materials should allow high lithium ion diffusivity and reasonable electronic conductivity. In this work are discussed NMR studies conducted on Li(M, M')PO₄ (M= Mn, M'=Fe) single crystals. These materials belong to the olivine family and exhibit exceptionally high applicability for electrochemical energy storage in lithium-ion secondary batteries due to their charge storage capacity, chemical and thermal stability, and cost. Special attention is given to mixed transition metal ion compounds LiFeₓMn₁₋ₓPO₄ due to the fact that the redox voltage increases when Fe is substituted by Mn, and the mixed compounds can be tailored for specific applications.

1.5 Electrolytes

Electrolytes used in most commercial LIBs are comprised of lithium salts dissolved in non-aqueous solutions or gels. The electrolyte serves as the medium through which Li-ions move between the positive and negative electrodes during charge and discharge processes. The basic requirements of a suitable electrolyte for LIBs are: high ionic conductivity over a wide range of temperature, good chemical stability and compatibility with the electrode materials. Safety concerns over the risk of fire and explosion hazards, has led towards the study of inflammable electrolytes. In this area of research solid polymer electrolytes (SPEs) have been developed with
some better properties over traditional liquid electrolytes. These properties include low flammability, high electrochemical stability and mechanical stiffness. Reported in this study are self-diffusion coefficients for a polystyrene-\textit{block}-copolymer (PS-\textit{b}-PEO) mixed with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) [16]. The self-diffusion coefficients were determined using pulse field gradient (PFG) NMR.
Chapter 2

2.1 Nuclear Magnetic Resonance

This thesis employs nuclear magnetic resonance (NMR) as a spectroscopic tool to obtain information about the physical and chemical microscopic environments of atoms and ions in the various systems of interest. The NMR experiment is observed for a nucleus possessing magnetic moment $\mu$ (a consequence of non-zero spin), and the phenomenon can be described for an individual moment as follows. When this nucleus is subjected to a static magnetic field $B_0$ oriented along the $z$-direction, it will experience a torque and precess about this field direction at a rate (Larmor frequency) governed by its magnetogyric (gyromagnetic) ratio. From a classical point of view, this precession is due to the torque exerted on the magnetic moment $\tau = \mu \times B_0$, where $\mu = \gamma I$ and $I$ is the nuclear magnetic spin angular momentum. The symbol $\gamma$, is the magnetogyric ratio, i.e. the proportionality constant between the magnetic moment and the spin, and nuclear magnetic precession can be clockwise for $\gamma>0$ or counterclockwise for $\gamma<0$. The energetics between the magnetic field and the nuclear moment is called the Zeeman interaction and is summarized below.

![Figure 2.1 Spin precession around an applied magnetic field $B_0$](image)
Since spin angular momentum is quantized along \( I_z \), the nuclear magnetic moment \( \mu \) will be:

\[
\mu_z = \gamma I_z \quad (2.1)
\]

where \( I_z = I, I-1, I-2, \ldots, -I+1, -I \), and will assume all discrete number of possible orientations with respect to \( \mathbf{B}_0 \). There are \((2I+1)\) possible values for \( I_z \). The Zeeman energy of this system is the magnetic potential energy allowed

\[
E = -\mu \cdot \mathbf{B}_0 = -\gamma I \cdot \mathbf{B}_0 \quad (2.2)
\]

If we consider \( \mathbf{B}_0 = B_0 \mathbf{e}_z \), this equation can be rewritten as:

\[
E = -\mu_z B_0 = -\gamma I_z B_0 \quad (2.3)
\]

In this form it is clear that the energy of the system depends on the \( z \)-component of the spin.

As stated, \( I_z \) is quantized in units of \( \hbar \):

\[
I_z = m\hbar \quad (2.4)
\]

and \( m \) assumes all possible integer values between \( I \) and \(-I\). There are therefore \((2I+1)\) energy levels. The substitution of (2.4) into (2.3) gives:

\[
E = -\mu_z B_0 = -\gamma m\hbar B_0 \quad (2.5)
\]

As a result of (2.5) the difference in energy between two consecutive energy levels is:

\[
\Delta E = \gamma \hbar B_0 \quad (2.6)
\]

It is clear that the difference in energy between these two adjacent states depends on the intensity of the applied field. If the nucleus is also exposed to a second magnetic field that oscillates at the
precession rate (radio-frequency field), the nuclear magnetic moment will respond to this field as well and can be forced to change its direction or flip. In other words, the change in the nucleus’ magnetic potential energy (as supplied by the rf-field) forces the change of direction of its magnetic moment. A nucleus can absorb radio-frequency energy equal to $h\nu_0$, and thereby reside in a higher energy state. From here the nucleus can de-excite or relax by emitting a photon with the same amount of energy $\Delta E = h\nu_0$. In effect, this excitation/de-excitation can be driven towards resonance under favorable thermodynamic conditions and only when the excitation frequency equals the Larmor frequency, given by:

$$\nu_0 = \gamma B_0 \quad (2.7)$$

It is this forced manipulation of the nuclear moment’s direction that is the core concept of the resonance experiment. The so-called “spin-flipping” phenomenon in NMR is a reflection of the nuclear spin making transitions between adjacent magnetic energy levels as it absorbs and emits a quantum of energy $h\nu_0$.

Up to now, only one nucleus was considered, but typical systems suitable for study are often large populations of interacting nuclei. For this reason it is necessary to use a statistical approach as the NMR signal is the collective result of a large ensemble of nuclear magnetic moments. Boltzmann statistics gives an adequate description of a nuclear spin ensemble over a wide temperature range. Therefore as an example of this thermodynamic approach for a $I=1/2$ system, populations between the two energy levels are related as follows:

$$\frac{N^-}{N^+} = e^{\frac{\Delta E}{kB_T}} \quad (2.8)$$
where $N$ is the number of nuclei in the lower energy level, $N^+$ is the number of nuclei in the higher energy level, $k_B = 1.3181 \cdot 10^{-23} J K^{-1}$ is the Boltzmann constant and $T$ is the temperature in Kelvin. For nuclear spin systems at equilibrium at room temperature in typical laboratory field strengths, one finds: $N^+ \approx N^-$, with $N$ only slightly larger than $N^+$. The sample magnetization at equilibrium ($M_0$) is therefore proportional to the population difference: $N^- - N^+$. It is clear that the magnetization $M$ describes the collective behavior of spins in a system as it is defined as the vectorial sum over the ensemble of the nuclear magnetic moments in the sample:

$$M = \sum_i \mu_i = \sum \mu^+ + \sum \mu^- \quad (2.9)$$

It is important to understand that at equilibrium the magnetization component along the applied $B_0$ field ($M_\| \text{ or } M_z = M_0$, called a “population”) is non-zero, whereas the components of $M$ that are orthogonal to the applied field ($M_\perp \text{ or } M_{x,y}$, referred to as coherences) are zero (Figure 2.2a).
The intensity of the NMR signal is, then, proportional to:

1. The numerical difference of the nuclei population in the two states \( N^+ - N^- \)

2. The transition energy \( \Delta E = \gamma \hbar B_0 \)

Now, as in the single spin case described above, application of an rf field, \( B_1 \) orthogonal to \( B_0 \), with resonance frequency \( \nu_0 \), forces a change in the direction of the initial net magnetization \( M_0 \), such that it will tilt away from the \( z \)-direction in the lab frame as it attempts to precess about the resultant field \( B_0 + B_1 \). It is advantageous to view this scenario from the point of view of the precessing spin. A rotating frame can be imagined that follows the spin as it precesses at the Larmor frequency. From this view, the spin only ‘sees’ \( B_1 \) as in this frame the effect of \( B_0 \) isn’t apparent. In the rotating frame, the magnetization attempts to precess about \( B_1 \), but only as long as \( B_1 \) is present. The degree of ‘tipping’ can be controlled by duration of \( B_1 \). Therefore, if \( B_1 \) is pulsed “on” for a time \( \tau \), just so as to rotate \( M_0 \) precisely into the \( x \)-\( y \) plane in the rotating frame.
the spin system will be forced from equilibrium and the orthogonal $M_x$ and $M_y$ components can be non-zero and observable (Figure 2.2b).

The tip or flip angle $\theta$ can be expressed as:

$$ \theta = \gamma \tau B_1 = 2\pi \nu_1 $$

(2.10)

with $\omega_1 = \gamma B_1 = 2\pi \nu_1$. Clearly, the tip angle depends on the strength of $B_1$, the duration of the pulse $\tau$ and the gyromagnetic ratio $\gamma$. For example, an RF pulse which rotates the magnetization $M_z$ into the x-y plane is called a 90°-pulse (Figure 2.3).

**Figure 2.3** Behavior of the net magnetization under a 90° RF pulse.

In order to better understand the action of a 90°-pulse, it is useful to consider the time evolution of the magnetization components separately. Immediately after the pulse, $M_z$ will be identically 0, and the system is no longer at thermal equilibrium. Over time, as the system recovers, $M_z$ builds towards the equilibrium value $M_0$. The time constant by which $M_z$ recovers is called the spin-lattice relaxation time, $T_1$. The behavior of $M_z$ during the recovery period as a function of time is:
\[ M_z(t) = M_0(1 - e^{-t/T_1}) \] (2.11)

**Figure 2.4** \(T_1\) Relaxation Curve

After a 90°-pulse the magnetization lies within the x-y plane, and \(M = M_x + M_y\). In the lab frame, \(M_{x,y}\) not only rotates around the z-axis with a frequency equal to the Larmor frequency, but undergoes phase dispersion due to the various interactions that each nuclear magnetic spin \(\mu_l\) experiences. These interactions affect the local magnetic fields about the nuclei, resulting in distributions of resonant frequencies.

This phenomenon which creates dephasing of the \(M_x-M_y\) coherence is called *spin-spin relaxation* and the time constant which describes the gradual reduction of the transverse magnetization to zero is known as the *spin-spin relaxation time* \(T_2\). Like \(T_1\), this can be represented by an
exponential function. In the simplest description, $M_x - M_y$ can be written by the following expressions:

\[
M_x = -M_0 \sin(2\pi \nu_0 t) e^{-\frac{t}{T_2}} \quad (2.12)
\]

\[
M_y = M_0 \cos(2\pi \nu_0 t) e^{-\frac{t}{T_2}} \quad (2.13)
\]

**Figure 2.5** $T_2$ Relaxation Curve

It is important to remember that, although these two relaxation processes are described separately, they occur simultaneously as the spin system evolves in time.
2.2 Solid State NMR

Typically in solution-state NMR, spectra consist of very sharp resonances with line widths on the order of a few Hz or less, due to the averaging of interactions by fast isotropic molecular tumbling. In solid-state NMR, this tumbling motion is usually absent or largely hindered. As a consequence, the resonances much broader (usually on the order of 10kHz - 100 kHz), as the full effects of interactions are observed in these spectra. Line broadening interactions have the significant disadvantage of lowering the spectral resolution, yet on the other hand contain important structural and dynamic information.

Solid-state NMR spectroscopy is a very powerful tool and can often be employed to study:

I. amorphous and inhomogeneous substances;
II. crystalline structure;
III. solid-state dynamic phenomena.

The primary interactions often encountered for the study of solids are given by the following Hamiltonian [17]:

\[
H_{NMR} = H_{\text{External}} + H_{\text{Internal}} = (H_Z + H_{RF}) + (H_D + H_Q + H_S) \quad (2.14)
\]

The external contributions (interactions with \( B_0 \) and \( B_1 \) fields) are the Zeeman (\( H_Z \)) and radiofrequency terms (\( H_{RF} \)). The remaining interactions are usually much smaller than the Zeeman term and can be treated as perturbations. For instance, through-space homo and heteronuclear magnetic dipolar interactions (\( H_D \)) in the solid state rarely surpass ~100 kHz in breadth, as compared to the ~10-100 MHz Zeeman interaction. Most ground state nuclei have
spin greater than 1/2, and therefore possess electric quadrupole moments. These nuclei can interact so strongly with their surrounding electric field gradients (EFG, generated by surrounding electrons) such that in many instances their quadrupole interactions ($H_Q$) are of the order 1-100 MHz or more, as these cases need no applied magnetic field for study (pure nuclear quadrupole resonance, NQR). For the cases described in this thesis the electric quadrupole coupling ($H_Q$) is small relative to $H_Z$, and can be treated perturbatively. The last internal term, $H_S$ represents all the various ‘shifts’, ‘shielding’ and ‘antishielding’ interactions such as:

I. Chemical shift (indirect magnetic interaction of the nuclear spins with the external magnetic field as mediated by a non-spherical distribution of electronic currents)

II. Susceptibility (long-range through space magnetism) [18]

III. Knight shift (magnetic field due to local electronic environment; typical in metals and superconductors) [17]

IV. Hyperfine or paramagnetic shift (given by two contributions: the “Fermi hyperfine contact’ directly proportional to the amount of unpaired electron spin density that is ‘in contact’ with the nucleus, and the “pseudocontact”, a through-space coupling between ligand nuclei and unpaired electrons on the metal ion)[19].
2.3 NMR Interaction Tensors

In general, the interactions that a nuclear spin experiences within a local magnetic field in the solid state can be expressed as a tensor product:

\[ H = \hat{i} \mathbf{A} \hat{B} \quad (2.15) \]

Where \( \mathbf{A} \) is a second rank Cartesian tensor of this interaction:

\[
\mathbf{A} = A_{\alpha\beta} = \begin{pmatrix}
A_{xx} & A_{xy} & A_{xz} \\
A_{yx} & A_{yy} & A_{yz} \\
A_{zx} & A_{zy} & A_{zz}
\end{pmatrix} \quad (2.16)
\]

In most cases, it is convenient to represent the interaction within its own principal axes, so that it can be described by a diagonal tensor of the form:

\[
\mathbf{A} = \begin{pmatrix}
A_{11} & 0 & 0 \\
0 & A_{22} & 0 \\
0 & 0 & A_{33}
\end{pmatrix} \quad (2.17)
\]

**Figure 2.6** Principal components of the interaction tensor
Such interaction tensors are commonly pictured as ellipsoids, with the $A_{33}$ component assigned to the largest principal component (Figure 2.6).

### 2.3.1 Dipolar Coupling Interaction

The interaction energy of magnetic moments $\mu_1$ and $\mu_2$ separated by a distance $r_{1,2}$ (Figure 2.7) is given classically by (2.18).

$$E = \frac{\mu_0}{4\pi} \left[ \left( \frac{\mu_1 \cdot \mu_2}{r^3} \right) - \frac{3(\mu_1 \cdot \vec{r}) (\mu_2 \cdot \vec{r})}{r^5} \right]$$

(2.18)

Where $\mu_0$ is the permeability constant, equal to $4\pi \times 10^{-7} \frac{kg}{s^2 A^2}$. The general expression of the dipolar Hamiltonian can be written in terms of spin operators as:

$$\hat{H}_{jk}^D = b_{jk} (3(\vec{I}_j \cdot \vec{e}_{jk})(\vec{I}_k \cdot \vec{e}_{jk}) - \vec{I}_j \cdot \vec{I}_k)$$

(2.19)

where $\vec{e}_{jk}$ is the unit vector parallel to the line connecting the jth and the kth nuclei (Figure 2.7) and $b_{jk}$ is the coupling constant [4]:

$$b_{jk} = \frac{\mu_0}{4\pi} \frac{\gamma_j \gamma_k h}{r_{jk}^3}$$

(2.20)

Where $\gamma_j$ and $\gamma_k$ are the gyromagnetic ratio values for j and k nuclei and r is the distance between them.
**Figure 2.7** The dipolar coupling between spins $\mu_j$ and $\mu_k$ at distance $r$ and forming the angle $\theta_{jk}$ with the direction of the magnetic field $B_0$

There are several important facts to note about the dipolar coupling interaction. Firstly, the magnitude of the coupling constant $b_{jk}$ is proportional to the product of the gyromagnetic ratios; secondly, the dipolar coupling interaction depends on the orientation and finally, the interaction is inversely proportional to $r_{jk}^{-3}$. This interaction can be very informative for molecular structure studies.

In a system of many spins, the dipolar coupling Hamiltonian can be written as:

$$H_D = \sum_{j<k} H_{D,jk} \quad (2.21)$$

The form of the secular part of the dipolar coupling depends on whether the spins $I_j$ and $I_k$ are of the same type (homonuclear) or different type (heteronuclear). For the homonuclear case:

$$H_{D,jk} = d_{jk} \left( 3 I_{jz} I_{kz} - \mathbf{I}_j \cdot \mathbf{I}_k \right) \quad (2.22)$$
where \( d_{jk} \) is the secular dipole-dipole coupling. Equation (2.22) can be represented as:

\[
d_{jk} = b_{jk} \frac{1}{2} \left( 3 \cos^2 \theta_{jk} - 1 \right) \tag{2.23}
\]

In the heteronuclear case, the interaction is given by:

\[
\tilde{H}_{D,jk} = d_{jk} 2 I_{jz} I_{kz} \tag{2.24}
\]

In both cases the interaction depends on the orientation of the internuclear vector \( r_{jk} \) relative to \( B_0 \), through the angle \( \theta_{jk} \). In this case the secular part \( d_{jk} \) is equal to zero when the condition in eq. 2.24 is satisfied:

\[
3 \cos^2 \theta_{jk} - 1 = 0 \tag{2.25}
\]

The solution of this equation is called “magic angle” [17]:

\[
\theta_{\text{magic}} = \arctan \sqrt{2} = 54.74^\circ \tag{2.26}
\]

### 2.3.2 Quadrupolar Interaction

The nuclear electric quadrupole interaction can be the largest of all the perturbative phenomena in solid state NMR, as it encompasses the electronic interaction between the nuclear charge distribution and the surrounding electric field gradient (EFG). This is experienced only by nuclei with spin greater than \( \frac{1}{2} \) (Figure 2.8).
Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries

Figure 2.8 Nuclear charge distribution for spin $\frac{1}{2}$ and greater than $\frac{1}{2}$.

The quadrupolar interaction Hamiltonian can be expressed as [20]:

$$
\hat{H}_Q = \frac{e^2 q Q}{4I(2I-1)} \left[ 3I_z^2 - I(I + 1) + \eta(I_x^2 + I_y^2) \right]
$$

(2.27)

which results after diagonalizing the second-rank electric field gradient tensor. The EFG principal components satisfy the relation $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, $e\text{q}$ represents the $z$-component ($V_{zz}$), $\eta$ is the asymmetry parameter (which reflects the deviation from cylindrical symmetry of the EFG), $Q$ is the nuclear quadrupole moment, $I_z, I_x$, and $I_y$ are the spin angular momentum operators [4]:

$$
\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, \quad e\text{q} = V_{zz}
$$

(2.28)

The magnitude of the quadrupolar interaction scales with the quadrupolar coupling constant $Q_{cc} = e^2 q Q/h$, and the symmetry of the nuclear environment (bond geometry, number of neighboring atoms, etc.) is provided by $\eta$. In the case that the EFG has axial symmetry, i.e. $V_{xx} = V_{yy}$, the Hamiltonian of the quadrupolar interaction can be re-expressed in the form:

$$
\hat{H}_Q = \frac{e^2 q Q}{4I(2I-1)} \left[ 3I_z^2 \cos^2 \theta + 3I_x^2 \sin^2 \theta + (I_z^2 I_x^2 + I_x^2 I_z^2) \sin \theta \cos \theta - I(I + 1) \right]
$$

(2.29)
When the quadrupolar interaction is much smaller than the Zeeman term, eq. 2.27 can be treated perturbatively, giving the following expressions correct to second-order for the transition energies [4]:

\[
\hbar \nu = \hbar \nu_0 - \frac{\hbar \nu Q}{2} (m - \frac{1}{2}) [3 \cos^2 \theta - 1 - \eta \cos 2\phi \sin^2 \theta] \\
+ \frac{\hbar \nu_0}{12} \left[ \frac{3}{2} \sin^2 \theta [(A + B) \cos^2 \theta - B] + \eta \cos 2\phi \sin^2 \theta [(A + B) \cos^2 \theta + B] + \right. \\
\left. \frac{\eta^2}{6} [A - (A + 4B) \cos^2 \theta - (A + B) \cos^2 \phi (\cos^2 \theta - 1)^2] \right] 
\]

(2.30)

where

\[
\nu_Q = \frac{3e^2 qQ}{2l(l-1)} 
\]

(2.31)

\[
A = 24m(m - 1) - 4I(I + 1) + 9 
\]

(2.32)

\[
B = \frac{1}{4} [6m(m - 1) - 2I(I + 1) + 3] 
\]

(2.33)
with \( m \) as the magnetic quantum number, and \( \{ \theta, \phi \} \) as the set of polar and azimuthal angles specifying the orientation of the EFG principal axis with respect to the magnetic field (along the \( z \)-axis) (Fig. 2.9). In this expression only \( \Delta m = \pm 1 \) transitions have been considered. The second term in eq. 2.30 comes from first-order effects, the third term arises from second-order effects. Note that the second-order correction depends on the inverse of the Larmor frequency. Therefore, second-order quadrupole effects (typically observed as splittings and linewidths of the central transition) are reduced upon measurement at higher fields. By plotting the number of combinations of \( \theta \) and \( \phi \) versus the respective resonance frequency \( v \), one obtains the “powder pattern” for the sample (Figure 2.10)[5].
Figure 2.10 Schematic representation of the nuclear energy levels due to the effect of the quadrupolar coupling for spin $I=3/2$. Corresponding pattern for a first-order quadrupolar interaction and the second-order quadrupolar interaction when $\eta=0$. For the second order picture the frequency scale is in units of $\frac{v_0}{144v_0} \left[ l \left( l + 1 \right) + \frac{3}{4} \right]$ (CT=central transition, ST= satellite transition) [4, 5].
In that the electron distributions that generate the EFG tensor determine the strength of the quadrupole-coupling constant $Q_{cc}$ and the value of the asymmetry parameter $\eta$, it is clear that NMR spectra can provide very precise information regarding the nature of bonding in the solid state.

2.3.3 Chemical-Shielding and Anisotropy

Nuclear spins are susceptible to the small local magnetic fields, $B_{\text{ind}}$, generated by the circulation of the surrounding electrons. These currents are induced by the static external magnetic field, and the larger the external field the larger these local fields become with corresponding effects on the nuclear magnetization. In other words, the magnitude of the net local field is proportional to the external applied magnetic field $B_0$. Therefore the total effective magnetic field, $B_{\text{eff}}$, experienced by the nucleus is the sum of the external field and the net induced field:

$$B_{\text{eff}} = B_0 + B_{\text{ind}} = B_0 - \sigma B_0 = (1 - \sigma)B_0$$  \hspace{1cm} (2.34)

The change in magnetic field at the nuclear site due to an induced local field results in a “shift” ($\sigma$) of the resonance frequency away from the Larmor frequency ($\omega_0 = \gamma B_0$). This phenomenon is called the chemical shift interaction, and is formulated by the following Hamiltonian

$$\hat{H}_{cs} = \gamma I \cdot \sigma \cdot B_0$$  \hspace{1cm} (2.35)

$$\sigma_{PAS} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$  \hspace{1cm} (2.36)

where $\sigma$ is generalized as the shielding tensor. Typically, the shielding tensor is given in diagonal form (see further discussion in chapter 5) and specified by its principal components $\sigma_{11}$,
\( \sigma_{22} \) and \( \sigma_{33} \) such that \( \sigma_{11} \leq \sigma_{22} \leq \sigma_{33} \). The trace of this tensor, defines the isotropic chemical shift:

\[
\sigma_{iso} = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (2.37)
\]

In the solid state, where rapid spin orientation is hindered, the spectroscopic effects of nuclear shielding depend on the orientation of the shielding tensor with respect to the external magnetic field. The orientational dependence is formulated through the direction cosines of the tip and azimuthal angles, \( \theta \) and \( \varphi \), such that for a powdered material [4, 21]:

\[
u = \nu_0 [(1 - \sigma_{11}) \sin^2 \theta \cos^2 \varphi + (1 - \sigma_{22}) \sin^2 \theta \sin^2 \varphi + (1 - \sigma_{33}) \cos^2 \theta] \quad (2.38)
\]

The principal components of the shielding tensor can be obtained from the discontinuities (peaks and shoulders) in the NMR powder patterns. NMR shifts are expressed in normalized frequency units, i.e. parts-per-million (ppm) units, rather than in absolute frequencies (Hz). Modern convention defines the chemical shift: \( \delta = -\sigma \). The ppm scale is employed as follows:

\[
\delta = \frac{\nu - \nu_{ref}}{\nu_{ref}} \quad (2.39)
\]

with Hz frequency units in the numerator, and MHz units in the denominator.

### 2.3.4 Isotropic Shift in Paramagnetic Materials

There are several contributions to the general nuclear shielding formulism as described by eq. 2.34, and paramagnetic shielding can similarly be approached, except that paramagnetic shielding is that the induced field does not arise from induced electron currents. For instance, the presence of localized paramagnetic entities (unpaired electron moments associated with ionized transition metal elements, structural defects, paramagnetic molecules, etc.) and delocalized unpaired spin density (through-bond, molecular orbital contributions, etc.) can also yield
resonance shifting in NMR spectra. A general relation suitable for paramagnetic shift interactions in NMR is:

\[ \delta_p = - \frac{A_H}{\omega_0 h} \langle S_z \rangle \]  

(2.43)

where the hyperfine constant \( A_H \) is a measure of the coupling between the paramagnet and the nucleus of interest. The size and sign of this constant are particularly important since from them it is possible to extract interesting features of molecular electronic structure and understand the origin of many spectral features. The hyperfine coupling constant is generally expressed as the sum of two contributions:

\[ A_H = A_F + A_P \]  

(2.44)

where \( A_F \) is the Fermi contact term and \( A_P \) the pseudocontact term [22].

The paramagnetic interaction is particularly strong for contact shifts. As the name implies, this term originates from the through-bond coupling between the nuclear moment and the unpaired electron density on the paramagnet. The interaction can in principle be analyzed by assessing the amount of electron spin density at the nuclear site (through the \( s \)-character electron density). The Fermi contact Hamiltonian can be expressed in the form:

\[ \hat{H}_F = \frac{8\pi}{3} g_e g_n \mu_B \mu_n I \cdot S \delta(r) \]  

(2.45)

The constants in eq. 2.45 are: the Bohr magneton \( \mu_B = \frac{|e|\hbar}{2m_e} \), the nuclear magneton \( \mu_n = \frac{|e|\hbar}{2m_n} \), the electron \( g_e \) factor and the nuclear \( g_n \) factor [18, 19]. The Fermi contact shift can be obtained by dividing the contact coupling energy by the nuclear Zeeman energy [22]:

\[ \delta_{FC} = \frac{A}{\hbar \mu_0 \gamma_n g_e \mu_B} \]  

(2.46)
Where \( \chi \) is the magnetic susceptibility, \( \mu_0 \) is the permeability of free space and \( A \) is the contact coupling constant:

\[
\frac{A}{\hbar} = \frac{2}{3} \mu_0 Y_n g_e \mu_B |\phi(0)|^2 \tag{2.47}
\]

The contact coupling constant is related to the unpaired spin density and it is proportional to the probability density associated with the electron wavefunction at the nucleus.

A direct consideration of localized unpaired paramagnetic moments and their effect on nuclear moments can be assessed by the dipolar Hamiltonian expressed analogous to eq. 2.18, in the form:

\[
\mathcal{H}_D = -\frac{\mu_0}{4\pi} \hbar Y_n Y_e \sum_i \left( \frac{3 (r_i \cdot s_i) (r_i \cdot I)}{r_i^5} - \frac{(s_i \cdot I)}{r_i^3} \right) \tag{2.48}
\]

Where \( I \) and \( s \) are the spin operators associated with the nucleus and the unpaired electron respectively and \( r_i \) is the nucleus-paramagnet spatial separation vector. The sum covers atomic pair sites in the entire lattice. This is a through-space coupling and does not arise from a through-bond interaction, as described above for the Fermi contact interaction. The pseudocontact shift can be expressed in the form:

\[
\delta_{PC} = \sum_i \frac{1}{4\pi r_i^3} \left[ I - 3 (e_i \otimes e_i) \right] \cdot \chi \tag{2.49}
\]

Just like the Fermi contact (eq. 2.46) this term depends on the magnetic susceptibility\( \chi \). In this thesis the hyperfine interaction plays a major role in the \(^7\)Li and \(^{31}\)P NMR shifts described in Chapter 5.
Chapter 3

3.1 Solid State NMR Techniques

In this chapter are described the NMR techniques used throughout this thesis to characterize the structure and dynamics of the materials introduced in Chapter 1.

All NMR experiments described in this work were performed using the following:

- A Varian-S Direct Drive 300 (7.1 T) spectrometer (proton frequency of about 300 MHz)
- A Bruker Avance III HD 400 (9.4 T) spectrometer
- A Varian/INOVA 500 (11.7 T) spectrometer
- Apollo Tecmag spectrometer (2.1T).

The pulse sequences used in this research are described in this section.

3.1.1 Basic NMR Pulse Sequences

3.1.1.1 Single Pulse

The single pulse experiment is the simplest of all pulsed NMR procedures. It works by subjecting the sample of interest to a single rf pulse (applied orthogonal to $B_0$). This excites the sample magnetization and creates coherences which can be detected as a free induction decay signal (FID). The time domain FID can be measured, stored and converted into a spectrum via Fourier transformation. Figure 3.1 illustrates this pulse in a generalized form. A $\pi/2$-pulse creates a transverse magnetization which produces an FID, typically measured by the spectrometer receiver after a suitable receiver delay (DE). This sequence is repeated after a time
d₁ (recycle delay), and the signals from the first and all subsequent repetitions of the sequence are averaged within the spectrometer computer memory until a sufficient signal-to-noise ratio is achieved.

![Figure 3.1 Single Pulse Sequence](image)

The recycle delay is chosen to ensure that the longitudinal nuclear magnetization has recovered to equilibrium following the excitation pulse. Usually it is sufficient to set \( d₁ \geq 7 \times T₁ \), in order to maintain a well-defined initial condition for the sample magnetization. If the magnetization is not allowed to relax to equilibrium before applying the RF pulse, signal saturation will progress as more pulses are applied. Immediately after the pulse, the receiver is not fully functional due to the shock of the high-power rf pulse; this period is called the dead time. The receiver delay, DE, is minimally adjusted for the time between the end of the pulse and the start of acquisition of the FID. DE can easily be 10 to 20 \( \mu \)s, since this is typically the time required for the receiver to recover after the rf pulse. From a mathematical point of view it is interesting to see how a simple NMR spectrum is generated. After we apply a \( \pi/2 \)-pulse the transverse magnetization components described in equations 2.12 and 2.13 as a function of time, start to oscillate with frequency \( \omega₀ \) (Larmor frequency) and eventually will decay with time \( T₂ \). The signal stored in
digital form appears as exponential decay in the time domain. Using numerical calculations, the signal is Fourier transformed to obtain the typical NMR spectrum in the frequency domain.

![Simple NMR spectrum](attachment:image.png)

**Figure 3.1.1** Simple NMR spectrum

The function shown in Fig.3.1.1 is known as Lorentian and has the following mathematical expression:

$$ S(\omega) = \frac{\lambda}{\lambda^2 + (\omega - \omega_0)^2} \quad (3.1) $$

The parameter $\lambda$ is known as the *coherent decay rate constant* and it is the inverse of the decay time $T_2$. This tells us that a slow decay of the transverse magnetization corresponds to a narrow spectral peak while a fast decay will correspond to a broad spectral peak.
3.1.1.2 Spin Echo Pulse Sequence

Perhaps the most significant advancement of pulsed NMR was the discovery of the spin echo [23]. Spin echos are the magnetization responses to the implementation of two or more pulses, such that coherences, created by a single pulse, can become refocused by additional pulses. There are many instances where spin echo methods are used; however, the most fundamental applications are with spin-spin relaxation and diffusion. On a practical level, the spin echo methods provide convenient ways to minimize the effects of receiver dead time. A spin echo can be generated using a two pulse sequence, as shown in Figure 3.2. The pulse sequence consists of two rf pulses in sequence, namely a $\pi/2$ and $\pi$ pulse respectively separated by a delay $\tau$ [24].

![Spin Echo Pulse Sequence](image)

**Figure 3.2 Spin Echo Pulse Sequence**

Differently from the FID produced from a single pulse, when we apply two rf pulses we generate a Spin Echo. This represents the regeneration of the spin information that is apparently lost after the first rf pulse. In fact, after the first pulse, most of the FID signal seems to vanish, this because relaxation and local magnetic field inhomogeneity cause spins throughout the sample to process differently. By applying the second rf pulse, certain dephased components of the original FID can be refocused into a spin echo.
3.1.2 Magic Angle Spinning (MAS) NMR

MAS NMR is a technique for obtaining high resolution data from solids. Contrary to solution NMR, where anisotropic interactions are averaged by rapid tumbling of molecules, NMR performed in the solid-state are characterized by angularly dependent interactions (sec. 2.3 chemical shift, dipolar and quadrupolar couplings) yielding much larger lineshapes and typically lower resolution. The MAS technique improves the resolution issue by averaging the interaction over the time span of a measurement. To achieve this, the sample under study is physically rotated (~ kHz) about an axis that is tilted at $\theta = 54.74^\circ$ (the magic angle) with respect to the direction of the external magnetic field $B_0$ as shown in Figure 3.3.

![Figure 3.3 Schematic representation of the MAS technique [25].](image)

Spinning the sample at the magic angle during measurement, averages the angularly dependent perturbation terms in the Hamiltonian (i.e. $3\cos^2(54.74^\circ) - 1 = 0$), thereby diminishing their effect on the lineshape. The averaging becomes more efficient when the spin rate exceeds the spectral linewidth, such that in the infinite spinning speed limit the anisotropic angular terms, except the 2\textsuperscript{nd}-order quadrupole terms, are averaged to zero.\[24\] In this way only the isotropic values will be observable in the spectra.
It is not always possible to spin at a rate exceeding the static linewidth. When this is the case, incomplete averaging of the angular terms leads to the occurrence of rotational spin echoes in the time-domain FID. These will give rise to spinning sidebands in the corresponding frequency-domain spectrum. At low spin rates the sideband manifolds map out the those parts of the lineshape that arise from the angular dependence. Sideband peaks are separated by a frequency that is equivalent to the spin rate. As the spinning rate increases, the sidebands become narrower and more sparsely distributed about the associated isotropic peak. As the spinning rate increases, the isotropic peak remains invariant in position, narrows to the pure isotropic distribution and gains in intensity at the expense of the sideband intensity. MAS NMR allows a better resolution for the resonance, and is especially powerful when more than one isotropic component is present.

### 3.2 Diffusion NMR

Pulsed Field Gradient (PFG) NMR is a very powerful, noninvasive technique to investigate transport properties in condensed matter. The measurement of ion transport in materials developed for the electrochemical storage of energy (such as batteries, fuel cells, or supercapacitors) is of primary importance for the understanding of their electrochemical properties.

PFG-NMR allows the extraction of a very valuable parameter known as self-diffusion coefficient. By definition, self-diffusion is the displacement due to random translational motion (or Brownian motion), driven by thermal agitation of chemical entities (molecules, ions, complexes, etc.). It is characterized by a self-diffusion coefficient $D$, expressed usually in units of $m^2/s$ (or $cm^2/s$). It is important not to confuse self-diffusion with mutual diffusion. In fact, mutual diffusion arises from a concentration gradient which results in mass transfer to even out the
concentration gradient. The force behind mutual diffusion is the gradient of the chemical potential [26].

The diffusion process, from a mathematical point of view, is connected to Fick’s first law, which states that the transfer of particles across a given plane is proportional to the concentration gradient across the plane:

\[ J = -D \frac{\partial C(x,t)}{\partial x} \quad (3.1) \]

Where \( J \) represents the flux, \( D \) the diffusion coefficient of the particles moving in the solvent and \( \frac{\partial C(x,t)}{\partial x} \) is the concentration gradient. The negative sign is used to indicate the motion of the particles towards the regions of lowest concentrations.

Fick’s second law predicts how diffusion causes the concentration to change with time

\[ \frac{\partial C(x,t)}{\partial t} = -\frac{\partial J}{\partial x} \quad (3.2) \]

or, from Fick's First Law,

\[ \frac{\partial C(x,t)}{\partial t} = -D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (3.3) \]

where we suppose that the diffusion coefficient is independent of position.

In an isotropic system, where there are no thermal or concentration gradients, the average molecular displacement is equal to zero, but the mean square average three-dimensional displacement is non-zero and equal to:

\[ \langle r^2 \rangle = 6Dt \quad (3.4) \]
NMR experiments for the measurements of self-diffusion are based on the use of magnetic field gradients. Consider a constant magnetic field ($B_0$) and a magnetic field gradient (of amplitude $g$), both aligned along the $z$-axis. The magnitude of the total magnetic field at the vertical position $z$ is given by:

$$B(z) = B_0 + g \cdot z \quad (3.5)$$

Consider a sample made of an ensemble of equivalent spins. The Larmor frequency of these spins will then become spatially dependent (Figure 3.4):

$$\omega_z = \omega_0 + \gamma g z \quad (3.6)$$

Field gradients can thus be used to assign a vertical position via a $z$-dependent Lamor frequency. The system can be then visualized by imagining layers of the sample perpendicular to the $z$-axis that are thin enough to experience a uniform magnetic field but thick enough to contain a large number of spins [27].

**Figure 3.4** Larmor frequency in the presence of a static magnetic field and a magnetic field gradient.
A basic pulse sequence is shown below to illustrate the effect of the pulsed field gradient (Fig. 3.5). While the sample is under the sole influence of the static field $B_0$, a $90^\circ$ RF pulse rotates the net magnetization into the $xy$ plane. The Larmor frequency of the spins is the same all along the $z$-axis ($\omega_0$). Under the application of the first gradient pulse (of amplitude $g$ and duration $\delta$), the spins experience different magnetic fields depending on their position along the $z$-axis. The magnetizations fan out into a helical pattern along the $z$-axis. The second gradient pulse of same duration and amplitude but with opposite polarity, immediately applied after the first gradient pulse, counteracts the first gradient and allows the perfect refocusing of the spins at their original Larmor frequency.

**Figure 3.5** Schematic of the effect of pulsed field gradients on the macroscopic magnetization vectors.
If a delay that allows the spins to move from one layer to another is introduced between the two gradient pulses (Fig 3.6), the magnetizations after the second gradient pulse will not precess exactly at the $\omega_0$ frequency and thus will not be perfectly refocused. Consequently, the refocused signal is less intense. This decrease in the signal intensity is directly correlated to the mean square average displacement (hence the self-diffusion) of the spins along the $z$-axis.

**Figure 3.6** Schematic of the effects of pulsed field gradients and spin diffusion on the macroscopic magnetization vectors

In order to minimize the dephasing of the spins due to local static field disturbances (transverse magnetization inhomogeneity), the pulse sequence described in Figure 3.6 is modified with a Hahn spin-echo. Because the 180° pulse inverts the spin orientation, the second gradient pulse must be of the same polarity as the first one in order to attempt to refocus the spins. This
pulse sequence, proposed by Stejskal and Tanner in [6], is called the Pulsed Field Gradient Spin Echo (PFGSE) sequence and is the most fundamental sequence for diffusion measurements by PFG NMR (Fig. 3.7).

The expression of the amplitude of the signal is given by the Stejskal-Tanner equation [6]:

\[ I = I_0 e^{-\gamma^2 \delta^2 g^2 D (\Delta - \delta)} \]  \hspace{1cm} (3.7)

Where \( I_0 \) is the signal when no gradient is applied, \( \Delta \) is the diffusion time, \( \delta \) is the gradient pulse duration, \( g \) is the gradient strength and \( D \) is the self-diffusion coefficient.

PFG NMR implies the use of a probe equipped with a coil, coaxial with RF coil, able to produce pulsed magnetic field gradients.

A typical PFG NMR experiment to measure self-diffusion consists in acquiring multiple spectra while varying the strength of the magnetic field gradient. The signal integral is then plotted as function of the gradient strength (Fig. 3.8) and the resulting attenuation plot is fitted according to eq. 3.12 to determine the self-diffusion coefficient \( D \).
Figure 3.8 Example of NMR diffusion attenuation plot (dots: data points; red curve: fit).

**Technical considerations.**

The lifetime of the magnetization over the course of a Hahn spin-echo is ruled by the transverse relaxation time $T_2$. In many cases involving slow molecular tumbling, $T_2$ are very short in comparison with $T_1$. (Fig 3.9).

Figure 3.9 $T_1$ and $T_2$ relaxation times behaviors as function of the molecular correlation time $\tau_c$ (the time needed for molecules to rotate one radian). Adapted from the BBP model [7].
In the case where $T_1 >> T_2$, the PFG stimulated echo (PFG STE) sequence should be adopted (Fig 3.10). The purpose of this sequence is to minimize the time during which the “information” (i.e. the magnetization) is stored in the $xy$ plane, where the relaxation is extremely fast due to a very short $T_2$. After the first gradient pulse (the position-encoding gradient), a 90° RF pulse is applied so the magnetization is stored along the longitudinal axis, where spin relaxation depends on a more favorable (i.e. slower) mechanism: the spin-lattice relaxation ($T_1$). A final 90° RF pulse is applied prior to the second gradient pulse (position-decoding gradient).

![Figure 3.10 Schematic of stimulated echo (STE) sequence with pulse field gradient](image)

The use of bipolar gradient pulses helps minimize the non-linear effects of the eddy currents produced by the repetition of strong pulsed field gradients. Cotts et al. (1989) proposed a modified STE pulse sequence with bipolar gradient pulse pairs (STE BPP) [9]. This is the pulse sequence we have used in our study of transport properties in solid polymer electrolytes (Chapter 6).
Figure 3.11 Schematic of the stimulated echo pulse sequence with bipolar gradient pulse pairs (STE BPP) [9].

For the studies of diffusion in crystalline polymer electrolytes, presented in Chapter 6, we observed a deviation from the single-exponential decay typical of isotropic samples and we have explored two models to describe the ionic diffusion:

- a model with 2 types of isotropic diffusion regimes: a fast diffusion within the crystalline domains and a slow diffusion mechanism representing the crossing of the interphase between 2 crystallites (grain boundary);
- a model where the oriented diffusion within the crystallites can be extended to a macroscopic scale.
3.2.1 PFG NMR Diffusion in Heterogeneous Systems

Heterogeneous materials are often characterized by a complex morphology and for this reason performing self-diffusion measurements and extracting meaningful data can be very challenging. In the case of heterogenous polymers, where several type of domains coexist, the diffusion of small molecules can be described by the general equation below:[28]

\[
\int \frac{L}{I_0} = \sum_{i=1}^{n} p_i e^{-r^2 \delta^2 g^2 D_i t} \tag{3.8}
\]

Where \( D_i \) is the self-diffusion coefficient of the fraction of molecules \( p_i \) in the \( i \) domain.

In polycrystalline materials, crystallites have a definite size and are separated by grain boundaries. The self-diffusion at the macroscopic length scale of small molecules/ions in these materials can be thus described by 2 regimes: one in the crystallites, and one through the grain boundaries. Of course, the contribution of each regime to the NMR attenuation plot will depend on the length scale probed by the NMR experiment. The diffusion time \( \Delta \) and the square root of the mean square displacement (of dimensionality \( n \)) are related according to the follow equation:

\[
\sqrt{\langle r^2 \rangle} = \sqrt{2nDA} \tag{3.9}
\]

When we increase the diffusion time, more molecules will be restricted by the boundaries, giving a lower value for the apparent self-diffusion coefficient. Thus, it is very important to know the grain size and the length scale probed.
3.2.2 Anisotropic Diffusion

If the diffusion is anisotropic, which is expected in non-amorphous solids, the displacement of the species under investigation will depend on the orientation of the system with respect to the gradient axis. The directionality of a diffusion process can be described by the diffusion tensor \( \mathbf{D} \), which is diagonal in its principal axis system. It is characterized by three orthogonal components \( D_{xx} \neq D_{yy} \neq D_{zz} \)

In order to be able to perform self-diffusion measurements with a one-axis gradient experimental setup, favorable conditions must be satisfied. First of all, a full distribution of the microscopic orientations is needed. In the case of crystalline samples, a fine powder is required. Secondly the signal attenuation equation has to be simplified by reducing the number of parameters. This depends of the degree of symmetry of the structure.

In the case of a powder, we can calculate the signal attenuation as the integral over all possible orientations \((\theta, \varphi)\) of the crystallites with respect to the magnetic field, with \(0 \leq \theta \leq \pi, 0 \leq \varphi \leq 2\pi\). (Fig. 3.12) [10]:

\[
\psi(g\delta,\Delta) = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{\pi} \exp \left[ -(g\delta)^2 \Delta (D_{xx} \sin^2 \theta \cos^2 \varphi + D_{yy} \sin^2 \theta \sin^2 \varphi + D_{zz} \cos^2 \theta) \right] \sin \theta d\theta d\varphi \quad (3.15)
\]
Figure 3.12 representation of the Diffusion tensor in the general case of anisotropic diffusion for a powder sample [10]

In the case of cylindrical symmetry of the crystalline structure, the diffusion tensor can be greatly simplified since $D_{xx} = D_{yy} \neq D_{zz}$. We can distinguish two components of the self-diffusion: an axial diffusion, $D_{zz}$, corresponding to the diffusion along the crystalline axis of symmetry, and a radial diffusion, $D_{xy}$, within a plane orthogonal to the axis of symmetry (Fig 3.13). The signal attenuation can be then expressed as:

$$
\psi (g\delta, \Delta) = \frac{1}{2} \int_{0}^{\pi} \exp \left[ - (g\delta)^2 \Delta (D_{zz} \cos^2 \theta + D_{xy} \sin^2 \theta) \right] \sin \theta d\theta
$$

(3.10)
Figure 3.13 representation of the Diffusion tensor in the case of anistropic diffusion for a powder crystalline sample with a cylindrical symmetry [10]

This method has already been successfully applied for measuring diffusion in crystalline powders such as mesostructured silica (MCM-41) or solid-state ionic lithium nitride (Li$_3$N) [29]:

In Chapter 6, we will see that for the system under investigation, the lamellar structure of our samples will allow to simplify the calculations of the self-diffusion coefficients by adopting a similar cylindrical symmetry.
Chapter 4

$^{23}$Na and $^{27}$Al Nuclear Magnetic Resonance Studies on NaAlH$_4$ Based Anode Materials for Li-Ion Batteries

Abstract

Sodium alanate has proven to be a feasible candidate for electrochemical applications. Within a lithium cell, NaAlH$_4$ closely approaches its theoretical capacity of 1985 mAh/g upon the first discharge. However, despite its high specific capacity, NaAlH$_4$ suffers from poor cycle efficiency. This mostly happens due to a severe volume expansion, following the conversion reaction, and leads to mechanical damage in the electrode. Synthesis of an appropriate composite alanate/carbon by High Energy Ball Milling demonstrates an ability to mitigate these deleterious effects. Also, one method that has been shown to highly enhance the cycle life stability is that of dispersing the active material in a nanoporous carbon matrix. Solid state NMR, together with other techniques, has been used to study the impact of ball milling on the NaAlH$_4$ crystal structure and to investigate structure and morphology of the same material nanoconfined in a mesoporous carbon. Finally, new evidence concerning the reversibility of the conversion process has been obtained by ex-situ NMR measurements on cycled electrodes.
4.1 Investigation of the Effects of Mechanochemical Treatment on NaAlH$_4$
Based Anode Materials for Li-ion Batteries[15]

4.1.1 Introduction

Metal hydrides recently emerged as new anodic materials for lithium ion batteries. Studies on MgH$_2$[30] and TiH$_2$ [31]-[32] have already proved that metal hydrides can react in lithium cells through a conversion mechanism (Hydride Conversion Reaction, HCR) [33] following the scheme: $M_xM'_yH_z + ze^- + zLi^+ \rightleftharpoons M_xM'_y + zLiH$, where $e^-$ and $Li^+$ are the electron and the lithium ion, respectively. Besides the studies on the binary hydride systems, also lightweight complex hydrides have been recently reported as conversion anode materials in lithium cells [34]-[35]. Among them, NaAlH$_4$ deserves high consideration due to the high specific capacity this compound developed during its first discharge step (>1700 mAh/g) through a reversible process [34].

The NaAlH$_4$ conversion reaction occurs in a potential range between 0.7-0.01V and consists of a multistep process involving the formation of hexa-alanate phases (LiNa$_2$AlH$_6$ and Na$_3$AlH$_6$) followed by their decomposition to metallic Na and Al. Mechanochemical treatments have been reported to improve the electrochemical reactivity of sodium and lithium alanates. From previous studies [34], a cell efficiency close to 70 % has been achieved using a NaAlH$_4$/C composite anode prepared by high energy ball milling. Apparently ball milling with carbon affects both the shape of discharged/recharged profiles and the reversibility of the electrochemical processes. Our data suggest that ball milling treatments promote the creation of an intimately mixed carbon-hydride composite material with improved electrodic kinetics. Moreover this composite material is able to mitigate the electrode pulverization upon cycling, which occurs due to a very large
volume variation thus preventing the loss of electronic contact between particles upon full discharge/charge.

In this chapter new insights into the role of mechanochemical treatments on the properties of NaAlH$_4$ are discussed, Na and Al environments in NaAlH$_4$/C composites have been probed by solid state NMR. Other studies involving thermal programmed desorption (DPT) analysis to evaluate the hydrogen content, electrochemical impedance spectroscopy (EIS) to study the electrodic kinetics were conducted by our collaborators and described in detail in ref. [15].

4.1.2 Experimental

**Sample preparation**—All samples were provided by our collaborators Dr. L. Silvestri, Dr. P. Reale, Dr. S. Panero from Dipartimento di Chimica, Sapienza Universita’ di Roma, Italy and ENEA Centro Ricerche Casaccia, Roma Italy.

NaAlH$_4$ (hydrogen grade) was purchased from Sigma-Aldrich and used as received. All manipulations have been carried out in a Jacomex Argon filled glove box, with controlled humidity and oxygen content at room temperature. NaAlH$_4$ was activated by High Energy Ball Milling (HEBM) using a SPEX mill M400 Shaker [34]. Within the glove box, the NaAlH$_4$ powder was placed into a stainless steel jar along with 10 mm diameter stainless steel balls. The powder to combined steel balls weight ratio was 1:20. Milling sessions were carried out intermittently for 15 minutes followed by 30 minutes of rest to avoid thermal deterioration of the samples. The HEBM protocol involved two steps: 1) the pristine NaAlH$_4$ powder was milled for 15 hours, then 2) conductive carbon Super P was added to the milled powder (NaAlH$_4$/C weight ratio = 0.625:0.375) and the sample was milled further for 5 hours. The sample obtained has been labeled as B15D5. The effects of carbon and milling were studied by comparing the above
sample with three alanate references: pristine NaAlH₄ (labeled as B0), NaAlH₄ ball milled for 15 hours (labeled as B15) and a mixture of NaAlH₄ and Super P, obtained by hand grinding in a mortar (labeled as B0D0). Reported in ref. [34] is the detailed characterization of all the prepared materials by x-ray diffraction, transmission electron microscopy and infrared spectroscopy. These results show that ball milling without carbon leads to a progressive decrease of the average crystallite size from 110 nm (in B0) to 30 nm (mean particle diameter in B15). Apparently as a result of ball milling, minor traces of the hexahydride Na₃AlH₆ were observed in the B15 sample.

*Advanced characterization*-Static and magic angle spinning nuclear magnetic resonance (MAS) measurements were performed on a Varian Direct Drive 300 MHz spectrometer with a magnetic field of 7.1 T operating at Larmor frequencies of 79.4 MHz for $^{23}\text{Na}$ (spin 3/2) and 78.2 MHz for $^{27}\text{Al}$ (spin 5/2). Samples are highly sensitive to ambient laboratory conditions, therefore in preparation for NMR study, samples were packed into 1.6 mm zirconia rotors inside a glove box within an Argon atmosphere. In order to maintain the integrity of the samples during measurement dry N₂ gas was used for both MAS and purge. Data were gathered using single pulse and rotosynchronized echo pulse sequences ($\text{pulse - } \tau - \text{pulse} - \tau - \text{acquire}$, $\tau = 50\mu s$). High power short pulses ($1\mu s$) were employed in order to minimize artifacts and phase distortions in the lineshapes. Spectra are referenced to 1M NaCl aqueous solution for $^{23}\text{Na}$ and to 1M AlCl₃ aqueous solution for $^{27}\text{Al}$.

$^{23}\text{Na}$ static lineshapes were typically broadened by 1ˢᵗ-order quadrupolar effects, and spectral parameters (coupling constant $Q_{cc}$, asymmetry parameter $\eta$, dipolar width and distributions) were extracted via computer simulation of the experimental powder patterns. These results are
summarized in Table 4.1.1. $^{27}$Al static spectra were analyzed according to 2\textsuperscript{nd}-order quadrupolar and chemical shift anisotropy powder pattern contributions to the central transition. It is probable that some NMR signal intensity is lost due to very short $T_2$ (spin-spin relaxation) effects and therefore not fully represented in the spectra. Besides $^{23}$Na and $^{27}$Al static measurements, there is analysis of the isotropic values of the observable resonances through MAS. MAS NMR experiments were performed using spinning rates from 25 kHz to 40 kHz on materials recuperated after cycling in lithium cells (EP samples, see below). The isotropic peaks in the MAS spectra were analyzed as superpositions of Lorentzian/Gaussian lineshape contributions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{23}$Na</th>
<th>$^{27}$Al</th>
<th>$^{27}$Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{cc}$\textsuperscript{a}</td>
<td>dipolar fwhm\textsuperscript{b}</td>
<td>$Q_{cc}$\textsuperscript{a}</td>
</tr>
<tr>
<td>B0</td>
<td>0.150</td>
<td>8.5</td>
<td>3.15</td>
</tr>
<tr>
<td>B0D0</td>
<td>0.150</td>
<td>8.0</td>
<td>3.15</td>
</tr>
<tr>
<td>B15</td>
<td>$\sim$ 0.150 (std. dev $\approx$ 60)</td>
<td>9.0</td>
<td>$\sim$ 3.15</td>
</tr>
<tr>
<td>B15D5</td>
<td>$\sim$ 0.160 (std. dev $\approx$ 60)</td>
<td>6.0</td>
<td>$\sim$ 3.15</td>
</tr>
</tbody>
</table>

\textsuperscript{a} quadrupolar coupling constant values in MHz and distribution (Gaussian standard deviation) values in kHz; EFG asymmetry parameter is zero for both $^{23}$Na and $^{27}$Al; \\
\textsuperscript{b} dipolar fwhm in kHz; \\
\textsuperscript{c} CSA principal components in ppm.

Table 4.1.1 $^{23}$Na and $^{27}$Al simulation results for NaAlH$_4$ samples.

The electrochemical characterization has been performed by our collaborators. Working electrodes for electrochemical tests were prepared from B0D0 and B15D5 samples. The powders were pressed on 10 mm diameter Cu disks using a Specac hydraulic press. In this way, electrodes containing 1-2 mg/cm$^2$ of active material were obtained. Three-electrode electrochemical cells
were assembled using lithium metal foil both as counter and reference electrodes and electrolyte LP30, (Merck; 1M LiPF$_6$ in 1:1 v/v ethylene carbonate–dimethyl carbonate) embedded in a Whatmann borosilicate fiber disk, potentiodynamic cycling with galvanostatic acceleration (PCGA) and electrochemical impedance spectroscopy (EIS) measurements were carried out using a Biologic VSP potentiostat. PCGA tests were performed in the potential range of 2.5-0.01 V, with 10 mV steps and a cutoff current equal to C/20, calculated as the current to deliver in 20 hours the full theoretical conversion capacity [34]. Impedance spectra were collected by applying a 10 mV amplitude signal in a frequency range of 100 kHz - 0.01 Hz. Galvanostatic experiments for post mortem analysis were carried out with a MACCOR cycler in galvanostatic mode at a C/20 rate. In particular both B0D0 and B15D5 electrodes in the fully discharged state (0.01 V vs Li) and in a fully recharged state (2.5 V vs Li) have been recuperated from the lithium cells after their disassembly inside an argon-filled glove box. The extracted electrodes were then washed with dimethyl carbonate and dried. The final Electrode Powder was prepared for NMR by the procedure outlined above (these will be referred to as “EP” samples).

4.1.3 Results and discussion

Effect of ball milling on sodium alanates: NMR characterization

Static $^{23}$Na and $^{27}$Al NMR provides some insight into the effect of ball milling for NaAlH$_4$ and NaAlH$_4$/C composite materials, as shown respectively in Figs. 4.1.1 and 4.1.2. The $^{23}$Na lineshape for pristine NaAlH$_4$ (B0) shows the typical 1$^\text{st}$-order quadrupolar powder pattern for a spin 3/2 nucleus. $^{23}$Na spectra consists of a central transition (-1/2 ↔ 1/2), two satellites divergences (3/2 ↔ 1/2 and -1/2 ↔ -3/2) and two shoulders. For NaAlH$_4$, there is a single sodium site, where the Na$^+$ cation has eight nearest H neighbors at the vertices of a distorted...
triangular dodecahedron[36]. From another perspective, the Na$^+$ site is the center of an axially distorted tetrahedron where the H atoms are proximately arranged 2 per vertex (see Fig. 4.1.3). Correspondingly, the NMR shows the site to be axially symmetric ($\eta = 0$), as is evident by the divergence and shoulder features separated in frequency by $Q_{cc}/4$[37].

The degree of structural variation is reflected in the satellite spectral features as they are extremely sensitive to the crystalline environment. Ball milling reduces the average particle size, yet as seen in the NMR satellite transitions, also creates a larger variation in bond angles about Na and Al atoms without destroying the basic crystal structure. The NMR provides evidence that ball milling effectively impacts length scales below the 30 nm particle size referred to in ref.[34]. In the case of $^{23}$Na static lineshapes, the effect of ball milling was analyzed via the satellite features (Fig. 4.1.1), and satisfactory simulations were made by incorporating normal distributions in $Q_{cc}$. 
Figure 4.1. $^{23}$Na static NMR spectra for uncycled samples. Top: pristine NaAlH$_4$ (B0) and mixed NaAlH$_4$/C (B0D0); bottom: ball-milled NaAlH$_4$ (B15) and mixed ball-milled NaAlH$_4$/C (B15D5).
Figure 4.1.2 $^{27}\text{Al}$ static NMR spectra of pristine and ball-milled NaAlH$_4$ and NaAlH$_4$/C samples (top), and detail of the central transition in ppm (bottom).
A simple point-charge model suggests that ball milling must impact the electric field gradient (EFG) about these ionic Na sites to a radial length scale of the order of 100Å. The analysis was done by summing the EFG contributions from surrounding Na, Al and H atoms. In order to see the convergence, summations were truncated at particular values of radial distances ($r_{\text{max}}$) using the EFG tensor components given by:

$$V_{xi xj} = \frac{e}{4 \pi \varepsilon_0} \sum_{n}^{r_{\text{max}}} Z_n \left[ (r_n^2 \delta_{ij} - 3 x_{in} x_{jn}) / r_n^5 \right]$$  \hspace{1cm} (4.1)$$

$$\vec{r}_n = (x_{1n}, x_{2n}, x_{3n}) \quad \text{and} \quad i, j = 1, 2, 3.$$ \hspace{1cm} (4.2)

with the electronic charge $e$, vacuum permittivity $\varepsilon_0$, partial charge parameters $Z_n$ (i.e. $Z_{Na}$, $Z_{Al}$ and $Z_{H}$). The principal components, $V_{XX}$, $V_{YY}$ and $V_{ZZ}$, for the EFG tensor were gathered upon diagonalization. The associated $Q_{cc}$ can be calculated from the z-component of the EFG using the following:

$$Q_{cc} = (1 - \gamma_\infty) \frac{eQV_{zz}}{h}$$  \hspace{1cm} (4.3)$$

where $h$ is Planck’s constant, $Q$ the nuclear quadrupole moment, and $\gamma_\infty$ the Sternheimer antishielding value. No optimization was made, as the calculation uses the partial charge parameters for the constituent atoms from ref. [38] ($Z_{Na} = 1.45$, $Z_{Al} = 0.5$ and $Z_{H} = -0.49$). The results presented in fig. 4.1.4 show that the Na site calculation converges, for summations carried out with $r_{\text{max}} > 70$ Å, to nearly $Q_{cc} = 160$ kHz and $\eta = [V_{XX} - V_{YY}] / V_{ZZ} \approx 0$. This compares favorably with the experimental value of 150 kHz and lends credence to the idea that ball milling for samples B15 and B15D5 impacts the structure (i.e. $Q_{cc}$ distribution) down to a length scale of roughly 100Å.
Figure 4.1.3 Structure model for NaAlH₄, revealing Na (white) and Al (black) sites surrounded by their respective nearest neighbors H, in (gray). Four unit cells were constructed for the purpose of viewing all eight H surrounding Na, in a distorted triangular dodecahedron. In the same four cells, the [AlH₄]⁻ anion of tetrahedral geometry is visible. The cells were constructed using the crystallographic parameters given by Silvestri et. al.[8] (lattice parameters: a = 4.994 Å, b = 4.994 Å, c =11.089 Å) and software Diamond 3.2

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Figure 4.1.4 Result for point-charge EFG summation about sodium sites. The calculation results are given by the discrete points, and the continuous line is strictly a guide.

Next, $^{27}$Al powder patterns for these samples, displayed in figure 4.1.2, are discussed. For NaAlH$_4$ the observation of five transitions is generally possible because of the fairly large quadrupolar interaction in this case. However, only the $\pm 3/2 \leftrightarrow \pm 1/2$ satellites and $+1/2 \leftrightarrow -1/2$ central transition are analyzed here due to poor resolution. $^{27}$Al MAS data (not shown) reveal a single Al peak at $+96$ ppm (NaAlH$_4$), for these samples. The Al site is a tetrahedral with four H nearest neighbors (AlH$_4$); however, an EFG is present which indicates a non-spherical charge distribution. Consistent with previous measurements [39], a quadrupolar coupling constant of 3.15 MHz can be determined from the satellite positions near $\pm 230$ kHz.
The $^{27}$Al central transition is convoluted by chemical shift anisotropy (CSA), 2nd-order quadrupolar and dipolar effects. These contributions can be separated and analyzed via lineshape simulation.

Particularly for the ball milled samples, the $^{27}$Al satellite transitions are not well resolved, in comparison to the $^{23}$Na case, due to distributions over a much larger $Q_{cc}$. A simulation is attempted here primarily for the central transition, and the results are summarized in Table 1. As shown in fig. 4.1.2, the dramatic effect on the central transition lineshape due to ball milling, originates mostly from distributions in the CSA, as opposed to 2nd-order quadrupolar effects. This is reasonable since the EFG arises from fairly local charge distributions about the nuclear site (within 100Å), and apparently ball milling does not significantly affect the crystal structure inside this range. On the other hand, the length scale of the CSA can be relatively large (to crystallite proportions, as with the magnetic susceptibility). As seen in the $^{27}$Al central transition details of samples B15 and B15D5, the CSA contributions to those lineshapes (e.g. the shoulders) are significantly distributed with ball milling. Attempts to perform a simple point-charge EFG computation for the Al site, in order to ascertain a lower limit length scale for ball milling effects, was not compatible with the experimental $Q_{cc}$ value of 3.15 MHz. This is not surprising considering the degree of covalency between the Al and H atoms in the AlH$_4^-$ tetrahedron.

In summary, NMR data show that ball milling of the alanate promotes an increase of the microstructural disorder. It seems likely that this occurs within finely produced powder and on particle surfaces as stipulated by the NMR lineshapes (large $Q_{cc}$ and CSA distributions).
Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries

**NMR Monitoring of electrochemical processes**

In order to consolidate the reversibility of the conversion mechanism and highlight the effect of the performed mechanochemical treatment, $^{23}\text{Na}$ and $^{27}\text{Al}$ MAS NMR experiments were performed on fully discharged (0.01 V) and charged (2.5 V) EP samples. The relevant spectra are shown in figure 4.1.5 for EP B0D0 and B15D5, where the focus is on resonances of NaAlH$_4$ and associated reaction products (lower ppm range) and metallic signals (upper ppm range). Peak assignments have been made according to figure 4.1.6 and earlier reports. It is of interest to compare the NMR results with electrochemically driven conversion reaction described in ref.[34].

Beginning with the $^{23}\text{Na}$ spectra for B0D0 (upper left of fig. 4.1.5), the fully discharged EP B0D0 shows a 1:2 signal intensity respectively for the two peaks associated with Na$_3$AlH$_6$ near +20 ppm and -13 ppm. The assignments reported here are slightly more shielded from those given by refs [40] and [41]. An additional peak near -18 ppm is assigned to LiNa$_2$AlH$_6$, and together with the resonances from Na$_3$AlH$_6$, comprise much of the observed signal in this range. The small shoulder near -10 ppm is assigned to unreacted NaAlH$_4$. Along with these are the large Knight shifted metallic Na resonance at +1135 ppm and an anomalous metallic peak at +1120 ppm. It has been shown that Knight-shifted $^{23}\text{Na}$ resonances can bifurcate if coexisting bulk and nanoconfined metallic environments are present [42]. The corresponding $^{27}\text{Al}$ resonances for the fully discharged EP B0D0 are observed in the upper right quadrant of figure 4.1.5. The peak at -43 ppm is attributed to the hexa-alanate species (corresponding to Na$_3$AlH$_6$ and LiNa$_2$AlH$_6$) and the peak near +1640 ppm is the Knight shifted metallic Al resonance. There is a very small $^{27}\text{Al}$ contribution near +96 ppm, assigned to the residual NaAlH$_4$. The large complex of
resonances comprising peaks within $+150 \text{ ppm}$ and $+200 \text{ ppm}$ are attributed to 4-coordinated alkyl-Al compounds \[43 \] that probably result from the undesired reactions of metallic aluminum nanoparticles produced upon conversion and DMC used to wash the cycled electrodes. Metallic aluminum is more abundant and more highly exposed in the discharged electrode than in the recharged electrode, where Al has partially been converted to the alanate phase.

In contrast, the fully recharged situation for EP B0D0 reveals some large relative intensity changes. For the $^{23}\text{Na}$ spectrum (fig. 4.1.5, for the dotted line spectrum, upper left), there is a large relative increase in the spectral contributions associated with $\text{Na}_3\text{AlH}_6$, $\text{LiNa}_2\text{AlH}_6$, and $\text{NaAlH}_4$. It stands to reason that the most significant difference is the additional intensity from the $\text{NaAlH}_4$ component, although it overlaps with the neighboring $\text{Na}_3\text{AlH}_6$ peak. It might also be that this feature arises from the convolution of a $\text{Na}_3\text{AlH}_6$ phase with $\text{NaAlH}_4$ as it emerges from oxidation. This enhanced intensity comes at the expense of the metallic Na, as there is a corresponding reduction of the $+1135 \text{ ppm}$ peak. From the $^{27}\text{Al}$ perspective, there is an enhancement of the metallic Al signal relative to the peak at $-43 \text{ ppm}$. Also, the complex of overlapping resonances ($+150$ to $+200 \text{ ppm}$) is significantly reduced, and any signal near $+96 \text{ ppm}$ associated with $\text{NaAlH}_4$ is not resolved. Since the signal for $\text{NaAlH}_4$ appears in the corresponding $^{23}\text{Na}$ spectrum, there must be a large isotropic distribution rendering poor resolution for this phase in the $^{27}\text{Al}$ spectrum.

A comparison can now be made with measurements performed on the cycled EP B15D5 sample. Considering the $^{23}\text{Na}$ results presented in the bottom left quadrant of figure 4.1.5 for the fully discharged spectrum, the double peaked contribution from the $\text{Na}_3\text{AlH}_6$ phase is obvious as the most intense peaks at $+20 \text{ ppm}$ and $-13 \text{ ppm}$. Comparing with the discharged EP B0D0 $^{23}\text{Na}$
spectrum, note the relatively less intense metallic peak at +1135 ppm and the absence of the anomalous (possibly nanoconfined) metallic peak at +1120 ppm. There is a small component at -18 ppm due to a LiNa$_2$AlH$_6$ phase. $^{23}$Na features for any residual NaAlH$_4$ phase are unresolved here. The $^{27}$Al spectrum of this discharged sample (fig. 8, bottom right) mainly shows a feature near +190 ppm (i.e. 4-coordinated alkyl-Al compounds) and the relatively large metallic Al peak at +1640 ppm. There are two small peaks at -43 ppm and +96 ppm, due to the hexa-alanates and residual NaAlH$_4$ respectively; and a very small peak at +16 ppm. This last peak, is assigned to aluminum oxides probably produced during the brief exposure to the air during sample transfer.

Finally, the scenario for the fully charged EP B15D5 sample is explored (dotted line spectrum in lower quadrants of fig. 4.1.5). In the $^{23}$Na spectrum, there is a small signal from the LiNa$_2$AlH$_6$ phase, but more striking is the absence of signal associated with the Na$_3$AlH$_6$ and metallic Na. There is also a corresponding increase of the NaAlH$_4$ peak near -10 ppm comprising over 90% of the spectral intensity. The small peak near +10 ppm is more likely due to sodium aluminum hydroxide, as such products have been identified in oxidized NaAlH$_4$ [44]. As far as the sodium behavior is concerned, this is a much improved cycling performance, as compared to that given by the B0D0 sample. Accordingly, the $^{27}$Al spectrum (lower right quadrant, dotted line spectrum), besides a large metallic Al peak, reveals a clear NaAlH$_4$ signal at +96 ppm, which was not resolved in the spectrum for the fully charged B0D0. It is assumed for EP B15D5 as well that a large isotropic distribution is responsible for the low peak intensity with this NaAlH$_4$ phase on recharging. Although alkyl-Al resonances were lessened upon charging in the EP B0D0 sample, they are virtually absent for the fully charged EP B15D5 sample. The $^{27}$Al spectrum reveals a small hexa-alanate peak at -43 ppm (consistent with its $^{23}$Na spectrum) and a small aluminum oxide peak near +16 ppm.
Figure 4.1.5 $^{23}$Na and $^{27}$Al MAS NMR spectra of the EP B0D0 (top) and B15D5 (bottom) samples discharged (solid line) at 10 mV and recharged (dotted line) at 2.5 V in galvanostatic mode using a C/20 rate.
Figure 4.1.6 $^{23}$Na and $^{27}$Al MAS NMR for reference compounds: NaAlH$_4$, Na$_3$AlH$_6$ and LiNa$_2$AlH$_6$. 
From these NMR data it is clear that the conversion reactions of B0D0 and B15D5 samples proceed along the same lines, although differing in the efficiency and reaction route depth. Upon discharge, NaAlH$_4$ is consumed through a conversion reaction that evolves firstly to form hexa-alanate intermediate phases (Na$_3$AlH$_6$ and LiNa$_2$AlH$_6$). Products continue to follow the discharge route, such that final picture is comprised of metallic Al and Na. As a consequence of ball milling, despite a shallower discharge profile, EP B15D5 seems to recharge more efficiently as evidenced by relatively simpler NMR spectra, revealing zero alkyl-Al compounds, zero Na$_3$AlH$_6$, zero metallic Na, reduced LiNa$_2$AlH$_6$ and reduced metallic Al signals after charging. These findings are consistent with the higher reversibility of the conversion process observed in electrochemical experiments with the B15D5 sample.

### 4.1.4 Conclusions

A NaAlH$_4$/C composite has been prepared by high energy ball milling. The local structure as a function of the performed treatment has been studied by solid state NMR under MAS and static conditions. From the results obtained on the cycled materials the implications of mechanochemical processing on the electrochemical reversibility are indisputably positive. Both electrochemical tests and NMR measurements confirmed the superior reversibility of the composite B15D5 sample conversion.
4.2 NaAlH₄ Nanoconfinement in a Mesoporous Carbon for Application in Lithium Ion Batteries [45].

4.2.1 Introduction

Has already discussed in par. 4.1.1, anodic materials based on conversion chemistries could represent a viable alternative to the classical intercalation materials currently used in lithium ion devices, in fact from the results shown in the previous section it is evident that mechanochemical treatments can provide an effective solution towards improving the electrochemical performance of sodium alanate in lithium cells. One method that has been shown to highly enhance the cycle life stability [14] [46] is that of dispersing the active material in a nanoporous carbon matrix. Besides preserving conductivity, the presence of carbon is beneficial towards preventing grain growth and sintering by limiting the large volumetric changes encountered during lithium incorporation/de-incorporation [47]. Along these lines, in order to improve the performance of sodium alanate in electrochemical cells, a nanocomposite of sodium alanate confined in a mesoporous carbon host matrix has been developed by our collaborators in Rome. They adopted a solvent-assisted infiltration method to highly disperse NaAlH₄ as well as facilitate a close contact with the carbon material [48]. The success of the infiltration method was gauged by morphological and thermal analysis. The interaction between the carbon matrix and the sodium alanate was studied by solid state NMR. Infrared spectroscopy and galvanostic measurements were performed by our collaborators and described in detail in ref. [45].
4.2.2 Experimental

**Materials**- NaAlH₄ (hydrogen grade), resorcinol (≥ 99 %), formaldehyde (37 wt % in H₂O) and anhydrous tetrahydrofuran (≥ 99.9 %) were purchased by our collaborators from Sigma Aldrich and used without any pretreatment. Anhydrous sodium carbonate was purchased from Carlo Erba Reagents.

**Sample preparation**- All samples were prepared and provided by L. Silvestri, P. Reale, S. Panero from Dipartimento di Chimica, Sapienza Universita’ di Roma, Italy and ENEA Centro Ricerche Casaccia, Roma, Italy.

The carbon aerogel was synthesized by polycondensation of resorcinol with formaldehyde according to a method developed by Pekala et al.[49], followed by solvent exchange and pyrolysis. In particular, 4 g of resorcinol (C₆H₄(OH)₂) were dissolved in 5.88 g of distilled water with 7.62 mg of sodium carbonate (Na₂CO₃) as the basic catalyst. 5.83 g of formaldehyde (CH₂O) were added and the resulting solution was stirred for 1 hour at room temperature. Then, the solution was aged 12 hours at 90° C. Following this, the batch was cooled to room temperature, washed with acetone three times to remove the excess water and catalyst and allowed to dry in air. The resulting formaldehyde-resorcinol aerogel sample was pyrolyzed in a tube furnace under an argon atmosphere at 750° C for 4 hours, yielding a carbon aerogel (CRF). Before using, the carbon aerogel was further subjected to a 500° C thermal treatment under vacuum for 20 hours, in order to remove any adsorbed species. The product was then moved to an argon filled glove box.

In order to prepare the NaAlH₄/carbon nanocomposite, a quantity of sodium alanate was measured in order to fill 50% of the total porous volume of the carbon host. This corresponded to
a carbon/NaAlH$_4$ weight ratio equal to 0.624/0.376. Infiltration was carried out as follows: the NaAlH$_4$ and carbon aerogel powders were mixed in a mortar, anhydrous tetrahydrofuran (THF) was added dropwise to promote the alanate dissolution and precipitation into the carbon pores. The mixture was then dried under vacuum for 5 hours in order to drive-off the solvent and allow for the complete recrystallization of NaAlH$_4$. The NaAlH$_4$/carbon nanocomposite obtained was labeled $si$. Also, a control sample was prepared by mixing the same dry quantities of NaAlH$_4$ and carbon aerogel using a mortar and pestle. This control sample was labeled as $ni$. Table 4.2.1 summarizes the preparation for the two samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CRF:NaAlH$_4$ molar weight</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ni$</td>
<td>0.624:0.376</td>
<td>Physical mixing</td>
</tr>
<tr>
<td>$si$</td>
<td>0.624:0.376</td>
<td>Solvent assisted impregnation</td>
</tr>
</tbody>
</table>

Table 4.2.1 List of the samples under investigation

**Solid State NMR characterization**- Magic angle spinning nuclear magnetic resonance (MAS) measurements were performed on a Varian Direct Drive 300 MHz spectrometer with a magnetic field of 7.1 T operating at Larmor frequencies of 79.4 MHz for $^{23}$Na (spin 3/2) and 78.2 MHz for $^{27}$Al (spin 5/2). Samples are highly sensitive to ambient laboratory conditions, therefore in preparation for NMR study, samples were packed into 1.6 mm zirconia rotors inside a glove box within an Argon atmosphere. In order to maintain the integrity of the samples during measurement dry N$_2$ gas was used for both MAS and purge. MAS rates between 35 kHz and 40 kHz were used. Data were gathered using single pulse and rotosynchronized echo pulse sequences ($pulse - \tau - pulse - \tau$ – acquire, 25 $\mu$s $\leq \tau \leq 30\mu$s). High power short pulses (1$\mu$s) were
employed in order to minimize artifacts and phase distortions in the lineshapes. Spectra are referenced to 1M NaCl aqueous solution for $^{23}\text{Na}$ and to 1M AlCl$_3$ aqueous solution for $^{27}\text{Al}$.

4.2.3 Results and discussion

Before performing the solid state NMR characterization, our collaborators employed N$_2$ physisorption to evaluate the effect of the infiltration process on the porous structure of the carbon aerogel. Subsequently, the sample morphologies before and after infiltration have been analyzed by both scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM). X-ray diffraction (XRD) measurements were acquired to analyze the phase nature of the samples, while infrared spectroscopy (FTIR) was used to reveal aspects of the sample local structure. The results of these studies can be found in detail in ref. [45].

Finally, further insights were obtained from solid state $^{23}\text{Na}$ and $^{27}\text{Al}$ MAS NMR measurements. A few alanate infiltrated samples were prepared and since a fair degree of NMR spectral intensity variation was observed, it is concluded that some heterogeneity exists between these identically prepared materials. The infiltration of NaAlH$_4$ into the carbon matrix strongly affects the NMR spectra in the differences of constituent peak positions and isotropic distributions.

Figure 4.2.1 compares NMR spectra for $si$, $ni$ and reference materials (NaAlH$_4$ and Na$_3$AlH$_6$). The spectra are interpreted in terms of contribution resonances from constituent phases.
Figure 4.2.1 $^{23}\text{Na}$ (top) and $^{27}\text{Al}$ (bottom) MAS NMR spectra for infiltrated NaAlH$_4$/carbon and reference compounds NaAlH$_4$ and Na$_3$AlH$_6$. 
The $^{23}\text{Na}$ spectrum for the $ni$ sample is entirely due to $\text{NaAlH}_4$ with no resonances associated with metallic Na or $\text{Na}_3\text{AlH}_6$. The $^{27}\text{Al}$ spectrum for $ni$, shows the large alanate component as well as a small oxide peak. These observations are consistent with the simple alanate-carbon mix description for the fabrication procedure of $ni$, although there is some slight reaction likely between the alanate and oxygenated carbon species.

An altogether different picture emerges for the $si$ sample. In this case, due to the decrease in particle size and structural distributions with infiltration there are correspondingly large distributions in the quadrupolar coupling constant for both $^{23}\text{Na}$ and $^{27}\text{Al}$ spectra. As a consequence, spinning sidebands are broad with greatly reduced intensity (as compared to the $ni$ spectra). The lineshape variations between the different $si$ samples, indicate the overall $^{23}\text{Na}$ signal is a composite of a number of overlapping resonances from distinct Na sites. Isotropic peaks are evident at -9 ppm and +4 ppm (no metallic $^{23}\text{Na}$ resonances are observed), and there is a broad unresolved feature underneath the peaks. Freitas et al. [50] measured the $^{23}\text{Na}$ resonance within the range of 0 and -30 ppm for $\text{Na}^+$ infused carbon (with a much smaller average pore width measured by our collaborators to be approximately 16 nm). This Na site was characterized by a large quadrupolar coupling constant of about 1.2 to 1.8 MHz. Their results are interpreted along the lines of $\text{Na}^+$ bound to oxygenated carbon groups (i.e. carbonyl) at pore surfaces. A similar description may account for the broad feature encountered here. The small resonance at -9 ppm reveals a portion of the initial $\text{NaAlH}_4$ that survived infiltration. The dominant $^{23}\text{Na}$ peak centered near +4 ppm is due to Na sites influenced by substantial interaction with electron withdrawing oxygen species such as carbonates [51] and peroxides [52].
Unfortunately the -9 ppm signal is not easy quantified here since the unresolved sideband structure is an unknown mixture of 1st-order quadrupolar satellites intensity from the various Na sites. In principle it is possible to obtain an estimate of the alanate content from the $^{27}$Al NMR, but these MAS results show no evidence of a signature peak near +96 ppm. Instead the $^{27}$Al spectrum shows three resonances near +70, +35 and +4 ppm. There is also a large metallic Al signal at +1640 ppm (not shown), the intensity of which varies roughly between 20% and 50% of the overall detected signal with the sample heterogeneity. Some likely assignments include 4-coordinated Al-oxides (from about +50 to +85 ppm) [41] and 6-coordinated Al-oxides (from -20 to +35 ppm) [43], and Al-carboxylates (~0 ppm)[53],[54]. It is noted that both $^{23}$Na and $^{27}$Al signatures for \textit{si} somehow resemble spectra of an amorphous (unannealed) phase of NaAl$_9$O$_{14}$ by MacKenzie at al. [55], although those $^{23}$Na and $^{27}$Al resonances display large 2nd-order quadrupolar interactions, have somewhat more shielded shifts and probably display intense sidebands manifolds. In addition to the site distribution, some broadening and shifts observed for \textit{si} might be attributed to the susceptibility of the carbon matrix [41]. This effect has been observed, but only accounts for a shielding of roughly -2 ppm; not nearly enough to draw the attention to the +70 ppm peak. However, large distributions are present and the presumed one $^{27}$Al signal intensity attributable to NaAlH$_4$ is likely within this unresolved portion.

In summary, both FTIR and NMR spectroscopies show that strong chemical interactions occur between NaAlH$_4$ and the carbon support upon infiltration. Some NaAlH$_4$ survived infiltration intact, although the absolute content is not readily available from the data. All signals observed for \textit{si}, e.g. the $^{23}$Na NMR, $^{27}$Al NMR and Al-H stretching mode from FTIR, are broadened (in the case of NMR by discrete isotropic distributions) and are greatly different from the NaAlH$_4$
reference, as for si they reflect altogether different Na and Al environments due to nanoconfinement.

4.2.4 Conclusions
A carbon aerogel was synthesized as host for alanate nanoparticles. As a result, a mesoporous carbon was obtained consisting of spherical nanoparticles interconnected to form a nonporous structure characterized by a total porous volume of 1.33 cm$^3$/g and pores of 16 nm diameters.

In order to improve the dispersion of particles into the carbon matrix, a solvent assisted method was chosen. The result was a nanocomposite with a homogeneous morphology consisting of alanate particles permeated into the carbon matrix. Nevertheless, the resulting nanoconfined material was highly reactive and therefore complex to manage: it easily burns upon exposure to air, and starts to desorbs hydrogen already below 100°C. Furthermore, despite elemental analysis performed on carbon revealed just 1.75 wt.% of residual oxygen, the interactions between alanate and carbon are intensive. Either FTIR and solid state NMR analyses revealed a rather alanate oxidation, and thermal analysis demonstrated that only 54% of the total infiltrated hydride was preserved after confinement [45]. Despite these issues, such nanocomposite demonstrated improved cyclability in a lithium cell. Apparently confinement is effective in reducing electrode pulverization following the huge volume variations to which the hydride is subjected upon lithium conversion.

In summary, alanate infiltration into a carbon aerogel appears to be a promising method to confine a hydrogen rich material capable to give a reversible conversion reaction in lithium cells. However, the optimization of the infiltration method is necessary in order to avoid the extensive decomposition of the sample. Further improvements might be obtained by optimizing the
solvent-assisted infiltration method, for instance, by improving the solvent purity, increasing carbon porosity, and grinding under a reducing hydrogen atmosphere (by ball milling in closed anaerobic vials). Also, the use of alternative melt infiltration techniques should be explored [56]. Enhancement of the reversible cycled capacity, which might be made starting with sample quality improvements, is essential for this composite material to be considered for application in electrochemical devices.
Chapter 5

Single Crystal NMR Studies on Paramagnetic Lithium Transition-Metal Phosphates Crystals \((\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4 \text{ with } x=0, 0.25, 0.5, 0.6, 0.75, 1)\)

Abstract

Lithium transition-metal (TM) phosphates \(\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4\) with olivine-type structure are considered one of the most promising next generation lithium ion battery cathodes. While these crystals possess very attractive properties for battery applications, it is of interest to further understand the characteristic properties with respect to the compositional parameter \(x\). Along these lines, NMR spectroscopy was used to gain insight into the magnetic structure of \(\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4\) single crystals. By measurement of the \(^7\text{Li}\) and \(^{31}\text{P}\) NMR frequencies with crystal orientation, i.e. \(\nu = I \cdot \sigma \cdot B_0\), where \(B_0\) is the applied field and \(I\) is the nuclear spin, the magnitudes of the components of the interaction tensors giving rise to the lithium and phosphorus shifts can be determined (\(\sigma = \text{hyperfine, susceptibility, etc.}\)). Generally, the anisotropic frequency shift range for \(^7\text{Li}\) is roughly ±1000ppm (centered at 0ppm) depending on crystal orientation relative to the external magnetic field. \(^{31}\text{P}\) shifts (measured only for \(x = 0\) and 1) show an anisotropy of about ±2000ppm; however, in contrast with \(^7\text{Li}\) shifts, the \(^{31}\text{P}\) shift range is centered at about +8000ppm and +3500ppm from the \(\text{H}_3\text{PO}_4\) reference for \(x = 0\) and 1 respectively. The shielding tensors vary greatly for Li sites and P sites in both magnitude and direction. Furthermore, there are large differences in the paramagnetic shifts depending on the TM \([2, 57]\). The results are interpreted along the lines of a through-space paramagnetic
susceptibility shift for $^7\text{Li}$ (more-or-less diagonal along the lattice vectors) and highly directional contact interactions for $^{31}\text{P}$ (not diagonal along the lattice vectors).

### 5.1 Introduction

The increasingly widespread use of battery-powered devices requires new, cheaper and safer electrode materials with higher energy densities. A very interesting class of compounds that received attention as promising cathode materials for lithium ion batteries is composed of the olivine-type compounds LiFe$_x$Mn$_{1-x}$PO$_4$ which are made by mixing together LiFePO$_4$ (LFP) and LiMnPO$_4$ (LMP). In fact, pure LFP although widely used, does not possess a sufficiently high energy density for many applications, and apparently pure LMP requires a costly preparation in order to become sufficiently activated for higher voltage applications. However, mixtures of LFP and LMP, generally show better electrochemical performance than either pure material. Some have attributed this enhancement to the local and long-range distortions caused by TM substitution. Insight into the local structural distortions is considered essential towards understanding the electrochemical properties of these materials [1]. Contributions made in regard to the compositional aspects of LiFe$_x$Mn$_{1-x}$PO$_4$ have been few. In this thesis is reported an NMR study employing low-field $^7\text{Li}$ and $^{31}\text{P}$ as probes of the local magnetic environments of Li and P sites associated with TM substitution. One goal of this study is to search for connections between the interaction tensors and the type and positions of atoms in the lattice.
5.2 Experimental

LiFe$_{x}$Mn$_{1-x}$PO$_4$ ($x=0$, 0.25, 0.5, 0.6, 0.75, 1) single crystal samples were provided by Dr. Y. Janssen from the Department of Chemistry, Stony Brook University. Crystals of size 20-30mm$^3$ were fabricated by a salt flux method and extracted from larger parent crystals [58]. The fabrication of the crystals starts with powdered pre-made LiFePO$_4$ and LiMnPO$_4$, mixed with LiCl.

Crystal integrity was checked by x-ray diffraction at New York University using a Bruker AXS APEXII Single Crystal Diffractometer (New York University). This instrument is capable of providing an image of the crystal with lattice axes clearly marked (Figure 5.1 and 5.2). The diffraction results allowed for any twinning to be identified, as well as helped map the crystal axes (i.e., [1 0 0] relative to crystal surfaces), and lattice constants ($a \approx 10.3\text{Å}$, $b \approx 6.0 \text{ Å}$, and $c \approx 4.7\text{Å}$). The x-ray results were invaluable in orienting the crystals for NMR study. The studied crystals were thereby all confirmed to possess the orthorhombic unit cell and point symmetry known for Li(TM)PO$_4$. Once lattice parameters pictures and angular data were obtained for the principal orientations [100], [010], and [001], the crystals were made ready for NMR rotation studies.
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Figure 5.1 Photo of Bruker AXS APEXII Single Crystal Diffractometer

Figure 5.2 Images of LiMnPO₄ (a), LiFe₀.₂₅Mn₀.₇₅PO₄ (b), LiFe₀.₅Mn₀.₅PO₄ (c), LiFe₀.₆Mn₀.₄PO₄ (d) and LiFe₀.₇₅Mn₀.₂₅PO₄ (e) crystals with crystallographic axes.

NMR measurements were made using a 2.1 T permanent magnet and a Tecmag Apollo Spectrometer operating at approximately 35MHz and 36MHz for $^7$Li and $^{31}$P respectively. Typically, solid state NMR is conducted using large field strengths (> 7T); however, since large paramagnetic shifts are observed for these crystals, better resolution of the resonances, within a reasonable spectral window (i.e., 1 MHz), can be achieved using a smaller field. For this purpose a simple pulsed spectrometer system, Tecmag Apollo HF2, was employed using an older Varian 2.1 T permanent magnet.
A spin-echo pulse sequence was used \((\pi/2-\tau-\pi-\tau\text{-acquire})\) for \(^{31}\text{P}\) NMR, with \(\tau\) typically within 25\(\mu\text{s}\) to 40\(\mu\text{s}\). For \(^{7}\text{Li}\), a solid-echo pulse sequence \((\pi/2-\tau\text{-} \pi/2-\tau\text{-acquire})\) was used in order to enhance detection of the satellites contributions. All data were gathered using high power pulses such that pulse widths \((\pi/2)\) were typically less than 3\(\mu\text{s}\). Recycle delays of 0.25s or more were used (with no signal saturation), and reasonable signal-to-noise was obtained after the accumulation of 10000 to 30000 scans depending on the crystal. All data were taken at room temperature. Spectra are presented as rotation plots in ppm units and referenced to the standard diamagnetic substances 85\% \(\text{H}_3\text{PO}_4\) and aqueous \(\text{LiCl}\) for \(^{31}\text{P}\) and \(^{7}\text{Li}\) respectively.

In order to obtain the interaction tensors, the \(^{7}\text{Li}\) and \(^{31}\text{P}\) peak frequencies were measured with respect to crystal orientation (i.e. rotation angle \(\theta\) and initial orientation with either [100], [010] and [001] relative to \(B_0\)). This was done by gathering spectra as a function of rotation angle \(\theta\),
Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries

for each of the three orthogonal axes. The crystal is initially oriented by hand, following which spectra are recorded as the crystal is rotated about the lab frame $x$-axis. The probe geometry accommodated this arrangement such that the rotation angle $\theta$ could be freely varied. This was accomplished by mounting the oriented crystal onto the end of a 15inch plastic vertical shaft in such a way that upon positioning this crystal/shaft assembly into the probe coil, one crystallographic axis is made parallel to the coil axis (along the lab frame $x$-axis), while the other two axes lie in the (lab frame $y$-$z$) plane that includes the applied field $B_0$. For instance, suppose the crystal [1 0 0] is oriented along the coil axis (lab frame $x$-axis). In this case, spectra will be recorded with respect to the crystal direction that is parallel to the lab frame $z$-axis (corresponding to the crystal orientations within the [0 1 0] - [0 0 1] plane as the crystal is rotated about the lab frame $x$-axis). Rotations were performed smoothly by fixing the shaft to a goniometer, as shown in the right-hand picture of Fig. 5.4. To facilitate the process, the goniometer was connected to a computer-controlled stepper motor for a more precise adjustment of the rotation angle. Remote measurement was also made possible through the use of a camera and remote control software. Some of the probe details are shown in Figure 5.5. As mentioned above, measurements were done per each rotation axis, therefore, the crystal had to be removed from the probe and reoriented correspondingly by hand (e.g. [0 1 0] along the lab $x$-axis) for the next set of measurements. A partial data set was compiled from spectra recorded every 15° rotation increment of the goniometer shaft throughout the range $0^\circ < \theta < 360^\circ$. A full crystal set is comprised of all data (i.e. 24 spectra for each rotation axis [100], [010] and [001], $3 \times 24 = 72$ spectra). Upon completion of the NMR experiments, the full newly minted data set is analyzed in “one-shot” by a visual fitting method. In this analysis all 72 spectra are loaded into the program XTALFIT and the data are fit simultaneously and interactively (with the aid of
additional programs TENSOR, XTALFIT, and XTALFIT2) in order to determine the interaction tensor eigenvalues and eigenvectors for the $^7$Li and $^{31}$P environments. The programs were written in Matlab code by Dr. Phillip Stallworth and extended for scalable use by Fernando Villafuerte.

**Figure 5.4** Single crystal probe details. The red arrow points to an enlargement representing the crystal position relative to the applied field $B_0$ oriented along $z$ and rotating inside the coil along the x axis.

The analysis gives the interaction tensors in their PAS, as well as in the crystal frame, where greater insight may be gained. The context of the interaction tensor is that of the crystal lattice, and unfortunately this perspective is all but lost in polycrystalline NMR studies. Some guidance on navigating the frame transformations (LAB ↔ crystal ↔ PAS) is provided by the analysis in this thesis, as one of the goals of this study is to find relationships between the interaction tensors at lithium and phosphorus sites and the transition metal atoms. Since the NMR data is gathered
in the LAB frame and the x-ray data in the crystal frame, the computer analysis uses transformations to tie all the data together in order to determine the tensors in the PAS. The transformations are applied as follows:

\[
\sigma_{\text{LAB}} = R_{\text{crystal to LAB}}^{-1} R_{\text{PAS to crystal}}^{-1} \sigma_{\text{PAS}} R_{\text{PAS to crystal}} R_{\text{crystal to LAB}}
\]

\[
= R_{\text{coil}}(\theta)^{-1} R_{||B_0}^{-1} \sigma_{\text{crystal}} R_{||B_0} R_{\text{coil}} \quad (5.1)
\]

where the transformation from the crystal to lab frame is, \( R_{\text{crystal to LAB}} = R_{||B_0} R_{\text{coil}} \) with \( \sigma_{\text{crystal}} = R_{\text{PAS to crystal}}^{-1} \sigma_{\text{PAS}} R_{\text{PAS to crystal}} \). For example, orienting the crystal x-axis to be coaxial with the NMR coil (Figure 5.4), the following crystal orientation and rotation transformations can be used:

\[
R_{||B_0} = R_{||B_0}^{-1} = \hat{\Gamma} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (5.2)
\]

\[
R_{\text{coil}} = R_{\text{cwrot}}^x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \quad (5.3)
\]

where \( \sigma_{\text{crystal}} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} \quad (5.4) \)

In this case, the final result for the measured NMR frequency shift can be written as

\[
\sigma_{\text{LAB33}}(\theta) = \sigma_{22} \sin^2 \theta + \sigma_{33} \cos^2 \theta - 2\sigma_{23} \cos \theta \sin \theta \quad (5.5)
\]

Another example can be given when the crystal y-axis is coaxial with the NMR coil and the crystal z-axis (at \( \theta=0^\circ \)) is along the applied field \( B_0 \):
Inserting eq. 5.6 into eq. 5.1 gives us:

$$\sigma_{LAB33}(\theta) = 1 \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & cos\theta & -sin\theta \\ 0 & sin\theta & cos\theta \end{pmatrix} = \sigma_{11} sin^2\theta + \sigma_{33} cos^2\theta - 2\sigma_{13} cos\theta sin\theta$$  (5.7)

This outlines the basic procedure for obtaining the shielding tensor in the crystal frame from the data. Once the crystal tensor is obtained, an additional final transformation is required to obtain the tensor in the PAS frame, as Figure 5.5 shows this will involve Euler transformations (angles $\alpha, \beta, \gamma$).
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Figure 5.6 XTALFIT program interface
As discussed above analysis of $24 \times 3$ data sets simultaneously was carried out using XTALFIT (Fig. 5.6). This first program tool uses a graphical user interface (gui) with 6 sliders ((Fig. 5.6 (A)) so the user can adjust the tensor components and visually match Gaussian peaks to the spectral peaks. The optimized tensor components are then imported into a second program tool, called TENSOR (Fig. 5.7), which allows the user to diagonalize the lab frame shielding tensor ((Fig. 5.7 (B))and obtain a visual of the tensor geometry relative to the lab or crystal frames ((Fig. 5.7 (C)). The refined results for each crystal included the six tensor components ($9 - 3 = 6$).
components, since by symmetry $\sigma_{ij} = \sigma_{ji}$, along with the single eigenvector set ((Fig. 5.7 (D)) in the case of $^7$Li data and two eigenvector sets for the $^{31}$P data.

The presence of two sets of eigenvectors make the analysis of the $^{31}$P data a little bit more complicated, for this reason TENSOR program was used together with other two programs: XTALFIT1 and XTALFIT2. XTALFIT1 allows to fit only one rotation set from one crystallographic axis and to calculate the Euler Angles arising from the misalignment of the crystal when it was mounted. XTALFIT 2 is designed to fit simultaneously two tensors by adjusting the Euler angle that these form, this is the case described later for $^{31}$P spectra for LiMnPO$_4$.

### 5.3 Results and Discussion

Figure 5.8 shows the unit cell of the LiMnPO$_4$ olivine; by replacing Mn with Fe yields the LiFe$_x$Mn$_{1-x}$PO$_4$ olivines. The transition metals ($M$=Fe, Mn) are coordinated with six oxygen atoms, in distorted $MO_6$ octahedra, and are interconnected by covalent phosphate PO$_4$ tetrahedral units.
Figure 5.8 Orthorhombic unit cell for the phospho-olivine compound LiFe$_x$Mn$_{1-x}$PO$_4$. The unit cell was built using the software package VESTA [11].

From previous studies it known that pure LiFePO$_4$ exhibits a very stable structure due to the strong covalency of the P-O bonds in the (PO$_4$)$_{3-}$ tetrahedron [59, 60]. As a result, there is a very small percentage (less than 7%) of structural distortion that usually occurs during Li$^+$ ions intercalation/deintercalation [61]. LiMnPO$_4$ on the other hand, exhibits a higher redox potential than LiFePO$_4$ but, unfortunately demonstrates poor kinetics during charging/discharging [62].

The replacement of Mn$^{2+}$ for Fe$^{2+}$ in the LiFePO$_4$ lattice yields LiFe$_x$Mn$_{1-x}$PO$_4$, which is stable throughout the composition range $0 \leq x \leq 1$. This material has been studied by many groups [63-66] and it is conclusive that the presence of Mn$^{2+}$ increases both the energy density (by nearly 20%) and the capacity with respect to pure LiFePO$_4$. For this reason LiFe$_x$Mn$_{1-x}$PO$_4$ has attracted much interest.
There are some unanswered questions pertaining to the underlying physical mechanisms governing the interesting electrochemical properties of this system. One of the outstanding issues is concerned with the Mn/Fe spatial distribution inside the lattice. Since $^7$Li and $^{31}$P can serve as probes of the local magnetic environments, this NMR study may be able to offer new insights into the transition metal distribution.

The main interactions are fundamentally paramagnetic, highly anisotropic, and as previously described are responsible for the large frequency shifts and broadening observed in both $^7$Li and $^{31}$P spectra. The interactions are characteristic of through-space (pseudocontact) nuclear-paramagnet dipolar interactions and through-bond electron mediated contact interactions. Although both through-space and through-bond phenomena are present in the spectra, this work provides an opportunity for possibly sorting out the contributions directly from the NMR data. Grey et al. [67] were able to calculate the Fermi contact contribution for $^7$Li and $^{31}$P centers via density functional theory (DFT) calculations. From their studies, combined with MAS NMR results, they found that the distribution of Mn and Fe cations in LiFe$_x$Mn$_{1-x}$PO$_4$ materials is random across $x=0.25, 0.5$ and $0.75$ phases and the substitution of Mn and Fe induces very little distortion in the mixed phase.

All data given here for LiFePO$_4$ where acquired previously and is included in the thesis work of T. Nosach[68]. The present work focuses primarily on $^7$Li; however, there are some new $^{31}$P results for LiMnPPO$_4$ and a further refinement of the $^{31}$P data for LiFePO$_4$ and using XTALFIT and XTALFIT2.
5.3.1 $^7$Li NMR

In the case of $^7$Li the primary spectral features arise from two terms in its Hamiltonian

$$v_{Li} \propto I \cdot (D + A) \cdot \chi \cdot B_0 + I \cdot Q \cdot I \quad (5.1)$$

$I$ is the nuclear magnetic moment, $\chi$ is the paramagnetic susceptibility, $D$ is the dipolar through-space paramagnetic or pseudocontact interaction tensor, $A$ is the hyperfine Fermi contact interaction tensor, $B_0$ the external magnetic field and $Q$ is the interaction tensor between the $^7$Li electric quadrupole moment and the surrounding electric field gradient (EFG) [69]. As mentioned earlier (Chapter 2, eq. 2.42) the NMR frequency (shift, using the $\delta$ -notation) is related to the tensor components and rotation angle $\theta$ as follows:

$$\delta_{shift} = \delta_i \cos^2 \theta + \delta_{ij} \sin^2 \theta - 2\delta_{ij} \cos \theta \sin \theta \quad (5.2)$$

In most instances with these spectra, the satellite contributions are not clearly resolved, and for this reason, no analysis of the quadrupole interaction is presented. It suffices to say that the relatively large spectral widths observed here are compounded by the presence of the $m = \frac{3}{2} - \frac{1}{2}$ quadrupole broadened satellites. Therefore, the central transition peak position provides all the necessary information pertaining to the $D + A$ interaction tensor of equation (5.1).

The data for $^7$Li were collected for all three orthogonal crystallographic directions for 6 crystals LiFe$_x$Mn$_{1-x}$PO$_4$ (x=0, 0.25, 0.5, 0.6, 0.75, 1) and fitted with Gaussians. In figures 5.9-5.14 are shown the three rotation patterns and the simulations (in red) for each single crystal.
Figure 5.9 $^7$Li rotation plots ($0^\circ \leq \theta \leq 360^\circ$) about the three crystallographic axes X, Y and Z for LiFePO$_4$. 
Figure 5.10 $^7$Li rotation plots ($0^\circ \leq \theta \leq 360^\circ$) about the three crystallographic axes X, Y and Z for LiFe$_{0.75}$Mn$_{0.25}$PO$_4$. 
Figure 5.11 $^7$Li rotation plots ($0^\circ \leq \theta \leq 360^\circ$) about the three crystallographic axes X, Y and Z for LiFe$_{0.6}$Mn$_{0.4}$PO$_4$
**Figure 5.12** $^7\text{Li}$ rotation plots ($0^\circ \leq \theta \leq 360^\circ$) about the three crystallographic axes X, Y and Z for LiFe$_{0.5}$Mn$_{0.5}$PO$_4$
Figure 5.13 $^7$Li rotation plots ($0^\circ \leq \theta \leq 360^\circ$) about the three crystallographic axes X, Y and Z for LiFe$_{0.25}$Mn$_{0.75}$PO$_4$
Figure 5.14 $^7$Li rotation plots ($0^\circ \leq \theta \leq 360^\circ$) about the three crystallographic axes X, Y and Z for LiMnPO$_4$. 
Starting with LiFePO$_4$ (Fig. 5.9), large positive shifts (~+1300ppm) are observed for rotations about the crystal Y and Z axis, while large negative shifts of the same order are recorded for rotations about X and Z, satellites are clearly observed for rotations about Y, but not well resolved for the other two axes. Previous studies [70] conducted on the same sample report the quadrupolar coupling constant to be equal to 65 kHz. Unfortunately, no resolved satellites are visible on all the other samples, which may be related to structural disorder in the mixed TM crystals, resulting in broad spectra. For LiFe$_{0.75}$Mn$_{0.25}$PO$_4$ (Fig. 5.10), the largest negative shifts (~-500ppm) characterize the rotations about the X and Z axis and positive shifts (~+800ppm) for X and Y. For LiFe$_{0.6}$Mn$_{0.4}$PO$_4$ (Fig. 5.11), the largest negative shift (~-880ppm) and positive shift (~+1137ppm) characterize the pattern obtained for rotations about X. In the case of LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ (Fig. 5.12) the largest positive (~+900ppm) and negative (~-600ppm) shifts are evident for rotations around Z axis while for LiFe$_{0.25}$Mn$_{0.75}$PO$_4$ (Fig. 5.13) the largest positive (~+1240ppm) and negative (~-900ppm) shifts occur for rotations around Y axis. To complete the picture, the other end point, LiMnPO$_4$ (Fig. 5.14), shows the largest positive shift (~+900ppm) when rotating the crystal around the Y axis and the largest negative shifts (~-600ppm) for rotations around X axis. By looking at the values for the shifts it is clear that all lithium shifts lie in a range that goes from approximately +1000 ppm to -1000 ppm, this range can be interpreted as the range in which “through-space” interactions are predominant. The result extracted using TENSOR and XTALFIT programs are given below.
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<table>
<thead>
<tr>
<th>LiFe$<em>x$Mn$</em>{1-x}$PO$_4$</th>
<th>PAS Eigenvalues</th>
<th>$\delta$iso</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>x=1</td>
<td>$\delta_{11} = -1093, \delta_{22} = -89, \delta_{33} = 1142$</td>
<td>-13</td>
</tr>
<tr>
<td>x=0.75</td>
<td>$\delta_{11} = -806, \delta_{22} = 236, \delta_{33} = 850$</td>
<td>93</td>
</tr>
<tr>
<td>x=0.6</td>
<td>$\delta_{11} = -773, \delta_{22} = -283, \delta_{33} = 1222$</td>
<td>53</td>
</tr>
<tr>
<td>x=0.5</td>
<td>$\delta_{11} = -638, \delta_{22} = -25, \delta_{33} = 1058$</td>
<td>132</td>
</tr>
<tr>
<td>x=0.4</td>
<td></td>
<td>42 (C)</td>
</tr>
<tr>
<td>x=0.25</td>
<td>$\delta_{11} = -624, \delta_{22} = -49, \delta_{33} = 879$</td>
<td>69</td>
</tr>
<tr>
<td>x=0</td>
<td>$\delta_{11} = -703, \delta_{22} = 143, \delta_{33} = 888$</td>
<td>109</td>
</tr>
</tbody>
</table>

Table 5.1 $^7$Li interaction tensor eigenvalues and eigenvectors in its PAS. $\delta$iso represents the average eigenvalue expressed in units of ppm. The value for $\delta$iso in column (A) are given in ref.[1], for column (B) in ref.[2] and the value (C), matching x=0.4 is reported in ref. [3]

In Table 5.1, the first column indicates the sample, the second column gives the eigenvalues ($\delta_{11}, \delta_{22}$ and $\delta_{33}$) for the interaction tensor, in the third column are listed the values for the isotropic shifts obtained as the average eigenvalue in this work, and the last two columns report results from studies conducted on polycrystalline samples.
All results reported for (A), (B) and (C) were obtained combining static and MAS NMR experiments, in particular for the values in column (A) Ultrafast MAS technique was used to improve sensitivity and resolutions of the NMR spectra. For an easier visualization, the data given in Table 5.1 are plotted versus $x$ in LiFe$_x$Mn$_{1-x}$PO$_4$:

![Graph showing Li single crystal and MAS NMR shifts of LiFe$_x$Mn$_{1-x}$PO$_4$](image)

**Figure 5.15** $^7$Li single crystal and MAS NMR shifts of LiFe$_x$Mn$_{1-x}$PO$_4$

From the above figure, it is clear that a good agreement is found for $x=0.25$ and $x=1$, as for the remaining values, the difference between single crystal and MAS data is relevant. This
disagreement can be attributed partially to temperature gradients. In fact, paramagnetic materials are characterized by temperature-dependent shifts, as an example in Fig 5.16 we report $^7$Li MAS NMR measurements of LiMnPO$_4$ at a different temperature conducted by Reimer et. al. [2]

![Figure 5.16](image)

**Figure 5.16** $^7$Li NMR shift measurements of LiMnPO$_4$ taken at various temperature in a 1.54 T magnet [12]

When performing MAS or ultrafast MAS experiments, because of the spinning motion the sample’s temperature will increase due to friction (up to 70 °C for ultrafast MAS).

An interesting aspect emerging from our results is the large isotropic shifts measured for $x = 0.5$ and 0.75, apparently the presence of Mn atoms affects the system considerably around lithium sites in such a way that the contribution to isotropic shift, entirely attributed to the pseudo contact interaction, is perhaps also due to Fermi contact interaction. Unfortunately we do not know how the different transition metal atoms arrange in the structure and we cannot separate
the contributions but we believe, in contrast with previous studies [1], that the substitution on Mn and Fe actually induces a distortion in the mixed phases especially when x ≤ 0.75.

5.3.2 $^{31}$P NMR

In the case of $^{31}$P experiments, the approach to acquire and analyze the data is similar to the one used for $^7$Li. The NMR frequency for $^{31}$P resonances is proportional to:

$$
v_p \propto I \cdot (D + A) \cdot \chi \cdot B_0 \quad (5.4)
$$

and in the same way described for $^7$Li, the NMR frequency shift is linked to the tensor components with respect to the crystal axes and rotation angle $\theta$ as shown in eq. 5.2. No quadrupolar splitting appears in the NMR spectra when investigating the phosphorous sites, since $^{31}$P nuclei have spin $\frac{1}{2}$.

As mentioned previously, acquiring $^{31}$P NMR spectra from compounds like LiFe$_x$Mn$_{1-x}$PO$_4$ is very challenging due to the large paramagnetic shifts and shift anisotropies caused by the paramagnetic transition metal ions. In fact, several trials were done to center the acquisition window.

Below in Fig. 5.17 are displayed the data for $^{31}$P. In the same way described in the previous section, the spectra were collected for all crystallographic axes denoted as X, Y and Z. For each axis, 24 spectra were acquired every 15°. In this thesis, the only $^{31}$P spectra reported are the ones taken for LiMnPO$_4$, the results shown for LiFePO$_4$ come from previous studies conducted by P.Stallworth and T. Nosach.
By looking at the three rotation plots the shift range goes from approximately +2000 ppm to -500 ppm, a range similar to the one seen in $^7$Li data. Even if not shown, the same shift range applies for $^{31}$P data of LiFePO$_4$ [70]. The main difference arising when comparing $^7$Li and $^{31}$P for LiMnPO$_4$ is the presence of two resonances for all three axes and for the majority of the rotation.
angles. Having two sets of resonances lead us to think that two tensors arise when investigating phosphorous environments. In fact, from structural considerations, two resonances are expected from rotations about the Y-crystal axis since the xz plane contains two magnetically inequivalent phosphorus sites, but from Fig. 5.16 we can see two peaks for rotations about all three crystallographic axes. With this idea in mind, the fitting of the phosphorous data was done first, by focusing only on one tensor using XTALFIT, the fit for each axis was then refined with XTALFIT1, finally all data and fits were exported into XTALFIT2 from which we extract the angles between the two tensors components. The final values where then imported into TENSOR from which the interaction tensor components in its PAS were obtained. Unfortunately, up to now we were not able to separate the two tensors so all results given for $^{31}$P data are expressed in terms of only one tensor.

In Table 5.2 are shown the results for the tensor components and the value for the isotropic shift for LiMnPO$_4$ compared with values reported in previous studies.

<table>
<thead>
<tr>
<th></th>
<th>PAS Eigenvalues</th>
<th>$\delta_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>(A)</td>
</tr>
<tr>
<td>LiMnPO$_4$</td>
<td>$\delta_{11} = -772$, $\delta_{22} = 360$, $\delta_{33} = 1332$</td>
<td>8137</td>
</tr>
<tr>
<td>LiFePO$_4$[D]</td>
<td>$\delta_{11} = 4351$, $\delta_{22} = 3380$, $\delta_{33} = 3289$</td>
<td>3673</td>
</tr>
</tbody>
</table>

*Table 5.2* $^{31}$P interaction tensor eigenvalues and eigenvectors in its PAS. $\delta_{iso}$ represents the average eigenvalue expressed in units of ppm. (A) and (B) are the same studies referenced in Table 5.1, while (D) is reported in ref.[70]
All results obtained from $^{31}\text{P}$ single crystal NMR studies, find good agreement with previously reported MAS results. One important thing to notice is that for LiMnPO$_4$ the frequency scale in Fig. 5.15 does not match the table entry for $\delta$iso, this because, as mentioned earlier, our zero was shifted by +8000 ppm. This tells us that phosphorous environments are characterized by two different types of interactions: the Fermi contact interaction responsible of large positive shifts of +8000 ppm and +3500 ppm and the pseudo contact interaction responsible for the approximately 2000 ppm range.

### 5.4 Conclusions

$^7\text{Li}$ and $^{31}\text{P}$ single crystal NMR spectroscopy has the potential to provide a very detailed characterization of the local magnetic structure of LiFe$_x$Mn$_{1-x}$PO$_4$ ($x=0$, 0.25, 0.5, 0.6, 0.75, 1) crystals. Using computer simulations we were able to calculate the components of the interaction tensor in its PAS giving rise to the lithium and phosphorous shifts. The values obtained for the isotropic shifts were compared with previously reported static and MAS data conducted on polycrystalline samples. In the case of $^7\text{Li}$, we found a good agreement for the pure Fe and for LiFe$_{0.25}$Mn$_{0.75}$PO$_4$, it seems to be that the biggest discrepancy arises for pure Mn, LiFe$_{0.75}$Mn$_{0.25}$PO$_4$ and LiFe$_{0.5}$Mn$_{0.5}$PO$_4$. This can be linked to two possible reasons: the first is that the MAS data reported where acquired without taking into considerations the effects on the shifts due to temperature variations and the second is that the presence on Mn atoms in the structure induces an additive contribution to the shift due to Fermi contact interaction and this can be also related to a possible distortion of the structure. The rotation plots observed for all samples show that the pseudo contact shifts, in the case of $^7\text{Li}$ lies in a range of frequencies that
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goes from approximately +1000 ppm to -1000 ppm. Up to now, we cannot quantify the possible contribution arising from the Fermi contact interaction.

In the case of $^{31}$P, only two single crystals were investigated using single crystal NMR, LiFePO$_4$ and LiMnPO$_4$. Our results for the isotropic shifts are in good agreements with the ones reported for the polycrystalline samples. Similarly to the $^7$Li results, the $^{31}$P shifts occur in the ±1000 ppm range for LiFePO$_4$ and from 0 to 2000 ppm for LiMnPO$_4$, so we can affirm that the phosphorous environments are also effected by the pseudo contact interaction. But an additional shift of +3500 ppm for LiFePO$_4$ and +8000 ppm LiMnPO$_4$, tells us that another interaction is present that does not appear in the case of lithium, and that is the Fermi contact interaction.

![Figure 5.18](image)

**Figure 5.18** Representation of the two mechanisms responsible for the NMR shifts for $^7$Li and $^{31}$P. The range defined by the red arrows, represents the contribution arising from through-space paramagnetic susceptibility effect common to both nuclei. The arrows in grey describe the contribution to the shift due to Fermi contact interaction.

Unfortunately, we still need to perform $^{31}$P NMR on all samples to achieve a better understanding of the magnetic environment around the phosphorous sites in the mixed TM compounds.
As for $^7$Li, we are currently trying to understand how the interaction tensor is oriented with respect to the crystal frame. Unfortunately, numerous alignment errors between the XRD and the determined principal axes resulted in inconsistent results. Accordingly, these measurements must be repeated in the future.

As for the different contributions to the shift, one way to confirm our results, would be to compute the dipole sums, described in Chapter 3 Section 2.2 eqs 2.46 and 2.49, to numerically calculate the NMR shifts arising from pseudo and Fermi contact terms.

To conclude, it is important to add that except for the pure Fe and pure Mn samples, there are no single crystal studies in the literature on the other mixed phases and this makes the presented work very challenging and unique. In fact, the ability to extract magnitude and orientation of the interaction tensor components permits to understand the connection between transferred spin density, bonding and local field distribution leading to emphasize the sensitive link between interaction tensor orientation with respect to the crystal axes and molecular and electronic structure. These notions can only be gained analyzing the anisotropic phenomena, which are lost when performing MAS NMR on polycrystalline samples. Our hope, once the phosphorus characterization is complete is to gain a better knowledge of the local and long range distortion due to the cation mixing, and possibly determine whether or not the cation mixing follows a random site distribution.
Chapter 6

Self-Diffusion Coefficient Measurements on PS-PEO (16-16) LiTFSI 
(0.06≤r≤0.30)

6.1 Introduction

Future success of high-energy rechargeable batteries will require large improvements in cell safety and cycle life. These improvements are connected to increasing the stability between lithium conducting electrolytes and high energy electrode materials. Nowadays one of the biggest challenges in the manufacture of lithium-based rechargeable cell with excellent energy density, cycle life and safety, is to fight the instability between high energy electrode materials and the conventional liquid electrolytes [14, 71].

Solid polymer electrolytes have been widely studied as an alternative to organic liquid electrolytes because of their appealing features such as: low flammability, high electrochemical stability and mechanical stiffness [14]. In particular a subset of solid polymer electrolytes, block copolymers mixed with lithium salts, are particularly interesting because they have the advantage of microphase separation to decouple the materials responsible for ion transport and mechanical stiffness [72]. Here we consider the system polystyrene-\textit{block}-poly(ethylene oxide) (SEO) mixed with lithium bis-(trifluoromethanesulfonyl) imide salt (LiTFSI) (figure 6.1). The polystyrene (PS) block provides mechanical stiffness and the poly(ethylene oxide) (PEO) block solvates and transports ions derived from LiTFSI [73].
In particular we explore the transport properties of block copolymer electrolytes over a wide range of salt concentrations for the system polystyrene-\textit{block}-poly(ethylene oxide) (PS-\textit{b}-PEO, SEO) mixed with lithium bis-(trifluoromethanesulfonyl) imide salt (LiTFSI). The polymers under study are PS-PEO(16-16) over the salt concentration range $r=0.06$-$0.30$, where $r$ is the molecular ratio of salt to ethylene oxide moieties. Recent studies \cite{74} have showed that in these block copolymers the conductivity is maximized at a salt concentration of $r=0.1$. However from other studies conducted by Hudson et al. at University of California, Berkley \cite{16}, it is in the high salt regime that the conductivity of PS-PEO is maximized. Thus, it is important to further investigate such behavior, and for such purpose the ion self-diffusivities for each salt concentration were measured by pulsed field gradient nuclear magnetic resonance spectroscopy (PFG-NMR, in this work we focused our attention on lithium cations and fluorinated anions. From previous Small Angle X-ray Scattering (SAXS) studies used to characterized morphology and grain size of PS-PEO(16-16), it is evident that at all salt concentration the block polymer exhibits a lamellar morphology.
6.2 Experimental

Sample preparation and previous characterization - All samples were designed, prepared, and provided by our collaborators from the Department of Materials Science and Engineering and the Department of Chemical and Biomolecular Engineering at the University of California, Berkeley: K. Timachova, Dr. I. Villaluenga, and Prof N. P. Balsara. The electrolytes and sample preparation are described in detail in ref. [16]. In the same study are reported the results obtained from Small-angle X-ray Scattering (SAXS), scanning transmission electron microscopy (STEM) and differential scanning calorimetry experiments to characterize the morphology (figure 6.2), grain size and crystallinity of the samples, while ac impedance spectroscopy was used to measure the ionic conductivity as a function of temperature. Below $r=0.11$, the grain size $L$ is relatively large (~90 nm), it decreases with the increase of salt concentrations and it reaches an average minimum value of 39 nm for $r \geq 0.21$.

Figure 6.2 Dark field STEM images of PS-PEO(16-16) at several salt concentrations, increasing from left to right. The white bar on the bottom left for $r=0$ represents 100 nm, and it applies to all images.
By looking at the STEM images, it seems that the lamellar structure observed for low salt concentrations \( r \leq 0.18 \) changes becoming perforated at higher salt concentration. But the SAXS profiles show the suppression of the even order peaks, indicating a nearly symmetric lamellar structure for all salt concentrations below \( r=0.55 \).

**Diffusivity measurements** - NMR measurements were performed on a Varian Direct Drive 300 MHz spectrometer (\( B_0=7.1T \)) and using a DOTY Z-Gradient Diffusion probe (max. gradient 1200 G/cm). To maintain the integrity of the samples, these were prepared and packed in NMR tubes under Argon to avoid direct contact with air. Temperature was maintained at 90°C above the melting point of the ethylene oxide block. A bipolar pulse pair stimulated echo sequence was used for all experiments (Chapter 3, Sec.2).

The diffusion experiments were performed by repeating the pulse sequence 32 times incrementing the gradient strength, an intensity versus gradient strength plot is the result of each experiment.

\(^7\)Li diffusion NMR was used to investigate the diffusion behavior of the Li cations, and \(^{19}\)F diffusion NMR was used for the TFSI anions.

In order to obtain self-diffusion coefficients appropriate for the domain size probed, several experiments on each sample, and for both nuclei, were performed by varying the diffusion time \( \Delta \). We attempted to use the same values of \( \Delta \) for each sample \( (40 \, ms \leq \Delta \leq 600 \, ms) \), but unfortunately with the increase of salt concentration it was not possible to obtain a full attenuation in intensity (at least 95% of the signal) for \( \Delta \leq 100 \, ms \).
6.3 Results and Discussion

As mentioned in the experimental chapter (3.2), we observed a deviation from the single-exponential decay typical of isotropic samples and we have explored two models to describe the ionic diffusion:

- a model with 2 types of isotropic diffusion regimes: a fast diffusion within the crystalline domains and a slow diffusion mechanism representing the crossing of the interphase between 2 crystallites (grain boundary);

- a model where the oriented diffusion within the crystallites can be extended to a macroscopic phenomenon.

6.3.1 ‘Fast and Slow’ diffusion regimes

As discussed Chapter 3 Section 2.1, multi-exponential decays in diffusion experiments are typically fitted to the sums of exponentially decaying components when investigating heterogeneous systems. In our models, the signal attenuation can be simulated with a bi-exponential fit:

\[ I = P_s e^{-\gamma^2 \delta^2 g^2 D_{slow} \left( \frac{\Delta B}{3} \right)} + (1 - P_s) e^{-\gamma^2 \delta^2 g^2 D_{fast} \left( \frac{\Delta B}{3} \right)} \]  \hspace{1cm} (6.1)

where \( P_s \) is the relative amplitude (‘slow’ population) of the component with slow diffusion \( D_{slow} \), characteristic of diffusion across grain boundaries, and the component with fast diffusion is described by \( D_{fast} \), characteristic of diffusion through a single grain. Using three independent
fitting parameters leads to several solutions, so for this reason the following constrains were used:

1. Discard the diffusion profiles not achieving at least 95% signal attenuation.
2. For each sample composition, find the most accurate fits and use these values as reference data for the other fits. These starting points are highlighted in yellow in Table 6.1 and 6.2.
3. The remaining data were then fitted constraining the values of $D_{\text{fast}}$ and $D_{\text{slow}}$ to fluctuate approximately ±20% from the reference data (the ones highlighted in yellow in Table 6.1 and 6.2) and the weights ($P_f$ and $P_s$) were obtained accordingly. The constraints on the self-diffusion coefficients are justified by the independence of their values with respect to $\Delta$, in which no measurements were taken for $\Delta<40$ ms.

As an example, below are shown two bi-exponential fits obtained for the sample at lowest salt concentration for both $^7\text{Li}$ and $^{19}\text{F}$.
Figure 6.3 $^7$Li and $^{19}$F PFG Diffusion NMR data for PS-PEO(16-16) at $r=0.06$, fitted with a bi-exponential curve.

For higher salt concentrations, $r=0.3$ and in some cases for $r=0.24$, a very satisfactory fit was obtained by a single-component fit. This is consistent with a high degree of disorder in samples with high salt concentrations.

In the tables below are summarized the values obtained for $D_{\text{slow}}$ and $D_{\text{fast}}$ with the correspondent relative amplitude $P_s$ (‘slow’ population) and $P_f = 1 - P_s$ (‘fast’ population).

<table>
<thead>
<tr>
<th>$r$</th>
<th>$D_{\text{slow}}$ (*10$^{-12}$ m$^2$/s)</th>
<th>‘Slow’ Population</th>
<th>$D_{\text{fast}}$ (*10$^{-12}$ m$^2$/s)</th>
<th>‘Fast’ Population</th>
<th>$\Delta$(ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
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Table 6.1 $^7$Li PFG-NMR: ‘Slow’ and ‘Fast’ self-diffusion coefficients
Table 6.2 $^{19}$F PFG-NMR: ‘Slow’ and ‘Fast’ self-diffusion coefficients

For an easier visualization the diffusion data summarized in the two tables above are displayed in figure 6.4. The fast and slow diffusion coefficients are compared with the average diffusion obtained using the equation:

$$D_{ave} = P_s \times D_{slow} + P_f \times D_{fast}$$  \hspace{1cm} (6.2)
For both anions and cations, the value of the diffusion coefficients decreases over the range of salt concentrations. As expected for low salt concentrations ($r=0.06$) the fast component is approximately four times bigger than the slow one for both Li cations and TFSI anions. Another common feature to both nuclei is that fast and slow diffusion coefficients become almost undistinguishable when approaching $r=0.3$. This is consistent with the high degree of disorder in samples with high salt concentration.

The main difference between the two graphs resides in the behavior of the average diffusion (in blue). In fact in the case of $^7$Li, the average diffusion is closer to the fast component values and
this is due to the fact that for low salt concentrations the population of fast-diffusing species is much higher than the slow-diffusion one. While for $^{19}$F, it seems that the two populations are relatively similar for all salt concentrations.

### 6.3.2 Anisotropic Diffusion

The theory behind anisotropic diffusion is explained in Chapter 3, Section 2.2.

For our system, due to lamellar structure, we assume the symmetry of our system to be cylindrical ($D_{xx} = D_{yy} \neq D_{zz}$), the signal attenuation can be then expressed as:

$$
\psi(g\delta, \Delta) = \frac{1}{2} \int_0^\pi \exp \left[ -(\gamma \delta g)^2 \Delta (D_{zz} \cos^2 \theta + D_{xy} \sin^2 \theta) \right] \sin \theta d\theta \quad (6.4)
$$

Under these assumptions, we can distinguish two components of the self-diffusion: a radial diffusion $D_{xy}$, which occur parallel to the lamellae, and an axial diffusion $D_{zz}$, orthogonal to the previous one. The axial and radial diffusion coefficients were obtained from eq.6.4 under the condition that $D_{xy} > D_{zz}$, since we expect, at least for low salt concentrations, higher values for the diffusion coefficients along the lamellae than across it. The results of our calculations are summarized in Table 6.3 and Table 6.4.
Below are displayed the axial and radial data for both nuclei and for the different values of $\Delta$.
Figure 6.5 $^7$Li and $^{19}$F PFG-NMR on PS-PEO (16-16)/LiTFSI ($0.06 \leq r \leq 0.3$): axial (in red), radial (in black) diffusion values Vs. salt concentration r.
For both Li cation and TFSI anion, it is clear that for low salt concentrations ($r=0.06$) the radial diffusion is much greater than the axial (almost an order of magnitude). This is consistent with the lamellar morphology of the samples; with the increase in salt concentration the two diffusion coefficients converge, in fact the average value of axial and radial diffusion for $r=0.30$, is compatible to the value obtained from a single-exponential fit within 5% uncertainty.

### 6.4 Conclusions

$^7$Li and $^{19}$F PFG-NMR experiments were conducted on PS-PEO (16-16)/LiTFSI over a salt concentrations range $r=0.06$-$0.3$. From the results obtained, we observed a deviation from a single-exponential decay and we have explored two models to explain this phenomenon.

In the case of domain-restricted diffusion, in both Li cations and TFSI anions the self-diffusion coefficients decrease of almost a factor of 4 from $r=0.06$ to $r=0.3$, and these two coefficients become approximately the same when the salt concentration reaches its highest value. This is consistent with the high degree of disorder in samples with high salt concentrations.

For the anisotropic diffusion model, a cylindrical symmetry is considered. This arises from the lamellar structure of the samples and leads to distinguish two self-diffusion coefficients: the axial diffusion and the radial diffusion, parallel to the lamellae and larger than the axial one since higher value for the diffusion coefficients along the lamellae than across it are expected.

For both nuclei, the radial diffusion decreases of almost an order of magnitude with the increase in salt concentration while the axial diffusion does not experience such fast decrease. As predicted the radial diffusion is higher than the axial diffusion for low salt concentrations ($r=0.06$); and the two diffusion coefficients reach almost the same value when $r=0.3$. 
From the results of both models we can affirm that increasing salt concentration slows ionic motions; in particular we proved that for $r=0.3$, the signal attenuation versus the gradient strength can be fit with a single exponential decay which implies that there is only one self-diffusion coefficient. This, in contrast with the X-ray diffraction results, can be attributed to a possible change of the sample morphology when we add salt, in fact the perforated lamellae scenario seems more accurate at high salt concentrations. Another important result derives from the anisotropic model, the presence of a radial and axial self-diffusion coefficients shows that there is a directional and length dependence on the ion conduction pathways.

This work is still under investigation and we hope it helps to understand how the increase in salt concentrations effect the dynamical properties of block copolymers.
List of References


Nuclear Magnetic Resonance Studies of Electrode and Electrolyte Materials for Li-Ion Batteries


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