# EXPLORING ION DYNAMICS IN SOLID-STATE ELECTROLYTES THROUGH SOLID-STATE NMR

## EXPLORING ION DYNAMICS IN SOLID-STATE ELECTROLYTES OF LITHIUM-AND SODIUM-ION BATTERIES THROUGH SOLID-STATE NUCLEAR MAGNETIC RESONANCE

By MENGYANG CUI, B.Sc., BSE,

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Author: Mengyang Cui

Supervisor: Professor Gillian R. Goward

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#### Lay Abstract

All-solid-state batteries, which utilize thermally stable solid-state electrolytes, are considered the potential candidates for the next generation of batteries. An important aspect in their performance is ion transport within the electrolytes, though these dynamics are often slower than in liquid electrolytes and not fully understood. Further research is needed to improve ion dynamic in such materials. In this thesis, various nuclear magnetic resonance (NMR) techniques were used to explore ion transport properties across different materials from molecular level to macro-scales. This work demonstrates how advanced NMR techniques can provide valuable insights into the mechanisms and rates of ion dynamics within solid ionic conductors, enhancing our understanding of battery performance and potentially offering to greener, safer, and more efficient energy storage solutions to the public.

#### Abstract

This body of work applies various solid-state nuclear magnetic resonance (ssNMR) techniques to study the ion transport phenomena within different solid-state electrolytes (SSEs) for energy storage devices. The investigation covers length scales ranging from atomic-level ion hopping to microscale ion diffusion, extending further to macroscopic electrode-electrolyte interfacial stability. <sup>7</sup>Li NMR diffusometry was employed to probe the Li<sup>+</sup> transport in polymer electrolytes upon structural modifications. Additionally, pressure-treated crystalline electrolytes were analyzed with diffusometry and relaxometry, to explore how mechanical stress impacts ion transport as a result of micromorphological changes of the crystalline materials. Furthermore, with the combination of ssNMR and computational methods, the crystallographic Na<sup>+</sup> site exchange mechanism in a novel crystalline sodium ion conductor was also explored. Finally, in situ <sup>7</sup>Li ssNMR spectroscopy and magnetic resonance imaging (MRI) were employed to correlate stack pressure with metallic Li microstructures formed at the Li-electrolyte interface in a hybrid electrolyte. In summary, the work presented in this thesis demonstrates the robustness of ssNMR in delivering detailed insights into ion dynamics and molecular structures, from molecular scale to macroscopic interface stability. It provides valuable information for battery research, enhancing our understanding of material properties and performance in energy storage applications.

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# List of Abbreviations (Alphabetical)

3QMAS	Triple-quantum magic-angle spinning
a. u.	Arbitrary unit
ASSB	All-solid-state battery
ASSNIB	All-solid-state sodium-ion battery
ВСР	Block copolymers
BO	Butylene oxide
BPP (for diffusometry)	Bipolar-pulse-pair
BPP (for relaxometry)	Bloembergen-Purcell-Pound
BVEL	Bond-valence energy landscape
CASTEP	CAmbridge Serial Total Energy Package
CPMG	Carr-Purcell-Meiboom-Gill
CSA	Chemical shift anisotropy
CSI	Chemical shift imaging
СТ	Central transition
DAS	Dynamic-angle spinning
DC	Direct current
DEC	Diethyl carbonate
DFT	Density functional theory
DMC	Dimethyl carbonate
DOR	Double-rotation experiment
DOSY	Diffusion ordered spectroscopy
EC	Ethylene carbonate
EFG	Electric field gradient
EIS	Electrical impedance spectroscopy
EMC	Ethyl methyl carbonate
EO	Ethylene oxide

EV	Electric vehicles
EXPRESS	EXchange Program for RElaxed Spin System
F1	Indirect dimension in a 2D NMR spectrum
F2	Direct dimension in a 2D NMR spectrum
FEC	Fluoro-ethylene carbonate
FIB-SEM	Focused ion beam scanning electron microscopy
FID	Free induction decay
FOV	Field of view
FWHM	Full-width-at-half-maximum
GB	Grain boundary
GHG	Greenhouse gas
GIPAW	Gauge-including projector augmented wave
HE	Hybrid electrolyte
HPLC	High-performance liquid chromatography
IE	Imaging echo
IL	Ionic liquid
LA0/LA500	LAGP prepared at 0(powder)/500 MPa
LAGP	$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$
LAMP	$Li_{1+x}Al_x(M)_{2-x}(PO_4)_3$ (M = Ge, Ti, Zr, Sn)
LCO	LiCoO <sub>2</sub>
LE	Liquid electrolyte
LED	Longitudinal eddy current delay
LFP	LiFePO <sub>4</sub>
LGPS	$Li_{10}GeP_2S_{12}$
LIB	Lithium-ion battery
LiFSI	Lithium bis(fluorosulfonyl)imide
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
LLZO	Li7La3Zr2O12

LLZTO	$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$
LMB	Lithium metal battery
LPSC	Li <sub>6</sub> PS <sub>5</sub> Cl
LS0/LS250/LS500	LSnPS prepared at 0(powder)/250/500 MPa
LSnPS	$Li_{10}SnP_2S_{12}$
MAE	Mean absolute error
MAS	Magic-angle spinning
MD	Molecular dynamic simulation
MQ/3Q/1Q/ZQ	Multiple-/ triple-/ single-/ zero-quantum transitions
MQMAS	Multiple-quantum magic-angle spinning
MRI	Magnetic resonance imaging
NASICON	Na SuperIonic CONductor
NIB	Sodium-ion battery
Ni-MH	Nickel-metal hydride
NMC	LiNi <sub>x</sub> Mn <sub>y</sub> Co <sub>1-x-y</sub> O <sub>2</sub>
NMR/MR	Nuclear magnetic resonance/magnetic resonance
01	Transmitter frequency offset
OCV	Open circuit voltage
PAF	Principal axis frame
PBE	Perdew-Burke-Ernzerhof
PC	Propylene carbonate
PE	Polyethylene
PEEK	Polyether ether ketone
PEO/PEG	Poly-ethylene oxide/polyethylene glycol
PFG	Pulsed-field gradient (NMR diffusometry)
PGSE	Pulse-gradient spin-echo
PGSTE	Pulse-gradient stimulated echo
PHEV	Plug-in hybrid electric vehicles

PLION	Plastic lithium-ion battery
РО	Propylene oxide
PS	Polystyrene
PXRD	Powder X-ray diffraction
RF	Radio frequency
RMSD	Root mean square deviation
RT	Room temperature
S.H.E.	Standard hydrogen electrode
SCE	Solid crystalline electrolyte
SGE	Solid glass electrolyte
SCXRD	Single-crystal X-ray diffraction
SG	Spoiler gradient
SN	Succinonitrile
SNR	Signal-to-noise ratio
SPE	Solid polymer electrolyte
SSE	Solid-state electrolyte
ssNMR	Solid-state nuclear magnetic resonance
ST	Satellite transition
TD	Time domain
ТМ	Transition metal
ТО	Triethylene oxide
UNFCCC	United Nations Framework Convention on Climate Change
VT	Variable temperature
WCA	Weakly-coordinated anion
XCT	X-ray computed tomography

# List of Symbols (Alphabetical)

$a_{Li}$ +	Activity of Li <sup>+</sup>
$\vec{B}_0$	External magnetic field
$\vec{B}_1$	RF-excited field
$\widehat{H}_{CS}/\widehat{H}_J/\widehat{H}_D$	Hamiltonians of CSA/scalar coupling/dipolar coupling
$\widehat{H}_D^{homo}/\widehat{H}_D^{hetero}$	Homonuclear/heteronuclear dipolar coupling Hamiltonians
$\widehat{H}_P / \widehat{H}_K$	Hamiltonians of paramagnetic/Knight shifts
$\widehat{H}_Q$	Hamiltonian of quadrupolar coupling
$\widehat{H}_{RF}$	Hamiltonian of RF pulse
$\widehat{H}_z$	Zeeman Hamiltonian
$\vec{M}_0$	Net magnetization aligns with the external magnetic field
$\vec{M}_{xy}$	Magnetization at the xy-plane
$\widehat{S_e}(\vec{r})$	Electron spin as a function of $\vec{r}$ from the nucleus
$\bar{V}_m$	Partial molar volume of Li at room temperature
$A_{electrode}$	Li foil surface area
$C_Q$	Quadrupolar coupling constant
c <sup>i</sup>	Charge carrier concentration
$C_k^I(m)$	Coefficient of the k <sup>th</sup> -rank term in $E_m^2$
$D^{+}/D^{-}$	Cationic/anionic diffusivity
$D^i$	Diffusion coefficient of specie <i>i</i>
$E_{I,m} I,m\rangle$	Eigenvalue (energy level) of $\hat{H}_z$ for the spin state I
E <sub>a</sub>	Energy of activation
E <sup>exp</sup>	Experimental potential
$E_m^1/E_m^2$	1 <sup>st</sup> -/2 <sup>nd</sup> -order energy perturbation of the quadrupolar effect
E <sup>o</sup>	Standard reduction potential
$\vec{G}(z)$	Magnetic field gradient

$P_F$	Averaged density of conduction $e^-$ over the Fermi level
$P_Q$	Quadrupolar product
<i>R</i> <sub>1</sub>	$R_1$ relaxation rate $(1/T_1)$
$R_2$	$R_2$ relaxation rate $(1/T_2)$
Ŝ	Spin angular momentum
<i>T</i> <sub>1</sub>	Longitudinal (spin-lattice) relaxation
<i>T</i> <sub>2</sub>	Transverse (spin-spin) relaxation
$V_{00}^Q/V_{20}^Q/V_{40}^Q$	$0^{\text{th}}$ -/ $2^{\text{nd}}$ -/ $4^{\text{th}}$ -rank tensors for the $1^{\text{st}}$ -order quadrupolar effect
$V_{k0}^Q$	Spherical tensor of the corresponding k <sup>th</sup> -rank term
$W_{20}^{Q}$	2 <sup>nd</sup> -rank spherical tensor for the 1 <sup>st</sup> -order quadrupolar effect
$d_D$	Dipolar coupling constant
e <sup>-</sup>	Electron
$\vec{k}$	Reciprocal of Cartesian space ( $\vec{k}$ -space)
$k_B$	Boltzmann constant
k <sub>reaction</sub>	Rate constant for thermally activated process
$m_I$	Nuclear spin state
$p_{\Psi}$	Spin population of each eigenstate
<i>t</i> +	Cation transference number
$t_p$	RF pulse length
$v_0$	Larmor frequency in MHz
$z^i$	Number of charges on the specie <i>i</i>
$\alpha_I/\beta_I$	$\alpha/\beta$ spin state for <i>I</i>
$\beta_p$	Flip angle of the net magnetization
$\delta_{11}^{PAF}/\delta_{22}^{PAF}/\delta_{33}^{PAF}$	Principle values of the shielding tensors at laboratory frame
$\delta_{F1-3QMAS}$	The isotropic shift in the indirect dimension of 3QMAS
$\delta_{F2}$	Center of gravity shift
$\delta_{iso}$	Isotropic chemical shift

$\delta_{qis}$	Quadrupolar induced shift
$\eta_{CS}$	Asymmetric parameter for CSA
$\eta_Q$	Quadrupolar asymmetry parameter
μ̂	Spin magnetic moment
$\mu^+/\mu^-$	Cationic/anionic mobility
$\mu_0$	Vacuum permeability factor
$\mu_B$	Bohr magneton
$\sigma_{\Delta}$	Anisotropic term in the shielding tensor
$\sigma^i$	Ionic conductivity
$\sigma_{iso}$	Isotropic shielding tensor
$\sigma_{iso}^{ref}$	Shielding of the reference compound
$\sigma_{\chi\chi}^{PAF}/\sigma_{yy}^{PAF}/\sigma_{zz}^{PAF}$	Diagonal elements in the shielding tensor respect to PAF
$ au_c$	Correlation time
$ au_g$	Gradient stabilization delay
$ au_{vc}$	Evolution time used in the Hahn echo sequence
$ au_{vd}$	Variable delay used in inversion-recovery experiment
XΡ	Pauli magnetic spin susceptibility per atom
$\omega_0$	Larmor frequency in rad s <sup>-1</sup>
$\omega_{CS}$	Shielding contribution to the frequency
$\omega_Q^1/\omega_Q^2$	1 <sup>st</sup> -/2 <sup>nd</sup> -order quadrupolar splitting
$\omega_{eff}(z)$	Effective Larmor frequency for spin under $\vec{G}(z)$
$\omega_g(z)$	Correction of Larmor frequency for spin under $\vec{G}(z)$
$\omega_p$	Frequency of the RF pulse
ω <sub>ref</sub>	Frequency of reference signal
Δ	Diffusion time in NMR diffusometry
$\Delta L$	Length of Li consumed/created
$\Delta V$	Volume of stripped/platted Li metal

$\Delta z$	Field of view
$\Delta \omega$	Offset of the frequency from the reference frequency
h	Planck's constant
ħ	Reduced Planck's constant
Ж	Knight shift
R	Ideal gas constant
η	Microstrain
Α	Pre-exponential factor
В	Exponential factor for the stretch exponential fit
D	Diffusion coefficient in NMR diffusometry
F	Faraday constant
Ι	Spin quantum number
Q	Nuclear quadrupole moment
Res.	Resolution of the image
S(g,t)	Measured signal intensity in NMR diffusometry
$S(\omega)$	Complex Lorentzian of NMR signal
$b/b_{BPP}$	Singal attenuation power of PGSE/BPP sequence
dV	Volume occupied by spins in the Cartesian space
е	Elementary charge
$eq/eq_{zz}^{PAF}$	EFG tensor/EFG tensor defined at the z-axis in the EFG
g	Gradient strength
i	Imaginary number
n	Number of electrons (or number points in imaging)
n(Li)1/n(Li)2	Number of mol of Li consumed/created at the electrode
r	Internuclear distance
s(t)	NMR signal as a function of time
t	Time
Ζ	Spatial position

$lpha/eta/\gamma$	Euler angles
γ	Gyromagnetic ratio
δ	Gradient encoding/decoding time in NMR diffusometry
$\delta(ec{r})$	Contact interaction
$ heta/\phi$	Angles at the laboratory frame deviates from PAF
λ	Wavelength of X-ray source
$\rho(z)$	Local spin density
σ	Shielding tensor

#### **Declaration of Academic Achievements**

The copolymer samples were synthesized by V. St-Onge from Professor J. P. Claverie's group at University of Sherbrook in **Chapter 3**, V. St-Onge also conducted the ionic conductivity and DC polarization measurements. In **Chapter 4**, Dr. J. D. Bazak provided instructions and engaged in discussions regarding the NMR diffusometry and relaxometry measurements. V. M. Jarvis contributed to the data collections and analyses for the powder X-ray diffraction. Dr. D. H. Brouwer contributed to the DFT calculation for the <sup>23</sup>Na NMR parameters, as well as the discussion of the calculation and experimental data. C. A. Gurwell prepared the MATLAB codes for the automatic processing of the EXPRESS package in **Chapter 5**. In **Chapter 6**, Dr. K. J. Sanders provided instructions on the MRI and CSI setup for the *in situ* experiments. Stack pressure calibration within the pencil cell was completed by C. A. Gurwell. The rest of the experimental designs, data collections, and analysis were performed by M. Cui.

## Chapter 1 – Introduction 1.1 Overview

Undoubtedly, mitigating climate change is one of the most critical challenges for current and future generations. In 2015, in the United Nations Framework Convention on Climate Change (UNFCCC), 196 countries reached the Paris Agreement – an international treaty to fight against climate change, which aims to hold the global average temperature to well below 2 °C above pre-industrial levels" and to "limit the global temperature rise below 1.5 °C".<sup>1</sup> Consequently, the long-term target is to reach net-zero greenhouse gas  $(GHGs, mainly CO_2)^2$  emission by the second half of this century. However, UNFCCC recently indicates that more actions are needed to achieve these goals.<sup>1</sup> Certainly, one promising approach to combating climate change is to reduce the reliance on fossil fuels. Thus, there is a growing demand worldwide to transition from fossil fuel energy consumption to renewable energy sources and storage solutions.<sup>2</sup> In the transportation industry, the large-scale adoption of electric vehicles (EVs) is expected to play a significant role in reducing the GHGs emissions. In the year of 2023, new EV sales has reached a peak of 14 million globally, including both pure battery EV and plug-in hybrid EV (PHEV), which together accounts for ~ 18% of all vehicles sold in 2023.<sup>3</sup> Unlike the traditional internal combustion engines that utilize gasoline or diesel as the fuels to power the vehicle. EVs, utilize a powertrain that includes motor, gearbox, and most importantly, a rechargeable *battery* for energy storage and conversion.<sup>4</sup>

There are a variety of types of battery chemistries, leading to the four most successful rechargeable battery adapted in commercial markets. They are lead-acid batteries invented by G. Plante in 1850; nickel-cadmium batteries introduced by W. Jungner in 1899; nickel-metal hydride (Ni-MH) batteries firstly commercialized in 1989; finally, Li-ion batteries (LIBs) that firstly commercialized in 1991 by Sony Corporation.<sup>5</sup> LIBs are now the most common type of power source used in the current generation of EVs and PHEVs. The reason that LIBs outperform other types of battery is mainly due to the properties of metallic Li. **Figure 1.1**<sup>6</sup> clearly illustrates the advantages of energy and power densities of Li-based battery chemistry in comparison with the others. Any Li-based batteries including the LIB, polymer-based electrolyte plastic Li-ion (PLION) battery, and Li metal batteries (LMBs) that utilizes metallic Li as electrode, exhibit significantly higher gravimetric and volumetric energy densities. In other words, they have much better *capacities* than the other battery chemistries can provide. Li is the most electropositive (-3.04 V vs standard hydrogen electrode, or S.H.E.) and the lightest metal (with the atomic mass of only 6.94 g mol<sup>-1</sup>), with low density of 0.53 g cm<sup>-3.2, 6</sup> Therefore, metallic Li was utilized as electrode materials in the early 70s, but soon abandoned due to safety concerns.

The subsequent improvements and modifications were conducted on LMBs, which utilizes *electrochemical intercalation* of Li<sup>+</sup> into crystalline layered structure, demonstrated by M. S. Whittingham and J. B. Goodenough.<sup>2, 7</sup> A. Yoshino, replaced the dangerous metallic Li with more chemically stable graphitic carbon. Owing to the huge success of LIB applications, the three above-mentioned founders of LIBs shared the 2019 Nobel prize in chemistry for their contributions to the invention of modern LIBs.



**Figure 1.1** Comparison of gravimetric (in W h kg<sup>-1</sup>) and volumetric (in W h L<sup>-1</sup>) energy densities and power densities of different battery technologies. Reprinted with permission from *Nature*. 414, 3590367.<sup>6</sup> Copyright © (2001) *Springer Nature*.

In the past several decades, the energy densities and cyclability of LIBs have been considerably improved. However, several challenges remain for large-scale applications of LIBs. The current LIBs still suffered from low capacity, which can be direct translated into "lower mileage" on the EVs upon full charge. Fast charging of the battery could also cause battery degradation and poor long-term cycling life. Finally, the most immediate concern is the safety. The conventional LIBs utilize organic liquid electrolytes (LEs) pose significant safety concerns as several undesirable processes such as mechanical abuse,
dendritic Li induced short-circuiting, or thermal runaway.<sup>7</sup> These processes can ignite the thermally unstable LEs and resulting in fire hazard as well as explosion.

To address these concerns, the most immediate method is adapting all-solid-state batteries (ASSBs), which replace the flammable LEs with more thermally stable *solid-state electrolytes* (SSEs). SSEs can be generally categorized based on their chemical properties: solid-polymer electrolytes (SPEs), inorganic solid crystalline electrolytes (SCEs), solid glass electrolytes (SGEs) and hybrid solid electrolytes (HEs, also known as "composite SEs") that combine elements from the above categories, including LEs.<sup>8, 9</sup> Despite numerous materials have been reported with excellent electrochemical/mechanical/chemical properties in the past decades. SSEs still face several limitations for practical ASSB application. In LEs, lithium ions are solvated and transported via solvation shells formed by organic solvent molecules. This offers rapid ion-transport which is not rate-limiting in terms of electrochemical performance. In contrast, a key issue in SSEs is the sluggish ion dynamics, which mostly arise from the slower solid-state transport mechanisms and undesirable mechanical properties that limit long-range transport of lithium ions. Thus, to tackle these challenges, it is necessary to explore various strategies for improving the ion dynamics of the well-established electrolyte candidates *via* chemical and mechanical modifications. Additionally, it is also critical to investigate the ion dynamics of the new candidates which could be promising materials for next generation of ASSBs. However, typical electrochemical characterization methods cannot provide insights of fundamental ion transport mechanisms at the molecular level. Thus, in this thesis, various magnetic resonance techniques were employed to not only characterize the local

environments of the novel electrolyte materials, but also to probe the ion dynamic information at the molecular level. The advanced nuclear magnetic resonance (NMR) techniques/experiments demonstrated in this work can provide comprehensive insights into ion dynamics of different materials, and potentially opens a door for improving the next generation of batteries.

## **1.2 Working Principles of LIBs**

Modern LIBs consist of three major working components, here, a simple schematic diagram is illustrated in **Figure 1.2**.<sup>10,11</sup> A *cathode* (positive electrode), an *anode* (negative electrode), and *electrolyte* in between that facilitates the transports of Li<sup>+</sup>. During discharging, the Li stored in between the graphite layers will be oxidized into Li<sup>+</sup>, and release electrons to the external circuit through Cu current collector. The oxidized Li<sup>+</sup> thus released into the bulk electrolyte through solvation shell provided by the electrolyte solvent molecules. The solvated ion will be further transported to the cathode side, where Li<sup>+</sup> released from the solvation shell and intercalate into the layered transition metal (TM) polyanion frameworks. The oxidation of Li<sup>+</sup>, with the electrons introduced from the external circuit through Al current collector. In addition, a Li<sup>+</sup>-permeable separator (usually polyethylene or polypropylene) is used to prevent the direct physical contact of the two electrodes. For the charging process, all the above-mentioned steps were reversed. The reversibility of the redox reactions at each electrode of the LIB enables the device to

function as rechargeable/secondary batteries, with the original example of  $LiCoO_2 (LCO)^{12}$  as the cathode and graphite as the anode. The reversible electrochemical reactions and the corresponding redox potential (vs Li<sup>+</sup>/Li) can be written as:<sup>2</sup>



**Figure 1.2** Schematic diagram of the basic components and the working principles of LIBs upon discharging process. The LIB utilizes a layered transition metal (TM) oxide as the active cathode material and graphite as the active anode material, and the conventional LEs as the Li<sup>+</sup> transport medium.

Cathode: 
$$LiCo^{III}O_2 \leftrightarrow Li_{1-x}Co^{IV}O_2 + xLi^+ + xe^- \quad 0 < x < 0.5 \quad E^o = 3.9 V$$
  
Anode:  $6C + xLi^+ + xe^- \leftrightarrow Li_xC_6 \qquad x = 1 \qquad E^o = 0.2 V$   
Net reaction:  $6C + LiCo^{III}O_2 \leftrightarrow Li_xC_6 + Li_{1-x}Co^{IV}O_2 \qquad E^o = 3.7 V [1.1]$ 

Equation [1.1] demonstrates both the cathodic and anodic half cell reactions, as well as the net reaction of the LIB.  $E^o$  is the *standard reduction potential* of the redox process, which can be correlated with the generic *Nernst equation* shown in Equation [1.2]:<sup>2</sup>

$$E^{exp} = E^o - \frac{RT}{nF} \ln(a_{Li^+})$$
 [1.2]

where  $E^{exp}$  is the experimental reduction potential (or cell voltage when compared two electrodes), which is a correction to the  $E^o$  under more "practical" conditions, such as variable temperature *T* and activity  $a_{Li^+}$ . *R* is the ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), *n* is the number of electrons involved in the redox reaction, and *F* is the *Faraday constant* (96485 C mol<sup>-1</sup>). This equation provides the practical evaluation for different redox chemistries, making it possible to assess the cell voltage based on the cathodic and anodic reactions under variable conditions.

Over the years, various cathode and anode materials have been developed. For the cathode side, with the LCO (practical capacity of 140 mAh g<sup>-1</sup>) being the first successful commercialized battery material, introduced by Sony Corporation in 1991.<sup>2, 13</sup> Following this, polyanion oxide LiFePO<sub>4</sub> (LFP) and its derivatives have higher capacities (~ 30% higher) as well as remarkable reversibility, though they are limited by a narrow operating voltage window.<sup>2, 14</sup> The LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>1-x-y</sub>O<sub>2</sub> (NMC) class of materials presents an excellent balance of capacity and voltage window.<sup>13</sup> However, the broader application of NMC is constrained by issues related to structural and thermal stabilities, as well as the high costs associated with Ni and Co.<sup>15</sup> In contrast to the diverse array of materials used for the

cathode side, the anode side in LIBs is predominantly graphite in the commercial market. The idea of lithium-intercalated graphite is considered as the 1<sup>st</sup> example of the anodic component in modern LIBs, introduced by A. Yoshino (petroleum coke was used originally). For years, it has been considered by far the most ideal role for the main anode material, because graphite has a low average de-/lithiation potential (mostly operated at 0.1 -0.3 V vs Li/Li<sup>+</sup>),<sup>16, 17</sup> making high voltage LIBs possible when used against most of cathodes  $(3.0 - 4.5 \text{ V vs Li/Li}^+)$ .<sup>18</sup> In addition, the delocalized  $\pi$ -bonds resulted from the  $sp^2$  hybridization of carbons facilitates efficient electron transport, resulting in fast kinetic for the reduction of Li<sup>+</sup> or oxidation of Li during charging and discharging, respectively. Finally, the strong covalent bonds between the carbons with low ionicity contributes to the ability of weakly bonding lithium, making them undergo fast ion transport (diffusion) upon interaction and de-intercalation.<sup>16</sup> Silicon can also be an anode of interest because it can offer much higher theoretical capacity (4200 mAh g<sup>-1</sup>), making it advantageous over the graphite.<sup>2</sup> This high theoretical capacity of Si is attributed to its alloying mechanism, which accommodates more Li per Si than per C (Li<sub>4.4</sub>Si vs LiC<sub>6</sub>).<sup>2</sup> However, Si anode suffers from substantial volume expansion (300 - 400%) during cycling,<sup>2, 18</sup> which can lead to mechanical failures in batteries. As a result, it is now more common to implement Si as an additive in anode mateirals, such as trapping small amounts of Si nanoparticles in between the graphite sheets.<sup>2</sup> This approach improves the overall battery capacity and also mitigates the volume expansion issue.<sup>2</sup>

For the traditional LEs, there are a lot more options in the selection of materials. Nevertheless, they are basically the combinations of two core components – Li salt and organic solvents. The Li salts are usually composed of Li<sup>+</sup> and a weakly-coordinated anion (WCA, also known as "non-coordinated anion"), the presence of WCA will decrease the ionicity between the Li<sup>+</sup> and the anion, providing efficient disassociation when dissolving in the solvent and thus release free Li<sup>+</sup>. The common examples for lithium salts are lithium hexafluorophosphate (LiPF<sub>6</sub>), lithium bis(fluorosulfonyl)imide (LiFSI), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).<sup>7, 19, 20</sup> Organic carbonate solvents are widely adapted for the LE solvents. They can be vaguely categorized into two groups based on their carbon backbone structures. The 1<sup>st</sup> group contains the cyclic carbonates, such as ethylene carbonate (EC) and propylene carbonate (PC), or fluoro-ethylene carbonate (FEC).<sup>7, 19, 20</sup> The cyclic carbonates typically possess high dielectric constants, making them favourable for interact with Li<sup>+</sup> via dipole-dipole force and form solvation shells.<sup>19</sup> However, this property also increases the molecular interaction between the solvents, resulting in an increase in the solvent's viscosity.<sup>19</sup> The 2<sup>nd</sup> type consists of carbonates with linear chains, such as dimethyl carbonate (DMC), diethyl carbonate (DEC), or ethyl methyl carbonate (EMC). They have much better flowability but weaker dipole interaction with Li<sup>+</sup> in comparison to the cyclic ones.<sup>19</sup> To balance the ionic conductivity and the solution viscosity, a combination of carbonates from each group are usually required.<sup>19</sup>

So far, the basic working principle of LIB is discussed for the LE system. In this thesis, most of the materials presented in this work will be focusing on SEs. Thus, in the following section, the transport mechanisms in different SEs will be discussed in detailed.

### **1.3 Ion Transport Mechanisms in Solid-State Electrolytes**

LIBs have achieved great market success since the first commercialization in the 90s. However, critical safety issues arise because of the usage of highly flammable organic LEs, primarily due to the low flash points of those linear carbonates (around 0 - 30 °C).<sup>19</sup> The flammability of LEs raises serious safety concerns for large-scale applications (such as in EVs). Hence, introducing thermally and chemically stable ASSBs can thoroughly address the safety concerns associated with the organic LEs. Other than the thermal and chemical stabilities, as the core component of ASSBs, SSEs are usually required to possess the following properties:<sup>7, 8, 20-25</sup>

- 1. High ionic conductivity of at least 10<sup>-4</sup> S cm<sup>-1</sup>, the SSE materials that with the conductivities higher than this value can be considered practical.
- 2. Electronically insulating, so that the redox chemistry cannot occur within the electrolytes during charging and discharging processes.
- 3. Wide electrochemical stability windows. The redox reactions within the electrolyte cannot occur when in contacts with strongly oxidizing cathodes or reducing anodes, with the working potentials of 3.0 4.5 V and 0 0.3 V (vs Li/Li<sup>+</sup>), respectively.
- 4. Good mechanical properties (low Young's modulus) to achieve intimate contacts in between the electrode-electrolyte and electrolyte-electrolyte interfaces.
- 5. Easy to fabricate with affordable prices for the purposes of large-scale manufacturing and commercialization purposes.

In the past few decades, extensive efforts have been made for the material explorations, and numerous versions of SSE materials have been reported since then. SSEs can be categorized into two general groups – the organic solid polymer-based (SPEs) and the inorganic SSEs.<sup>26</sup> For the 1<sup>st</sup> group, SPEs are composed with Li salt and macromolecular polymeric backbones. Even while they are organic materials as well, SPEs possess much better thermal stabilities than the LEs.<sup>20, 23</sup> The 2<sup>nd</sup> group contains both solid ceramic electrolytes (SCEs) and solid glass electrolytes (SGEs), which utilize crystalline or amorphous inorganic frameworks to conduct Li<sup>+</sup>. Due to the nature of non-combustible inorganic substances, this class of material have outstanding thermal stabilities,<sup>9, 21, 25</sup> allowing the battery operation at higher temperatures.

The successful commercialization of SSEs is nevertheless hindered by one of the major barriers – the slow practical ionic conductivities at room temperature (RT). Unlike the traditional LEs facilitate Li<sup>+</sup> transport through solvation structure by the highly mobile solvent molecules in the liquid phase (vehicular transport), the ion transport mechanisms are significantly different in across various types of SSEs. These transport mechanisms typically limited by many different intrinsic and extrinsic factors for the ASSB applications. Ion conduction in SPEs is enabled by dissolving lithium salts into polymeric backbones, the dissolved Li<sup>+</sup> can be transported by the coordination sites from the polar groups within the polymers, based on the Lewis acid-base theory.<sup>26</sup> The first type of ion transport mechanism in SPE is realised by the polymer chain mobilities (segmental motion).<sup>8,26</sup> The long-range ion motion results from the interactions between Li<sup>+</sup> and adjacent coordinated polar groups. Due to the highly mobile polymer chains, Li<sup>+</sup> changes its coordination rapidly

in between the polymer chains, as shown in **Figure 1.3a**. This is believed to be the dominant factor influencing the ion conductivity in SPEs. This often occurs in the amorphous regions above the glass transition temperature  $T_g$ , whereas the crystalline regions in the SPEs are much more rigid due to the interlock channels formed by firmly stacked polymer chains (**Figure 1.3b**), which cause the lost of chain flexibility to participate in segmental motion.<sup>23, 26, 27</sup> Nevertheless, ion conduction in this region is still possible *via* the second type of transport mechanism– *ion hopping*, though most researchers believe this is not the major role in the ionic conduction for SPEs.<sup>8, 23, 26</sup> In this case, the Li<sup>+</sup> transport is achieved by the association and disassociation between the Li<sup>+</sup> and the surrounding polar groups within the polymer chains. This mechanism was reported for the one of the most common SPEs – poly-ethylene oxide (PEO), which remains mostly crystalline (~ 80%)<sup>26</sup> below 65 °C.<sup>23, 28</sup>



**Figure 1.3** Li<sup>+</sup> conduction mechanisms in the SPEs, where (**a**) demonstrates the conduction within the amorphous phase, and (**b**) illustrates the conduction in the crystalline phase.

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In the electrolyte, charge transport is achieved *via* mobility of both cations moving towards the cathode and anions moving towards the anode. With that, the *transference number*  $t_+$  of Li<sup>+</sup> can be defined for LIBs as follow:<sup>8, 29</sup>

$$t_{+} = \frac{\mu^{+}}{\mu^{+} + \mu^{-}} \tag{1.3}$$

where  $\mu^+$  is the cationic mobility and  $\mu^-$  is the anionic mobility under electric field (in m<sup>2</sup> s<sup>-1</sup> V<sup>-1</sup>).<sup>8</sup> Polymeric conductors contain both mobile cations and their counter anions due to the disassociation of Li salts. While Li<sup>+</sup> play the key role in the redox (Faradaic) processes, the presence of counter anions can lead to increased resistivity and polarization in the SPE.<sup>30</sup> Typically, the  $t_+$  values in SPEs are lower than 0.3, meaning that most of the charge is actually carried by the movement of the anions.<sup>8</sup> Ideally, the  $t_+$  values are preferred to be equal or closed to 1 (no counter ion movements). The ionic mobility can be directly correlated to *ionic conductivity*  $\sigma$ , measured with *electrical impedance spectroscopy* (EIS) – a common tool for characterizing the ionic conductivity of materials using equivalent circuit models to mimic different Faradaic or non Faradic processes.<sup>31</sup> The conductivity of charged species  $\sigma^i$  can be expressed *via:*<sup>8, 29</sup>

$$\sigma^{i} = \sum \mu^{i} c^{i} |z^{i}| F$$

$$\tag{1.4}$$

where  $c^i$  is the charge carrier concentration in mol L<sup>-1</sup>,  $z^i$  is the number of charges on the species *i* (unitless, e.g. +1 for Li<sup>+</sup>).<sup>29</sup> By examining **Equation [1.4]**, one can observe the trend that the electrical conductivity is proportional to the ion mobility, indicating the ion dynamic plays a crucial role in the performance of electrolyte. The ion mobility, electrical conductivity can be further correlated with the *diffusion coefficient*  $D^i$  (m<sup>2</sup> s<sup>-1</sup>) of the charged species, by the Nernst-Einstein relation:<sup>29, 32</sup>

$$D^i = \frac{k_B T \mu^i}{|z^i|F} = \frac{RT\mu^i}{|z^i|F}$$

and 
$$\sigma^{i} = \sum \frac{|z^{i}|^{2} F^{2} c^{i} D^{i}}{RT} = \frac{F^{2} c^{i} (D^{+} + D^{-})}{RT}$$
 (for monovalent salt) [1.5]

where  $k_B$  is the Boltzmann constant (1.38066 × 10<sup>-23</sup> J K<sup>-1</sup>),<sup>29</sup> D<sup>+</sup> and D<sup>-</sup> are the cationic and anionic diffusivities after ionization of the salt (measured by EIS). The significance of **Equation [1.5]** is that it links the *mass transport* property of the conductive ion species at the molecular level to the cell performance at the macroscale. The slower the charged species migrate, the lower the conductivity (or higher the resistivity in other words), leading to higher Ohmic polarization during the battery operation. Thus, in this work, we employed magnetic resonance to study the cationic and anionic diffusivity for different SPE materials, in order to investigate the mass transport properties of these novel electrolytes.

SCE materials have attracted significant research interests over the past few decades, primarily due to their superior thermal stabilities and  $t_+$  of unity. To date, many different families of SCEs for LIBs have been developed, including oxide, sulfide, and halides, all of which share similar ion conduction mechanisms. In SCEs, ion diffusion channels are usually formed by the spatial arrangements of static polyanionic frameworks.<sup>8</sup> Ion transportation occurs through diffusion in between the vacancies within these channels *via* three major mechanisms shown in **Figure 1.4**:<sup>8, 33</sup>

- Vacancy hopping, also known as vacancy migration. The mobile ion moving through adjacent vacancies generated by Schottky defects,<sup>8</sup> it leaves its previous occupied site into an available vacant, allowing for the occupation of another neighbouring ion. The continuous cycle of ion movement facilitates ion transportation within the material.<sup>8</sup>
- 2. *Interstitial hopping*. This is achieved by the interstitial ions diffuse through the void spaces created by the *Frenkel defects*.<sup>8</sup>
- 3. *Interstitial substitutional* mechanism, also known as interstitial knock-off mechanism. It can be considered as an extension of the previous interstitial hopping, where the moving ions displacing those adjacent ions that located at the original crystallographic sites.<sup>8</sup>

Even though the ion conduction mechanisms discussed above are different in terms of different crystal defects, nevertheless, they can all be classified as the "*ion hopping*" mechanism, dictating the ion dynamic in SCEs. Additionally, these mechanisms are not construed only to specific class of materials. In fact, significant efforts were made to create different types of defects within the SCE materials, to enhance the ion diffusion/conduction. Different strategies were employed such as creating cationic vacancies or interstitial sites *via* aliovalent *doping*,<sup>34-36</sup> or introducing local defects and disorders within the crystalline through mechanical modifications.<sup>37, 38</sup>



**Figure 1.4** Illustration of  $Li^+$  conduction mechanisms in the SCEs, and the energy landscape of ion hopping. Adapted with modifications from *Energy Sci Eng.*, *10*(5), 1645, Yang (2022).<sup>8</sup>

**Figure 1.4** illustrates an energy landscape for the ion hopping from site to site. The current understanding of long-range ion diffusion in SCEs is based on the hypothesis that individual hopping processes between the crystallographic sites, dictated by the polyanionic frameworks of the crystal structures.<sup>39</sup> Here, an *activation energy* can be defined as the minimum amount of energy required for such hopping process to occur. The value of the activation energy can be determined by examining the ion hopping rate as a

function of temperature, for any kinetic processes. Thus, the universal Arrhenius equation can be applied as the following equation:

$$k_{reaction} = Aexp(-\frac{E_a}{RT})$$
[1.6]

 $k_{reaction}$  represents the rate constant corresponding to for thermally activated processes, such as local ion hoppings,<sup>40</sup> long-range ion diffusion (*D*) within the crystalline,<sup>41</sup> as well as the macroscopic ionic conductivity ( $\sigma$ ).<sup>8, 40, 41</sup> *A* is the pre-exponential factor that measures the rate of temperature-independent kinetic process which is irrespective of its energy,<sup>42</sup>  $E_a$  is the energy of activation related to the ion migrations.

Typically, a low activation barrier is preferred, as it ensures the smooth transportation of mobile charge carriers in the SCE crystallines.<sup>39, 40</sup> For bulk ion diffusion within the SCE, the activation barriers of diffusion can be correlated to the highest energy of the energy landscape along the diffusion path.<sup>39</sup> However, when measuring the ion transportation of SCE by EIS at a macroscale, an important energy barrier needs to be considered – *grain boundaries* (GBs).<sup>8, 25</sup> As SCEs are typically utilized in polycrystalline forms in the ASSBs, GBs are the local crystal structural perturbations within the polycrystalline, often resulting from the high concentration of local defects.<sup>21, 25</sup> The presence of GBs can significantly restrict the rate of ion transport, and increase the activation barrier for the long-range ion transportation, it is usually the rate-limiting step hindering the ion migrations in the SCEs in real ASSBs application.

Up to this point, the fundamental ion transport mechanisms in SPEs and SCEs have been briefly covered, along with the discussions of the energy barriers involved in these processes. The following sections will provide some basic discussions about the SSEs that used in this thesis, including their historical developments, advancements, as well as current challenges.

#### **1.4 Electrolyte Materials**

#### 1.4.1 PEO-Based Solid Polymer Electrolytes (SPEs)

Polyethylene oxide (PEO), also known as polyethylene glycol (PEG), is a polyether compound with the chemical structure of H-(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>-OH, normally with a molecular weight of > 20000 g mol<sup>-1</sup>.<sup>28</sup> PEO is the most extensively researched polymer host material among all the polymers.<sup>23</sup> The successful applications of PEO as the host material can be mainly correlated to its good ductility,<sup>43</sup> good solubility of lithium salt,<sup>28</sup> and good interfacial electrochemical stability against electrodes.<sup>26</sup> However, the Li<sup>+</sup> dynamics in PEO-based SPEs are considered slow at RT.<sup>8, 23, 26</sup> As previously discussed, the Li<sup>+</sup> transport in PEO-based SPEs are primarily attributed to the amorphous phase of the PEO matrix, where the formation of crystalline PEO matrix is considered as the major barrier for Li<sup>+</sup> transports, as shown in **Figure 1.3**. Most of the PEO-based SPEs have the melting temperature T<sub>m</sub> of ~ 65 °C, below which the presence of crystalline phase could contribute to up to 80% of the host matrix,<sup>26</sup> hindering the application of SPEs at around RT.

Thus, researchers are primarily attempting to supress the crystallinity of PEO and enhance the percentage of amorphous region for better Li<sup>+</sup> transport at RT. Different strategies were explored to achieve this goal. One of the approaches is to incorporate additives into the polymer matrixes to disrupt the long-range order in the crystalline region of the PEO.<sup>28</sup> These additives include inorganic nanofillers (mostly Li<sup>+</sup>-conductive SCEs), short PEO oligomers onto the PEO backbone,<sup>28</sup> as well as the non-ionic plasticizer with succinonitrile (SN) being one of the most commonly reported plasticizer additives.<sup>28, 44</sup> As illustrated in **Figure 1.5**, Li<sup>+</sup> transport occurs through coordination between the polar groups – ethylene oxide (EO) units,<sup>28, 44</sup> the molecular size of SN (NC-CH<sub>2</sub>-CH<sub>2</sub>-CN) matches quite closely with the distance between Li<sup>+</sup> binding site within one EO unit (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-),<sup>44</sup> allowing SN to easily incorporate between the EO units/chains, which inhibits the crystallization of PEO and facilitates the Li<sup>+</sup> transport within a more homogeneous amorphous region. This approach leads to the remarkable ionic conductivity of > 10<sup>-4</sup> S cm<sup>-1</sup> at RT, in contrast to the non-modified PEO with the conductivity of about two magnitudes lower.<sup>44</sup>



**Figure 1.5** Graphical illustration of  $Li^+$  conduction mechanisms in the PEO-based SPEs, where (a) and (b) represents the intramolecular and intermolecular  $Li^+$  transports when no plasticizer SN is incorporated, respectively. (c) and (d) demonstrates the effect of addition of plasticizer SN for each process, respectively. Adapted with modifications from *Adv*. *Funct. Mater.*, *30*, 2007172, Xu (2020), open access.<sup>44</sup>

One other common strategy is to modify the PEO structure via copolymerization of other comonomers, also known as "block copolymers" (BCPs).<sup>28, 30</sup> These BCPs incorporate EO units with different side chains, disrupting the long-range order of the EO chain, reducing the crystallinity of the PEO host. This method requires rational design of the polymeric macromolecular architecture to effectively alter the PEO structure with minimum amounts of comonomers.<sup>30</sup> It can also provide other preferred mechanical properties to form free-standing polymer film using other blocks such as polystyrene (PS) and polyethylene (PE).<sup>28</sup> In summary, decreasing the crystallinity in PEO is an important approach to enhance the Li<sup>+</sup> dynamics. This thesis presents our collaborative study of the Li<sup>+</sup> dynamics in PEO-based SPEs under structural modifications of the PEO matrix, detailed discussions and results of which will be presented in **Chapter 3**.

#### 1.4.2 Solid Crystalline Electrolytes (SCEs)

Enormous research efforts have focused on the SCEs owing to their excellent thermal stability and good ionic conductivity. SCEs can be generally categorized into a few different groups based on their anionic compositions; the three representative groups are the oxides (phosphates), sulfides, and halides.<sup>8, 25</sup> For the oxide group, one of the promising candidate classes of materials is the aluminium-doped NASICON-type  $Li_{1+x}Al_x(M)_{2-x}(PO_4)_3$  (LAMP, M = Ge, Ti, Zr, Sn).<sup>25</sup> The name "NASICON" standing for Na SuperIonic CONductor, was first proposed for a fast sodium conductor with the parent phase composition of NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, reported by J. B. Goodenough et al. in 1976.<sup>45</sup> While this name was originally used to describe the materials with fast Na<sup>+</sup> conductivity, it is now

more commonly referred to as a specific type of crystal structure with space group of  $R\bar{3}c$ ,<sup>21</sup> rather than its literal meaning,<sup>46-49</sup> owing to the classic and iconic crystallographic frameworks of the NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The unit cell and the Li<sup>+</sup> conduction pathways in the NASCON Li<sub>1+x</sub>Al<sub>x</sub>(M)<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> is shown in **Figure 1.6**.<sup>50</sup>



**Figure 1.6 (a)** NASICON unit cell structure of the LAMP SCEs, the blue octahedra are  $MO_6$  and the violet tetrahedra are  $PO_4$  units respectively. (b) represents the conduction bottleneck in between the M1 (green) and M2 (yellow) sites between the two  $MO_6$  octahedra, with oxygen atoms shown in red. (c) demonstrates the conduction pathways of the M1 and M2 sites. Reprinted with permission from *J. Phys. Chem. C.*, *119*(29), 16432, Francisco (2015).<sup>50</sup> Copyright © (2015) *American Chemical Society*.

The backbone of NASCION structure is constructed by  $[MO_6]$  (blue) octahedron units corner-sharing alternatively with  $[PO_4]$  tetrahedron units, forming a 3D interconnected channels. In the undoped parent phase (LMP), Li<sup>+</sup> preferentially fill into the distorted octahedral sites between two antiparallel  $[MO_6]$  with coordination of 6 oxygens,<sup>25</sup>, <sup>51</sup> these are called Li1/M1 sites (6*d*, green spheres). Upon doping of trivalent Al to replace the tetravalent M cations at the octahedral sites, the charge imbalance introduces more Li<sup>+</sup> into the structure, occupying the Li2/M2 sites (18*e*, yellow spheres) in between the two Li1 sites, with 10-fold oxygen coordination.<sup>25</sup> The introduction of extra Li<sup>+</sup> at the Li2 sites form the "zig-zag" style Li<sup>+</sup> diffusion pathway between the Li1 and Li2, as shown in **Figure 1.6c**.<sup>25, 50</sup> The "bottleneck" of this diffusion is mainly controlled by the size of the [MO<sub>6</sub>] units, as illustrated in **Figure 1.6b**. This thesis mainly focuses on the study of the germanium analog of this class – LAGP,<sup>47</sup> which shares the same structure and Li diffusion pathways as the other NASICON, the relevant works will be presented in **Chapter 4** and **6**.

In 2011, Kamaya et al. reported a type of sulfide SCE material – the thiophosphate superionic conductor  $Li_{10}GeP_2S_{12}$  (LGPS), with the remarkable ion conductivity of 12 mS cm<sup>-1</sup>, which is nearly two orders of magnitude higher compared to the other oxide phases, <sup>52</sup> making it competitive to the LEs. The ground-breaking discovery of LGPS led to booming research for material explorations within this family. One of the most promising phases is the Sn analog  $Li_{10}SnP_2S_{12}$  (LSnPS), as it adapts the same structure as the LGPS.<sup>53</sup> The LSnPS material has a bulk conductivity of 7 mS cm<sup>-1</sup>, but the cost of this material is

reduced by 3-fold due to the replacement of expensive Ge by Sn, making them affordable for potential large-scale commercialization of ASSBs.<sup>53</sup>



**Figure 1.7** Singal crystal structure of thiophosphate LSnPS lithium superionic conductor. Reprinted with permission from *J. Am. Chem. Soc.*, *135*(42), 15694, Bron (2013).<sup>53</sup> Copyright © (2013) *American Chemical Society*.

**Figure 1.7** presents the single crystal structure of LSnPS, with the space group of  $P4_2/nmc.^{53}$  Similar to LGPS,<sup>52</sup> the framework of LSnPS is constructed by one-dimensional chains with edge-sharing [LiS<sub>6</sub>] octahedrons (not shown) and [Sn/PS<sub>4</sub>] tetrahedrons (light green) with the Sn2 : P2 = 1 : 1 at this site. The 1D chains are further interconnected with

[PS<sub>4</sub>] tetrahedrons (P1, pink) to from the 3D framework. The fast Li<sup>+</sup> conduction is realised by the partially occupied Li1 and Li2 located at the 16*h* sites along the c-axis, while the Li<sup>+</sup> transport at the ab-plane is predominantly contributed from the Li3 at the 4*d* positions, and the Li4 at the 4c position is believed to possess slow dynamic at a short timescale due to its coordination environments.<sup>53</sup> Nevertheless, the total Li<sup>+</sup> ion conductivity of the LSnPS can still achieve remarkable total conductivity of up to 4 mS cm<sup>-1</sup>, including the resistive component of GBs.<sup>53</sup>

While the sulfide-based materials benefit from the fast ion conduction, owing to the weaker electrostatic interaction between Li<sup>+</sup> and S<sup>2-</sup> in comparison with O<sup>2-,25</sup> One key drawback of this class of material is their significantly narrowed electrochemical windows. This is due to the oxidation of S<sup>2-</sup> at high potential (~ 2 V vs Li/Li<sup>+</sup>) and the reduction of P<sup>5+</sup> at low potential (~ 1 V vs Li/Li<sup>+</sup>).<sup>8</sup> In addition, it is well known that sulfide-based SCEs can undergo hydrolysis and generate toxic H<sub>2</sub>S upon contact with atmosphere, further hindering the application of thiophosphate materials for the next generation of ASSBs.

#### **1.4.3 Hybrid Electrolytes (HEs)**

As discussed earlier, various types of SSEs each have their own set of advantages and disadvantages. For example, PEO-based SPEs offer good mechanical processability and excellent chemical and electrochemical stabilities, but they have low Li<sup>+</sup> transference number and suffer from poor Li<sup>+</sup> conductivity at RT. Oxide-based polycrystalline SCEs exhibit good bulk ionic conductivity, yet their Li<sup>+</sup> transport is hindered by highly resistive grain boundaries and poor interparticle contacts. Sulfide-based SCEs, while known for their excellent ionic conductivity and high ductility, are limited by poor electrochemical and chemical stabilities.

Therefore, since a single-component SSE generally cannot fulfill all the requirements for ASSBs, a common strategy is mixing two or more electrolytes (and/or additives) to combine their complementary properties. These mixed electrolytes, often referred to as hybrid solid electrolytes (HEs),<sup>54-57</sup> also known as pseudo-, quasi-,<sup>57-60</sup> and composite solid electrolytes.<sup>60-62</sup> They are designed to enhance the overall performance of the SSEs by combining the advantages across different SSE materials, allowing the flexible modification of the electrolyte properties. For the PEO-based electrolytes, it is common to make HE with it by incorporating additives which can sufficiently suppress the crystallinity of the PEO. These additives can be generally categorized as active fillers and passive fillers. The active fillers refer to the additives that contain Li<sup>+</sup> and can provide Li<sup>+</sup> transportation pathway, such as various types of  $Li^+$ -conductive SCEs. Whereas the passive fillers are non-Li containing, such as plasticizer SN mentioned previously. The presence of fillers suppresses the recrystallization tendency of the PEO chains, creating considerably more amorphous phases of PEO and facilitate Li<sup>+</sup> transport.<sup>8, 26, 54, 55</sup> Additionally, in the PEObased HEs, the Li<sup>+</sup> transport cannot always be treated as Li<sup>+</sup> conduction in two distinct region, rather influenced by the interaction between the components of the hybrid structure. Previous studies conducted by Hu's group, utilizing <sup>6</sup>Li  $\rightarrow$  <sup>7</sup>Li isotope exchange NMR reveal a strong correlation of Li<sup>+</sup> migration pathway as a function of the weight ratio between the SCEs and PEO, for both sulfide and oxide SCEs.<sup>63, 64</sup>

The other HE system combines SCEs and ionic liquids (ILs) as the additive, which also has attracted extensive research interest. ILs are the organic salts (or "molten salts") with the melting points below 100 °C.<sup>56, 65</sup> They are composed of large and bulky organic cations, where the positive charge is shielded in the center by the alkyl groups, and the WCAs that have delocalized electrons from several possible resonance structures. Both of these factors cause ILs to remain in liquid form due to the weak electrostatic interactions.<sup>65</sup> Their good wettability allows them to facilitate the Li<sup>+</sup> transport at the SCE interfaces, reducing the resistivity of the electrolyte.<sup>57, 66</sup> Nevertheless, mixing different electrolyte phases can significantly alternate the mechanical properties, and there's still limited information regarding how the mechanical modifications can affect these HEs when in cooperation with Li anode.

#### **1.5 Pressure Effects in SCEs**

The development of superionic crystalline conductors in recent decades has significantly advanced the potential utilization of SCEs in ASSBs. SCEs offer excellent thermal stability and high ionic bulk conductivity. However, their mechanical properties often pose challenges for practical application. Specifically, the unstable and slow ion transport at particle interfaces and GBs can limit ion conduction at a macroscale. To address this issue, mechanical pressure is often applied during conductivity measurements and electrochemical cycling with the SCEs, which helps create better interfacial contacts between the SCEs and the electrolyte-electrode interface thereby enhancing ion transport.

There are two different definitions of mechanical pressures for SSEs and ASSBs, namely *fabrication* pressure and *stack* pressure.<sup>67, 68</sup> The fabrication pressure is a singletime compression for preparing SCE pellet from polycrystalline powder, usually with the levels of hundreds of MPa.67, 69, 70 The fabrication pressure will be released after the compression process is completed. Stack pressures is the constant pressure hold for maintaining good contacts between all the components in the ASSBs. The values of stack pressures are usually much lower, ranging from a few MPa up to several dozens of MPa.<sup>68,</sup> <sup>71-76</sup> Generally, high fabrication pressure level on the SCE is believed to be helpful to create intimate particle-particle contacts and facilitate ion transport at the GBs. Doux et al.<sup>67</sup> reported that a higher fabrication pressure can greatly improve the ionic conductivity for the argyrodite Li<sub>6</sub>PS<sub>5</sub>Cl (LPSC), which can be correlated with the enhanced GB transport due to the decreased porosity of the SCE pellet (Figure 1.8), visualized by focused ion beam scanning electron microscopy (FIB-SEM).<sup>67</sup> Kodama et al.<sup>70</sup> applied X-ray computed tomography (CT) to study the morphological change of the LPSC particle after application of pressure. The results showed that compression led to an increase in both the contact ratio and sphericity, which in turn contributed to the enhanced ionic conductivity.<sup>70</sup>



**Figure 1.8** The FIB-SEM images of the LPSC pellet prepared at the fabrication pressure of (a) 50 MPa and (b) 370 MPa, together with the corresponding 3D reconstruction shown in (c) and (d), respectively. (e) The ionic conductivity and the calculated relative density as a function of fabrication pressure. Reprinted with permission from *J. Mater. Chem. A.*, 8(10), 5049-5050, Doux (2020).<sup>67</sup> Copyright © (2020) *Royal Society of Chemistry*.

Most recent studies have shown that pressure effects can induce mechanical strain and stress, altering the local atomic structure of the SCE crystal.<sup>37, 38, 69, 77</sup> While some of these studies were conducted under active pressure conditions, it is still possible to attribute these effects to the fabrication pressure, as they are solely applied to the SCE at ultra-high pressure levels (ranging from hundreds of MPa to GPa). Therefore, even though fabrication pressure can significantly increase the overall conductivity of the SCE to some extent, it can also impart strain, hindering the local ion transport, eventually decrease the overall conductivity once exceed some thresholds.<sup>37, 38</sup> Thus, it is essential to carefully assess the fabrication pressure effect on ion dynamics in SCEs to distinguish between the contributions of improved particle contacts and grain boundary conductivity, versus the potential reduction in ion mobility due to structural alterations caused by pressure-induced mechanical strain.

The effect of stack pressure is also crucial to the functioning of ASSBs, so this aspect is extensively studied. Wang et al.<sup>71</sup> investigated the stack pressure effect on a Li/Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO)/Li symmetric cell, where a few cells were prepared to be cycled at different constant current density ranging from 50 to 400  $\mu$ A cm<sup>-2</sup>. Starting from the highest stack pressure of 3 MPa, then lowering the pressure stepwise to observe the voltage response (**Figure 1.9**).<sup>71</sup> It was found that with higher stack pressure, the cell can be cycled at a relatively high current density. When the pressure is below some thresholds at the corresponding current density, the cell will undergo significant polarization due to the void formation at the Li-electrolyte interface. This is the consequence of insufficient replenishment of Li metal from the stack pressure-induced mechanical deformation compared to the stripping rate of metallic Li foil from the galvanostatic test.<sup>71</sup> From this study, they defined "critical stack pressure", which means the minimum stack pressure required to maintain good Li-electrolyte contact under a fixed current density.<sup>71</sup> Although higher stack pressures can be favourable to the ASSBs cycling against Li metal as it decreases the overall resistance, studies also suggest that applying too much stack pressure could lead to cell short-circuiting for the cells prepared with LPSC.<sup>68, 73, 74, 76</sup> Because Li metal has a very low yield of 0.41 - 0.89 MPa,<sup>68, 74</sup> it can be extruded/creeped through the pores, voids, and GBs within the SCE pellet under high stack pressure. The extrusion and creeping of the soft Li metal leads to mechanically induced short-circuiting, introducing





**Figure 1.9 (a)** Potential response of Li/LLZO/Li as a function of current density at varying stack pressure. **(b)** Proposed mechanism of Li microstructure at the interface when the stack pressure is above the critical stack pressure so that the contact between Li and LLZO can be maintained **(c)** While the pressure is below the critical stack pressure, resulting in void formation at the interface. Reprinted with permission from *Joule*, *3*(9), 2165-2178, Wang (2019).<sup>71</sup> Copyright © (2019) *Elsevier*.

In summary, the effects of both fabrication and stack pressures are crucial to the operation of ASSBs. To better understand them, we investigated the ion dynamics as a function of fabrication pressure on oxide and sulfide SCEs in **Chapter 4**. In **Chapter 6**, we

investigated how the stack pressure effect influences the interfacial Li morphology for a HE systems that using LAGP SCE and IL, to reveal the information of interfacial mechanical stability for this class of electrolyte candidates.

#### 1.6 In Situ MR Method for Studying SSEs

**Chapter 6** investigates the stack pressure effect on the interfacial Li microstructure formation during galvanostatic cycling for a HE-based symmetric cell. A symmetric cell design with two Li foils as the electrodes were utilized to simulate the stripping and plating processes in the LMB operation. In this study, an *in situ* NMR setup<sup>78-82</sup> was employed to probe these processes. The term "*in situ*" originates from Latin expression, meaning "in position" or "on site", signifying that the electrochemical processes occurring within the cell are detected and analyzed directly in their original locations, without the need to disassemble the cell. This methodology allows for the acquisition of direct and real-time data that reflects the battery operation in real life, providing valuable insights compared to conventional *ex situ* methods – which involves qualifying and quantifying the chemistries only after disassembling the cell. Similarly, another common term, *operando* experiments<sup>83, 84</sup> refers to the experiments in which data is actively acquired during the electrochemical cycling of the cell.

MR setups for *in situ* studies have been widely used due to their non-invasive nature, high sensitivity to <sup>7</sup>Li, and ability to detect both amorphous and crystalline phases, unlike *in situ* X-ray methods that are significantly restricted by these issues.<sup>85</sup> However, the in situ

MR setups also pose a few issues. For example, the cell design needs to minimize magnetic field inhomogeneity as introduction of metallic components can affect the MR signals. To achieve artifact-free <sup>7</sup>Li spectra and images, Aguilera et al.<sup>86</sup> designed a parallel plate resonator that provides a sufficient sample volume as well as homogenous MR signal excitation across the cell volume. Nevertheless, the spectral resolution achievable in such cell will be limited as there will be several diamagnetic Li species overlapping at ~ 0 ppm and further blurred by other broad <sup>7</sup>Li peaks.<sup>83</sup> To obtain high resolution NMR spectra, Freytag et al.<sup>78</sup> prepared an *in situ* magic-angle spinning (MAS, Section 2.3.3) cell that can be used to perform high-resolution NMR experiments, however, achieving stable spinning with conductive components in the MAS rotor requires complicated preparation of the cell.<sup>78</sup> Krachkovskiy et al.<sup>79, 82, 84</sup> utilized a "pencil cell" modified from HPLC (highperformance liquid chromatography) fittings conducted several experiments on the Li<sup>+</sup> transport and distribution in the graphite anode with <sup>7</sup>Li MR methods. The hollow cell body can be filled with electrolyte and sealed by two threaded nuts at both ends, allowing a "sandwich" style connection. Similar designs have also been utilized for studying SSEs in situ, using <sup>7</sup>Li NMR spectroscopy and various imaging techniques,<sup>80, 81, 87</sup> as it can provide sufficient stack pressure to the ASSBs by tightening the nuts, maintaining the contacts of the internal components. Motivated by this cell design, we conducted the study of variable stack pressure on the microstructual Li formation at the Li-electrolyte interface for a HEbased ASSB system, using in situ NMR and MRI. The details of this work will be presented in Chapter 6.

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# **Chapter 2 – Methods**

This chapter focuses on describing the major NMR methods used in this thesis. A brief conceptional introduction of the basic NMR phenomenon will be presented, followed sequentially by introducing the more complicated interactions that affect the NMR spectra. Afterwards, the working principles of more advanced NMR techniques, such as pulse-field gradient (PFG) NMR (NMR diffusometry), magic-angle spinning (MAS) NMR, multiple-quantum MAS (MQMAS) NMR are presented. These methods were extensively utilized in characterizing the ion dynamics and revealing the local chemical environments for Li and Na-based SEs. Finally, magnetic resonance imaging (MRI) techniques such as imaging echo (IE) and chemical shift imaging (CSI) are explained. These methods were used to investigate the *in-situ* ASSB study.
## 2.1 NMR Spectroscopy Fundamentals

## 2.1.1 Nuclear Spins and Nuclear Zeeman Splitting

In classical physics, the rotational motion of a macroscopic object possesses angular momentum. Imagining the rotation of an object around with a fixed axis, the classical "right-hand rule" can be applied to determine the orientation of angular momentum.<sup>1</sup> In quantum mechanics, *quantum angular momentum* also exists in the particles such as protons and electrons, known as *spin*.<sup>1</sup> Atomic nuclei, made of protons and neutrons, also possess spin properties and it is usually referred as the nuclear spin quantum number I. In a classical manner, a nuclear spin can be viewed as a spinning positively charged particle, which generates a loop of current and thus creates a small local magnetization via right-hand rule. However, it is inappropriate to describe the particles are physically "rotating" in the quantum world, but it is the intrinsic property of the elementary particles.<sup>1</sup> Predicting the nuclear spin quantum number is not trivial, however, it is possible to generally categorize the nuclei based on the number of protons and neutrons into three groups. For the first group, if a nucleus has both even numbers of protons and neutrons, then its net magnetic moment will be zero, I = 0. The second group contains the nuclei that with integer I values, when they possess odd numbers for both protons and neutrons, for example, <sup>2</sup>H, <sup>14</sup>N, and <sup>6</sup>Li all have the spin quantum number I = 1; <sup>10</sup>B has a I = 3.<sup>2</sup> Finally for the third category, if one of the numbers of protons and neutrons is even, whereas the other is odd, then the nucleus will have a half-integer spin  $(I = \frac{n}{2})$ , such as <sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P, <sup>119</sup>Sn  $(I = \frac{1}{2})$ ; <sup>7</sup>Li, <sup>23</sup>Na, and <sup>79</sup>Br  $(I = \frac{3}{2})$ ; <sup>17</sup>O and <sup>27</sup>Al  $(I = \frac{5}{2})$ , etc.<sup>2</sup> In fact, many NMR

active nuclei fall into this group, making them significant for magnetic resonance applications.

It is important to note that, in NMR measurement, the spin  $I > \frac{1}{2}$  nuclei exhibit very different characters than the ones with spin  $I = \frac{1}{2}$ , this are known as the effect of *quadrupolar* interaction. More detailed description of the quadrupolar NMR effects will be further extended in the following **Section 2.2.3**.

Spin angular momentum  $\hat{S}$  ("~" is used for notation of mechanic operator) of a nucleus is quantized, and its value can only be expressed using the following Equation [2.1]:<sup>1,3</sup>

$$\widehat{\mathbf{S}} = \hbar \,\widehat{\mathbf{I}} = \hbar \,\sqrt{I(I+1)} \tag{2.1}$$

where the  $\hbar$  is the reduced Planck's constant, and  $\hat{I}$  is the nuclear spin operator. As when I = 0,  $\hat{S}$  will be 0 as well. This type of nuclei fall into the first category as mentioned, and they are NMR-inactive, such as <sup>12</sup>C (6 protons and 6 neutrons) and <sup>16</sup>O (8 protons and 8 neutrons).<sup>2</sup> However, the nuclei with non-zero *I* values will have spin angular momentum and are measurable with NMR, such as <sup>13</sup>C ( $I = \frac{1}{2}$ , 6 protons and 7 neutrons) and <sup>17</sup>O ( $I = \frac{5}{2}$ , 8 protons and 9 neutrons).

The spin state of an NMR-active nucleus is degenerate (at ground state) by the product of  $(2I + 1)^1$ . Thus, the only possible values of the nuclear spin state (with integer separation)  $-m_I$ ,  $m_I = -I$ , -I + 1, ..., +I, therefore the transition can only happen in

between the two energy states that  $\Delta m_I = 0, \pm 1$ . This is also known as *selection rule*. The degenerated nuclear spin states will be split into different energy levels under applied magnetic field, this is known as *nuclear Zeeman splitting*.<sup>1</sup> This is the dominant interaction in all the NMR experiments, other interactions can be viewed as the small perturbation added on the Zeeman interaction, which will be further discussed in **Section 2.2**. For example, <sup>1</sup>H with  $I = \frac{1}{2}$  will split into two different energy states under magnetic field  $(2 \times \frac{1}{2} + 1 = 2)$ . The *nuclear Zeeman Hamiltonian*  $\hat{H}_z$  on a nuclear spin under an external magnetic field  $\vec{B}_0$  be expressed in **Equation [2.2]**:<sup>3</sup>

$$\widehat{H}_z = -\widehat{\mu} \cdot \overrightarrow{B}_0 \tag{2.2}$$

The corresponding spin magnetic moment ( $\hat{\mu}$ ) can be proportionally related to the angular momentum:<sup>1</sup>

$$\widehat{\boldsymbol{\mu}} = \boldsymbol{\gamma} \cdot \widehat{\boldsymbol{S}}$$
 [2.3]

where  $\gamma$  is the gyromagnetic ratio (also known as magnetogyric ratio)<sup>1, 2</sup>. Like the definition of spin, it is also an intrinsic property of a specific nucleus. Normally, it is reported in the form of angular frequency over magnetic field strength, in rad s<sup>-1</sup> T<sup>-1</sup>, or frequency in MHz T<sup>-1</sup> (noted as " $\gamma/(2\pi)$ "). The gyromagnetic ratio could have both positive and negative signs. If a nucleus has a positive  $\gamma$ , then its magnetic moment is parallel to the angular momentum, otherwise, it will align anti-parallel to the angular momentum. The nuclear Zeeman Hamiltonian  $\hat{H}_z$  on nuclear spin I generating different energy state m can be expressed using Dirac's bra-ket notation in **Equation [2.4]**:<sup>3</sup>

$$\widehat{H}_{z}|I,m\rangle = E_{I,m}|I,m\rangle$$
[2.4]

where  $E_{I,m}$  is the *eigenvalue* of  $\hat{H}$ , it is also the energy of the eigenstate of  $|I, m\rangle$ , combining **Equation** [2.1] – [2.3] gives:

$$\hat{H}_z = -\hat{\mu} \cdot \vec{B}_0 = -\gamma \cdot \hat{S} \cdot \vec{B}_0 = -\gamma \hbar \hat{I} \vec{B}_0$$
[2.5]

Substituting Equation [2.5] into Equation [2.4] gives:

$$\widehat{H}_{z}|I,m\rangle = -\gamma\hbar\,\widehat{I}\overrightarrow{B}_{0}|I,m\rangle \qquad [2.6]$$

Since  $|I,m\rangle$  is the *eigenfunction* of  $\hat{I}$ , with the corresponding eigenvalue m, therefore,  $-\gamma \hbar \vec{B}_0 \cdot \hat{I} |I,m\rangle = -\gamma \hbar \vec{B}_0 \cdot m |I,m\rangle$ . Equation [2.7] can be obtained by substituting Equation [2.6] into [2.4]:

$$E_{I,m}|I,m\rangle = -\gamma \hbar \vec{B}_0 \cdot m|I,m\rangle$$
$$E_{I,m} = -\gamma \hbar \vec{B}_0 \cdot m \qquad [2.7]$$

Thus, a simple relationship can be acquired between the energy of the eigenstate as the functions of  $\gamma$  and  $B_0$ . For the nuclei with higher  $\gamma$  values, the energy separation  $\Delta E_{I,m}$ in between different spin states will be more pronounced under the same magnetic field, this provides the high sensitivity of the NMR experiments. An example illustrating the Zeeman splitting effects under  $B_0$  for spin  $I = \frac{1}{2}$  and  $I = \frac{3}{2}$  nuclei are shown in **Figure 2.1**. For  $I = \frac{1}{2}$ , when  $m = +\frac{1}{2}$ , the nuclear spin is at the lower energy state  $E_{\frac{1}{2}, +\frac{1}{2}} = -\gamma \hbar \vec{B}_0 \cdot$  $\left(+\frac{1}{2}\right) = -\frac{\gamma \hbar B_0}{2}$ ; when  $m = -\frac{1}{2}$ , the spin is at higher energy state  $E_{\frac{1}{2}, -\frac{1}{2}} = +\frac{\gamma \hbar B_0}{2}$ . The spin population  $p_{\Psi}$  of each eigenstate can be found using Boltzmann distribution over two possible states:

$$p_{\Psi} = \frac{\exp\left(\frac{E_{I,m}}{-k_BT}\right)}{\sum_{m'} \exp\left(\frac{E_{I,m'}}{-k_BT}\right)}$$
[2.8]

Nuclei such as <sup>1</sup>H (most sensitive nucleus,  $\gamma/(2\pi) = 42.577$  MHz T<sup>-1</sup>, 99.9885%) and <sup>19</sup>F ( $\gamma/(2\pi) = 40.078$  MHz T<sup>-1</sup>, 100%) are two examples of these nuclei. <sup>7</sup>Li ( $\gamma/(2\pi) = 16.548$  MHz T<sup>-1</sup>, 92.41%), is nearly 1/3 of the sensitivity as the <sup>1</sup>H and <sup>19</sup>F.<sup>2</sup> While  $\gamma$  is the intrinsic property of nuclei, the NMR sensitivity can only be increased by adjusting  $B_0$  (using  $B_0$  from here emphasizes the field strength). NMR experiments performed in this thesis are under the field strength of 7 to 20 T, the transitions between spin states will generate energy spectra which form the core of NMR phenomena, this will be discussed in the following section.



**Figure 2.1** Illustration of Zeeman splitting effects of a  $I = \frac{1}{2}$  (left) and  $I = \frac{3}{2}$  (right) nucleus under an external magnetic field B<sub>0</sub>. Adapted with modification from Levitt, 2001.<sup>1</sup>

### **2.1.2 Larmor Frequency**

The energy of nuclear spin states was previously discussed. Taking  $I = \frac{1}{2}$  as an example, the two spin states were calculated above as  $= -\frac{\gamma \hbar B_0}{2}$  and  $+\frac{\gamma \hbar B_0}{2}$  for  $m = +\frac{1}{2}$  and  $m = -\frac{1}{2}$ , respectively, the separation of the energy levels  $\Delta E_{I,m}$  (from lower  $\rightarrow$  higher energy state) can be calculated as:

$$\Delta E_{I,m} = E_{\frac{1}{2},-\frac{1}{2}} - E_{\frac{1}{2},+\frac{1}{2}} = +\frac{\gamma \hbar B_0}{2} - \left(-\frac{\gamma \hbar B_0}{2}\right)$$
$$\Delta E_{I,m} = \gamma \hbar B_0$$
[2.9]

The generic Planck's radiation law relates the frequency of radiation to energy by the equation  $E = hv_0$ , by substituting the into **Equation [2.9]**:

$$h\nu_0 = \gamma \hbar B_0$$
  
 $\nu_0 = \frac{\gamma B_0}{2\pi}; \quad \text{or} \quad \omega_0 = \gamma B_0$ 
[2.10]

where  $v_0$  is the *Larmor frequency* (in MHz), and  $\omega_0$ , with the same physical meaning, but in rad s<sup>-1</sup>. They are the frequency of the Zeeman energy transition under a given  $B_0$ ,<sup>1</sup> For convenience, most of the Larmor frequency presented in this section will be in " $\omega_0$ ". The concept of Larmor frequency is important for understanding the interactions between spin system and  $B_0$ , as well as the electromagnetic radio frequency (RF) pulse in the following section, where the introduction of vector model will be shown.

### 2.1.3 Vector Model

As it has been previously discussed, intrinsic particle spins are fundamentally quantum mechanic phenomena and cannot be perfectly described with classical physis. However, in order to understand the basic working principle of NMR, it is often convenient to employ a classical analogy to help illustrate how the spin can be affected by  $B_0$  and RF pulses. The Vector model is usually utilized to simplify the key concepts in NMR, mostly commonly coupled with  $I = \frac{1}{2}$  nucleus due to their simplicity. In a sample containing numerous amounts of  $I = \frac{1}{2}$  nuclei, the nuclei can be approximated as individual nuclear magnetic moments<sup>3</sup> (or tiny magnetic bars). When no  $B_0$  presents, the *net magnetization* of the spin system  $\vec{M}$ , is 0. Under  $\vec{B}_0$ ,  $\vec{M}$  of the spin system will be gradually orientated parallel to the field in a period. At this stage, the spin system reaches a thermal equilibrium state, the period required to reach this state is call " $T_1$  relaxation". This process will be discussed in more detailed in Section 2.1.5. If we set the orientation of the external magnetic field  $\vec{B}_0$ as the "z-axis", then the net magnetization  $\vec{M}_0$  will be along the z-axis, and there is no magnetization in the transverse xy-plane. When a RF pulse is applied  $(\vec{B}_1)$  at the Larmor frequency that is perpendicular to the z at the xy-plane,  $\vec{M}_0$  is "flipped" around the  $\vec{B}_1$  axis. The perturbation  $\vec{M}_0$  from the thermal equilibrium state will result in z- and xy- components, noted as and  $\vec{M}_z$  and  $\vec{M}_{xy}$  (shown in Figure 2.2), they are also typically known as "longitudinal magnetization" and "transverse magnetization", respectively, where the later one is directly related to the origin of the NMR signal.

If the RF pulse is turned off after the short amount of time, then the net magnetization will precess around the z-axis at a *flip angle*  $\beta_p$  (**Figure 2.2**). The change of the orientation of the rotational axis is known as *precession*.



**Figure 2.2** Graphical representation of net magnetization  $\vec{M}_0$  is perturbated by RF pulse  $(\vec{B}_1)$ , leading to the off-equilibrium state of the magnetization, generating xy- and z-components under the influence of RF pulse.

The flip angle can be related to the RF pulse time as:<sup>1</sup>

$$\beta_p = \omega_p \, t_P \tag{2.11}$$

where  $\omega_p$  is the frequency of the RF pulse  $(\vec{B}_1 = \gamma \ \omega_p)$ , it has to be closed to  $\omega_0$  so the spins are "on resonance", and  $t_p$  is the pulse length (duration), respectively. Different  $\beta_p$  can be achieved by varying the duration of the RF pulse. Typically, 90° of  $\beta_p$  is preferred as it provides maximum signal intensity in the NMR experiment, where the  $\vec{M}_{xy}$ will be closest to the net magnetization  $\vec{M}_0$ , while  $\vec{M}_z$  is nearly 0. The precession of the magnetization at the xy-plane can be further decoupled to two set of oscillating magnetizations,  $\vec{M}_y$  and  $\vec{M}_x$  respectively. After the implementation of RF pulse, the macroscopic magnetization components after time t will be:<sup>1</sup>

$$\vec{M}_{y} = -\vec{M}_{0} \cos(\omega_{0}t) \exp\left(\frac{-t}{T_{2}}\right)$$
$$\vec{M}_{x} = \vec{M}_{0} \sin(\omega_{0}t) \exp\left(\frac{-t}{T_{2}}\right)$$
[2.12]

The two components in the xy-plane can be acquired using *quadrature detection*,<sup>1</sup> this could be simply imagined as two receiver coils pointed perpendicular to the sample to receive x- and y-components simultaneously. The quadrature detector compares the NMR signal that oscillates at  $\omega_0$  to a reference signal oscillates at  $\omega_{ref}$ , here one can defined  $\Delta \omega = \omega_0 - \omega_{ref}$ , where the  $\Delta \omega$  is the offset of the frequency of the measured spin that deviates from the "on-resonance"  $\omega_p = \omega_0$  scenario.

Another important NMR concept is brought up here –  $T_2$  relaxation. As opposed to the  $T_1$  longitudinal relaxation,  $T_2$  is known as "transverse relaxation". It dictates the NMR signal evolution during the detection, and its duration is typically the determining factor of the appearance of NMR line shape for the spectra of  $I = \frac{1}{2}$  nuclei. The details about mathematical expressions of  $T_1$  and  $T_2$ , as well as how to acquire these values from NMR measurements will be described in the following section.

### 2.1.4 One-Pulse Experiment and the Origin of NMR Spectrum

A few concepts are already covered up to this point, they are:

- 1. The NMR signals are generated by perturbating the spin system under static  $\vec{B}_0$  using RF pulse at the field strength of  $\vec{B}_1$ .
- 2.  $\vec{M}_{xy}$  will oscillate in xy-plane under the transverse relaxation time  $T_2$  at the Larmor frequency  $\omega_0$ , generating detectable magnetization.  $\vec{M}_{xy}$  can be further deconvolute into two oscillating magnetizations with a 90° phase shift (sin vs cos).
- 3. Evolution of the  $\vec{M}_{xy}$  signal as a function of time will eventually decay due to the process of transverse relaxation.

With that, the simplest one-pulse NMR experiment can be performed, with a pulse of 90° tip angle  $\beta_p$ . The experiment's pulse sequence and data acquisition can be illustrated in **Figure 2.3**.



**Figure 2.3** Basic components in an one-pulse NMR experiment, after a duration of waiting the system to reach thermal equilibrium, a 90° RF excitation pulse is applied, followed by signal acquisition of FID (detection of  $\vec{M}_{xy}$ ).

There are three major components in this pulse sequence:

A waiting period D1, the purpose of waiting is simply to let the spin system reach thermal equilibrium. The value of D1 is typically set to 5 times of  $T_1$  of the sample. Common  $T_1$  values are within the range of from a few milliseconds to dozens of minutes, depending on the sample physical properties and the nucleus being measured.

When the thermal equilibrium is reached, a RF 90° pulse is applied to disturb the thermal equilibrium. It has a frequency  $\omega_p$  that is close to the Lamor frequency, it also has an "turned on time"  $t_p$  to control the tip angle, in this case, 90°. It also has a phase component (*x*), denoting that the pulse is applied along the x-axis.

Finally, the  $\vec{M}_{xy}$  evolution in the xy-plane, presented as an oscillating signal, which eventually decays to zero intensity, this evolution is known as *free induction decay* (FID) in the *time domain* (TD). The NMR signal acquisition is completed during this period, this can be treated as "raw NMR data" and requires further processing to create NMR spectrum.

Here, the simplest NMR experiment is introduced. However, it is very difficult to directly get detailed information from the FID signal. Herein, a mathematical transform can be applied to convert the TD signal to frequency domain (FD) signal, that is, Fourier Transformation (FT).<sup>1</sup> FT is a tool that converts a function of time into a function of frequency, thus, the individual components in the NMR signal can be separated and visualized better in the NMR spectrum, making them more interpretable to human's eye. First, we will need to modify **Equation [2.12]**, by converting  $\vec{M}_y$  and  $\vec{M}_x$  into detectable NMR signal s(t) in a from of complex conjugate, this can be achieved by *Euler's formula* 

 $e^{ix} = cosx + isinx$  (where *i* is the imaginary part), thus, the TD NMR signal upon detection can be written as:<sup>1</sup>

$$s(t) = M_0 \exp(i\Delta\omega t) \exp\left(\frac{-t}{T_2}\right)$$
[2.13]

 $M_0$  (without the vector notation) is the amplitude of the signal. If the sample has a long  $T_2$  relaxation time (imagining  $T_2 \rightarrow \infty$ ), then the TD signal will still present significant oscillating intensity even after a long evolution over time, resembling a nearly sinusoidal function. However, the  $T_2$  decay is usually within the range of microseconds to tens of milliseconds, and the FID signal will decay to 0 accordingly. Now, FT operation can be performed on the modified TD signal<sup>1</sup>:

$$S(\omega) = \int_0^\infty s(t) \exp(-i\omega t) dt$$
$$S(\omega) = M_0 \int_0^\infty \exp(i\Delta\omega t) \exp(-i\omega t) \exp(\frac{-t}{T_2}) dt$$
$$S(\omega) = M_0 \int_0^\infty \exp(i\Delta\omega t) - i\omega t + \frac{1}{T_2}) dt$$

After integrating the previous equation, we have:<sup>1</sup>

$$S(\omega) = M_0 \left[\frac{1}{1/T_2 + i(\omega - \Delta\omega)}\right]$$
[2.14]

**Equation [2.14]** is defined as *complex Lorentzian*, it can be decoupled into a *real* part and an *imaginary* part by multiplying a complex conjugate to both of its numerator and denominator, this gives **Equation [2.15]**:<sup>1</sup>

$$S(\omega) = M_0\left[\frac{1}{1/T_2 + i(\omega - \Delta\omega)}\right] = M_0\left[\frac{1}{1/T_2 + i(\omega - \Delta\omega)}\right] \times \frac{1/T_2 - i(\omega - \Delta\omega)}{1/T_2 - i(\omega - \Delta\omega)}$$



**Figure 2.4** FT operation on a set of time domain FID data to frequency domain data, where an absorptive Lorentzian NMR line shape can be obtained from the raw FID signal (both real and imaginary) after properly phasing. 1D NMR spectrum can be acquired (with the frequency horizontal axis with the unit in Hz).

Figure 2.4 presents a graphical schematic diagram, demonstrating how FT works on the TD signal and converts it into FD signal. In this example, only the absorptive Lorentzian line shape is depicted in the NMR spectrum. Based on **Equation [2.15]**, the peak position of the Lorentzian line is when  $\omega = \Delta \omega$ , and the *full-width-at-half-maximum*  (FWHM) is  $\propto \frac{1}{T_2}$ .<sup>1</sup> Practically, labeling the spectrum with frequency in Hz is somewhat inconvenient, since running the same NMR experiments at different magnetic field strengths will result in inconsistent results, due to the different Larmor frequencies during the data collection. Thus, the most common practice is to measure the frequency difference from a reference and then scale it relative to the field strength. This is the field-independent *chemical shift*, it is defined as  $\delta$ , where  $\delta$  (*in ppm*) =  $\frac{\Delta \omega}{\omega_0} \times 10^6$ .

So far, the simplest one-pulse NMR experiment and the origin of the classic Lorentzian NMR line shape has been briefly introduced. Next, more advanced pulse sequences that contain more components will be presented in the following section for  $T_1$  and  $T_2$  relaxation measurements.<sup>4</sup>

### 2.1.5 $T_1/T_2$ Measurements

As previously stated,  $T_1$  is the time required for the spin system to re-establish thermal equilibrium state after perturbation by the RF pulses.  $T_1$  is also referred to as "longitudinal relaxation" or "spin-lattice relaxation". The first term emphasizes that the  $T_1$ is the process of net magnetization returning to the longitudinal orientation, while the second term highlights the interaction that causes the relaxation process, that is, fluctuating magnetic fields at the sites of spins caused by motions of molecules,<sup>1, 4</sup> thus the spins exchange their magnetizations to the surrounding environment. As opposed to the "longitudinal" and "spin-lattice" relaxation for describing  $T_1$ ,  $T_2$  relaxation is referred to "transverse" and "spin-spin" relaxation, is the process that nuclear spins interact with each other and cause the loss of phase coherence of spins.<sup>1,4</sup> This effect leads to the signal decay in the FID.

The fundamental origin of relaxation is complicated, yet a generic model that describes relaxation with molecular motion is important for the experimental works here. That is, *Bloembergen-Purcell-Pound* relaxation theory (*BPP*, noted in italic to be distinguished from another acronym "BPP", bipolar-pulse-pair in the **Section 2.3.1**). *BPP* relaxation theory correlates the relaxation mechanism to the effect of averaging *dipolar coupling* interaction from molecular motions. Herein,  $R_1$  relaxation rate, can be defined as the reciprocal value of  $T_1$ , with the unit of Hz. Same principle can be applied to  $T_2$  (=  $1/R_2$ ). For  $n = \frac{1}{2}$  nuclei, the  $R_1$  and  $R_2$  can be defined using *autocorrelation function*,<sup>1, 4</sup> based on *BPP* relaxation theory:

$$R_1 = \frac{3\mu_0^2}{160\pi^2} \frac{\hbar^2 \gamma^4}{r^6} \left[ \frac{\tau_c}{1+\omega_0^2 \tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2 \tau_c^2} \right]$$
[2.16]

$$R_2 = \frac{3\mu_0^2}{320\pi^2} \frac{\hbar^2 \gamma^4}{r^6} \left[ 3\tau_c + \frac{5\tau_c}{1+\omega_0^2 \tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2 \tau_c^2} \right]$$
[2.17]

 $\mu_0$  is the vacuum permeability factor,  $\tau_c$  is the *correlation time*, it can be considered as the time required for molecular tumbling motion. r is the internuclear distance for *dipolar coupling* (will be introduced in **Section 2.2.3**). A graphical schematic of the relationships between  $R_1/R_2$  and  $\tau_c$  is shown in **Figure 2.5**, modified from Callaghan, 1991.<sup>4</sup>



**Figure 2.5**  $R_1$  and  $R_2$  relaxation rates as a function of the product of molecular tumbling rate  $\tau_c$  and Larmor frequency  $\omega_0$ . The change in tumbling rate can be related to the temperature change. Adapted with modifications from Callaghan, 1991.<sup>4</sup>

As shown in **Figure 2.5** that the behaviour of  $R_1$ : initially, it increases as the  $\tau_c$  decreases, reaching a maximum value when the molecular tumbling rate  $(\tau_c^{-1})$  is close to the Larmor frequency  $\omega_0$ . This happens when the relaxation is most effective. Beyond this point, the  $R_1$  will keep decreasing as the  $\tau_c$  decreases. The trend of  $R_2$  change exhibits a constant reduction as the temperature increases. Thus, it can be roughly concluded that a smaller  $R_2$  can be related to the faster molecular dynamics, thus averaging the local dipolar interaction. It is evident that at lower temperature  $R_2 > R_1$  ( $T_1 > T_2$ ), when the motion

significantly surpasses Lamor frequency, then they are essentially equals. In this case, the dipolar interaction is sufficiently averaged, thus the transverse component relaxation is now dominated by the process where the spins return to thermal equilibrium. While the interpretation for molecular dynamic based on only one  $R_1$  value might be less straightforward, a series of temperature measurements can provide a clearer picture of the molecular motion. The variable-temperature measurements of  $R_1$  will be an important aspect of understanding dynamic in the subsequent works presented in this thesis.

In addition to the fact that  $T_1$  and  $T_2$  ( $R_1$  and  $R_2$ ) are important for understanding the molecular dynamics. It is also critical to probe these values when setting up NMR experiments. As for  $T_1$ , a rule of thumb in regular NMR world will be setting the preparation period D<sub>1</sub> as 5 times of  $T_1$  to ensure the system has reached thermal equilibrium state.  $T_2$  is equally crucial, it dictates the signal decay during the FID acquisition. In other NMR explements, consideration is required when setting pulse durations or delays if the net magnetization is at xy-plane requires consideration. Thus, it is necessary to acquire  $T_1$ and  $T_2$  experimentally.

Inversion-recovery can be performed to probe  $T_1$ . The pulse sequence is shown in **Figure 2.6**. It contains two RF pulses, separated by a variable length of delays  $\tau_{vd}$ . The application of the 1<sup>st</sup> pulse with  $\beta_p$  of 180° inverts the net magnetization, then the magnetization will undergo  $T_1$  process during the delay period. Afterwards, a 90° pulse is applied to receive the FID signal (for simplicity, "FID" will be noted as a triangle instead of oscillating signal starts from here). If  $\tau_{vd}$  is set to 0 s, then it is expected to see the maximum negative value of the net magnetization after the acquisition pulse  $(-M_0)$ . If  $\tau_{vd}$  is sufficiently long (>> 5 times of  $T_1$ ), then the net magnetization will have enough time to return to its thermal equilibrium state, resulting in the maximum positive  $M_0$ . Any magnetization magnitude under a given  $\tau_{vd}$  can be calculated using the following equation:<sup>4</sup>

$$M_z(t) = M_0 [1 - 2\exp\left(-\frac{t}{T_1}\right)]$$
[2.18]

 $M_z(t)$  is the magnitude of z-component magnetization after a delay time t. By setting a series of  $\tau_{vd}$ , an exponential fit can be performed on the measured signal intensity as a function of t. Thus,  $T_1$  can be obtained.



**Figure 2.6** Inversion-recovery experiment for measuring  $T_1$  relaxation. The  $\tau_{vd}$  is varied during the experiment to probe the  $M_z(t)$  magnitude at different stage during the relaxation.

Determining  $T_2$  is less straight forward, because there are other factors that contribute to the signal decay in the transverse plane. One key factor is the inhomogeneous magnetic field, which causes the variations in the field strength across the sample. In such an inhomogeneous field, spins at different positions will experience different field strength, resulting in variation of their phase components in the xy-plane. This difference leads to the loss of phase coherence among the spins, causing rapid decay of the oscillating signal in the transverse plane, after the excitation pulse.

To tackle this problem, after the first 90° pulse followed by a waiting period –  $\tau_{vc}$ , an 180° RF pulse can be applied right afterwards. The loss of spin phase coherence happens during its evolution time  $\tau_{vc}$ . But the 180° pulse reverts the phases of each spin, by waiting for the exact same evolution period, the signal will be refocused and reach a maximum intensity when the second wait time equals to  $\tau_{vc}$ , and then decay again (echo signal). This "trick" that refocuses the spin in the transverse plane is known as *Hahn echo (spin echo)*.<sup>4</sup>



**Figure 2.7** *CMPG echo train* sequence for measuring  $T_2$  relaxation. The echo signal is produced by implementing an 180° pulse in between the two  $\tau_{vc}$  duration. Multiple echo loops will be applied to obtain the signal intensity as a function of number of total echo time.

Once the effect of field inhomogeneity is greatly supressed by implementing Hahn echo, the determination of  $T_2$  becomes possible:

$$M_{y}(t) = M_{0}[\exp\left(-\frac{t}{T_{2}}\right)]$$
[2.19]

where  $M_y(t)$  is the measured magnetization intensity at the echo time t, whereas  $t = 2\tau_{vc}$  + duration of 180° pulse. In order to fit the exponential curve to acquire  $T_2$  value, multiple experiments are required. Thus, successive echoes will needs be applied by repeating the echo loop, this is known as the *Carr-Purcell-Meiboom-Gill echo train*. The pulse sequence is shown in **Figure 2.7**. A modification to the previous t is essential at this point. Where  $t = n \times (2\tau_{vc} + \text{duration of } 180^\circ \text{ pulse})$ , n is the number of echo loops, usually set to a factor of 2.

Up to this point, the fundamentals of NMR experiment and signal generation were covered, altogether with an introduction of the basic concepts like  $T_1$ ,  $T_2$ , and their corresponding NMR measurements. These topics have primarily been explained using the vector model due to its simplicity. However, there are more complicated interactions that can significantly affect the NMR line shapes, which cannot be fully captured by the vector model. In the upcoming chapter, different nuclear spin interactions will be presented, which will highlight the significance of more advanced NMR techniques that will be discussed later.

# **2.2 Internal Spin Interactions**

While the external factors of  $\vec{B}_0$  and  $\vec{B}_1$  generates a basic NMR spectrum, other internal electric/magnetic interactions often play a crucial role to the features of NMR spectra as well. As they not only significantly complicate the interpretation of NMR line shapes but also provide valuable information for understanding the material's structures and dynamics. Hence, the internal spin interactions will be discussed in this section. First, to access the effect of internal spin interactions, one can consider the uses of *perturbation theory*.<sup>3</sup> This method treats the Zeeman splitting  $\hat{H}_z$  as the dominant interaction, assuming the spins in the system are in equilibrium at their quantized energy states. Additional internal nuclear spin interactions then can be added as the "perturbations" to the equilibrium state. Here, the total Hamiltonian  $\hat{H}_{Total}$  of the spin system can be written as:

$$\hat{H}_{Total} = \hat{H}_z + \hat{H}_{RF} + \hat{H}_{CS} + \hat{H}_J + \hat{H}_D + \hat{H}_Q + \hat{H}_P + \hat{H}_K$$

$$(2.20)$$

Internal

where  $\hat{H}_{RF}$  is the Hamiltonian of the RF pulse. The rest of the Hamiltonians from internal interactions resulting in the perturbation, they are corresponding to *chemical shielding* ( $\hat{H}_{CS}$ ), *J-coupling* or scalar coupling ( $\hat{H}_{CS}$ ), *dipolar coupling* ( $\hat{H}_D$ ), *quadrupolar coupling* ( $\hat{H}_Q$ ), *paramagnetic shift* ( $\hat{H}_P$ ), and *Knight shift* ( $\hat{H}_K$ ), respectively.

External

J-coupling arises from the indirect magnetic interactions of nuclear spins mediated through chemical bonds. The paramagnetic shift results from the nuclear spin interaction with unpair electrons, it is commonly observed for paramagnetic substances, such as the ones with transition metal cations. The effects of J-coupling and paramagnetic shift will not be covered in the following sections as they are less relevant with the current work.

### 2.2.1 Chemical Shielding and Chemical Shift Anisotropy (CSA)

Chemical shielding is a key concept in the NMR spectroscopy, because it describes how the nucleus is affected by the local electronic environments. Previously, the effect of Zeeman splitting of the spin system was discuss. However, the discussion assumed that the nucleus is "naked" and free of any external influence from the surrounding electrons. In reality, the nucleus is surrounded by electrons, which generate local magnetic fields and significantly affect the effective magnetic field experienced by the nucleus, resulting in different shifts in the NMR spectra. To correct this, the chemical shielding Hamiltonian acting on a spin can be presented by introducing a term called shielding tensor  $\sigma$ :<sup>1,3</sup>

$$\widehat{H}_{CS} = -\gamma \hbar \widehat{l} \cdot \sigma \cdot B_0 \qquad [2.21]$$

Nuclear spin interactions depend on the molecular orientation; therefore, the influence of the shielding tensor described with a second-rank Cartesian tensor – a 3 × 3 matrix that quantifies the extent of spatial contribution of the electronic environments. and it is possible to fix  $\sigma$  with respect to axis frame so that only the diagonal elements are presented, this is called the *principal axis frame* (PAF):<sup>1, 3</sup>

$$\begin{pmatrix} \sigma_{xx}^{PAF} & 0 & 0 \\ 0 & \sigma_{yy}^{PAF} & 0 \\ 0 & 0 & \sigma_{zz}^{PAF} \end{pmatrix}$$
 [2.22]

PAF is a combination of three specific orientations for the nucleus, where the induced field from chemical shielding is parallel to the external field, leaving the only isotropic components for the shielding tensors. From **Equation [2.22]**, the *isotropic* shielding tensor  $\sigma_{iso}$  can be acquired:<sup>1,3</sup>

$$\sigma_{iso} = \frac{1}{3} \left( \sigma_{xx}^{PAF} + \sigma_{yy}^{PAF} + \sigma_{zz}^{PAF} \right)$$
[2.23]

However,  $\sigma_{iso}$  is a particular case that all the three components are equal, if two or more principal values are different, then the chemical shift tensor will be anisotropic. This effect is known as *chemical shift anisotropy* (CSA). The anisotropy term  $\sigma_{\Delta}$ , and the asymmetry parameter of the chemical shielding  $\eta_{CS}$  can also be obtained, shown in **Equation [2.24]**:<sup>3</sup>

$$\sigma_{\Delta} = \sigma_{zz}^{PAF} - \sigma_{iso}; \qquad \qquad \eta_{CS} = \frac{\sigma_{yy}^{PAF} - \sigma_{xx}^{PAF}}{\sigma_{\Delta}} \qquad [2.24]$$

The CSA effect can significantly broaden the NMR spectral lines, as there are components that deviate from the isotropic values exist. With the consideration of shielding tensor, the correction to the Larmor frequency from the isotropic shift will be:<sup>3</sup>

$$\omega_{CS} = -\omega_0 \sigma_{iso} - \frac{1}{2} \omega_0 \sigma_\Delta (3\cos^2\theta - 1 + \eta_{CS} \sin^2\theta \cos 2\phi) \qquad [2.25]$$

where  $\theta$  and  $\phi$  are the angles that  $\vec{B}_0$  at the *laboratory frame* deviates from the PAF.<sup>3</sup> The above " $3cos^2\theta - 1$ " term will be re-occurring in the expressions of other interactions later, it is also an important factor that be removed by the *magic-angle-spinning* technique, which will be covered in **Section 2.3.2**.

We briefly defined the concept of chemical shift in **Section 2.1.1**. Herein, with the consideration of chemical shielding, the *isotropic shift* can be defined using the isotropic tensor from the sample and a reference compound at the laboratory frame:<sup>3</sup>

$$\delta_{iso} = \sigma_{iso}^{ref} - \sigma_{iso} = \frac{1}{3} (\delta_{11}^{PAF} + \delta_{22}^{PAF} + \delta_{33}^{PAF})$$
 [2.26]

where  $\sigma_{iso}^{ref}$  is the chemical shielding tensor of the reference compound,  $\delta_{11}^{PAF}$ ,  $\delta_{22}^{PAF}$ , and  $\delta_{33}^{PAF}$  are the principal values of the chemical shift tensors at the laboratory frame, instead of at the PAF. By convention,  $\delta_{11}^{PAF} \ge \delta_{22}^{PAF} \ge \delta_{33}^{PAF}$ .<sup>3</sup> Chemical shift anisotropy and asymmetry can be modified from **Equation** [2.24], where  $\delta_{\Delta} = \delta_{11}^{PAF} - \delta_{iso}$ , and  $\eta_{CS}(\delta) = \frac{\delta_{33}^{PAF} - \delta_{22}^{PAF}}{\delta_{\Delta}}$ .<sup>3</sup> To demonstrate the effect of CSA on the NMR spectrum of a static powder sample, a simulated spectrum is illustrated in **Figure 2.8**.



**Figure 2.8** Simulated NMR spectrum of a static powder sample, demonstrating the line broadening effect from CSA interaction. The positions of isotropic shift and the principal

chemical shift tensors are labelled with dash lines. The spectral simulation is completed using ssNake v1.3.2.<sup>5</sup>

### **2.2.2 Dipolar Interactions**

Dipolar interaction, also known as dipole-dipole coupling, arise from the direct nuclear spin interaction through space. Because nuclear spins are magnetic (except for those I = 0), when one nucleus is close to a neighbouring nucleus in proximity, it experiences a small magnetic field perturbation that is created by its neighboring nucleus. There are two types of dipolar interaction, namely, *homonuclear dipolar coupling*  $\hat{H}_D^{homo}$  from the same isotope, and *heteronuclear dipolar coupling*  $\hat{H}_D^{hetero}$  from a different nucleus/isotope. A thorough analysis of the dipolar interactions can be quite complicated when examining the Hamiltonian expression, but typically, only the first-order term(s) are considered to have the dominant contribution(s).<sup>3</sup> The corresponding Hamiltonians for the two types of dipolar interactions can be expressed more succinctly as follow:<sup>3</sup>

$$\hat{H}_{D}^{homo} = -d_{D}(3\cos^{2}\theta - 1)[\hat{I}_{z}\hat{S}_{z} - \frac{1}{2}(\hat{I}_{x}\hat{S}_{x} + \hat{I}_{y}\hat{S}_{y})]$$
[2.27]

$$\widehat{H}_{D}^{hetero} = -d_{D}(3\cos^{2}\theta - 1)\,\widehat{I}_{z}\widehat{S}_{z} \qquad [2.28]$$

$$\text{Term A} \qquad \text{Term B}$$

$$d_D = \hbar \left(\frac{\mu_0}{4\pi}\right) \frac{1}{r^3} \gamma_I \gamma_S \qquad [2.29]$$

 $d_D$  is the *dipolar coupling constant* (in rad s<sup>-1</sup>), represents the strength of the dipolar interaction, and it is dependent of the relative orientation of spin  $\hat{I}$  and  $\hat{S}$ . This constant is only sensitive to the gyromagnetic ratio as well as the internuclear distance r between the

two spins.  $\hat{I}_z$  and  $\hat{S}_z$  are the nuclear spin operators of spin  $\hat{I}$  and  $\hat{S}$ , with the spatial orientation respective to the laboratory frame z-dimension ( $\vec{B}_0$ ),  $\hat{I}_{x,y}$  and  $\hat{S}_{x,y}$  representing the other two dimensions, respectively.

It is notable that there's a key difference between the two Hamiltonians, where the one of homonuclear dipolar coupling  $\hat{H}_D^{homo}$  has a second term B (for two-spin considerations), which represents the effects of the transverse components of spin  $\hat{S}$  perturbate the local magnetic field of spin  $\hat{I}$ . In the case of dipolar coupling, both spins have similar  $\omega_0$  under  $\vec{B}_0$  due to the same gyromagnetic ratio, thus, spin  $\hat{S}$  will sufficiently induce perturbation of the local magnetic field around spin  $\hat{I}$  in the transverse plane. This perturbation effect can lead to NMR line broadening in system that has larger number of spins. An experimental example is illustrated in **Figure 2.9**,<sup>6</sup> where the <sup>7</sup>Li NMR spectra for three crystalline lithium borate samples were shown, both natural abundant <sup>7</sup>Li (92%)<sup>2</sup> or depleted <sup>7</sup>Li (5%)<sup>6</sup> are recorded for each sample. It is clearly that the <sup>7</sup>Li line shapes were narrowed in the depleted <sup>7</sup>Li sample, and much better site resolution can be achieved due to the decreases homonuclear dipolar coupling effect.<sup>6</sup>



**Figure 2.9** Diminishing homonuclear dipolar coupling effect in <sup>7</sup>Li NMR spectra by diluting the <sup>7</sup>Li with <sup>6</sup>Li isotope for three different diamagnetic lithium borates, the increases in resolution in the <sup>7</sup>Li depleted samples can be achieved. Reprinted with permission from *Chem. Mater.* 2018, 30, 5521–5526.<sup>6</sup> Copyright © (2018) *ACS*.

In contrast, for the heteronuclear Hamiltonian, term B vanishes because the two different isotopes  $\hat{I}$  and  $\hat{S}$  commute with each other in the xy-plane. From a physical

perspective, the two spins don't interact with each other in the xy-plane due to their differing Larmor frequencies.<sup>3</sup> Instead, according to the selection rule mentioned in **Section 2.1.1**, the transition can only be achieved with  $\Delta m_I = \pm 1$  and  $\Delta m_S = \pm 1$ . If we label the lower energy state as  $\alpha$  ( $m_I = \frac{1}{2}$ ), and the higher energy state as  $\beta$  ( $m_I = -\frac{1}{2}$ ). Then for term  $A - \hat{l}_z \hat{S}_z$ , only two transitions are possible when measuring spin *I*. They are  $\alpha_I \alpha_S \Rightarrow \beta_I \alpha_S$  and  $\alpha_I \beta_S \Rightarrow \beta_I \beta_S$ . Therefore, in a powder sample, the heteronuclear interaction results in two CSA patterns that are symmetrical to the  $\delta_{iso}$ . This occurs due to the same extent of local magnetic field perturbation of spin *I*, but with opposite polarity (referring to  $\Delta m_S = \pm 1$  transitions). An example of the powder line shape for heteronuclear dipolar interaction is shown in **Figure 2.10**. adapted from Duer 2004<sup>3</sup> with modification.



**Figure 2.10** The powder line shape of spin *I* under the influence of heteronuclear dipolar coupling, the distance between the two "horns" is the dipolar coupling constant. Adapted with modification from *Introduction to Solid State NMR Spectroscopy*, Duer, 2004<sup>3</sup> Copyright © (2004) John Wiley & Sons.

### 2.2.3 Quadrupolar Interaction

So far, we've introduced the basic internal nuclear spin interaction based on spin  $I = \frac{1}{2}$  nuclei. However, up to 74% of NMR active nuclei are having  $I > \frac{1}{2}$ , making them quadrupolar nuclei.<sup>3</sup> In fact, most of the NMR works will be presented later in this thesis are done on this type of nuclei. Unlike those spin-1/2, quadrupolar nuclei have nonspherical charge distributions within the nuclei, thus they possess *electric quadrupole* moment, which can interact with the electric field gradient (EFG) from the surrounding charges. The interaction is called *quadrupolar coupling* or *quadrupolar interaction*, with its strength depending on the electric quadrupole moment of the nucleus and the magnitude of the EFG resulting from the molecular structure. Under very specific circumstances, such as in solution state NMR, or when the measured spin site exhibits cubic symmetry in solidstate NMR (ssNMR), the EFG effect is absent, resulting in NMR peaks that resemble Lorentzian or Gaussian spectral line shapes. Nevertheless, in most ssNMR cases, quadrupolar coupling effect not only leads to broader line shapes, but also interfere with the Zeeman energy due to its large magnitude, causing non-trivial features in the line shapes, complicating the interpretation of NMR spectra.

The quadrupolar interaction Hamiltonian can be expressed in the PAF of the EFG tensor as:<sup>3</sup>

$$\hat{H}_Q = \frac{e^2 q Q}{4I(2I-1)\hbar} \cdot \left[3\hat{I}_{ZPAF}^2 - \hat{I}^2 + \eta_Q(\hat{I}_{XPAF}^2 - \hat{I}_{YPAF}^2)\right]$$
[2.29]

$$eq = eq_{zz}^{PAF}; \qquad \eta_Q = \frac{q_{xx}^{PAF} - q_{yy}^{PAF}}{q_{zz}^{PAF}}$$
[2.30]

where *e* is the elementary charge, *eq* is the EFG tensor at the nucleus, usually defined at the z-axis in the PAF ( $eq_{zz}^{PAF}$ ), to be distinguished from the laboratory frame. *Q* is the nuclear quadrupole moment,  $\hat{l}_{z PAF}$  is the spin operator at the z-axis of the PAF (same applies for  $\hat{l}_{x PAF}$  and  $\hat{l}_{y PAF}$ ).  $\eta_Q$  is the *quadrupolar asymmetry parameter*, it is restricted from 0 to 1. The quadrupolar coupling constant  $C_Q$ , can be written as (in the unit of Hz):<sup>3,7</sup>

$$C_Q = \frac{e^2 q Q}{h} \tag{2.31}$$

The quadrupolar interaction has been briefly introduced, which is based on the PAF of the nucleus. However, it is often more convenient to define PAF relative to the laboratory frame when dealing with NMR experiments, since the Zeeman interaction from the applied  $\vec{B}_0$  along the laboratory z-axis, is still the predominant effect to the NMR line shape.<sup>3</sup> This definition from PAF to laboratory frame can be achieved by rotating the PAF using two angles  $\theta$  and  $\phi$ , which defining the orientation of PAF relative to  $\vec{B}_0$  at the *laboratory frame*. In this scenario,  $\hat{H}_Q$  can be written in the laboratory frame by substituting the appropriate linear combinations of  $\hat{I}_{x,y,z}$  for further analysis (derivation not shown).<sup>3</sup>

From here, the 1<sup>st</sup>-order energy correction to the Zeeman interaction can be expressed as:<sup>3</sup>

$$E_m^1 = \frac{e^2 q Q}{4I(2I-1)} (3m^2 - I(I+1)) \cdot \left[\frac{1}{2}(3\cos^2\theta - 1) - \eta_Q \sin^2\theta \cos^2\phi\right]$$
[2.32]

where  $E_m^1$  is the 1<sup>st</sup>-order energy perturbation (1<sup>st</sup>-order quadrupolar coupling effect). Higher order terms of the quadrupolar interaction appear to be more complicated, but typically, consideration up to 2<sup>nd</sup>-order energy correction  $E_m^2$  to the Zeeman interaction

is enough, this correction can be expressed in the following **Equation** [2.33], adapted with modifications from Duer 2004:<sup>3</sup>

$$E_m^2 = -\left(\frac{e^2 q Q}{4I(2I-1)}\right)^2 \frac{1}{2\omega_0} \times \left\{-\frac{1}{5}\left[2m(I(I+1)-3m^2)\right](3+\eta_Q^2)\right] \qquad 0^{\text{th}-\text{rank}}$$

$$+\frac{1}{28}\left[2m(8I(I+1)-12m^2-3)\right]\left[(\eta_Q^2-3)(3\cos^2\theta-1)+6\eta_Q\sin^2\theta\cos^2\right] 2^{\text{nd}-\text{rank}}$$

$$C_2^I(m)$$

$$+\frac{1}{8}\left[2m(18I(I+1)-34m^2-5)\right]\left[\frac{1}{140}\left(18+\eta_Q^2\right)(35\cos^4\theta-30\cos^2\theta+3)\right] \qquad 4^{\text{th}-\text{rank}}$$

$$C_4^I(m)$$

$$+\frac{3}{7}\eta_Q\sin^2\theta(7\cos^2\theta-1)\cos^2\phi + \frac{1}{4}\eta_Q^2\sin^4\theta\cos^4\phi]\right\} \qquad [2.33]$$

There are three terms in the 2<sup>nd</sup>-order corrections – the  $0^{th}$ -rank, the  $2^{nd}$ -rank, and the  $4^{th}$ -rank terms, as labelled above.  $C_k^I(m)$  is the coefficient for k<sup>th</sup>-rank term at spin state m, and  $V_{k0}^Q$  is the spherical tensor of the corresponding k<sup>th</sup>-rank term.<sup>3</sup> Clearly, the 1<sup>st</sup>- and 2<sup>nd</sup>-order corrections not only exhibit distinct orientational dependencies but also influence different transitions in various ways, for different quadrupolar nuclei. In addition, there are a few notable phenomena arise from **Equation [2.32]** and **[2.33]**:

For any half-integer quadrupolar nuclei, the E<sup>1</sup><sub>m</sub> correction has no influence on the central transition + <sup>1</sup>/<sub>2</sub> → -<sup>1</sup>/<sub>2</sub>, because ΔE<sup>1</sup>/<sub>1/2</sub> → <sup>1</sup>/<sub>2</sub> is 0. For any integer quadrupolar nuclei, Δm = ±1 will generate pairs of transitions, with opposite polarities, e.g. +1 → 0 and 0 → -1 for spin I = 1.

- 2.  $E_m^1$  has the same molecular orientation dependency as the heteronuclear dipolar interaction and CSA interaction.<sup>3</sup> For a powder sample, this will result in a similar line shape of the satellite transitions for the spin I = 1 and  $I = \frac{3}{2}$ .<sup>3</sup>
- 3. An orientational-independent isotropic term exists in the 2<sup>nd</sup>-order correction, indicating a perturbation of the Zeeman interaction always presents.<sup>3</sup> But the entire 2<sup>nd</sup>-order term scales inversely proportional to the magnetic field strength. If the magnetic field is much stronger than quadrupolar coupling constant, the 2<sup>nd</sup>-order quadrupolar coupling effect can be neglected.
- 4. Even within the 2<sup>nd</sup>-order correction, the 2<sup>nd</sup>-rank and the 4<sup>th</sup>-rank has different magnitude and angle-dependency of  $\theta$  and  $\phi$  at the laboratory frame.

To further examine the quadrupolar effects on the transition energies, the quadrupolar coupling tensors can be firstly transformed into the laboratory frame. This is done by rotating the PAF of quadrupolar tensor around its  $z \rightarrow y \rightarrow z$  axes sequentially by the angles of  $\alpha \rightarrow \beta \rightarrow \gamma$ , respectively (ZYZ convention). This set of angles are known as *Euler angles*.<sup>3,7</sup> From here, the *quadrupolar splitting*  $\omega_Q^1$  and  $\omega_Q^2$  for the transition energies (in frequency unit) at the laboratory frame are given in **Equation [2.34]** and [2.35]:<sup>3</sup>

$$\omega_Q^1 = \frac{e^2 q Q}{4I(2I-1)} (3m^2 - I(I+1)) W_{20}^Q; \qquad W_{20}^Q \propto (3\cos^2\beta - 1)$$
 [2.34]

$$\omega_Q^2 = -(\frac{e^2 q Q}{4I(2I-1)})^2 \frac{1}{\omega_0} \times [C_0^I(m) V_{00}^Q + C_2^I(m) V_{20}^Q + C_2^I(m) V_{40}^Q]$$

$$V_{20}^Q \propto (3\cos^2\beta - 1); \qquad V_{40}^Q \propto (35\cos^4\beta - 30\cos^2\beta + 3) \quad [2.35]$$

where  $W_{20}^Q$  is the second-rank spherical tensor for the 1<sup>st</sup>-order quadrupolar interaction,  $V_{00}^Q$ ,  $V_{20}^Q$ , and  $V_{40}^Q$  are the tensors corresponding to the 0<sup>th</sup>-, the 2<sup>nd</sup>-, and the 4<sup>th</sup>-terms in **Equation** [2.33].



**Figure 2.11** Graphical illustration of the 1<sup>st</sup>- and the 2<sup>nd</sup>-order energy corrections to the Zeeman interaction. "ST" stands for satellite transition, and "CT" is central transition.<sup>7</sup>

Recall from **Figure 2.1**, where the Zeeman splitting for the spin  $I = \frac{3}{2}$  nuclei was shown without the effects of 1<sup>st</sup>- and 2<sup>nd</sup>-order quadrupolar interactions. **Figure 2.11** further illustrates the effect of them. As previously mentioned, the 1<sup>st</sup> order correction has no effect on the central transition (CT), but for the satellite transitions (ST), an energy shift of  $2\omega_Q^1$ for the two ST presents, where  $\omega_Q^1$  is the *quadrupolar splitting* of the 1<sup>st</sup>-order correction.

Its value can be calculated using **Equation [2.32]**. If the  $C_Q$  is small, then only the 1<sup>st</sup>-order correction needs to be considered,<sup>1, 3</sup> the corresponding powder line shape is shown in Figure 2.12a. The approximation to the 1<sup>st</sup>-order quadrupolar interaction is usually true for the nuclei that has small quadrupole moment, such as for <sup>7</sup>Li ( $Q = -4.01 \ fm^2$ ),<sup>2</sup> where the central transition and satellite transitions are closed in frequency and can be observed simultaneously in the NMR spectra. However, if  $C_0$  is large (up to MHz level), 2<sup>nd</sup>-order quadrupolar interaction contribution needs to be taken into account.<sup>3</sup> This can be quite common for the nuclei that with large quadrupole moment, such as  $^{23}$ Na (Q = $10.01 fm^2$ ).<sup>2</sup> Under this scenario, the Zeeman energy state of the CT and the STs are both perturbated by the 2<sup>nd</sup>-order quadrupolar effect, and this effect does not shift each transitions uniformly. In the 0<sup>th</sup>-rank term, the  $\eta_0$  value has dominant the contribution. In 2<sup>nd</sup>- and the 4<sup>th</sup>-rank term, the CT and ST transitions are not only orientationally dependent on the " $3cos^2\theta - 1$ ", but also dependent on the more complicated  $V_{40}^Q$  term, leading to the asymmetrical broadening of CT. In addition, the significant 2<sup>nd</sup>-order perturbation introduced by large  $C_Q$  can lead the STs non-observable in the NMR spectra, because they are well off-resonance.<sup>3</sup> Thus, it is typical to only observe the CT for the spectra that suffered from the  $2^{nd}$ -order interaction. Figure 2.12c – f illustrates the central transitions of spin  $I = \frac{3}{2}$  that with different  $C_Q$  and  $\eta_Q$  values.



**Figure 2.12** The contributions of quadrupolar coupling in the NMR spectra for spin  $I = \frac{3}{2}$  nuclei. Where (**a**) represents effect of 1<sup>st</sup>-order quadrupolar coupling, (**b**) illustrates that in a cubic symmetry environment, no quadrupolar effect is present because of the absence of EFG, (**c**) – (**f**) considers the contributions of 2<sup>nd</sup>-order quadrupolar coupling, with different values of  $C_Q$  and  $\eta_Q$ , only CT can be observed in the spectra because of the STs are off-resonance. The spectral simulations were completed using ssNake v1.3.2.<sup>5</sup>

Up to this point, the consideration of quadrupolar couplings perturbate the Zeeman interaction have been discussed. The various orientational dependencies for the different

components in the 1<sup>st</sup>- and 2<sup>nd</sup>-order quadrupolar interactions can be challenging to grasp, yet they have significant effect on the observed line shapes in ssNMR spectra. The quadrupolar interactions will be further discussed in **Section 2.3.2** and **2.3.3**, where the different techniques to remove/average them in practice will be introduced.

### 2.2.4 Knight Shift

In the later part of this thesis, measurements of metallic Li metal are involved because Li metal is one of the most common anodes used in different electrochemical studies. The NMR shifts of conductive metals is dominated by the interaction between the nuclei and the conduction electrons, which align paramagnetically to  $\vec{B}_0$  and produce strong polarization. The strong polarization of these electrons introduces significant internal magnetic field, resulting in dramatic shifts in the NMR spectrum. For simple metals that the only needs consideration of *s*-orbital electrons (such as Li), the Hamiltonian of the conductive *s*-electron and nuclear interaction  $\hat{H}_K$  can be expressed as (with the omission of nucleus-electron dipolar and quadrupolar couplings):<sup>8, 9</sup>

$$\widehat{H}_{K} = \frac{16\pi}{3} \mu_{B} \gamma \hbar \, \widehat{I} \, \widehat{S}_{e}(\vec{r}) \, \delta(\vec{r}) \qquad [2.36]$$

where  $\mu_B$  is the Bohr magneton,  $\hat{S}_e(\vec{r})$  represents the electron spin as a function of its position vector  $\vec{r}$  from the nucleus.<sup>8, 9</sup>  $\delta(\vec{r})$  is the contact interaction that samples the probability density of the electrons at the nucleus.<sup>9</sup> The perturbation of spin generated from this interaction is called *Knight shift*, denoted as  $\mathscr{K}$ :<sup>9</sup>
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$$\mathscr{H} = \frac{8\pi}{3} \chi_P P_F \tag{2.37}$$

 $\chi_P$  is the Pauli magnetic spin susceptibility per atom, and  $P_F = \langle \psi(0)^2 \rangle$ , representing the averaged density of conduction electrons at the nucleus over the Fermi surface. For <sup>7</sup>Li NMR, the shift value of metallic Li is around 240 – 280 ppm (compared from typical diamagnetic shifts ~ 0 ppm), which makes them distinguishable from other species in the <sup>7</sup>Li NMR spectra.



**Figure 2.13** An <sup>7</sup>Li NMR spectrum recorded for a symmetric *in-situ* cell using metallic Li as electrode, on a Bruker AV300 spectrometer. The shift of Li electrode shows up at ~ 250 ppm, making it distinguishable from the diamagnetic shift of the solid electrolyte.

## **2.3 Advanced NMR Methods**

### 2.3.1 NMR Diffusometry

NMR diffusometry, pulse-field-gradient (PFG) NMR, or "DOSY (Diffusion Ordered Spectroscopy)" NMR, also referred to as "NMR chromatography" in solution NMR world, essentially are the exact same pulse sequence. This sequence is a powerful tool to measure molecular dynamics at microscale, firstly proposed by E. O. Stejskal and J. E. Tanner in 1965.<sup>10</sup> The previous discussion in this chapter mostly assumes the nuclear spin with  $I = \frac{1}{2}$  under an uniform and static external field  $\vec{B}_0$ , thus they share the same precession frequency across the entire sample volume, resulting in an *in-phase* scenario for all the spins in the transverse plane and therefore resulting in high signal intensity (recall from discussion for  $T_2$  in **Section 2.1.5**). The trick of NMR diffusometry is to introduce an artificial factor that purposely "de-synchronizes" the phase of each spin aligns z-axis, by applying a linear change of the magnetic field strength along  $\vec{B}_0$ . This is achieved by applying *magnetic field gradient*,  $\vec{G}(z)$ , typically written in the units of T m<sup>-1</sup> or G cm<sup>-1</sup>. The spin at different position z will "feel" different effective Larmor frequency,  $\omega_{eff}$ , which can be calculated as:<sup>11</sup>

$$\omega_{eff}(z) = \omega_0 + \omega_g(z) = \gamma[\vec{B}_0 + z \cdot \vec{G}(z)]$$
[2.37]

where  $\omega_g(z)$  is the correction to the effective Larmor frequency for a specific spin at z-position.  $z \cdot \vec{G}(z)$  is the effective gradient at z-position. After the application of the gradient pulse for a short period of time, the spins will acquire phase shifts based on their locations. This process labels the nuclear spins, known as *phase-encoding*. However, a single encoding gradient pulse will just dephase the NMR signal and cannot provide any useful information. A decoding gradient pulse is required to refocus the NMR signal, it possesses the same gradient strength but opposite polarity. Here, a simple pulse sequence for measuring diffusivity – pulse-gradient spin-echo (PGSE) is presented in **Figure 2.14**, together with the phase evolutions of the nuclear spins along z-axis.



**Figure 2.14** Graphical illustrations of (**a**) pulse sequence of PGSE, and (**b**) the phase evolutions of the nuclear spins corresponding to their positions, throughout the PGSE sequence.<sup>12, 13</sup>

In **Figure 2.14**, an initial 90° RF pulse excites all the spins in the sample, generating a phase-coherent NMR signal align the z-axis. Afterwards, a gradient pulse is applied to linearly encode the spins, the phase coherence is lost across the sample, which is illustrated in **Figure 2.14b** from spin 1 – 5. The spins might undergo translational motions for a fixed period (denoted as " $\Delta$ ", diffusion time). During this time, spins with different phase elements can displace from their original positions; for simplicity, it can be illustrated here by exchanging the positions between spin 2/3 and 4/5. The following, a 180° pulse reverse the phases of each spin to cancel the inhomogeneity of  $\vec{B}_0$  after time  $\tau$  (recall from the Hahn echo in **Section 2.1.5**).

Afterwards, the decoding gradient pulse is employed, since the phases of the spins have been reverted by the 180° pulse, the decoding gradient pulse, which supposed to have an opposite phase with the first encoding gradient pulse, now shares the same polarity as the encoding gradient pulse instead. At this point, two scenarios can exist. For the first scenario, the decoding gradient effectively refocuses the coherence of the non-dynamic spins, because they are static at their original positions throughout the entire process, do not participate in any translational motion at all, (for example, spin 1). Thus, they receive the same magnitude of the decoding gradient power as the encoding one, or in other words, *net-zero phase shift*. Thus, their phase can be fully refocused, leading to a maximized NMR signal.

The second scenario, for spins 2/3 and 4/5, since they displaced from their original positions after the diffusion time  $\Delta$ , they do not receive the same gradient power from the decoding gradients. Hence, these spins will lose their phase coherences due to the discrepancies between the encoding and decoding gradients. In this case, the final detected NMR signal/echo will be attenuated due to the lost of phase coherence. This effect is also illustrated in **Figure 2.14b**, where the spin 2 – 5 are not "aligned" after the application of

decoding gradient. The decreased in total signal intensity, all together with the  $T_2$  relaxation effect in the transverse plane from **Equation [2.19]** (considering  $T_2 \ll T_1$ ):<sup>12</sup>

$$S(g,t) = S_0 \exp\left(-\frac{2\tau}{T_2}\right) * \exp\left[-\gamma^2 g^2 \delta^2 D\left(\Delta - \frac{\delta}{3}\right)\right]$$

$$(2.38)$$
Attenuation due Attenuation due to  $T_2$  relaxation to diffusion

where S(g, t) is the final measured signal intensity as a function of echo time  $\tau$ , as well as gradient power – g (in T m<sup>-1</sup> or G cm<sup>-1</sup>).  $\delta$  is the gradient encoding/decoding time, typically in a few milliseconds. D is the diffusivity of the nucleus being measured in m<sup>2</sup> s<sup>-1</sup>, and  $\Delta$  is the time that allows the nuclei to diffuse (diffusion time), typically in hundreds of milliseconds. Practically, NMR diffusivity experiment is often done by collecting a series of spectra with varying gradient power, after scaling the signal intensity relative to the spectrum with lowest g. In this case, the effect of  $T_2$  relaxation can be normalized out, because the spins in the transverse plane will have the same evolution time across all the spectra,<sup>11</sup> which resulting in the generic *Stejskal and Tanner* equation:<sup>12</sup>

$$S(g)/S_0 = \exp\left[-\gamma^2 g^2 \delta^2 D\left(\Delta - \frac{\delta}{3}\right)\right];$$

or

$$S(g)/S_0 = \exp\left[-bD\right];$$

where  $b = \gamma^2 g^2 \delta^2 \left( \Delta - \frac{\delta}{3} \right)$  [2.39]

S(g) represents the signal intensity of gradient power, *b* denotes the attenuation power, which is usually adjusted to accommodate different samples by modifying g,  $\delta$ , and  $\Delta$ . Below, a schematic illustration of one NMR diffusometry experiment is shown in **Figure 2.15**. This was conducted on a 1M LiPF<sub>6</sub> in EC/DMC (1:1, v/v) liquid electrolyte sample.



Figure 2.15 Schematic illustration of an NMR diffusometry experiment from data acquisition and processing to final analysis. (a) Collecting a series FIDs under variable gradient and (b) corresponding 1D spectra. (c) and (d) displays two different manners of plotting the integrated intensity as a function of g. This experiment was completed on <sup>7</sup>Li,

for a 1M LiPF<sub>6</sub> in EC/DMC (1:1, v/v) liquid electrolyte sample on a Bruker AV300 spectrometer (at ~ 295 K). The final calculated *D* is  $1.96 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>.

During the experiment, *g* was linearly incrementally increased in a series of steps to collect serveral FIDs (**Figure 2.15a**). After performing FT on all the FIDs, multiple 1D spectra were acquired. By plotting *g* against the integrated intensity across all the spectra, 2D plots can be generated. **Figure 2.15c** and **d** displays two different methods of plotting. The diffusivity *D*, can be calculated by fitting the resulting data points using the function indicated **Figure 2.15c** and **d**.

There are a few practical difficulties related to the PGSE sequence. The first difficulty is that the final signal will be significantly affected by  $T_2$  relaxation. In the PGSE sequence, the nuclear spins evolution time in the transverse plane is dictated by  $\Delta$ , which is usually set to dozens to hundreds of milliseconds. However, for solution state, the  $T_2$  values are usually up to a few milliseconds, therefore, even the effect of  $T_2$  is averaged out across the spectra, but the absolute signal intensity could still be greatly attenuated to an undetectable level, as indicated in **Equation [2.38]**. The second problem closely follows the previous one, for the sample that has slow dynamics, longer  $\Delta$  or  $\delta$  are required to observe efficient echo attenuation, while  $T_2$  relaxation will be even shorter for slow dynamics, based on the *BPP* theory, making it even more difficult to collect the echo signals. At this point, the only possible way is to increase g, without saturating the signal at the transverse plane due to  $T_2$  process. Here, the final difficult arises: the application of high

strength of gradient pulse within a short  $\delta$  can result in *eddy currents* in the xy-plane. Eddy currents can interfere with the magnetic field in the xy-plane, leading to diminished signal in the FID, or causing line shape distortions in the NMR spectra. The severity of the eddy currents is proportionally related to  $dI/d\delta$ , where *I* is the current being passed through the gradient coil here.<sup>12</sup> Rapidly increasing and decreasing the large gradient pulses within short period of time will be problematic for the diffusion measurements for slow diffusing samples. This could mean that the measured diffusivity might not be a result of kinetics, but rather a consequence of NMR artifact, potentially leading to an overestimation the diffusivity.

To address the first and the second issues, a pulsed-gradient stimulated-echo (PGSTE) sequence can be utilized, as illustrated in **Figure 2.16a**.<sup>12</sup> Instead of allowing the spins to evolve in the xy-plane during  $\Delta$ , a second 90° pulse is introduced after the encoding process, which brings the encoded spins to the negative z-axis. This z-storage minimizes  $T_2$  relaxation, allowing an extended  $\Delta$  to collect the diffusion coefficient at a longer length scale. However, the length of  $\Delta$  now should be manipulated based on the  $T_1$ , which is more tolerant to accommodate for experiments with longer diffusion time, given the fact that  $T_1 \gg T_2$ , and the effect of losing signal intensity due to  $T_1$  process can be averaged by collecting the spectra under a series of gradient strengths, just like the treatment for  $T_2$  from **Equation [2.38]** – **[2.39]**.





Regarding the third problem, Wu et al.<sup>14</sup> proposed a more robust sequence that modified from the PGSTE sequence. This new sequence is known as *bipolar-gradientpulse-pair* sequence (BPP, distinct from the *BPP* relaxation discussed in **Section 2.1.5**). BPP sequence divides the encoding and decoding gradient pulses into two shorter gradient pulses with opposite polarities. The short gradient pulse pair is separated by a 180° pulse, which has negating effect on the phase change induced by the negative sign of the second gradient pulse, thus, the 180° sandwiched in between the gradient pulse pair can be treated as one gradient pulse in the PGSTE. During the encoding process, if eddy currents are induced by the gradient pulse with a positive polarity, the subsequent negative polarity gradient pulse will induce "negative" eddy currents, thus introduces self-compensating effects to the initial eddy currents. To further tackle the eddy current effects, longitudinal eddy current delay (LED)<sup>12</sup> component can be incorporated into the BPP sequence, together with spoiler gradients (SGs) that with low power and long activation time. LED component is applied at the end of the pulse sequence, it introduces a settling time that allows the eddy currents to dissipate, while the decoded spins are brought back into z-storage. During this period, SG is also applied, it acts as an "eraser" to dephase any remaining magnetization in the xy-plane, effectively reduces the eddy currents, and leads to undistorted line shapes of the final spectra. In addition, modulated gradient pulses can also be used to mitigate the eddy current effects. As previously mentioned, the severity of the eddy currents is proportional to  $dI/d\delta$ , it is an obvious method to slow down the rise and fall time of the gradient pulses by modulating them into shaped gradient pulses.<sup>12, 15</sup> One of the most common types is the sine-shaped pulse, which ramp up and down the gradient pulse in a more gentle manner.<sup>12</sup> Herein, the sum of the modifications to the PGSTE is denoted as "BPP-STE-LED", which is the most common sequence used in this thesis, illustrated in Figure 2.16b. Certainly, by modifying PGSTE sequence with BPP, LED, and shaped pulse requires amendments to the original Stejskal and Tanner equation, for the BPP-STE-LED sequence, it can be written as:<sup>15</sup>

$$S(g)/S_{0} = \exp[-\gamma^{2}g^{2}\delta^{2}D\frac{4}{\pi}\left(\Delta - \frac{5\delta}{16} - \frac{\tau_{g}}{2}\right)$$
$$b_{BPP} = \gamma^{2}g^{2}\delta^{2}\frac{4}{\pi}\left(\Delta - \frac{5\delta}{16} - \frac{\tau_{g}}{2}\right)$$
[2.40]

Here,  $\tau_g$  represents the stabilization delay between the gradient pulse and the subsequent RF pulse,<sup>15</sup>  $b_{BPP}$  is the attenuation power specific to this sequence. Additional modified equations that account for various combinations of BPP, LED, and shaped pulses were described elsewhere.<sup>12, 15</sup>

One last note for the NMR diffusometry measurement is the variable  $\Delta$  and the corresponding diffusion length scale. For a case of free diffusion (such as free Brownian motion in pure liquid), the measured diffusivity is not affected by  $\Delta$ . However, in practical, the observed diffusivity value in anisotropic phase (porous solid or powder) might be varied by the length of  $\Delta$ , as the longer the  $\Delta$ , the more likely the nuclei reach diffusion barriers, such as the diffusive species reach GBs at the interfaces of the solid particles. This effect leads to an inversed  $\Delta$ -dependency of D; That is, the apparent diffusivity  $D_{app}$  tends to decrease as  $\Delta$  increases. This phenomenon is known as *restricted diffusion*.<sup>11, 16</sup> This mechanism will be further presented in the context of <sup>7</sup>Li diffusion behaviour in the crystalline solids, as discussed later in the thesis.

### 2.3.2 Magic-Angle Spinning (MAS) NMR

Previously, different internal nuclear spin interactions were addressed to highlight their significance in altering NMR line shapes. These interactions exhibit orientational dependency and can introduce anisotropic components in the NMR spectra. When the NMR experiment is conducted on a solution sample, the molecules in solution can rapidly tumbling, which sufficiently averages out these interactions, resulting in "net isotropic" environments around the nuclei. Thus, the resulting spectra are usually well-resolved and simple to interpret for solution NMR (even with J-coupling). However, the main issue with these interactions arises in ssNMR experiments, where the samples are typically powder, which consists of many crystallites with random orientations. While the nuclei within the powder sample are more static, the orientational dependency of the spin interactions will contribute to broad and anisotropic line shapes, consequentially leads to the NMR lines that are difficult to analyze.

To acquire high-resolution ssNMR, it is essential to employ certain techniques to remove the above-mentioned anisotropic interactions. *Magic-angle spinning* (MAS) is a routine practice that used extensively in the ssNMR world. It utilizes the fact that most of the nuclear spin interaction has orientational dependency on the second-rank tensor on a specific term " $3cos^2\theta - 1$ " (as discussed in **Section 2.2**). When  $\theta$  is set to 54.74° relative to  $\vec{B}_0$ , this term vanishes.<sup>3</sup> MAS mimics the "molecular tumbling" effect observed in the solution samples by mechanically spinning the solid powder sample.

The sample spinning is realised by using a cylindrical sample holder called *rotors*, they equipped with fins at one end. By applying a gas flow on the fins, the rotor is driven to spin, together with another gas flow to "float" the rotor inside the stator of a MAS probe. The rotor, aligns to the spinning axis at 54.74° relative to the external field  $\vec{B}_0$ , is illustrated below in **Figure 2.17**.



**Figure 2.17** Schematic of a rotor positioned at the magic-angle of 54.74°, which is also the axis for the rotor spinning. Adapted with modifications from Duer 2004.<sup>3</sup>

To effectively remove the anisotropic interactions, the rotor spinning frequency typically needs to be a factor of 3 - 4 times greater than the strength of the anisotropic interactions.<sup>3</sup> Figure 2.18 illustrates the simulated NMR spectra demonstrating increased resolution through MAS.



**Figure 2.18** Simulating the effects of MAS-enhanced NMR spectral resolution, (**a**) – (**b**) the effect of CSA (MAS = 10 kHZ); (**c**) – (**d**) 1<sup>st</sup>-order as well as (**e**) – (**h**) 2<sup>nd</sup>-order quadrupolar interactions (MAS = 5 kHz). Spinning sidebands are marked with asterisks. The spectral simulations were completed using ssNake v1.3.2.<sup>5</sup>

It is important to note that spinning the sample can also introduce artifact signals in the NMR spectra, known as *spinning sidebands*, which appear at the flanks of the isotropic peaks in the NMR spectra, separated by spinning frequency (marked with asterisks).<sup>3</sup> Suppose a magnetization evolve in the xy-plane, the frequency of this magnetization is dictated by  $\vec{B}_0$  and chemical shielding. However, during MAS, the evolution of the magnetization is also modulated by the orientation of the crystallites, as the rotor spins, the frequency in the FID varies as the orientations of the crystallites change. Once a full rotation is completed, the frequency returns in its maximum signal, resulting a series of *rotational echoes*,<sup>3</sup> modulated by the spinning frequency, which results in the formation of spinning sidebands.<sup>3</sup>

MAS can induce line-narrowing effects on the NMR spectra. in **Figure 2.18a** and **c**, where the NMR spectra are experiencing with CSA and 1<sup>st</sup>-order quadrupolar interactions, the MAS can sufficiently average out the anisotropic terms and lead to isotropic peaks in **Figure 2.18b** and **d**. However, for the spectra that suffered from 2<sup>nd</sup>-order quadrupolar interaction, MAS cannot completely narrow the peaks down to isotropic line shape (**Figure 2.18e** – **h**). This is mainly attributed to the 4<sup>th</sup>-rank tensor (**Equation 2.35**) in the 2<sup>nd</sup>-order quadrupolar interaction, which has a different orientational dependency as the "3*cos*<sup>2</sup> $\theta$  – 1". To mitigate this issue, combinations of MAS and other techniques are necessary to resolve this type spectra, they will be introduced in the subsequent section.

### 2.3.3 Multiple-Quantum MAS (MQMAS) NMR

As previously discussed, regular MAS can introduce averaging effects on the 2<sup>nd</sup>order quadrupolar interactions, but due to the 4<sup>th</sup>-rank tensor, MAS cannot completely cancel the 2<sup>nd</sup>-order interaction at 54.74°. In a mathematical expression, the 4<sup>th</sup>-rank tensor, which is proportional to  $(35cos^4\theta - 30cos^2\theta + 3)$ , can only be removed when  $\theta$  equals to 30.56° or 70.1°. Thus, there's not a single spinning axis that can simultaneously cancel out the 4<sup>th</sup>-rank term in the 2<sup>nd</sup>-order quadrupolar interaction and other anisotropic interactions, such as CSA, dipolar coupling, and 1<sup>st</sup>-order quadrupolar coupling.

The most direct method to tackle this issue is to introduce a second spinning axis other than the regular one at 54.74° respective to the external field. This is known as the *double-rotation* experiment, or DOR, proposed by Pines, Samoson, and co-workers in 1988.<sup>3, 17, 18</sup> In this setup, a larger size rotor aligns at 54.74°, which contains a smaller size rotor in it aligns at 30.56° relative to  $\vec{B}_0$ , respectively. The simultaneous spinning of the two rotors can cancel the 2<sup>nd</sup>-rank and 4<sup>th</sup>-rank terms in the 2<sup>nd</sup>-order quadrupolar effects, altogether with other anisotropic nuclear spin interactions with the " $3cos^2\theta - 1$ " dependency. However, the setup of DOR is relatively complicated. In addition, spinning a small rotor inside a large rotor is not-trivial, achieving high and stable spinning frequencies of both rotors can be challenging.<sup>3</sup> Shortly after the invention of DOR, Llor and Virlet introduced *dynamic-angle spinning* (DAS) to the field,<sup>19, 20</sup> this method only requires the spinning of a single rotor, but at two different angles,  $\theta_1$  and  $\theta_2$ . The pulse sequence generally consists three components:<sup>3</sup> a selective excitation of the CT  $(+\frac{1}{2} \rightarrow -\frac{1}{2})$  at angle

 $\theta_1$  for an evolution time of  $t_1$ ; following by another selective pulse that brings the magnetization to z-storage; finally, after flipping the spinning angle to  $\theta_2$ , a subsequent selective pulse return the evolution of the magnetization at transverse plane for a period of  $kt_1$  (k is a constant), which will be refocused into an echo.<sup>21</sup> By allowing the 2<sup>nd</sup>-rank and 4<sup>th</sup>-rank anisotropy terms to proceed at two different evolution times at each angle. It is possible to find solutions to cancel the two terms after reaching an echo:<sup>3, 21</sup>

$$C_{2}^{I}(m)V_{20}^{Q}(\cos\theta_{1})t_{1} + C_{2}^{I}(m)V_{20}^{Q}(\cos\theta_{2})kt_{1} = 0$$

$$C_{4}^{I}(m)V_{40}^{Q}(\cos\theta_{1})t_{1} + C_{4}^{I}(m)V_{40}^{Q}(\cos\theta_{2})kt_{1} = 0$$
For CT,  $m = +\frac{1}{2} \rightarrow m = -\frac{1}{2}$ 
[2.40]

Multiple solutions for the two angles are possible, for example, when  $\theta_1$  and  $\theta_2$  are set to 37.38° and 79.19°,  $V_{20}^Q(\cos\theta_1) = -V_{20}^Q(\cos\theta_2)$ , and  $V_{40}^Q(\cos\theta_1) = -V_{40}^Q(\cos\theta_2)$ .<sup>20, 21</sup> In this case, the two evolution times can be set to equal (k = 1), and the 2<sup>nd</sup>-order quadrupolar broadening effect can be cancelled, leading to the observable isotropic term. However, like DOR, DAS experiment also requires a specialized probe with a complicated hardware setup,<sup>20</sup> which limits its applicability for a wider range of users.

Nevertheless, the DAS method demonstrates cancelling of the 2<sup>nd</sup>-order quadrupolar effect, by creating an echo that is varied by spinning angle. It provides an idea for the subsequent method – *multiple-quantum magic-angle spinning*, or MQMAS. This is a pulse sequence firstly proposed by Frydman et al. in 1995,<sup>22, 23</sup> instead of varying the spinning angles for the single-quantum transition  $(1Q, +\frac{1}{2} \rightarrow -\frac{1}{2})$  to remove the 2<sup>nd</sup>-rank

and 4<sup>th</sup>-rank terms like in the DAS; MQMAS removes the 2<sup>nd</sup>-rank term by conventional MAS, and varies the *coefficients* of the 4<sup>th</sup>-rank terms –  $C_4^I(m)$  between the 1Q and MQ transitions. The removal of 4<sup>th</sup>-rank terms is realised by modulating the evolution times in between the 1Q and the MQ. The convenient utilization of MQMAS making it an extremely advantageous method compared to the DOR and DAS, as it can be done on any regular high-power ssNMR probe without any hardware modifications. Furthermore, spinning the rotors at 54.7° is usually desirable as it can induce averaging effects to CSA, dipolar coupling, etc. **Figure 2.19** shows a simple MQMAS sequence for a 3Q excitation (3QMAS) scenario;<sup>3, 22</sup>



**Figure 2.19** Pulse sequence of 3QMAS experiment. Adapted with modification from Duer 2004<sup>3</sup> and Frydman et al. 1995.<sup>22</sup>

First, a 3Q excitation pulse is applied to generate  $+\frac{3}{2} \rightarrow -\frac{3}{2}$  coherence following by an evolution time  $t_1$ ; the second pulse converts the 3Q to 1Q transition; after the second evolution period for the 1Q transition  $kt_1$ , an echo can be reached at the start of signal acquisition time  $t_2$ . For a spin  $I = \frac{3}{2}$  nucleus, the evolution of 1Q and 3Q in 3QMAS can be calculated accordingly from **Equation [2.33**]:

$$C_{4}^{I}\left(\frac{1}{2}, 1Q\right) = 2 \times \frac{1}{2} \times \left[18 \times \frac{3}{2}\left(\frac{3}{2}+1\right) - 34\left(\frac{1}{2}\right)^{2} - 5\right] = 54$$
$$C_{4}^{I}\left(\frac{3}{2}, 3Q\right) = 2 \times \frac{3}{2} \times \left[18 \times \frac{3}{2}\left(\frac{3}{2}+1\right) - 34\left(\frac{3}{2}\right)^{2} - 5\right] = -42 \qquad [2.41]$$

When the sample is spun at the magic-angle, the 2<sup>nd</sup>-rank term vanishes, only the sum of the evolution of the 4<sup>th</sup>-rank terms in **Equation** [2.40] needs to be considered:

$$C_{4}^{I}\left(\frac{3}{2}, 3Q\right)V_{40}^{Q}\left[\cos(54.74^{\circ})\right]t_{1} + C_{4}^{I}\left(\frac{1}{2}, 1Q\right)V_{40}^{Q}\left[\cos(54.74^{\circ})\right]kt_{1}$$

$$C_{4}^{I}\left(\frac{3}{2}, 3Q\right)t_{1} + C_{4}^{I}\left(\frac{1}{2}, 1Q\right)kt_{1} = -42t_{1} + 54kt_{1} \qquad [2.42]$$

When *k* equals to  $\frac{7}{9}$ , the 4<sup>th</sup>-rank terms of the 1Q and 3Q can cancel each other, this will result in a pure isotropic shift if the evolutions of the two transitions are controlled. This is achieved by setting a two-dimensional NMR experiment, where the evolution of  $t_1$  is stepped through a series of increment time periods, creating the second dimension (or indirect dimension, also referred to as "*F*1") for the NMR spectrum. After applying a shearing transformation, with the shearing factor equals to *k*, the isotropic shift of the signal can be identified in the indirect isotropic dimension. An example of a 2D sheared-3QMAS spectrum for <sup>27</sup>Al ( $I = \frac{5}{2}$ ) of a crystalline LiAlCl<sub>4</sub><sup>24</sup> is shown in **Figure 2.19**, where only one Al site is expected in this material, so as in the indirect isotropic dimension. In the case of  $I = \frac{5}{2}$ , the shearing factor *k* is equal to  $\frac{19}{12}$  here.<sup>25</sup>



**Figure 2.20** <sup>27</sup>Al 2D-sheared 3QMAS spectrum for LiAlCl<sub>4</sub>, the direct dimension is the conventional NMR spectrum. The indirect dimension is the pure isotropic dimension after removal of the 2<sup>nd</sup>-order broadening effect by refocusing the 4<sup>th</sup>-rank terms between the 1Q and 3Q transitions. This experiment was conducted on a Bruker AV850 spectrometer, using a 1.9 mm double-resonance probe with the rotor spinning at 54.74°, MAS frequency was set to 20 kHz. The material was provided by collaborator Dr. Insang You from Prof Nazar's group at University of Waterloo.

Up to this point, the concept of quadrupolar NMR and the important MQMAS technique has been introduced. To further quantify the isotropic component contributed from the 2<sup>nd</sup>-order quadrupolar effect from the MQMAS spectra, more mathematical expressions and analyses are required but omitted here, they will be presented in **Chapter 5** instead, during the discussions of the works for <sup>23</sup>Na ssNMR.

### 2.3.4 Imaging Echo and Chemical Shift Imaging (CSI)

Undoubtedly, one of the most common magnetic resonance applications is *magnetic resonance imaging* (MRI), as it is a non-invasive method to probe information during the diagnostic in modern medicine. In **Chapter 6**, different magnetic resonance imaging sequences were employed to study the morphologies of metallic Li metal in SSB at the interfaces. Similar to the idea in NMR diffusometry, MRI also utilizes magnetic field gradient to encode the spins as a function of their positions. However, unlike NMR diffusometry, where the displacements of spins are allowed under a long diffusion time, to an extent that the spatial information cannot be refocused after decoding. In MRI, the spatial information of the nuclear spins is preserved. Here, an assumption can be made on the nuclear spins at position z within the sample, which occupying a small volume *dV* in the Cartesian space, this is defined as local spin density  $\rho(z)$ . By combining **Equation [2.13]** and **[2.37]**, one can derive the signal evolution of the nuclear spins as a function of the nuclear spins as the signal evolution of the nuclear spins as a function of the nuclear spins as the signal evolution of the nuclear spins as a function of time and spatial position under the influence of field gradient ( $T_2$  evolution is negligible because the gradient is sufficiently dominant):<sup>4</sup>

$$ds(\vec{G},t) = \rho(z)dV\exp\left[i\left(\gamma\vec{B}_0 + z\vec{G}(z)\right)t\right]$$
[2.43]

The term of  $\gamma \vec{B}_0$  can be normalized out once the spins are on-resonance, the effect of  $z\vec{G}(z)$  can be considered oscillating around the Larmor frequency. Hence, the integrated signal amplitude over Cartesian space can be written as:<sup>4</sup>

$$S(t) = \iiint \rho(z) \exp\left[i\gamma z \vec{G}(z)t\right] dz \qquad [2.44]$$

where dz represents the volume integration. In the previous discussion (see Section 2.1.4), the concept of converting TD signal to FD signal by integrating time (dt) to complete the FT operation. The same concept can pretty much be applied here for space as well. In Equation [2.44], here, to mimic the inversed relationship between time and frequency, the definition of inversed-Cartesian space can be introduced –  $\vec{k}$ -space (in the unit of m<sup>-1</sup> for 1D), it is the *reciprocal space vector*, which can be given as:<sup>4, 26</sup>

$$\vec{k} = \frac{\gamma \vec{G}(z)t}{2\pi}$$
[2.45]

By substituting the definition of  $\vec{k}$ -space into Equation [2.44], we have:<sup>4, 26</sup>

$$S(\vec{k}) = \iiint \rho(z) \exp(i2\pi \vec{k} \cdot z) dz$$
$$\rho(z) = \iiint S(\vec{k}) \exp(-i2\pi \vec{k} \cdot z) d\vec{k}$$
And  $d\vec{k} \cdot \Delta z = 1$  [2.46]

where  $\Delta z$  is the *field of view* (FOV) of the image of Cartesian space, and  $d\vec{k}$  is the increment of the  $\vec{k}$ -space measurement.<sup>4, 26</sup> Here, with the same idea of NMR spectroscopy, MRI, collects the data in  $\vec{k}$ -space, and processes the  $\vec{k}$ -space into Cartesian space in a same manner of FT. An 1D *imaging echo* (IE) MRI sequence is illustrated in **Figure 2.21**, together with the spin evolution and a sample data, collected for a ~ 4 mm thick LAGP pellet. The pulse sequence looks very similar to the PGSE sequence in **Figure 2.14**, where a combination of Hahn echo and a pair of encoding/decoding gradient pulses were applied. However, instead of utilizing phase-encoding, *frequency-encoding* is applied in the IE; the

gradient is activated during signal acquisition to encode spatial information and create an echo. Thus, the spins carry different frequencies along z-axis. Consequently, spins along the z-axis resonate at different frequencies, allowing the final "spectrum" to represent a composite of all linearly varied resonances, ultimately resulting in an MR image.



**Figure 2.21** (a) Graphical illustration of the pulse sequence of IE and spin evolution. (b) The direct collection of <sup>7</sup>Li MR signal in  $\vec{k}$ -space, for a cylindrical LAGP pellet (~ 4 mm thick) (c) The Cartesian image of the LAGP pellet after the FT operation. The experiment was performed on a Bruker AV300 spectrometer with a Diff50 probe.

To further correlate the experimental parameters to the final image, by relating **Equation [2.45]** and **[2.46]**, the FOV of the image can expressed as:<sup>26</sup>

$$\vec{G}(z) = \left(\frac{2\pi}{\gamma}\right) \cdot \frac{1}{2 \cdot t \cdot FOV(\Delta z)}$$

$$FOV(\Delta z) = \left(\frac{2\pi}{\gamma}\right) \cdot \frac{n}{2 \cdot t \cdot \vec{G}(z)}$$
[2.47]

*n* is the number  $\vec{k}$ -space sampling points, which corresponds to the number of data points in the TD. A factor of 2 introduced in denominator of **Equation [2.47]** is because considering the symmetrical sampling of  $\vec{k}$ -space from -k to +k (total of 2k).<sup>26</sup> Following by that, the *resolution (Res.)* of the image can be calculated as:<sup>26</sup>

$$Res. = \frac{FOV}{n}$$
[2.48]

It is notable that the *Res*. of the MR image is directly proportional to the gradient power, which is also proportional to the size of  $\vec{k}$ -space; in addition, an inversedproportional relationship can be observed in between the *FOV* and the magnitude of  $\vec{k}$  (as well as gradient power). Thus, to properly setup the IE, one should carefully manipulate the input parameters. For example, to increase the Res. of a previous image with the same FOV by a factor of 2, one should increase both of the  $\vec{G}(z) \cdot t$  and the number of sampling points by a factor of 2.

One major limitation of the IE sequence is that it loses frequency information during the frequency-encoding process, resulting in a purely image without any spectroscopic information. To preserve the spectroscopic information, an improved pulse sequence can be employed – *chemical shift imaging* (CSI).<sup>27</sup> This 2D technique relies solely on the phaseencoding gradient to generate echoes in the 2<sup>nd</sup> dimension, incrementing the gradient strength from -g to +g over n steps (where n corresponds to the calculations for FOV and *Res.*). By retaining frequency information, the spectroscopic data can be captured in the direct dimension. The pulse sequence of CSI is presented in **Figure 2.22**. Where a composite 180° pulse is used to cancel any possible imperfection of a single 180° pulse.



**Figure 2.22** Pulse sequence of CSI, with a composite  $180^{\circ}$  pulse in the RF channel to achieve the spin echo. Gradient strength was incremented from -g to +g over n steps to create the  $2^{nd}$  dimension, in addition to the spectroscopic dimension.

With the application of CSI sequence, it is possible to obtain the spatial information of different chemical species. In later of this thesis, the discussion of microstructures of metallic Li electrodes in ASSB will be presented, thanks to the unique Knight shift (see **Section 2.2.4**) of the Li metal provides a resolvable signal apart from the dominant electrolyte signal. Further spatial information from imaging dimension reveals location of the Li misconstrues. More detailed and analyses will be shown in **Chapter 6**.

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# Chapter 3 – Impacts on Li<sup>+</sup> Dynamics by Reducing the Crystallinities of PEO-Based SPE under Structural Modifications

This chapter reformatted the experimental results from a previous co-authored publication, where the author was the second author in this work. The paper was published in the *Communications Materials* (*Commun. Mater.*, **2021**, *2*(1), 83).<sup>1</sup> The author contributed to the solid-state <sup>7</sup>Li and <sup>19</sup>F NMR diffusometry and analyses to characterize the Li<sup>+</sup> dynamics and transference numbers upon structural modification of PEO *via* copolymerization. The copolymer samples were prepared and characterized by V. St-Onge (first author) from Prof J. P. Claverie's group at University of Sherbrooke. V. St-Onge also conducted all other electrochemical analyses on these materials. The initial idea was designed by J. P. Claverie, and the paper was written by V. St-Onge and J. P. Claverie with input and revisions from all authors. The project evolution was driven by V. St-Onge, J. C. Daigle, and J. P. Claverie. Prof G. R. Goward provides valuable instructions and guidance for the diffusometry measurements.

This publication presents a remarkable method for enhancing the Li<sup>+</sup> dynamics in the PEO-based materials. As discussion in **Chapter 1.4**, the main challenge of the PEObased SPIEs is the slow Li<sup>+</sup> transport at RT due to the significant crystallization of PEO below its melting temperature  $T_m$ . The research has been focusing on supressing the crystallinity of PEO at RT *via* different strategies. Specifically in this work, the PEO macromolecular architectures were modified by introducing small amounts of comonomers, which prevent the crystallization of the long PEO chain, increasing the amount of amorphous region and therefore increasing the ionic mobility of the Li<sup>+</sup>.

# **3.1 Introduction**

Polyethylene oxide (PEO)-based solid polymer electrolytes (SPEs) are one class of material that are promising to be applied in the next generation of all-solid-state batteries (ASSBs), because PEO has excellent mechanical stability,<sup>2, 3</sup> good solubility of lithium salt,<sup>4</sup> and a wide electrochemical stability window.<sup>5</sup> In addition, the adhesive property of polymers has the potential to form intimate contacts with the electrodes and ceramic electrolytes, making them promising to be utilized in composite electrolyte systems for ASSBs.<sup>5-7</sup> However, the Li<sup>+</sup> dynamics in PEO-based SPEs are very slow at room temperature (RT), attributed to the formation of crystalline regions in the PEO matrix (**Figure 1.3**).<sup>3, 5, 8</sup> Most PEO-based SPEs have a melting temperature T<sub>m</sub> of ~ 60 – 65 °C,<sup>9</sup> Below this temperature, the material tends to crystallize, with the crystalline phase potentially comprising up to 80% of the host matrix,<sup>5</sup> hindering the Li<sup>+</sup> transport at RT.

Reducing the crystallinity of PEO is the main strategy to realise the goal of applying PEO in ASSB practically. In the past, different methods have been explored, such as incorporating non-ionic plasticizer with succinonitrile (SN), which is one of the most commonly reported plasticizer additives.<sup>4, 10</sup> Inorganic ceramic fillers can also be incorporated such as Al<sub>2</sub>O<sub>3</sub> TiO<sub>2</sub> and SiO<sub>2</sub> nano-powders,<sup>5, 8</sup> these nanoscale fillers can prevent the local chain reorganization within the PEO, which inhibits the crystallization of

PEO and facilitates the Li<sup>+</sup> transport. However, these fillers are considered as "passive" because the core objective of these materials is to supress the PEO crystallinity and thus they are not necessarily Li<sup>+</sup>-conductive.<sup>5, 8</sup> Addition of "active" fillers is also possible, and these are made of Li<sup>+</sup>-conducting ceramics such as perovskite, garnet, or NASCION-type conductors.<sup>5</sup> However, owing to the high resistances of the polycrystalline active materials themselves, the increase in conductivity of the composite SPEs are typically far from ideal.<sup>5-7</sup>

Here in this work, a strategy is proposed to modify PEO macromolecular structures through the copolymerization with other comonomers, resulting in the creation of "copolymers." These copolymers combine the starting material ethylene oxide (EO) units with various comonomers that have different side chains, disrupting the long-range order of the EO chains at RT. This disruption enhances Li<sup>+</sup> mobility by increasing the amorphous region of the material. In this study, three copolymers were synthesized by collaborators from the University of Sherbrooke, the Li<sup>+</sup> dynamics and transport mechanisms were investigated using <sup>7</sup>Li and <sup>19</sup>F NMR diffusometry. The results demonstrate that solid-state NMR (ssNMR) can offer valuable microscale insights into ion transport, contributing to a better understanding of ion transport phenomena in such materials.

## **3.2 Methods**

# 3.2.1 <sup>7</sup>Li and <sup>19</sup>F NMR Diffusometry

<sup>7</sup>Li and <sup>19</sup>F NMR diffusometry (PFG) measurements for the copolymers were performed on a Bruker AVANCE III 300 MHz spectrometer using a Diff50 gradient probe with an 8 mm <sup>7</sup>Li/<sup>19</sup>F double resonance coil inserted. All the <sup>7</sup>Li and <sup>19</sup>F NMR spectra were referenced to 1M aqueous LiCl solution and pure CFCl<sub>3</sub> at 0 ppm. All the copolymer SPEs were prepared in an Ar-filled glovebox and the PFG experiments were conducted at 45 °C. The copolymer SPEs were packed into a 4 mm zirconia MAS rotor which was then placed into a thoroughly dried 5 mm Shigemi NMR microtube. The PFG measurements were achieved with the bipolar-gradient pulse pair coupled with stimulated-echo sequence (BPP-STE)<sup>11</sup> with longitudinal eddy current delay (LED),<sup>12</sup> the pulse sequence is shown in Figure 2.16b. A linear 16-step gradient ramp was used in each experiment with the maximum gradient strengths of 2725 and 1000 G cm<sup>-1</sup> for <sup>7</sup>Li and <sup>19</sup>F measurements, respectively. The gradient pulse length  $\delta$  was set from 1.3 to 2.5 ms depending on the  $T_2$ relaxation of each measurement. The diffusion time  $\Delta$  was fixed as 200 ms. The signal was averaged over 32 scans. The diffusion coefficients were extracted by fitting the PFG signal attenuation curves with Bruker TopSpin 4.1.0 software, with the modified Stejskal-Tanner equation for BPP-STE pulse sequence in Equation [2.40].

# **3.3 Results and Discussions**

### 3.3.1 Effects of Structural Modifications of PEO on Li<sup>+</sup> Dynamics

Three families of statistical copolymers (10 mol%) with LiTFSI salt (18 wt%, the O:Li ratio of 30:1) have been synthesized by the collaborators with three types of commoners, they are propylene oxide (PO), butylene oxide (BO), and triethylene oxide (TO). The methyl and butyl side chains in PO and BO units in the copolymers are believed to hinder the long-range order of the crystalline PEO components.<sup>1</sup> However, they do not contain any polar groups which can solvate and transport the Li<sup>+</sup>. Hence, the TO comonomer with 3 EO units was also investigated, as it potentially provides better conductivity in comparison with PO- and BO-modified ones. Prior to the ion dynamic study, the compositions and crystallinity contents of the copolymers were determined using <sup>1</sup>H and <sup>13</sup>C NMR.<sup>1</sup> Additionally, the thermal properties of these copolymers were studied, and it was found that a decreased in  $T_m/T_g$  were observed compared to the pristine PEO phase.<sup>1</sup> Furthermore, powder X-ray diffraction (PXRD) were conducted and noticeable diminished crystalline contents were observed for the copolymers. All of the above-mentioned evidence suggests the incorporation of different monomers decrease the crystallinity of PEO, more details were described in the published paper.<sup>1</sup>

The Li<sup>+</sup> dynamics of the SPEs were evaluated *via* conductivity measurements using EIS, shown in **Figure 3.1**. A generic common Randle circuit model<sup>13, 14</sup> was used to fit the Nyquist spectra with the example given in **Figure 3.1a**,<sup>1</sup> where  $R_s$  represents all the internal resistance contributed from wires and connections,  $R_b$  reflects the resistance for the Li<sup>+</sup>

transport within the bulk SPEs.  $R_t$  can be considered as the interfacial double layer at the surface of blocking electrode. The constant phase element (CPE), representing the imperfect capacitive behaviours associated with these processes. **Figure 3.1b** – **c** shows the variable temperature (VT)-EIS data of the PEOPO, PEOBO, and PEOTO, respectively, together with the pure PEO-LiTFSI SPE superimposed in each plot. It is remarkable that the ionic conductivity of the copolymers are more than two orders of magnitude higher than the unmodified pristine PEO at RT. In addition, even though the PEOTO copolymer show the highest ionic conductivity among the three, but the differences in conductivity between the PEOTO copolymer and the ones with alkyl PO and BO units are not very significant. This potentially indicates that the enhancement of Li<sup>+</sup> dynamics in the PEOTO copolymer is predominately contributed by the reduction of crystallinity, rather than it has a better solubility of LiTFSI salts with the short TO units.<sup>1</sup>

The behaviours of activation energy were also extracted from the Arrhenius plots of VT-EIS and presented for each of the copolymer in **Figure 3.1b** – **c**. PEOPO, PEOBO, and PEOTO exhibits decreased in activation energies for ion conduction. Where the pristine PEO-SPEs usually possess the activation energy of up to100 kJ mol<sup>-1</sup> below their T<sub>m</sub> (60 – 65 °C) and ~ 40 kJ mol<sup>-1</sup> above their T<sub>m</sub>.<sup>9</sup> Thus, from EIS studies show very good agreements with thermal properties (T<sub>g</sub> of -44 °C, -50 °C, and -72 °C)<sup>1</sup> and the crystallinity contents (19%, 12%, and 4%) for PEOPO, PEOBO, and PEOTO copolymers, respectively.<sup>1</sup> While EIS can provide the total ionic conductivity of the entire electrochemical system by modeling the equivalent circuits,<sup>13</sup> further evaluations are required to distinguish the cation and anion mobilities. Hence, we followed up with <sup>7</sup>Li and <sup>19</sup>F NMR diffusometry to probe the dynamics at the micro-level, aiming specifically to separate the cation and anion motions. The self-diffusion coefficient can be correlated with the ionic conductivity through Nernst-Einstein relation (**Equation [1.4]** – **[1.5]**), thus, a direct observation of high diffusivity usually indicates a higher ionic conductivity.



**Figure 3.1** Ionic conductivity from EIS measurements for the copolymer SPEs. (**a**) Exhibits an example of fitting the Nyquist plot using a Randles circuit model. (**b**) – (**c**) shows the variable temperature (VT) ionic conductivity of the copolymers prepared with PEOPO (red), PEOBO (blue), and PEOTO (green), respectively. These VT-EIS plots superimposed with the conductivity data collected for PEO (black).<sup>1</sup>

The <sup>7</sup>Li and <sup>19</sup>F self-diffusion coefficients for PEO and all the copolymers were recorded at 45 °C, presented in Figure 3.2. It is noteworthy that, across all the polymers, the diffusion of <sup>7</sup>Li is consistently slower than the <sup>19</sup>F, judging by the slower attenuation rate of the <sup>7</sup>Li signal intensities (blue) in comparison to the fast signal decays for the <sup>19</sup>F curves (red), as a function of gradient strength. After performing the fitting of these echo attenuation curves, we obtained the diffusivity values for both <sup>7</sup>Li and <sup>19</sup>F and tabulated them in **Table 3.1** and plotted in **Figure 3.3b**. The <sup>7</sup>Li diffusivity values are about an order magnitude lower than the <sup>19</sup>F ones for all the SPEs. The phenomena of faster anionic mobilities than the Li<sup>+</sup> have been previously reported before for other SPEs and LEs as well,<sup>9, 15-18</sup> despite Li<sup>+</sup> being much smaller in size than the TFSI<sup>-</sup>. This can be attributed to the consequence of high charge density of the Li<sup>+</sup>, making it strongly interact with the solvation shell (lager hydrodynamic radius<sup>17</sup>) or coordinated anions, while weaklycoordinated anion TFSI<sup>-</sup> does not interact with the PEO matrix significantly and therefore more easily to migrate.<sup>18-20</sup> The <sup>7</sup>Li diffusion coefficients of all three copolymer solid polymer electrolytes (SPEs) are higher than that of the pristine PEO. Among the copolymers, PEOTO exhibits the highest diffusivity, with nearly a 4-fold increase compared to the pristine PEO, while the PEOPO and PEOBO copolymers show an increase of about 2 to 3 times. These findings from <sup>7</sup>Li diffusometry are generally consistent with the results from electrochemical impedance spectroscopy (EIS) measurements.



**Figure 3.2** Echo attenuation curves obtained from <sup>7</sup>Li (blue) and <sup>19</sup>F (red) NMR diffusometry measurements at 45  $^{\circ}$ C.

**Table 3.1** Summary of the results from the <sup>7</sup>Li and <sup>19</sup>F NMR diffusometry for the SPEs. The transference numbers  $t_+$  obtained from electrochemical method are also listed below.<sup>1</sup>

Samples (Temp)	$D_{7Li} (\times 10^{-13} \text{ m}^2 \text{ s}^{-1})$	$D_{19F} (\times 10^{-12} \mathrm{m^2  s^{-1}})$	$t_+^{NMR}$	$t_+$ (RT)
PEO (45 °C)	2.99 (± 0.06)	1.19 (± 0.02)	0.201 (± 0.005)	0.21
PEOPO (45 °C)	5.8 (± 0.2)	2.63 (± 0.08)	0.180 (± 0.006)	0.58
PEOBO (45 °C)	8.9 ( <u>±</u> 0.2)	3.8 (± 0.1)	0.189 ( <u>±</u> 0.007)	0.4
PEOTO (45 °C)	12.40 (± 0.04)	3.45 (± 0.05)	0.26 (± 0.01)	< 0.1
PEOTO (25 °C)	2.5 (± 0.1)	0.80 (± 0.01)	0.24 (± 0.01)	N/A
#### 3.3.2 Correlating the Nature of Side Chain to Cation Transference Numbers

Following evaluations of the transference number  $t_+$  (Section 1.3) for Li<sup>+</sup> were performed for each SPE with direct current (DC) polarization method at 25 °C.<sup>1</sup> SPEs used in this work contain both  $Li^+$  and counter anion TFSI<sup>-</sup>. Since  $Li^+$  plays a major key role in the Faradaic processes, the exitance of TFSI<sup>-</sup> will contribute to increased resistivity and polarization within the SPE.<sup>1</sup> It is typical to observe the  $t_{+}$  values lower than 0.3 for various SPEs,<sup>8</sup> but ideally a higher  $t_{\pm}$  closed to 1 is preferred. The  $t_{\pm}$  for PEO (Figure 3.3a and Table 3.1) obtained from DC polarization measurement were determined to be 0.21, consistent with the other published works.<sup>8</sup> A lower  $t_{\pm}$  is attributed to the strong interaction between the Li<sup>+</sup> and the coordinated oxygens in the EO units (Figure 3.3c). Upon structural modifications with the PO and BO units, the SPEs exhibit outstanding  $t_{+}$  of 0.58 for PEOPO and 0.4 for PEOBO, indicating the weaken interaction between Li<sup>+</sup> and the coordinated oxygens. This can be correlated to the non-EO side chains that cannot solvate LiTFSI and coordinate with the Li<sup>+</sup> (Figure 3.3d). The PEOTO copolymer, which contains three polar EO units in its side chain, has the lowest  $t_{+}$  with the value of less than 0.1.<sup>1</sup> This low  $t_+$  can be attributed to the strong coordination of Li<sup>+</sup> with not only the EO units in the copolymer backbone, but also with the EO units from the side chains provided by comonomer TO. These interactions create a "cryptand" type environment for the Li<sup>+</sup>, which in terms restricts their mobility compared to the TFSI<sup>-</sup> under the same modification.<sup>1</sup>



**Figure 3.3 (a)** Cation transference numbers of all the SPEs probed by DC polarization method. **(b)** <sup>7</sup>Li (triangles) and <sup>19</sup>F (squares) diffusivity values obtained by NMR diffusometry at 45 °C. Proposed mechanisms of Li<sup>+</sup> (yellow spheres) with the SPEs in **(c)** PEO (red spheres represent EO units), in (d) PEOPO and PEOBO (the alkyl comonomers shown in blue spheres with sticks), and in (e) PEOTO copolymers, respectively.<sup>1</sup>

We also compared the cation transference number for the copolymer SPEs calculated from the NMR diffusometry  $(t_+^{NMR})$  to those obtained from electrochemical assessments, as seen in **Table 3.1**. The PEO shows excellent agreement in  $t_+^{NMR}$  and  $t_+$ ,

suggesting the consistency of the Li<sup>+</sup> and TFSI<sup>-</sup> diffusion values obtained from diffusion measurement and electrochemical characterization. The  $t_{+}^{NMR}$  values for PEOPO and PEOBO are a lot lower than the values reported in  $t_{\perp}$ . Additionally, the  $t_{\perp}^{NMR}$  value for the PEOTO is the highest among all the SPEs obtained from the NMR measurements, and further evaluation of  $t_{\pm}^{NMR}$  at 25 °C (same temperature as the polarization method) did not reveal any significant difference. However, it has the lowest  $t_{+}$  (Figure 3.3a) probed by the electrochemical method. A possible explanation of the contradiction could arise from the fact that NMR cannot distinguish between ionized and coupled <sup>7</sup>Li or <sup>19</sup>F, but DC polarization can only measure the charged species. In the PEOPO and PEOBO, LiTFSI has much lower solubility due to difficult of accessing polar EO groups from the bulky alky groups (Figure 3.3d), thus, less free Li<sup>+</sup> are available for diffusion, and the measured  $t_{\pm}^{NMR}$ values are more dominated by the immobile paired LiTFSI. On the contrary, the extra EO units in the PEOTO facilitate the disassociation of LiTFSI (Figure 3.3e), creating more amounts of free Li<sup>+</sup>, contributing to a higher  $t_{\pm}^{NMR}$ . It could also correspond to the reduction of anion movements (Figure 3.3b) due to the stronger columbic interaction between TFSIand the PEOTO framework. In summary, the ion transport mechanisms in the copolymers were tuned by introducing different comonomers, however, the exact Li<sup>+</sup> transport mechanisms are certainly more complicated than the current understanding, and future exploration is necessary for these materials.

# **3.4 Conclusion**

Copolymerization of PEO with different monomers – PO, BO, and TO units were conducted to reduce the crystallinity of the PEO matrix by our collaborators at University of Sherbrooke. It is discovered that adding only 10 wt% of comonomers can significantly supress the formation of crystalline PEO phase in the copolymers.<sup>1</sup> Li<sup>+</sup> dynamics were studied using EIS and <sup>7</sup>Li NMR diffusometry, it was observed that the ionic conductivity improved more than two order of magnitudes in the copolymers in comparison to the unmodified PEO, with the TO-modified analog shows the highest enhancements. Similar results can also be seen from <sup>7</sup>Li NMR diffusometry measurements, the PEOTO exhibits 4 times higher diffusivity than the pristine PEO, while the PEOPO and PEOBO demonstrate around 2 – 3 times higher diffusion coefficients. Though the conductivity of the copolymer SPEs were not significantly impacted by the nature of the side chains, the  $t_+$  analyses suggests that the incorporation of comonomers can easily alter the Li<sup>+</sup> transport mechanism in the copolymers, opening a possibility of tuning the PEO properties for future ASSB application.

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# Chapter 4 – Accurate Measurements of Li<sup>+</sup> Dynamics in Pressure-Treated Solid Electrolytes by Powder X-ray Diffraction and <sup>7</sup>Li Magnetic Resonance Diffusometry

This chapter is a re-written version of a study that was previously published in the *Journal of Physical Chemistry C (J. Phys. Chem. C.*, **2023**, *127*(51), 24498-24507). The author contributed to the method developments for sample preparations, NMR diffusometry and relaxometry characterization, and the preparation of the manuscript. Powder diffraction data were collected and analyzed by V. M. Jarvis at the McMaster X-ray diffraction facility. Y. Mozharivskyj contributed to the microstrain discussion and the editing of the relevant parts. J. D. Bazak and G. R. Goward contributed to the manuscript editing and final analysis.

In this chapter, a study was conducted by applying a series of pressures to two representative classes of SE materials in their powder forms – oxide Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP) and sulfide Li<sub>10</sub>SnP<sub>2</sub>S<sub>12</sub> (LSnPS), to mimic the fabrication process of all-solid-state batteries (ASSBs). <sup>7</sup>Li NMR diffusometry and relaxometry were performed to probe the ion dynamics of the materials after different pressure treatments. It was observed that the diffusivity of LSnPS reduced by 20% after the pressure treatment at 500 MPa, whereas no significant change was observed in LAGP electrolyte. <sup>7</sup>Li relaxometry also reveals that the local <sup>7</sup>Li dynamics diminished as a function of increasing fabrication pressure. These phenomena are counter-intuitive to most of the electrical impedance spectroscopy (EIS) measurements that have been previously reported, as it is believed that better interfacial

contacts between electrolyte particles can be achieved by increasing the fabrication pressure.

It is proposed that under higher pressure, mechanical modification can introduce changes in the micromorphology and the crystal lattice of the powder materials, these changes can be probed by NMR, which is more sensitive to the local environments. The diffraction data confirms the notable microstrain induced in the pellet form of the LSnPS, which can be correlated to the decrease in <sup>7</sup>Li dynamics. Pressure-treated LAGP does not show significant changes from its pristine condition. It is believed that the difference in response to pressure across the two classes of material can be correlated with their different Young's modulus.

# **4.1 Introduction**

As consumer willingness to embrace an electrified future grows, ongoing safety concerns regarding wide-spread use of lithium-ion batteries (LIBs) with flammable organic liquid electrolytes drive the search for alternatives. Undoubtedly, all-solid-state batteries (ASSBs) that utilize thermally stable or non-flammable electrolytes are promising candidates for next-generation energy storage devices. As one of the key components of the ASSBs, glass-ceramic inorganic solid-state electrolytes (SSEs) have been extensively studied in the past decade. The state-of-the-art SEs can be generally categorized based on their chemical properties, namely oxide- and sulfide-based materials. Oxide-based materials include the Na SuperIonic Conductor (NASICON family) Li<sub>1+x</sub>Al<sub>x</sub>M<sub>2-x</sub>(PO4)<sub>3</sub>

(LAMP, M = Ge, Ti),<sup>1-3</sup> protonated antiperovskites  $Li_{3-x}OH_xX$  (X = F, Cl, Br),<sup>4, 5</sup> garnettype  $Li_5La_3M_2O_{12}$  (LLMO, M = Nb, Ta), and the perovskite  $Li_{3x}La_{2/3-x}TiO_3$ .<sup>6, 7</sup> Sulfide materials include the thiophosphate  $Li_{10}XP_2S_{12}$  (LXPS, X = Ge, Sn)<sup>8, 9</sup> and argyrodite-type  $Li_{6-x}PS_{5-x}X_{1+x}$  (X = Cl, Br, I).<sup>10-12</sup>

Numerous studies have been reported for those excellent SE candidate materials. However, despite progress made on exploring the materials and studying their chemical and electrochemical properties at the laboratory scale, there is very limited research that focuses on the practical manufacturing process. Applying mechanical pressure to SE pellets during the fabrication and operation of solid-state cells/batteries is known to be a critical step to achieve intimate contacts of all the components. Doux et al.<sup>13</sup> studied the effect of mechanical stack pressure on Li metal ASSBs using the argyrodite Li<sub>6</sub>PS<sub>5</sub>Cl as the electrolyte. It was reported that applying too much pressure during battery operation could lead to mechanically-induced short circuiting, owing to the low yield strength of Li metal (0.8 Mpa).<sup>13</sup> A follow-up study using electrical impedance spectroscopy (EIS) provides a contrasting result that poor contacts within the SE particles under low fabrication pressure will lead to poor conductivity due to the presence of voids and pores.<sup>14</sup> Kodama et al.<sup>15</sup> applied in situ X-ray computational tomography (XCT) measurement to investigate the single-particle behavior of the  $Li_6PS_5Cl$  electrolyte under high mechanical pressure. Their results suggest that sulfide particles' contact ratio and sphericity can be increased with pressurization as the porosity decreases, which increases of ionic conductivity of the Li-<sub>6</sub>PS<sub>5</sub>Cl material.<sup>15</sup> Nevertheless, Famprikis et al.<sup>16</sup> previously reported the decreasing ionic dynamics under in-situ pressure (up to  $\sim 1$  GPa) for two compressed Na<sub>3</sub>PS<sub>4</sub> pellets, by the application of EIS. They concluded that the significant strain imparted on the material increases the activation volume, thus hindering ion transport during the EIS measurement. Monismith and Qu,<sup>17, 18</sup> demonstrated that the applied hydrostatic compression on the Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) electrolyte will increase the Li<sup>+</sup> diffusion activation energy due to the mechanically distorted lattice, using molecular dynamics (MD) simulations. Moreover, Zhang et al,<sup>19</sup> recently investigated the effect of one-time compression on ionic conductivity of the sulfide LSnPS pellets. They reported that the ionic conductivity initially increases as the pressure level, but then decreases when the pressure exceeds 1.8 GPa. By combining In-situ pressure and X-ray analysis they determined that the decrease in conductivity is caused by the stress-strain effect that contracted the lattice. Interestingly, the X-ray results show the lattice contraction already happens at ~ 500 MPa, but the EIS didn't detect the ion dynamic decrease until the pressure level exceeds 1.8 GPa.

The abovementioned contradictory conclusions from different studies are mainly attributed to the two opposing effects from the mechanical compression  $^{16, 19}$  – strain and consolidation (densification). While strain hinders ion transport, consolidation/densification enhances interparticle dynamic.<sup>16, 19</sup> As EIS measures the sum of averaged local dynamic at a large-scale, including grain-boundaries (GBs), it could be ambiguous to distinguish the mixed consequences from the pressure effects based on EIS results. In addition, EIS results depend on the active stack pressure that may be applied during the measurement. These extrinsic factors (applied stack pressure and pellet preparation) are variables that must be considered when studying the effect of pellet fabrication on ion dynamics.

Nuclear Magnetic Resonance (NMR) is a powerful method to probe the molecular dynamics of the SEs at atomic level, which is sensitive to the intrinsic properties of the materials. We previously investigated a series of Ca-doped argyrodite materials and extended the study to the effect of mechanical compression on the ion dynamics at the molecular level.<sup>20</sup> The study demonstrated that <sup>7</sup>Li relaxometry and diffusometry<sup>21</sup> (pulsedfield-gradient – PFG) NMR can be utilized to probe the changes of microscopic <sup>7</sup>Li dynamics under mechanical modifications. Here, we follow up the investigation using the similar methodology to evaluate the effect of mechanical compression on <sup>7</sup>Li dynamics at the molecular level of two representative materials from oxide and sulfide SEs, namely the Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP) and Li<sub>10</sub>SnP<sub>2</sub>S<sub>12</sub> (LSnPS). <sup>7</sup>Li relaxometry and diffusometry (PFG) NMR are applied to detect the change of dynamics after compression. These results are correlated to powder X-ray diffraction (PXRD) data, incorporated with material morphologies and lattice analysis to investigate potential changes. Here we demonstrate that the ionic dynamics in the sulfide SE are influenced even without active pressure, and this phenomenon could be accurately characterized using diffusometry NMR combined with PXRD. These results can motivate the future development of an apparatus to generate and progressively increase the pressure on solid-state *in-situ* NMR measurements.

#### 4.2 Methods

#### **4.2.1 Pellet sample Preparation**

The LSnPS and LAGP nano-powders were purchased from NEI cooperation (USA) and Toshima manufacturing Ltd (Japan) without further purification. The pellets were prepared with different axial fabrication pressures inside an Mbraun Ar-filled glovebox, utilizing a YLJ-15L laboratory hydraulic press (MTI Corporation, USA) with a 10 mm die set. The LSnPS pellets were prepared under 250 and 500 MPa (namely LS250 and LS500, respectively), the LAGP pellet was prepared at 500 MPa (LA500) only. The compressed pellets were compared against un-compressed LAGP and LSnPS powder (LA0 and LS0) to establish a performance baseline.

#### **4.2.2 Powder X-Ray Diffraction (PXRD)**

The phase purities of both LSnPS and LAGP materials were determined by performing PXRD measurements using Bruker D8 DISCOVER powder diffractometer equipped with a Vantec 500 2D detector. Cu K $\alpha_1$  radiation ( $\lambda = 1.5406$  Å) source was utilized here. LAGP powder was deposited on a Si single crystal wafer, and the LSnPS powder was sealed in a capillary for the measurements. The resulting PXRD patterns are shown in **Figure S4.1** and **S4.2**. The PXRD measurements for all the crystallite size and unit cell size analysis were performed with reflection geometry on a Bruker D8 Discover Vantec 500 diffractometer equipped with a Eiger2R 500K 2D detector, under the applied Co K $\alpha_{average}$  radiation ( $\lambda = 1.7903$  Å) source. The measured  $2\theta$  angle was set in between  $15 - 110^{\circ}$ . Inside the glovebox, the LA500 pellet were mounted parallel to a single-crystal

silicon wafer of a Bruker specimen holder, with an X-ray transparent polymer cap. For LA0 measurement, powder LAGP were homogenously deposited onto the Si wafer. Prior to the experiment, the sample height alignments were achieved using a laser-video Z-alignment system, with the polymer cap removed.

Due to the extreme chemical reactivity of the LSnPS, powder LS0 and pellet LS500 were prepared in a coin cell-type holder purchased from MTI Corp, with one side sealed with Kapton window, allowing X-ray interaction with the samples. The powder LS0 was carefully deposited onto the stainless-steel spacer and the overall height was fixed before crimping the coin cell holder. In order to fit the pellet in the cell perfectly, the overall thickness of the pellet sample within the headspace was controlled before crimping. Specifically, the overall height of LS0 powder was shimmed by a stainless-steel spacer to the overall height of 0.98 mm, and the overall thickness of the LS500 pellet sample was shimmed with a cardboard paper to 0.95 mm. After crimping the cell, a thin layer of epoxy was applied around the ring of the gap between the cap and the base of the cell to provide a better seal. The photos of these setups are shown in **Figure S4.3**. Again, laser-video Z-alignment system was used with fine-tuning the height alignment on the assembled coin cells.

The PXRD pattern refinements and crystallite size analyses for both LAGP and LSnPS were completed using Bruker TOPAS V6, silicon reference samples, which were assumed to have no specimen broadening contributing to the peak shapes, were measured for empirical determination of the instrument profile. A convolution of Lorentzian and Gaussian functions was applied to achieve a best fit. All refinable profile parameters were then fixed, and the resulting functions were implemented as the instrument function for deconvolution of physical microstructure information in the LAGP and LSnPS samples. In particular, the crystallite size and microstrain ( $\eta$ ) were determined using the double-Voigt approach<sup>22</sup> in the TOPAS software package. All refinements accounted for background and displacement error parameters. The refined profiles of both powder and pelletized forms of the LAGP and LSnPS, are shown in **Figure S4.4**.

#### 4.2.3 <sup>7</sup>Li NMR Diffusometry

The pelletized LSnPS and LAGP samples were trimmed into smaller pieces and fitted into a 5 mm Shigemi NMR tube inside the Ar-filled glovebox prior to the diffusometry measurements. The trimmed pellets were placed in a parallel stack inside the NMR tube by tamping the pellets with the Shigemi tube plunger to create a relatively homogenous and continuous sample distribution along the z-axis, which is the dimension of the applied magnetic field gradient used in the PFG sequence. The overall thickness of LS0, LS250 and LS500 in the Shigemi NMR tube are 3.2 mm vs ~4 mm, and for LA0 and LA500 are ~3.5 mm vs ~4 mm, respectively. The Shigemi tube was sealed with parafilm after sample packing. A demonstration that packing the NMR tube in this way will provide the most consistent diffusion measurements is provided in the SI (Figure S4.5, S4.6 and **S4.7**). The measurements were performed on a Bruker Avance III wide-bore 7.0 T NMR spectrometer, with a 5 mm <sup>7</sup>Li single resonance coil inserted in a Diff50 double-resonance gradient probe. A stimulated echo, bipolar-pair pulse sequence coupled with longitudinal eddy current delay (STE-BPP-LED, Figure 2.16b) was utilized to acquire the <sup>7</sup>Li diffusion data for both LSnPS and LAGP by incrementing the gradient strength over 16 steps, up to a maximum strength of 27.25 T/m.<sup>23</sup> The 1D <sup>7</sup>Li peak integral as a function of this gradient strength incrementation obtained from the measurements was fitted using **Equation [2.40]**, taking the sine-shaped gradient pulse and bipolar PFG sequence into account.<sup>24</sup> Variabletemperature (VT) data were collected under the control of a Bruker BCU-2 unit and the set temperatures were calibrated by measuring the chemical shifts of ethylene glycol (T >300 K) and methanol (T < 300 K). For all the measurements, the diffusion time  $\Delta$  was kept as 110 ms, unless specified otherwise, and the gradient duration  $\delta$  were varied from 1.2 – 2.7 ms under different temperatures.

#### 4.2.4 <sup>7</sup>Li Static Spectrum and VT-T<sub>1</sub> Measurements

<sup>7</sup>Li static spectra measurements were completed on a Bruker Avance III wide-bore 300 MHz spectrometer using a single-pulse acquisition. 1 M of LiCl aqueous solution was used for chemical shift referencing. With the same instrumental setup, VT-T<sub>1</sub> measurements were performed using the inversion-recovery pulse sequence over 16 delay steps, with the delay varied from 10  $\mu$ s to 3 s. Recycle delays for each experiment were set to at least 5 times of T<sub>1</sub> (previously measured) at the set temperature. A single-component fit was applied for the T<sub>1</sub> relaxation rates using Bruker Topspin relaxation module.

#### 4.2.5 Multinuclear ssNMR Measurements

Multinuclear NMR measurements were carried out to for the LS0 and LS500 to identify any local changes of the LSnPS at the molecular level after applying pressure. <sup>7</sup>Li, <sup>31</sup>P, and <sup>119</sup>Sn ssNMR spectra were recorded under 7.0 T, utilizing a 4 mm double-resonance MAS probe with the MAS spinning speed of 10 kHz. To achieve the stable

spinning, a fragment of LS500 was center-packed in the 4 mm rotor with loose KBr powder, PXRD confirms that no degradation has occurred by grinding LSnPS and KBr together. The detailed analyses were shown in **Table S4.5** and **Figure S4.12**.

## 4.3 Results & Discussion

#### 4.3.1 Powder Diffraction Studies of Structural Changes

To investigate the influence of pressure treatment to the grain morphology to the two different materials, their the PXRD patterns were acquired, for the LA0 and LA500, the patterns were shown in **Figure 4.1a**, and for the LS0 and LS500 were shown in **Figure 4.1b**, respectively. The PXRD measurement of the LS250 was completed using Bruker's air-tight specimen sample holder setup, its PXRD pattern and microstructual analysis is shown in **Figure S4.11** and **Table S4.4** together with the LS0 and LS500 that using the same approach for consistency. On top of both **Figure 4.1a** and **b**, a few enlarged patterns are shown in the insets of the figures at different 2 theta angles, for visual qualitative comparisons. Please note that refinements analysis has been carried out for all of the patterns below, and they are all have been corrected for sample displacement errors. The displacement errors for all the patterns are shown in **Table S4.1**.



**Figure 4.1 (a)** The PXRD patterns for LA0 (sky blue) and LA500 (orange) with the intensity shown in arbitrary unit (a. u.). The patterns of LS0 (dark blue) and LS500 (red) shown in (b). All the patterns have been corrected for sample displacement error, obtained from the Rietveld refinements. Insets showing the enlarged regions in both (a) and (b) for visual comparison.

Both LA0 and LA500 displayed in **Figure 4.1a** shows very similar patterns to each other, as can be seen in the selected enlarged diagrams across the 2 theta range. The unchanged peak shape of the LA500 pattern after pressure treatment implies that the compression on the LAGP sample has no impact on its grain morphology.

In **Figure 4.1b**, both PXRD patterns have a strong amorphous background at around the 2 theta of 20°. This is primarily owing to the presence of the Kapton windows. There are noticeable peak broadenings observed over the entire 2 theta range, the differences in peak shapes can be clearly seen in the insets of **Figure 4.1b**. The observed peak broadening with applied pressure could be attributed to two possible sources: either microstrain or decreasing crystallite size. Here, we primarily assign the peak broadening to microstrain, based on the refinement. The microstrain can be derived using Williamson-Hall method, and can be modelled independently from the influence from crystallite size.<sup>25</sup> It is the major factor that contributes to the broadening of the LS500 sample. Further justification of this consideration will be discussed in the SI and the NMR diffusometry measurement. The summarized microstrain effect of both materials before and after pressure treatments are plotted as bar graph in **Figure 4.2a** and **b**.



**Figure 4.2** The values of microstrain after pressure treatment are illustrated for (**a**) LA0 and LA500, and (**b**) LS0 and LS500, together with the error bars of each value.

In Figure 4.2 and Table 4.1, both LA0 and LS0 shows a non-zero microstrain value, even without pressure treatment, this is not uncommon for the nanosized materials, as microstrain is developed to accommodate for their large surface areas.<sup>26</sup> In Figure 4.2a, after compression, the strain value for LA500 is within the standard deviation of that for LA0, implying that there is no change in the strain from the applied pressure at 500 MPa for LAGP. However, there is a non-negligible increase in the microstrain in the LSPS sample after pressure treatment as seen in Figure 4.2b and Table 4.1. The microstrain change from LS0 to LS500 is significant and outside the experimental error bars, (0.064  $\pm$  0.02) % for the uncompressed LS0 vs. (0.086  $\pm$  0.03) % for LS500. Furthermore, the unit cell parameters and volumes for all four samples were refined and are given in Figure **54.8a**, **54.8b**, and **Table 4.1**. The unit cell volumes of both materials slightly decreased

after the pressure treatment, however, as discussed above there's no obvious pressure effects on the LAGP lattice crystallinity as judged from the strain values. In case of the LSnPS phase, besides some peak shifts related to the changes in the lattice parameters under pressure, there is a noticeable PXRD peak broadening indicative of the increased strain.

Sample ID	V (Å <sup>3</sup> )	Microstrain n (%)
LA0	$1216.7 \pm 0.1$	$0.031 \pm 0.003$
LA500	$1216.1 \pm 0.1$	$0.026 \pm 0.002$
LS0	$976.18 \pm 0.04$	$0.064 \pm 0.002$
LS500	$975.88 \pm 0.07$	$0.086 \pm 0.003$

**Table 4.1** Comparisons of the microstrain values of different LSnPS and LAGP samples

 based on the PXRD refinements.

In **Figure S4.8a** and **Table S4.2**, the lattice parameter *c* of LAGP is slightly decreased, while *a* remains unchanged, indicating the unit cell parameters exhibited some anisotropic compressibility. This anisotropic compressibility behavior of crystalline materials along different lattice dimension could be explained by the anisotropic properties of the crystal materials, as previously reported.<sup>27-29</sup> Interestingly, in LSPS the lattice parameter *a* decreases while *c* expands under pressure (**Figure S4.8b**). This is somewhat counter-intuitive, as one typically will expect the lattice parameters decrease under higher pressures. Here we hypothesize that the LSnPS lattice contracts in an "accommodative" way. The tetragonal LSnPS framework is constructed from the [PS4] (P at 2b) and [SnS4/PS4] (Sn/P at 4d) tetrahedra,<sup>8</sup> and we believe that the static electric repulsion between

the sulfur anions of the tetrahedra controls the compressibility. Here, we focus on the shortest S-S distances as highlighted in **Figure 4.3**.



**Figure 4.3** Illustration of the shortest S1-S3 bonds (labeled) in between the  $[SnS_4/PS_4]$  (4d) and  $[PS_4]$  (2b) polyhedrons in the LSnPS structure (Li atoms removed). Under pressure, the S1-S3 bends toward c-axis due to the have the shortest distance and cannot be further contracted, resulting in shorter a/b and longer c parameters.

These S1-S3 bonds of 3.584(4) Å<sup>30</sup> are between the [PS<sub>4</sub>] (2b) and [SnS<sub>4</sub>/PS<sub>4</sub>] (4d) tetrahedra and have contributions both along the *a/b* and *c* directions. The S1-S3 bonds give the LSnPS structure its layered appearance. The second shortest bond is the S2-S3 one of 3.853(4) Å<sup>30</sup> (not shown), is between the [SnS<sub>4</sub>/PS<sub>4</sub>] (4d) tetrahedra and almost purely along the *c* direction. The shortest S1-S3 bonds are expected to be rigid and are unlikely to contract much if at all under pressure. Therefore, we hypothesize that, to accommodate

large pressure, the angle between the S1-S3 bond bonds may become smaller, which would result in shorter a/b and longer c parameters. This would be consistent with the observation that the lattice constants display noticeable changes under pressure. Of course, to prove this hypothesis, further experiments such as MD simulations coupled with synchrotron X-ray diffraction would need to be carried out.

In summary, PXRD data is used to report on the structural changes and crystallinity experienced by the oxide and sulfide materials following pressure treatment. The fabrication pressure has a negligible effect on the lattice crystallinity for the LAGP, but a pronounced one for the LSnPS as judged from the microstrain values. This is in agreement with expectations considering the LSnPS has a low Young's modulus ( $\sim 30$  GPa<sup>31</sup>) comparing with the oxide SEs in general that have up to 100 - 200 GPa of Young's modulus.<sup>31, 32</sup> The pressure imparted for the LS500 reduces the crystallite (higher microstrain), and thus could alter the Li<sup>+</sup> dynamics in the materials. This will be further discussed in the following NMR section.

#### 4.3.2 NMR Diffusometry & Relaxometry Studies of Dynamics

Diffusometry, or PFG NMR is a well-established technique for probing dynamics of systems usually on a length scale of micrometers.<sup>33-35</sup> In contrast,  $T_1$  relaxometry can be used to probe locale dynamics, due to their sensitivity to local couplings.<sup>11, 36-38</sup> Here both strategies are implemented to differentiate how the local and long-range dynamics of the Li<sup>+</sup> are affected by applied mechanical pressure.

Here, NMR diffusometry experiments were firstly performed for the three LSnPS samples under 298 K, with the diffusion time  $\Delta$  varied from 30 – 500 ms, plotted in **Figure 4.4**. A sample data set for the signal attenuation for a fixed  $\Delta$  value of 110ms is given in **Figure S4.9** of the SI.



**Figure 4.4** Diffusivity of LS0, LS250, and LS500 plotted as a function of diffusion time  $(\Delta)$ .

It is noted that the measured diffusivity of all the LSnPS samples decrease as the diffusion time  $\Delta$  increases, which can be interpreted as restricted diffusion.<sup>39-41</sup> Where a fast initial decay of diffusivity at short  $\Delta$  indicates a less obstructed pathways for Li<sup>+</sup>, as  $\Delta$  increases, the diffusivity decay slows down, revealing that more Li<sup>+</sup> start encounter barriers

(grain boundaries). As is shown in Figure 4.4, the restricted diffusion behaviour is observed in all three polycrystalline samples. In addition, the diffusivity of all three samples starts plateauing at around the same  $\Delta$  region (~ 150 – 250 ms), this could be the evidence of an unchanged boundary conditions (no grain breakage after pressure treatment). Moreover, the diffusivity is consistently smaller for the LSnPS sample as the function of pressure over the entire range of diffusion time. The resulting Arrhenius plot from the VT experiments is plotted in **Figure 4.5**. A parallel investigation was performed for the LA0 and LA500 and plotted in Figure 4.5 as well. The diffusion coefficients of the LA0 and LA500 being within the error over the entire temperature range ( $\Delta$  time for LAGP included in **Table S4.3**). Dorai et al. previously reported the diffusometry studies in garnet-type SE Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>Ta<sub>0.5</sub>O<sub>12</sub> (LLZTO).<sup>40</sup> In their study, <sup>7</sup>Li diffusivity in the LLZTO fine powder is less than the diffusivity within LLZTO single crystal and coarse powder.<sup>40</sup> The diffusivity of the fine powder also has the strongest  $\Delta$ -dependency. These results are consistent with crystallite boundary conditions impacting the diffusivity.<sup>40</sup> In our study, we did not see any variation in the diffusivity for LAGP before and after compression, therefore we believe that the crystallite breakage is not present here for LAGP. Moreover, since LSnPS is softer than LAGP, it is unlikely that the LSnPS crystallites break under the equivalent pressure. This further strengthening our hypothesis that the broadening of the LS500 PXRD pattern is primarily contributing from the microstrain, instead of crystallite size variation.



**Figure 4.5** VT-NMR diffusometry Arrhenius plots for the three LSnPS samples. The diffusivity of the LA0 and LA500 samples are also plotted for comparison.

For the LSnPS, again, like the  $\Delta$ -dependency experiment, the diffusivity of pelletized LS250 and LS500 is decreased throughout the measured temperature ranges. The diffusivity and the activation energy values for all the samples measured by NMR diffusometry is shown in **Table 4.2**. Evaluating the activation energy (Ea) of Li<sup>+</sup> diffusion could provide better intuitive analysis of the activation barrier of different mechanism in

 $Li^+$  dynamics.<sup>42-44</sup> The activation energies of both LSnPS and LAGP were calculated from the VT diffusometry experiments, the diffusion Ea for LS0, LS250, and LS500 are within errors. Zhang et al. reported the Ea change from 0.257 to 0.244 eV<sup>19</sup> for the LSnPS prepared at low pressure and 1.8 GPa. Thus, the change in Ea can hardly be detected at the highest pressure of 500 MPa in this work.

**Table 4.2** Diffusivity of all samples at 298 K and the corresponding activation energy (Ea) values.

Sample ID	Diffusivity ( $\times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ )	Ea (eV)
LS0	$2.69 \pm 0.04$	$0.244 \pm 0.003$
LS250	$2.40 \pm 0.02$	$0.241 \pm 0.002$
LS500	$2.15 \pm 0.03$	$0.245 \pm 0.002$
LA0	$0.289 \pm 0.006$	$0.291 \pm 0.003$
LA500	$0.318 \pm 0.009$	$0.290 \pm 0.007$

The different response to the pressure treatment between the sulfide and oxide is intriguing, as well, the diminished diffusivity in sulfide after compression is somewhat unexpected, since most macroscopic studies of electrochemical performance described to date show that increasing pressure will enhance the interfacial contacts of SEs, thus improve the electrochemical performance. Nevertheless, this interesting trend is consistent to our previous PFG-NMR study,<sup>20</sup> where a slight reduction of the <sup>7</sup>Li diffusivity was observed for the Ca-doped argyrodite phase prepared under compression. This observation is also consistent to the EIS studies as a function of pressure,<sup>19</sup> where it is reported that the decrease in ion conductivity is observed as the pressure exceeding 1.8 GPa. Nevertheless,

the Li<sup>+</sup> diffusion decay of ~ 20% can already be detected using the diffusometry NMR, even under only 500 MPa applied pressure in this study. The explanation of decreased diffusivity in the NMR study can also be correlated to the strain effects reported before.<sup>16,</sup> <sup>18, 19</sup> This highlights the fact that the NMR diffusometry method is a robust tool to investigate the dynamic difference even under very subtle changes.

The functionality of crystalline solid-state ionic conductors relies significantly on the diffusion channels in lattice within the crystallite, and the conduction is achieved by Li<sup>+</sup> hopping in between neighbouring unoccupied vacancies along these channels (vacancy migration mechanism).<sup>45</sup> The microstrain effect induced by pressure treatment significantly distorted the crystallites, this micro-level effect further translates into the Li<sup>+</sup> diffusion channel distortion in the atomic level (increase activation volume), thus reduces the attempt frequency of these elementary local Li<sup>+</sup> hops. While the sulfide LSnPS is soft and could be deformed easily, the brittle oxide has a higher Young's modulus as stated above. The difference in mechanical properties of the two materials is in agreement with our PXRD analysis as well. Thus, the imparted microstrain effect exhibited in the sulfide material, is absence in the oxide. An illustration of the decreased ion dynamic under microstrain is shown in **Figure 4.6**.



**Figure 4.6** Illustration of the effect of decreased Li<sup>+</sup> diffusion due to the harsh mechanical condition for the soft sulfide LSnPS phase, in comparison with the oxide LAGP phase, which is not affected after the pressure treatment.

It also comes to our attention that Hayamizu et al. has recently studied the effect of pellet thickness on apparent diffusivity using LAGP pellet with the thickness varied from 0.5-4 mm.<sup>46</sup> They reported that the apparent diffusivity of pellet LAGP tends to be smaller than powder, due to the preferable diffusion along the sample geometry,<sup>46</sup> but with thicker pellet ( $\geq 3-4 \text{ mm}$ ) or longer diffusion time  $\Delta$  ( $\geq 30 \text{ ms}$ ) this variation will be negligible.<sup>46</sup> Here we did not see this kind of behavior in our test for LAGP. This could be because we are using thick LAGP pellet (3.5 mm) and long diffusion time ( $\geq 100 \text{ ms}$ ). However, it is unlikely that macroscopic packing thickness at the millimetre level will significantly affect the diffusivity measured by diffusometry NMR at the submicron level, as the authors proposed. Thus, an alternative explanation could be the variable pressure introduced

microstrain or crystallite breakage effects on their samples' morphologies, thus leading to the variation in ion dynamics.

#### 4.3.3 Static <sup>7</sup>Li NMR and Relaxometry Analysis for LSnPS

<sup>7</sup>Li is a quadrupolar nucleus, with a notably small quadrupolar moment (Q = -4.01fm<sup>2</sup>)<sup>47</sup>, thus the quadrupolar coupling constants,  $C_Q$  are usually small (tens of kHz<sup>38, 48-52</sup>) in lithium SE materials. Figure S10 shows the static <sup>7</sup>Li (spin I = 3/2) one-pulse spectra of the LSnPS samples under 7.0 T field at 298 K, with the characteristic quadrupolar line shape.<sup>53</sup> The central transition (-  $1/2 \rightarrow + 1/2$ ) occurs at 1.0 ppm, while the two satellite transitions (-  $3/2 \rightarrow -1/2$  and  $+1/2 \rightarrow +3/2$ ) are represented by the peaks at  $\pm 6.2$  kHz. This is caused by the orientational dependence of the crystalline materials relative to the external magnetic field of the quadrupolar nucleus NMR measurement.<sup>54</sup> All the LSnPS 1D <sup>7</sup>Li spectra have a calculated  $C_0$ , of 24.7 kHz and asymmetry factor ( $\eta_0$ ) of 0. The 1D <sup>7</sup>Li spectra do not differ significantly under static conditions. This is consistent with the PXRD findings above, as the lattice compression is modest, and thus the resulting impact on a small  $C_0$  such as <sup>7</sup>Li is negligible. This may be different for <sup>23</sup>Na, due to its larger quadrupolar moment ( $O = 10.155 \text{ fm}^2$ ).<sup>47</sup> Famprikis et al. studied the microstrain effect induced by mechanochemical synthesis in the sodium conductor (powders) using magicangle spinning (MAS) <sup>23</sup>Na NMR.<sup>16</sup> They were able to detect the difference of local <sup>23</sup>Na environments as the microstrain induced from mechanochemical synthesis, based on the relatively distinguishable second-order <sup>23</sup>Na  $C_Q$  of 1 to 2 MHz. Under static condition with the relatively small first-order  $C_Q$  (~ 25 kHz), differences between the <sup>7</sup>Li spectra are not measurable. Thus, <sup>7</sup>Li VT- $T_1$  relaxation experiments were performed to analyze the local <sup>7</sup>Li dynamics changes, using the inversion recovery sequence with the resulting plot provided in **Figure 4.7**.



**Figure 4.7** Comparison of  $T_1$  relaxation as the function of temperature of LS0, LS250 and LS500.

The  $T_1$  curves start to approach a minimum near 350 K. These behaviors are consistent with the well-known Bloembergen–Purcell–Pound type relaxation (*BPP*) theory,<sup>37</sup> similar to the observations reported for other lithium solid-state ionic conductors

previously.<sup>11, 20, 38, 48</sup> According to BPP theory,<sup>37</sup> nuclear spin relaxation is the result of local interactions which become more effective as the molecular tumbling rate increases, and the maximum relaxation rate is attained at the Larmor frequency. The same trend was observed in  $T_1$  curves across the three LSnPS samples. Thus, the fast  $T_1$  relaxation of the LS0 implies faster dynamic than the LS250 and the LS500. The relaxometry results are also in good agreement with the observations of the diffusometry study. This is expected as PFG-NMR measures the long-range of Li<sup>+</sup> mobility that could be considered as the statistical averaging of local Li<sup>+</sup> motions.

#### **4.4 Conclusions**

Investigations of the influence of pressure treatment on the oxide LAGP and sulfide LSnPS were conducted, with the corresponding change in Li<sup>+</sup> dynamics observed using static <sup>7</sup>Li diffusometry and relaxometry NMR. Firstly, the results show that the fabrication pressure at 500 MPa introduce non-negligible microstrain and distorts the sulfide LSnPS crystallite. Most significantly, <sup>7</sup>Li diffusometry data revealed a reduction of long-range Li<sup>+</sup> transport of about 20% following application of 500 MPa pressure, agrees with the NMR relaxometry study. We demonstrated that after such modest mechanical modification of hundreds of MPa, diffusometry and relaxometry NMR can be used for probing the <sup>7</sup>Li dynamic accurately across different SE materials, and this detectable difference is acquired even without applying active pressures. Finally, these mechanical effects have an inconsequential influence on the structure and ion dynamics in the reference ceramic LAGP

phase, owing to the high Young's modulus of oxide-based SEs. The measurable impact of pressure on the sulfide SE's dynamics imply that the pressure factor needs to be more carefully considered in ASSB engineering.

## **4.5 Supplementary Information**

The PXRD pattern for commercial LAGP powder was acquired. The results in **Figure S4.1** show that the intense peaks of the pattern correspond to the Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> phase (reference pattern in red) and that some minor impurity peaks were also detected, possibly including GeO<sub>2</sub>, which is the starting material commonly used in the solid-state synthesis of LAGP.<sup>52, 55</sup> Triclinic and orthorhombic aluminum phosphate AlPO<sub>4</sub> are also possible phase candidates for the observed weak peaks. Those impurities were also reported from other studies that using solid-state synthesis method.<sup>52, 56</sup> Nevertheless, the as-acquired LAGP powder possessed good purity for the NMR study as the impurities are non-Li-containing in addition to their minute amount.



**Figure S4.1** PXRD pattern for LAGP powder. GeO<sub>2</sub>, triclinic and orthorhombic aluminum phosphates were found to as possible phase candidates for the weak secondary phases.

The PXRD pattern for LSnPS using a thin boron glass capillary. The phase determination suggests the good quality of the acquired for powder LSnPS, any impurities were below detection.



Figure S4.2 PXRD pattern for powder LSnPS.



**Figure S4.3** LSnPS powder (left) and pellet (right) prepared in the coin cell holder with one side sealed with Kapton window. After crimping the cell an extra thin layer of epoxy was applied on the gap in between the cap and the base to ensure the good sealing.



**Figure S4.4** Experimental PXRD patterns, fittings, and the differences for a) LA0, b) LA500, c) LS0, and d) LS500.

Typically, Scherrer's method is limited for the crystallite size up to 100 - 200 nm,<sup>57,</sup> <sup>58</sup> the crystallite size above these value will lead to a very small broadening effect on the  $B_{size}$ , and it will be challenging to isolate their influence on the patterns.<sup>57</sup> In some extreme cases (very large crystallite), negative values for the crystallite size from the refinement are possible, but physically meaningless.<sup>25</sup>

**Table S4.1** Displacement errors, and the crystallite size analysis for all the samples based on the PXRD refinements. The refined crystallite sizes are not considered as accurate as the values are approaching or exceeding the limit of Scherrer's method.<sup>25, 57</sup>

Sample ID	Displacement (mm)	Crystallite size (nm)
LA0	$-0.071 \pm 0.002$	$190 \pm 40$
LA500	$-0.018 \pm 0.001$	$310 \pm 110$
LS0	$-0.039 \pm 0.001$	$130 \pm 10$
LS500	$0.064 \pm 0.001$	$2600 \pm 18100$

Pulsed-field-gradient (PFG)-NMR strongly relies on the gradient encoding and decoding process align with the z-dimension,<sup>59</sup> inhomogeneous sample distribution across the z-dimension could lead to significant artifact. To address this artifact, here we applied the packing method that ensure the small pellet fragments are stacked parallel to the bottom in the Shigemi NMR tube (**Figure S4.5a**), we call this a "homogenous stack packing". Briefly, a LSnPS pellet was prepared and broken into small fragments, then the fragments were further trimmed with tweezer so that they will have the similar diameters with the 5

mm Shigemi NMR tube. Then the pellet fragments were stacked parallelly to the ground level in the Shigemi tube. We also demonstrated that the artifacts could be significant if the pellet fragments are dropped randomly in the NMR tube in **Figure S4.5b**.



**Figure S4.5** (a) The homogenous stack packing method that applied in all the pelletized samples' measurements and (b) a demonstration of inhomogeneous packing of the pellet fragments by dropping the samples randomly in the Shigemi NMR tube.

Two trials of the homogenous packing are collected and shown in **Figure S4.6a** and **S4.6b**. The variable-temperature (VT) PFG-NMR experiments were performed, and the Arrhenius plots are shown. It is found that there will not be a significant different if the pelletized fragments were prepared by this packing method.


**Figure S4.6** (a) The VT-diffusion Arrhenius plot for the first trial of the homogenously packed LSnPS pellet fragments.



(b) The VT-diffusion Arrhenius plot for the second trial of the homogenously packed LSnPS pellet fragments.

The parallel measurement for the inhomogeneous-packed pellet was also conducted and the result is shown in **Figure S4.7**. Significant discrepancies were observed for both <sup>7</sup>Li diffusivities and the slopes of the Arrhenius plot, which essentially is the function of the diffusion activation energy.



**Figure S4.7** The VT-diffusion Arrhenius plot for the inhomogeneous packing pellet fragments (in red), in comparison to the results obtained from the homogenous packing (light blue).



**Figure S4.8** Lattice parameter and calculated unit cell volume change before and after pressure treatment for (a) LAGP and (b) LSnPS. The in both figures the *c* parameters are represented by circles, and *a* parameters are represented by triangles.

Sample ID	<i>a</i> (Å)	<i>c</i> (Å)
LA0	8.2812(3)	20.486(1)
LA500	8.2812(2)	20.477(1)
LS0	8.7412(2)	12.7755(3)
LS500	8.7379(2)	12.7814(4)

**Table S4.2** Lattice parameters for all the samples based on PXRD patterns.

**Table S4.3** shows the diffusion time  $\Delta$  under each temperature during the diffusometry experiments for LA0 and LA500.  $\Delta$  was set to noticeably longer for the diffusometry experiments at ~ 300 and 309 K, to achieve reasonable signal attenuations.

Temperature (K)	$\Delta$ (ms) for LA0	$\Delta$ (ms) for LA500
300	190	200
309	150	150
318	110	110
327	110	110
335	110	110
343	110	110
353	100	100

**Table S4.3** Diffusion time  $\Delta$  for LA0 and LA500 under different temperatures.



**Figure S4.9** Diffusion echo attenuation curves for the two LSnPS samples under 298 K, with the calculated fitting curve for each. Diffusion time ( $\Delta$ ) was kept as 110 ms for all the measurements.



**Figure S4.10** Static <sup>7</sup>Li one-pulse spectra for the three LSnPS samples collected under 7.0 T (298 K). The line shapes show a very generic static powder pattern for the nucleus with spin  $I = \frac{3}{2}$  nuclei. The calculated  $C_Q$  from the fittings are 24.7 kHz, with an  $\eta_Q$  value of 0. An example of fitted line shape for LS0 is shown in the inset in purple.



**Figure S4.11** PXRD patterns of LS0, LS250 and LS500 collected using Bruker air-tight X-ray specimen holder with displacement error corrected. The two insets shows that the

qualitative trend of peak broadening can be observed, which indicates the microstrain is introduced after pressure treatment of the LSnPS.

**Table S4.4** PXRD analysis of microstrain values and the displacement errors. These materials were prepared with a Bruker air-tight X-ray specimen holder, the data were not used in the PXRD analysis section due to poor signal/noise.

Sample ID	Microstrain (%)	Displacement (mm)
LS0	$0.05 \pm 0.03$	$0.184 \pm 0.008$
LS250	$0.06 \pm 0.03$	$0.146 \pm 0.004$
LS500	$0.09 \pm 0.04$	$0.147 \pm 0.006$

Multinuclear ssNMR analyses were carried out to for the powder and a pellet LSnPS sample (pressed at 500 MPa) to identify any local structural change at an atomic level. The results of <sup>7</sup>Li, <sup>31</sup>P, and <sup>119</sup>Sn ssNMR spectra analyses were shown in **Table S4.5** and **Figure S4.12**. <sup>7</sup>Li peaks for both LS0 and LS500 show up at ~ 0 ppm, which is within the typical range for diamagnetic <sup>7</sup>Li signals (~ 10 ppm).<sup>60</sup> The <sup>7</sup>Li NMR spectra are very similar between the two samples, with a small change of the chemical shift from 0.14 ppm after pressure treatment. The <sup>31</sup>P and <sup>119</sup>Sn spectra of both samples also exhibit similar line shapes, but the <sup>119</sup>Sn of the LS500 shows much higher noise level with the same experimental set as the LS0, this is due to the low natural abundance of <sup>119</sup>Sn (8.59%).<sup>47</sup> A fragment of LSnPS pellet contributes significantly smaller signal intensity compared to a fully packed rotor with the powder LSnPS. In <sup>31</sup>P ssNMR, three major <sup>31</sup>P environments can be seen, those at 77 and 93 ppm are corresponding to the P<sup>5+</sup> at 4d (P2) and 2b (P1)

sites, respectively,<sup>48, 61</sup> where the P<sup>5+</sup> at the 4d site shares equally in with the Sn<sup>4+,8</sup> and should ideally resulting into the same population of P1 and P2 sites. A signal at ~ 86 ppm (~ 3 - 4%) can be correlated to Li<sub>7</sub>PS<sub>6</sub>, which is commonly seen for this phase.<sup>48, 61</sup> The <sup>119</sup>Sn spectra exhibits a very intriguing line shape, other than the major peak (Sn1) corresponding to Sn<sup>4+</sup> peak at 87 ppm, there's a secondary peak at 78 ppm with high integral intensity (40%). This secondary <sup>119</sup>Sn peak (Sn2) has been reported before, and previously been proposed to be the disordered Sn<sup>4+</sup> that substitute the P<sup>5+</sup> at P1 sites.<sup>48, 61</sup> However, there's no enough evidence of supporting this hypothesis, hence, it is denoted as "disorder Sn2" in **Table S4.5**. In summary, no significant differences were detected on the multinuclear ssNMR spectra after pressure treatment, implying that the local structural changes at the atomic scale are modest, since the microstrain is an averaged effect over crystallites at a microscale.

Nucleus	Fitting parameters	LSO	LS500
<sup>7</sup> Li	δ (ppm)	0.66	0.80
	FWHM (Hz)	25	25
$^{31}P - P1$ (2b)	δ (ppm)	92.6	92.9
	FWHM (Hz)	428	434
	Integral (%)	55	56
$^{31}P - P2$ (4d)	$\delta$ (ppm)	77.0	77.2

**Table S4.5** Summary of the fitting parameters obtained from ssNMR analyses for the LS0and LS500.

	Integral (%)	41	41
	FWHM (Hz)	532	540
$^{119}$ Sn – Sn1 (4d)	$\delta$ (ppm)	86.9	87.1
	Integral (%)	60	60
	FWHM (Hz)	1017	979
<sup>119</sup> Sn – Sn2 (disorder)	$\delta$ (ppm)	77.7	77.5
	Integral (%)	400	40
	FWHM (Hz)	1115	1106



ssNMR spectra comparison between powder and pellet Sample spect

Sample spectral analyses for the powder

Figure S4.12 ssNMR spectral comparison between LSnPS powder and pellet (a) - (c) and the spectral deconvolution for powder LSnPS (d) - (e). Spinning sidebands are marked with asterisk.

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# Chapter 5 – Revealing the Na<sup>+</sup> Dynamics in Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> Solid Electrolyte Material Using <sup>23</sup>Na Solid-State NMR Spectroscopy and Computational Methods

This chapter reformatted the results from one previous publication and a current manuscript in preparation. The first contribution appeared in the *Inorganic Chemistry* (*Inorg. Chem.*, **2023**, *62*(39), 16068-16076), where the author was the third author, and contributed to the solid-state NMR measurements and analyses to characterize the structure of the Na<sub>4-x</sub>Sn<sub>2-x</sub>Sb<sub>x</sub>Ge<sub>5</sub>O<sub>16</sub>. The samples were prepared and characterized from diffraction analysis by S. A. Novikov (first author). The EIS measurements were conducted by C. J. Franko. Z. Yang performed the molecular dynamic simulation, G. R. Goward and Y. Mozharivskyj assisted the preparation of the manuscript and final analyses.

The second manuscript is in preparation. Here, as the first author, the author contributed to all the experimental NMR data collections and analyses, and the simulation of NMR line shape using EXPRESS package. C. A. Gurwell contributed to the preparation of scripts for the EXPRESS MATLAB automation program and the data analysis for simulated spectra. D. H. Brouwer completed the CASTEP calculations for the <sup>23</sup>Na quadrupolar parameters. K. J. Sanders and G. R. Goward participated in planning the NMR experiments, analyzing the quadrupolar NMR spectra and the discussion and editing of the manuscript.

This section primarily discusses the investigation of Na<sub>4-x</sub>Sn<sub>2-x</sub>Sb<sub>x</sub>Ge<sub>5</sub>O<sub>16</sub>, a novel Na<sup>+</sup> conductor that was discovered recently. This material has good ionic conductivity and could be a promising candidate for all-solid-state NIBs. SCXRD data shows that there are three Na sites – Na1 (8d) at a small channel, whereas Na2 (4c) and Na3 (4c) are occupying a larger channel, and they are expected to be more dynamic. To further understand Na<sup>+</sup> dynamics at the molecular scale, the pristine (x = 0) and the one with highest conductivity (x = 0.20) was characterized by <sup>23</sup>Na and <sup>119</sup>Sn ssNMR in the first publication. The <sup>119</sup>Sn spectra validated that the homogeneity of the Sb-doping phase, and the <sup>23</sup>Na NMR indicates that there are structural and environmental changes for the three Na sites.

The second manuscript focuses on probing the Na<sup>+</sup> dynamics at the molecular level. This study was conducted for the pristine phase (x = 0). A series of <sup>23</sup>Na ssNMR experiments were performed under multiple field strengths, in order to uniquely identify the three unique Na sites. However, the resolution of Na2 and Na3 cannot be achieved in the available temperature range. They are here denoted as Na2-3 peak, due to the observation that they are under rapid chemical exchange. The follow-up temperature- and field-dependent NMR relaxometry confirms the fast dynamics of Na2-3 peak, while the Na<sup>+</sup> at Na1 site is more static. To constrain the quadrupolar NMR parameters of the Na2-3 peak, the 3QMAS technique was employed, together with thorough spectral regression analyses under multiple fields (20, 11.7, and 7 T). CASTEP calculation was performed to further constrain the <sup>23</sup>Na quadrupolar NMR parameters. Finally, with these constrains, the coalesced Na2-3 <sup>23</sup>Na ssNMR lineshapes were successfully simulated with the EXPRESS program with one set of quadrupolar NMR parameters applied under all three fields, and

with the estimated exchange rate of  $2 \times 10^5$  Hz. These quadrupolar parameters found in EXPRESS simulation are very consistent with the constrains from the experimental and calculation results. Thus, we successfully demonstrated that the Na2 and Na3 sites are extremely dynamic in this structure at the molecular level. This work acquires a better understanding of the mechanisms of Na<sup>+</sup> conduction for the Na<sub>4-x</sub>Sn<sub>2-x</sub>Sb<sub>x</sub>Ge<sub>5</sub>O<sub>16</sub> series, and opens the door for studying and exploring Na<sup>+</sup> transport phenomena in the Na-based SCEs in the future.

#### **5.1 Introduction**

With the increasing demand for safer energy storage devices from the electric vehicles (EVs) and portable electronic markets, all-solid-state batteries (ASSBs) are recognized as one of the promising solutions to achieve this goal. Unlike the traditional batteries utilizing conventional liquid electrolytes with organic carbonate solvents, ASSBs employ polymers, inorganic glasses, and/or crystalline ion conductors as their solid-state electrolyte (SSE) materials, which are typically more thermally stable and therefore not prone to ignition, making ASSBs a promising candidate for the next generation of batteries.

As the pioneer in energy storage technology, lithium-ion batteries (LIBs) are extensively applied in various EV and electronic products, owing to their high gravimetric and volumetric energy densities.<sup>1</sup> However, the continuous utilization of LIBs has raised significant concerns regarding the limited availability and increasing cost of the lithium.<sup>2, 3</sup> Thus, it is necessary to explore other alternatives to replace the LIBs. Na-ion batteries

(NIBs) are one promising candidate, because sodium is the 6<sup>th</sup> most abundant element in the earth's crust,<sup>2</sup> and the performance of NIBs is comparable to LIBs.<sup>4</sup> While numerous Li-based SE materials have been explored and developed in the past decades<sup>5-8</sup> driven by huge markets for LIBs, there are still less reports for their sodium counterparts (all-solidstate Na-ion batteries, ASSNIBs). NASICON (NA SuperIonic CONductor)-type materials, which were first reported by Goodenough et al in 1976,<sup>9</sup> usually possess good ionic conductivities in the order of  $0.1 - 1 \text{ mS cm}^{-1}$  under room temperature (RT).<sup>2</sup> Na-conducting sulfide SGE 75Na<sub>2</sub>S-25P<sub>2</sub>S<sub>5</sub>, reported by Tatsumisago et al., exhibits a low elastic modulus which is preferable for ASSNIB manufacturing, thanks to the weaker ionic interaction between the Na<sup>+</sup> and the thiophosphate  $PS_4^{3-}$  anionic groups.<sup>10</sup> They also explored sulfide ceramic conductors based on the sodium thiophosphate glass, where a crystalline cubic Na<sub>3</sub>PS<sub>4</sub> structure was found to possess an ionic conductivity exceeding 0.1 mS cm<sup>-1</sup>.<sup>11</sup> Motivated by the lithium thiophosphate "LGPS" phase with a remarkable conductivity of 12 mS cm<sup>-1,8</sup> Zhang et al. reported a novel sodium superionic conductor analogue – Na<sub>11</sub>Sn<sub>2</sub>PS<sub>12</sub><sup>12</sup> which exhibits an outstanding ionic conductivity of 1.4 mS cm<sup>-1</sup>.<sup>12</sup> In general, the high conductivities of sulfide electrolytes can be attributed to the weaker cation-anion electrostatic interactions between Na<sup>+</sup> and S<sup>2-,2</sup> However, sulfide-based electrolytes are highly air-sensitive, prone to degradation through hydrolysis, and can produce poisonous H<sub>2</sub>S.<sup>2</sup> Additionally, sulfide-based sodium SEs have a narrow electrochemical stability window,<sup>13</sup> limiting the application range of the materials for high energy density sodium metal batteries. Thus, it is still important to explore other non-sulfur containing Na SE materials for ASSNIBs.

Very recently, a novel oxide Na conductor series, Na<sub>4-x</sub>Sn<sub>2-x</sub>Sb<sub>x</sub>Ge<sub>5</sub>O<sub>16</sub>, was reported with a maximum ionic conductivity of 0.11 mS cm<sup>-1</sup> (x = 0.20) under RT.<sup>14</sup> To understand the material structure, single-crystal X-ray diffraction (SCXRD) was performed on the parent phase (x = 0) (shown in **Figure 5.1**).<sup>14</sup> It adopts an orthorhombic crystal structure with space group Pbcn.<sup>14</sup> The polyhedron frameworks are built by stacking the corner-shearing [GeO<sub>4</sub>] (Ge occupies two 8d and one 4c positions) polyanionic chains parallel to the *bc*-plane. Interchain connections are realised by corner-sharing between the [GeO<sub>4</sub>] polyanionic chain and distorted [SnO<sub>6</sub>] octahedrons.<sup>14</sup> There are three crystallographically unique Na sites in the structure, with the molar ratio of Na1 (8d) : Na2 (4c) : Na3 (4c) of 2 : 1 : 1. The previous work shows that Na1 occupies smaller ion conduction channels, while Na2 and Na3 are situated in the larger channels, positioned further away from the Na1 sites along the *c*-axis.<sup>14</sup> By evaluating the results form leastsquares refinement, it was found that Na2 and Na3 have significantly larger displacement parameters in contrast to Na1,<sup>14</sup> which suggests that they contribute to the Na<sup>+</sup> ionic conductivity within the structure. Further investigation on Na<sup>+</sup> conduction pathways was performed on the Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> structure, utilizing bond-valence energy landscape (BVEL) calculations. The Na<sup>+</sup> diffusion activation energies ( $E_a$ ) were calculated as 0.30 and 0.43 eV along the *a*- and *b*-axes, respectively.<sup>14</sup> However, the calculated energy along the *c*-axis migration pathway is 1.27 eV. This value is significantly higher than the experimentally determined value from variable temperature (VT)-electrical impedance spectroscopy (EIS) measurements, which only exhibit an  $E_a$  of 0.33(1) eV.<sup>14</sup> Because the extracted  $E_a$  values from the VT-EIS measurement show good agreement with the calculated ones for a and baxes, we hypothesized the high calculated activation barrier along the c-axis elucidates that the slower dynamic Na1 is unlikely to interact with the Na2 and Na3. This argument is also in line with the observation for the crystal structure and the results from the least squared refinement analysis. Nevertheless, the Na<sup>+</sup> dynamic hypothesis has not yet been experimentally demonstrated at the molecular level.

Solid-state NMR is well-suited to study both structure and dynamics in the Na SE material, due to its potential of probing both unique crystallographic Na sites and dynamics. In this work, we investigated the Na<sup>+</sup> dynamics in Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> using <sup>23</sup>Na ssNMR. However, <sup>23</sup>Na ssNMR is usually influenced by asymmetric line broadening effects due to the presence of anisotropic components from the 2<sup>nd</sup> order quadrupolar coupling effect,<sup>15-</sup> <sup>17</sup> caused by the interaction between the nuclei with large electric quadrupole moment (Q $= 10.4 \text{ fm}^2 \text{ for } {}^{23}\text{Na})^{18}$  and electric field gradient (EFG) from the surrounding charges.<sup>15-17</sup> To address this, we conducted the  $^{23}$ Na ssNMR experiments under multiple fields (7, 11.7, and 20 T) and a series of subsequent analyses to determine the <sup>23</sup>Na quadrupolar parameters for unique Na sites. <sup>23</sup>Na NMR relaxometry was also performed, as it is proven to be an excellent tool to probe the dynamic information at the molecular scale.<sup>19-22</sup> Moreover, as previously discussed that Na2 and Na3 are hypothesized to be more dynamic in the abplane, their molecular-scale motions through chemical exchange could potentially influence their EFGs, therefore affecting the quadrupolar lineshapes in the NMR spectra. The EXPRESS program<sup>23</sup> is a MATLAB-coded script that can simulate effect of site to site exchange on NMR spectra of quadrupolar nuclei,<sup>24, 25</sup> potentially providing a method for modeling the <sup>23</sup>Na quadrupolar lineshapes under dynamics. Our current work illustrates the capabilities of <sup>23</sup>Na ssNMR to probe the nature of Na<sup>+</sup> dynamics in the Na-based SE, providing a better understanding of the Na<sup>+</sup> conduction mechanism in the novel Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub>SE material.



**Figure 5.1** Crystal structure of  $Na_4Sn_2Ge_5O_{16}$ . The polyhedron framework is built by corner-sharing [GeO<sub>4</sub>] (dark grey) and [SnO<sub>6</sub>] (orange). Sodium atoms are displayed in yellow and labeled according to their crystallographic sites.

#### **5.2 Methods**

#### 5.2.1 <sup>23</sup>Na Solid-State NMR

1D <sup>23</sup>Na NMR spectra were recorded under magic-angle spinning (MAS) conditions at 20, 11.7 and 7 T on Bruker HD 850 MHz, NEO 500 MHz and AV 300 MHz spectrometers, utilizing 1.9 mm, 2.5 mm and 4 mm double-resonance probes, with the corresponding spinning rates are 20, 20 and 10 kHz, respectively. The 1D spectra were collected with the RF powers varied from 120 kHz to 150 kHz across three fields. All the <sup>23</sup>Na spectra were referenced with respect to a 1 M aqueous solution of NaCl at 0 ppm using solid NaCl as a secondary reference by setting its signal to 7.21 ppm.<sup>26</sup> The VT-ssNMR experiments were performed with Bruker BCU-II VT unit. The <sup>119</sup>Sn chemical shifts of Sm<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> were used to calibrate the sample temperatures for the VT experiments, referenced to the standard SnO<sub>2</sub> at -604.3 ppm.<sup>27 119</sup>Sn NMR was carried out to identify the singular environment of the phase and validate the phase purity at 20 T from our previous work.<sup>14</sup> The <sup>23</sup>Na T<sub>1</sub> relaxation times under VT were extracted by performing inversionrecovery experiments, with two different set of experiments with the maximum delay times of 50 ms and 4 s each over 16 steps, to capture both the short and fast relaxation components of the sample. Signals were averaged over 32 scans for the experiments collected at 7 T and 16 scans for the ones collected at 11.7 and 20 T. The recycle delays were set to 3 to 4 s across all the inversion-recovery experiments under three fields. The fitting of <sup>23</sup>Na NMR spectra were performed with ssNake platform,<sup>28</sup> and the  $T_1$  relaxation curves were fitted with stretched exponential functions.

#### 5.2.2 <sup>23</sup>Na Triple-Quantum (3Q)-MAS Solid-State NMR

<sup>23</sup>Na 3QMAS experiments were conducted under field strengths of 20, 11.7, and 7 T at a spinning rate of 20 kHz under first two fields, and 40 kHz at the 7 T (1.3 mm MAS probe), respectively. A three-pulse 3QMAS pulse sequence that contains a z-filter was utilized (shown in Figure 5.2) for data acquisition,<sup>29</sup> with the first two hard pulses with the RF power of initiating triple-quantum (3Q) transition and conversion to zero-quantum (ZQ) respectively, with the RF powers from 120 to 150 kHz across the various fields. Followed by a selective pulse to achieve ZQ to single-quantum (1Q) conversion with the RF power varied from ~ 4 to 15 kHz depending on the line widths at different fields. The increment delay of the 3Q evolution time  $t_1$  was set to 50 to 25  $\mu$ s over 100 to 128 steps to create the indirect dimension, resulting in the indirect spectral widths ranging from 20 to 40 kHz across three fields, to accommodating for the spectral broadening effect from 20 T to 7 T. Number of scans were set to 48, 240, and 4320 to account for the phase cycling of 12n scans<sup>29</sup> for 20, 11.7, and 7 T, respectively. The z-filter delay time  $\tau$  was set to a constant of 20  $\mu$ s throughout all the 3QMAS experiments acquired at all three fields. The 3QMAS spectra were processed in Topspin 4.1.0, with the scaling factor of 34/9 in the indirect dimension and the shearing factor of 7/9.<sup>16</sup> The shift calibration of the indirect dimension axes was achieved *via* determining the center of mass shift of the well-defined Na1 peak, whose isotropic shift and quadrupolar NMR parameters are accurately determined from the experimental spectra in the direct dimension, under each field.



**Figure 5.2** Pulse sequence of z-filtered 3QMAS utilized under all three magnetic fields.  $t_1$  is the evolution time of the 3Q transition,  $\tau$  is the z-filter delay, and  $kt_1$  is the evolution time of 1Q transition, where k equals to the shearing factor of 7/9 for spin-3/2 nuclei in this case.<sup>15, 16</sup>

#### 5.2.3 DFT Calculations of <sup>23</sup>Na NMR Parameters

Density Functional Theory (DFT) calculations of <sup>23</sup>Na NMR parameters were carried out with the gauge-including projector augmented wave (GIPAW) method<sup>30</sup> using the NMR module<sup>30-32</sup> of the CASTEP program<sup>33</sup>. The Perdew-Burke-Ernzerhof (PBE) functional<sup>34</sup> was used for all calculations. On-the-fly pseudopotentials generated by the CASTEP program were used. Non-bonding forces were accounted by the semiempirical dispersion corrections of Tkatchenko and Scheffler.<sup>35</sup> The calculated <sup>23</sup>Na NMR parameters for NaH<sub>2</sub>PO<sub>4</sub> were found to converge with a planewave basis set energy cutoff of 800 eV and a Monkhorst-Pack<sup>36</sup> *k*-point spacing of 0.06 Å<sup>-1</sup> so these values were used for all calculations. Calculations were carried out on reported crystal structures without additional optimization. Calculated <sup>23</sup>Na isotropic chemical shielding values were converted to chemical shifts with a linear calibration equation established by comparing experimental shifts to calculated shielings for the series of sodium-containing materials reported by Koller et al.<sup>17</sup> (see **Supporting Information**). Similarly, the DFT-calculated quadrupolar coupling constants ( $C_Q$ ) were adjusted for comparison to experimental values based on a linear calibration equation established from the same dataset (see **Section 5.5**).

#### 5.2.4 EXPRESS Simulation of <sup>23</sup>Na ssNMR Spectra

EXPRESS (EXchange Program for RElaxing Spin Systems)<sup>23</sup> simulation was performed to model the <sup>23</sup>Na lineshape that is dominated by the chemical exchange of the Na2 and Na3 sites in the structure. The quadrupolar NMR parameters were stepped through a user-selected range using a MATLAB script. To achieve the best fit with the experimental spectrum, the simulated spectra were exported and plotted normalized to an experimental spectrum. The RMSE and the error in peak position were used to find the best fitting parameters. Simulated spectra were compared under 20, 11.7, and 7 T fields to ensure agreement between parameters. The ranges of the parameters attempted during the simulation are provided in **Table S5.3**.

#### 5.3 Results and Discussions

#### 5.3.1 Solid-State <sup>23</sup>Na NMR Spectra at Multiple Fields

The <sup>23</sup>Na ssNMR spectra under the influence of the 2<sup>nd</sup>-order quadrupolar interaction cannot be described by only an "isotropic chemical shift" which is caused from chemical shielding. Instead, the observed peaks in the direct dimension (here denoted as "F2" dimension) for a quadrupolar ssNMR spectrum should be defined with respect to the "center of gravity" or "center of mass" shift, due to the 2<sup>nd</sup>-order perturbation to the Zeeman energy states.<sup>29</sup> Under all conventional high-field NMR spectral conditions such as static, MAS, dynamic-angle spinning (DAS),<sup>37</sup> double-rotation (DOR)<sup>38</sup>..., the center of gravity shift, here we denoted it as " $\delta_{F2}$ ", can be expressed as:<sup>15, 39</sup>

$$\delta_{F2} = \delta_{iso} + \delta_{qis} \tag{5.1}$$

where  $\delta_{iso}$  (in ppm) represents the contribution from the isotropic chemical shift, and  $\delta_{qis}$  (in ppm) is the "quadrupolar induced shift", predominately contributed to from the 2<sup>nd</sup>-order quadrupolar interaction. This term is calculated as:<sup>15, 39</sup>

$$\delta_{qis} = -\frac{3}{40} * \left(\frac{C_Q}{\nu_0}\right)^2 * \frac{\left(l(l+1) - \frac{3}{4}\right)}{l^2(2l-1)^2} * \left(1 + \frac{\eta_Q}{3}\right) * 10^6$$
[5.2]

 $C_Q$  is the quadrupolar coupling constant (in MHz),  $v_0$  is the Larmor frequency (in MHz) under a certain field strength. *I* is the spin quantum number, and  $\eta_Q$  is the asymmetric parameter ( $0 \le \eta_Q \le 1$ ). For spin-3/2 nuclei (e.g. <sup>23</sup>Na), **Equation [5.2]** can be simplified to:<sup>15</sup> For spin-3/2 nuclei (e.g. <sup>23</sup>Na), Equation [5.2] can be simplified to:<sup>15</sup>

$$\delta_{qis} = -25000 \frac{P_Q^2}{\nu_0^2} \tag{5.3}$$

where  $P_0$  is the quadrupolar product which can be expressed as:<sup>15</sup>

$$P_Q = C_Q (1 + \frac{\eta_Q}{3})^{1/2}$$
[5.4]

For <sup>23</sup>Na ssNMR, the  $C_Q$  parameters are commonly between 1 – 4 MHz<sup>15, 17</sup> depending on the strength of  $C_Q$  interaction. However, accurately determining  $C_Q$  and  $\eta_Q$  from  $P_Q$  impossible using the preceding evaluation, as this usually requires fitting the quadrupolar lineshape under MAS.<sup>15, 17</sup>

<sup>23</sup>Na MAS NMR spectra recorded at 20 T, 11.7 T, and 7 T are shown in **Figure 5.3a** – **c**. It is notable that there are two regions of peak intensity in each of the <sup>23</sup>Na spectra. We note that our previous publication on this material included only the spectra at 20 and 7 T, and the deconvolution separated the high-frequency region into two peaks, while treating the broader low frequency resonance as a single peak. With the support of spectral acquisition at multiple fields and 3Q-MAS, we have determined that the high frequency region is more appropriately fitted as a single quadrupolar lineshape, and the broader low frequency region is likely to arise from the coalescence of two quadrupolar lineshapes due to fast sodium ion dynamics. Details of this assignment and the parameters for each peak are provided here. For the spectrum collected at 7 T (**Figure 5.3c**), the first peak (Na1, 8d) is found in the range of 0 to -50 ppm and exhibits a typical 2<sup>nd</sup>-order *C*<sub>Q</sub> lineshape. The other peak arises in the range of ~ -40 to -130 ppm and appears to be broader, does not

exhibit a typical 2<sup>nd</sup> order  $C_Q$  NMR lineshape. It is believed to be an overlapping resonance of both Na2 (4c) and Na3 (4c), and will be denoted as "Na2-3" in the following text. In addition, the peak integral area intensity ratio of the Na1 vs Na2-3 is approximately 1:1, which agrees with the Na site occupation ratio in the structure (Na1 : Na2 : Na3 = 2 : 1 : 1) from SCXRD analysis.<sup>14</sup> <sup>23</sup>Na NMR spectra collected at 11.7 and 20 T are also shown in **Figure 5.3a** and **5.3b**, respectively. Both spectra display similar lineshapes to the spectrum recorded at 7 T, but the Na1 and Na2-3 peaks are much narrower at higher field strengths. Furthermore, the  $\delta_{F2}$  of the Na1 and Na2-3 peaks progressively shift towards higher frequency as the magnetic field strength increases. This behaviour is consistent with the mathematical expressions in **Equation [5.1]** – **[5.2]**, where the effects of 2<sup>nd</sup> order  $C_Q$ interactions in NMR spectra were described.<sup>15, 39</sup>

The Na1 signal in the <sup>23</sup>Na spectra collected at multiple fields were fitted to extract its isotropic chemical shift and quadrupolar parameters. Na1 can be successfully modeled with the same set of parameters at all three fields (**Figure 5.3d** – **f**). The fitting parameters for Na1 are  $\delta_{iso} = -5.30$  ppm,  $C_Q = 2.24$  MHz, and  $\eta_Q = 0.42$ . The remaining broad signal of Na2-3 cannot be modeled as two distinct quadrupolar lineshapes with two sets of consistent quadrupolar parameters at all fields, due to the spectral overlap and indistinct features of the lineshape. The broadness and blurred singularities of this lineshape suggests that it arises from the coalescence of Na2 and Na3, potentially due to fast chemical exchange involving these sites. Notably, with the current experimental conditions, the Na2 and Na3 peaks cannot be resolved even at the lowest temperature of 270 K at 20 T that we could achieve (**Figure S5.1**), suggesting that the Na<sup>+</sup> dynamics are very fast. As discussed, the Na<sup>+</sup> dynamics were investigated using SCXRD and BVEL calculations based on the unit cell of the crystal structure.<sup>14</sup> Na2 and Na3 that occupying larger diffusion channels are likely the dominant contributors to the Na<sup>+</sup> ion transport, whereas Na1 appears to be comparatively slow, and does not interact with Na2 and Na3 along c-axis.<sup>14</sup> This is consistent with our observations of the 1D <sup>23</sup>Na ssNMR spectra. In this case, the dynamics between Na2 and Na3 generate a coalesced lineshape in the <sup>23</sup>Na NMR spectra as the Na2-3 peaks, as seen in **Figure 5.3a** from ~ -10 to -20 ppm, in **5.3b** from ~ -20 to -50 ppm, and in **5.3c** from ~ -40 to -130 ppm. It is difficult to accurately judge the left edges for the ones at 11.7 and 7 T because they are heavily overlapping with Na1 peak.

Before moving on to a detailed analysis of this complex Na2-3 lineshape, the next section provides additional and complementary evidence from <sup>23</sup>Na relaxometry measurements that supports the hypothesis that sodium ions in site Na1 are less dynamic and more isolated in its own channel, while the sodium ions in sites Na2 and Na3 are in rapid dynamic exchange.



**Figure 5.3** (a) – (c) <sup>23</sup>Na MAS NMR spectra of Na<sub>4</sub>SnGe<sub>5</sub>O<sub>16</sub> recorded at 20 T (top) under a MAS spinning rate of 20 kHz, and at 11.7 T (middle) under 20 kHz, and at 7 T (bottom) under 10 kHz. The spinning sidebands are labeled with asterisks. (d) – (f) Fitting for Na1 the three corresponding field strengths ( $\delta_{iso} = 5.30$  ppm,  $C_Q = 2.24$  MHz,  $\eta_Q = 0.42$ ). The simulated lineshapes are labeled as black dashed lines, and the experimental spectra are shown in blue under all fields.

## 5.3.2 Probing Na<sup>+</sup> Dynamics in Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> with <sup>23</sup>Na Relaxometry

A follow-up investigation of Na<sup>+</sup> dynamics using <sup>23</sup>Na ssNMR relaxometry was carried out at  $B_0 = 20$  T field strength. NMR relaxometry is a well-established method that

is used to probe local ion dynamics in both Li<sup>+</sup>- and Na<sup>+</sup>-based SEs.<sup>19-22</sup> The well-known Bloembergen-Purcell-Pound (BPP) relaxation theory<sup>40</sup> relates the molecular tumbling motion with  $T_1$  relaxation through an autocorrelation function, with the assumption that molecular dynamics is the predominant effect causing the spin-lattice relaxation. In Figure 5.4, the relaxation rates  $(R_1 = 1/T_1)$  for the Na1 and the Na2-3 peaks are graphed against inverse temperature in an Arrhenius plot. Two "dummy peaks" were used to model the total integral intensity of the Na2-3. An example of the integral fitting for the fully inverted and recovered Na2-3 peak at 301 K is shown in Figure S5.2. By evaluating the relaxation curves of Na1 and Na2-3, an immediate distinction can be detected by comparing the  $T_1$ values between the Na1 and Na2-3. At 301 K, Na1 has a  $T_1$  relaxation time of 647 ms, whereas Na2-3 has a relaxation time of 2.64 ms (Figure S5.3a and b), which is about two orders of magnitude smaller than Na1. Moreover, the Arrhenius plot for Na2-3 presents a negative slope, but the slope for Na1 is positive and closer to zero, implying that the relaxation mechanisms of Na2-3 and Na1 are dominated by completely different processes. In addition, the slope of Na2-3 is steeper than the one for Na1, indicating that it is more dependent on temperature change. The calculated activation energies E<sub>a</sub> for Na2-3 and Na1 are  $0.109 \pm 0.003$  eV and  $0.059 \pm 0.005$  eV, respectively. The above-mentioned evidence is consistent with that the relaxation rate of Na2-3 is dominated by a more thermally activated process from Na<sup>+</sup> dynamics, indicating the unresolved Na2-3 lineshapes are very likely to be the consequence of peaks coalescence of Na2 and Na3, due to fast chemical exchange. Nevertheless, the relaxation mechanism of Na1 is more likely to be modulated by local interactions such as 2<sup>nd</sup> order quadrupolar coupling, judging by its longer relaxation times and comparative insensitivity to change in temperature.



 $ln(R_1)$  as A Function of Temperature

**Figure 5.4.** <sup>23</sup>Na relaxation rate as a function of temperature. The integral intensity of Na2-3 has been modeled by two dummy peaks due to the lack of peak resolution. The fitting of the Na2-3 peak under full inversion and recovery is shown in **Figure S5.4**.

The relaxation times were also investigated under field strengths of 11.7 and 7 T at around RT (**Figure S5.3c** – **f**), as it is shown that  $T_1$  decreases significantly as the field strength increases for Na2-3, thus supporting the hypothesis of *BPP* relaxation. At temperature around RT, the Na2-3 exchange rate remains relatively constant, thus the faster relaxation observed at decreasing fields is explained by *BPP* relaxation theory, as the

Larmor frequency approaches the exchange rate, resulting in a faster relaxation.<sup>19, 20, 40, 41</sup> On the contrary, the  $T_1$  of Na1 only exhibits a modest change as a function of field strength (less than 10%). The slight change in  $T_1$  could be due to slightly different data acquisition conditions such as probe temperature, probe efficiency, frictional heating from MAS, etc. In summary, the relaxation study provides direct experimental evidence supporting that the Na<sup>+</sup> dynamic in this material is very likely dominated by Na2 and Na3 sites, but Na1 is not involved.

# 5.3.3 Constraining the NMR Parameters with Regression Analyses under Multiple Field Strengths and CASTEP Calculations

Vold and Hoatson developed the EXPRESS program,<sup>23</sup> which can simulate quadrupolar lineshape under the influence of chemical exchange. However, this could be quite challenging in the case of multiple overlapping sites, as there are several of unknown parameters involved ( $\delta_{iso}$ ,  $C_Q$ ,  $\eta_Q$ , exchange rates, three Euler angles for each site). There are more possible variables for the Na2-3 lineshapes than there are experimental constraints. Therefore, it is necessary to explore ways to constrain a reasonable range of the quadrupolar parameters to model this coalesced lineshape. This can be achieved with lineshape analyses of the 1D and 2D-3QMAS experiments under multiple fields. Since an inverse relationship between  $\delta_{qis}$  and the Larmor frequency  $v_L$  is given in **Equation [5.3]**,<sup>15</sup> from a change of  $\delta_{F2}$  as a function of magnetic field strength gives possible solutions for  $\delta_{iso}$  and  $P_Q$ . Herein, we quantified the average quadrupolar parameters for the Na2-3 peak, by plotting  $\delta_{F2}$  against 1000  $v_L^{-2}$  to obtain a linear regression. The regression analysis can further provide information for  $\delta_{F2}$  and  $P_Q$  by examining the slope and the intercept (details given in **Table S5.1**). In addition, we implemented the multiple-quantum MAS (MQMAS) method<sup>15, 16, 42</sup> to constrain the quadrupolar parameters for Na2-3 as well, since it can provide the pure isotropic component in the indirect dimension, by modulating the evolution times between the 3Q and 1Q transitions of the 4<sup>th</sup> rank anisotropy terms.<sup>42</sup> After applying proper shearing, scaling, and calibrating the 2D 3QMAS spectra, the observed isotropic shift in the indirect dimension can be expressed as **Equation [5.5]**:<sup>15, 16</sup>

$$\delta_{F1-3QMAS} = \delta_{iso} - \frac{10}{17} \delta_{qis}$$

$$[5.5]$$

In contrast to F2 for the direct dimension, the indirect dimension is labeled as "F1", and the observed isotropic shift is denoted as " $\delta_{F1-3QMAS}$ ". By comparing **Equations [5.1]** and **[5]**, there is a prominent inverse relationship of the  $\delta_{qis}$  contribution to the shift position in the F1 dimension of 3QMAS compared to the  $\delta_{F2}$ . **Figure 5.5a** – **c** shows the 2D-sheared <sup>23</sup>Na 3QMAS spectra of the Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub>, at field strengths of 20, 11.7, and 7 T respectively. Properly calibrating the isotropic dimension is usually non-trivial<sup>15, 16</sup> and requires a standard that has no influence from the 2<sup>nd</sup> order quadrupolar effect, where the peak position of this line should possess the same values in both direct and indirect dimensions.<sup>15</sup> Fortuitously, since the Na1 site is well-defined by one set of quadrupolar parameters under all three field strengths (**Figure 5.3d** – **f**), it is possible to treat the peak as an internal standard for the shift calibrations at the F1 dimension. Here, the isotropic shift values of the Na1 can be determined *via* calculating the  $\delta_{qis}$  from its quadrupolar

parameters and then applying **Equation** [5.5] for all three different field strengths. After calibrating the F1 dimension, the average NMR parameters of the Na2-3 peak can be further quantified.

Across the three 2D-sheared 3QMAS spectra as a function of field strength in **Figure 5.5**, a few trends appear. First, in the F1 dimension, the peak separations between Na1 and Na2-3 become more and more significant as the field strength decreases. Moreover, the broadening effect of both peaks in the F2 dimension is more pronounced at lower field. These effects are consistent with the contributions from  $\delta_{qis}$  as a function of magnetic field strength based on **Equations [5.1]**, [5.2], and [5.5]. Second, the Na2-3 shift has much lower signal intensity compared to Na1 in all three spectra. The reduced intensity can be correlated to the faster relaxation effects on the Na2-3 peaks because of their fast dynamics, as discussed in the previous section.



**Figure 5.5 (a)** Processed 3Q-MAS <sup>23</sup>Na spectrum at 20 T, where the horizontal axis is the <sup>23</sup>Na quadrupolar shift with anisotropic components, and the vertical axis is the isotropic <sup>23</sup>Na shift. An enlarge figure highlights the Na1 and Na2-3 peaks for clarity. (b) and (c) show the 3Q-MAS <sup>23</sup>Na NMR spectra with the same axial scales, collected at 11.7 T and 7 T respectively.

The Na2-3 peak also exhibits slightly tilted lineshapes in the F1 dimension for the 2D-sheared 3QMAS spectra, and this effect is more pronounced at 7 T. While it is well-documented that MQMAS experiments are prone to lineshape distortions,<sup>15, 16, 42, 43</sup> this tilted Na2-3 lineshape in the F1 dimension may also result from the different  $P_Q$  contributions from each individual static site, which is not fully averaged during exchange for the coalesced peak. For instance, if the  $P_Q$  for Na2 is larger, it will induce a more significant shift in the F1 dimension under a lower field. However, due to the peak coalescence for Na2-3 as well as low intensity due to faster relaxation, extracting an accurate set of quadrupolar NMR parameters from the individual sites is impossible. Therefore, we treated the center of this peak along the F1 axis as the average shift value (32.4 ppm, **Table S5.1**) of Na2-3 for the 3QMAS analyses.

Finally, **Figure 5.6** demonstrates the results for regression analyses of both  $\delta_{F2}$  and  $\delta_{F1-3QMAS}$  as a function of 1000  $v_L^{-2}$ . In **Figure 5.6a**, the center of gravity  $\delta_{F2}$  values were identified for both Na1 and Na2-3 (**Figure S5.4**). Since Na1 is used as the internal shift standard in 3QMAS, only the  $\delta_{F1-3QMAS}$  values of Na2-3 were plotted in **Figure 5.6b**. All plots in **Figure 5.6** were analyzed using linear regression with fitting qualities of R<sup>2</sup> > 0.999 (**Table S5.1**). The <sup>23</sup>Na quadrupolar NMR parameters were extracted and tabulated in **Table 5.1**, together with standard deviations calculated from linear regression using general error propagation analysis. In summary, the average  $\delta_{iso}$  and  $P_Q$  values for Na2-3 can be assessed from the regression analyses of both 1D <sup>23</sup>Na NMR and 3QMAS spectra. Then, from the average  $P_Q$  values, a range of possible average  $C_Q$  values can be proposed by
considering the range of possible  $\eta$  values between 0 and 1. These average values of  $\delta_{iso}$  and C<sub>Q</sub> determined from these spectra collected at multiple magnetic fields serve as an important constraint for the next step when we employ the EXPRESS program to model the complex coalesced Na2-3 lineshape that results from dynamic chemical exchange between the Na2 and Na3 sites.



**Figure 5.6.** Regression analyses of the <sup>23</sup>Na shift values as a function of the magnetic field strength, where (a) shows the relationship of observed center of gravity shift ( $\delta_{F2}$ ) for both

Na1 and Na2-3 as a function of 1000  $v_L^{-2}$ . (b) Na2-3 exhibits the isotropic shift obtained in the F1 dimension from the 3QMAS experiments ( $\delta_{F1-30MAS}$ ) as a function of 1000  $v_L^{-2}$ .

In order to further constrain the parameters for the EXPRESS simulations of the Na2-3 lineshape, DFT calculations of the <sup>23</sup>Na NMR parameters for the three Na sites in the reported crystal structure<sup>14</sup> of Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> were carried out using the CASTEP program. These calculations do not account for any dynamics, but they do provide estimates of what the <sup>23</sup>Na NMR parameters are for each Na site in the absence of motion and are important parameters for simulating the dynamically averaged lineshape with the EXPRESS program.

In order to assess the reliability of these calculations and to establish the relationship between calculated chemical shieldings and experimental chemical shifts, we first carried out DFT calculations of NMR parameters on a series of sodium-containing materials for which <sup>23</sup>Na NMR data has been previously reported,<sup>17</sup> a summary of which is given in the **Section 5.5**. A comparison of the calculated and experimental <sup>23</sup>Na isotropic chemical shifts ( $\delta_{iso}$ ) reveals decent agreement with a root-mean-square deviation (RMSD) of about 5 ppm, and a maximum deviation of 13.4 ppm. For the <sup>23</sup>Na quadrupolar coupling constants ( $C_Q$ ), the agreement between calculated and experimental values is also decent with an RMSD of 0.36 MHz, with a maximum deviation of 1.21 MHz. Finally, the agreement between calculated and experimental <sup>23</sup>Na asymmetry parameters ( $\eta_Q$ ) is fair, with an RMSD of 0.23 and maximum deviation of 0.62 due to the poor calibration curve established (**Figure S5.7**). The DFT-calculated <sup>23</sup>Na NMR parameters for the three Na sites in Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> are reported in **Table 5.1**. For the Na1 site, which is not involved in sodium ion dynamics, the calculated quadrupolar parameters ( $C_Q$  and  $\eta_Q$ ) are in excellent agreement with the experimental values obtained by fitting the downfield signal of the 1D spectra at multiple fields. The calculated  $\delta_{iso}$  differs from the experimental value by 11.2 ppm, which is just above twice the RMSD but less than the maximum deviation obtained from the calculations on the reference series of sodium-containing materials reported in the Supporting Information. A possible explanation of the poor agreement between the experimental and DFT-calculated isotropic chemical shifts may be the fact that none of the reference series of sodium-containing compounds used to calibrate the DFT calculations contain the heavier elements germanium and tin that are present in Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub>.<sup>17</sup>

The calculated values of the <sup>23</sup>Na NMR parameters for the Na2 and Na3 have no direct experimental data to compare to as they are believed to be coalesced (**Figure S5.5**), but rather serve to constrain the possible values used in the EXPRESS simulation of the dynamically-averaged Na2-3 lineshape. Based on the RMSD values obtained for the calculations on the sodium-containing reference compounds, and the deviation between the calculated and experimental values for the Na1 site reported above, we have constrained the isotropic chemical shifts and quadrupolar coupling constants for the Na2 and Na3 sites in the EXPRESS simulations to be within around  $\pm 10$  ppm and around  $\pm 1$  MHz (at least twice the RMSD, **Table S5.3**) of the DFT-calculated values. These constraints are combined with the previous constraints on the average isotropic shift and the average

quadrupolar coupling constant based on the analysis of the spectra collected at multiple magnetic fields.

#### 5.3.4 Modeling Na2-3 Lineshapes at Multiple Fields Using EXPRESS

Apparently, the static Na2 and Na3 peaks provided in the CASTEP calculations cannot directly account for the experimental lineshape of Na2-3 (**Figure S5.5**), due to the influence of rapid chemical exchange between Na2 and Na3 sites. However, the CASTEP calculations do provide another set of starting points on the quadrupolar parameters for Na2 and Na3, from where we can further constrain the ranges of the parameters tested for the EXPRESS program,<sup>23</sup> to simulate the Na2-3 lineshape under exchange conditions.

EXPRESS simulations were performed by stepping through a series of  $^{23}$ Na quadrupolar parameters for both Na2 and Na3. The set of parameters for Na2 and Na3 were chosen such that they agree well with the experimental  $^{23}$ Na lineshapes under all three fields (summarized in **Table 5.1**), along with a set of Euler angles (**Table S5.2**). The simulated spectra exhibit the best agreement when the Na2 and Na3 are under a chemical exchange rate at the level of ~ 2 × 10<sup>5</sup> Hz (different exchange rates were attempted at 20 T, examples given in **Figure S5.6**). This rate is much faster than the frequency differences between any of the Na sites (at the level of  $10^3$  Hz under 20 T), which explains why the Na2 and Na3 peaks are unresolvable under the NMR timescales. The comparison of the simulated and the experimental lineshapes are presented in **Figure 5.7**. For the unresolved Na2-3 peaks, reasonably good agreements can be seen for the shapes, frequency ranges and the

singularities under multiple fields. Furthermore, by simply averaging the parameters of Na2 and Na3, the mean quadrupolar NMR parameters obtained from the best fit of EXPRESS simulations are in good agreements with the parameters extracted from regression analyses for the F2 and F1-3QMAS, as shown in **Table 5.1**. Even though these quadrupolar parameters might not provide a unique solution, they are generally consistent with the constraints given by the experimental data. In addition, whether these are precise final parameters, the conclusion that Na2-3 sites are involved in the dynamics is well supported by these results. Interestingly, other than the regression analyses, the averaged Na2-3 quadrupolar parameters calculated from CASTEP calculation are similar to the results from EXPRESS as well.

**Table 5.1** A summary of the <sup>23</sup>Na quadrupolar NMR parameters obtained from CASTEP (original CASTEP parameters are available in **Table S5.4**), the regression analyses of F2 and F1-3QMAS, and the best fit from EXPRESS simulations. The estimated  $C_Q$  values from the  $P_Q$  parameters were calculated by setting the  $\eta_Q$  values from 0 - 1, the final range of the  $C_Q$  values include the considerations of error propagation for  $P_Q$ . The parameters of individual Na2 and Na3 sites acquired from CASTEP and EXPRESS are averaged, denoted as "Na2-3 (Avg)".

Sites	Parameter Sources	$\delta_{iso}$ (ppm)	$P_Q$ (MHz)	$C_Q$ (MHz)	$0 \leq \eta_Q \leq 1$
Na1	$\delta_{F2}$ – 1D Fitting	-5.30	2.30	2.24	0.42
	$\delta_{F2}$ – Regression	$-5.2 (\pm 0.2)$	2.32 (± 0.02)	$1.99 \leq C_Q \leq 2.34$	/
	CASTEP	5.91	2.25	2.18	0.45
Na2-3	$\delta_{F2}$ – Regression	-7.9 (± 0.3)	4.21 (± 0.02)	$3.63 \le C_Q \le 4.23$	/
	$\delta_{F1-3QMAS}$	-8.5 (± 0.3)	4.18 (± 0.02)	$3.60 \le C_Q \le 4.20$	/

Na2-3 (Avg)		-8.4	3.88	3.52	0.9
Na2	EXPRESS	0.4	4.47	4.06	0.8
Na3		-17.2	3.44	2.98	1
Na2-3 (Avg)		-6.82	3.61	3.56	0.29
Na2	CASTEP	6.05	4.90	4.85	0.25
Na3		-19.68	2.31	2.26	0.33



**Figure 5.7** A comparison of the experimental and the EXPRESS-simulated <sup>23</sup>Na NMR lineshapes. (a) – (c) are the experimental and (d) – (f) are the simulated spectra under field

strengths of 20, 11.7, and 7 T respectively, with the exchange rate of  $2 \times 10^5$  Hz. The spectra at different field strengths are plotted on varying scales and bounds to emphasize the strong agreements in the peak shapes across each spectrum.

## **5.4 Conclusions**

In summary, <sup>23</sup>Na ssNMR experiments were carried out for the novel Na<sup>+</sup> conductor Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> to reveal the Na<sup>+</sup> dynamics within the structure for unique Na sites. Due to the rapid chemical exchange of Na2 and Na3 sites, the broad lineshapes at lower frequency range in the 1D spectra cannot be resolved into individual Na2 and Na3 quadrupolar peaks, under available experimental conditions. Temperature- and field-dependent relaxation studies demonstrate that the relaxation rates of Na2-3 lineshapes are strongly influenced by their dynamics, suggesting that the unresolved broad lineshapes are the consequences of the Na2 and Na3 chemical exchange. The relaxation rate of Na1 is less affected by temperature and field strength, consistent with the hypothesis that Na1 is stationary within the structure. Conventional 1D and 2D-3QMAS NMR spectra were then analyzed with regression method under multiple fields, to quantify a set of "averaged" values for the NMR parameters of the Na2-3 peak. DFT calculations of <sup>23</sup>Na parameters were in good agreement with the experimentally measured values for the Na1 site and provided constraints on the possible values for the Na2 and Na3 sites. Subsequentially, by utilizing the EXPRESS program with the constraints acquired from the regression analyses and DFT calculations, we were able to simulate a series of 1D NMR spectra that fit reasonably well with the experimental spectra at multiple fields with one set of NMR and chemical exchange parameters. Those parameters are within a reasonable range as the estimated values from experimental data. All these experimental results provide strong evidence for the hypothesis that Na2 and Na3 are the major contributors to the Na<sup>+</sup> conduction in the Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> phase, but Na1 is not involved. This work can be further extended in the future for the Sb-doped Na<sub>4-x</sub>Sn<sub>2-x</sub>Sb<sub>x</sub>Ge<sub>5</sub>O<sub>16</sub> series,<sup>14</sup> which has a much higher ionic conductivity and presumably faster Na<sup>+</sup> dynamics. This methodology could provide insight into understanding the Na<sup>+</sup> transportation mechanisms, and potentially provide valuable information for tuning the crystal structure and composition of other analogue phases, triggering further exploration of better Na<sup>+</sup> conducting ceramic materials for the next generation of ASSNIBs.



## **5.5 Supplementary Information**

**Figure S5.1** VT-NMR experiments for the Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub>. (a) displays the 1D <sup>23</sup>Na spectra as a function of temperature. A change in signal intensity was detected due to the change in the Boltzmann distribution of the nuclear spins. However, Na2 and Na3 peaks cannot be resolved. (b) – (c) are the 2D-sheared 3QMAS spectra collected at 301 and 270 K. No significant difference can be seen between the two spectra.



**Figure S5.2** Examples of fitting the integral intensity of Na2-3 peak with two "dummy peaks" at 20 T (301 K), this approach provides a good description of the experimental spectra under both inversion and recovery conditions for the Na2-3 peak.

**Table S5.1** Summary of the results from the regression analyses, where the intercept values of the linear regression are directly calibrated to be the isotropic shifts\*. The slope is related the inversed squared of the quadrupolar product  $P_Q$  in (1/MHz<sup>2</sup>), with a factor of -1/25 in the  $\delta_{F2}$  analyses, and a factor of 17/250 in the  $\delta_{F1-3QMAS}$  analysis, respectively.

Analyses	Intercept – $\delta_{iso}$ (ppm)	Slope $-(1/MHz^2)$	$\mathbb{R}^2$
Na1			
$\delta_{F2}$ -Regression	-5.2 (± 0.2)	-134 (± 2)	0.99969
Na2-3			
$\delta_{F2}-Regression$	-7.9 (± 0.3)	-427 (± 1)	0.99942
$\delta_{F1-3QMAS}$	-8.5 (± 0.3)	257 (± 3)	0.99989

\*The isotropic shifts of Na2-3  $\delta_{F1-3QMAS}$  are measured to be -3.21, 6.02, and 32.4 ppm for the field strength of 20, 11.7, and 7 T, respectively.



**Figure S5.3**  $T_1$  relaxation fitting curves for Na1 and Na2-3 under the field strength of 20 (a) and (b), 11.7 (c) and (d), and 7 T (e) and (f), respectively. A stretch exponential function was employed for the fittings:  $M(t) = M(0)[1 - 2Ae^{\left(-\frac{t}{T_1}\right)^B}]$ . The *B* values under different magnetic field strengths for Na1 and Na2-3 are ranged from 0.6 – 0.8 and 0.8 – 0.9, respectively.

The center of gravity (C. G.) positions in the F2 dimension were identified, the C. G. of Na1 are obtained by taking the middle position of the two horns. While the C. G. for Na2-3 are primarily based on estimation under 20 T, as the best resolution can be obtained. The C. G. at 11.7 and 7 T are measured at the similar positions, they are slightly off to the right edge of the peak positions.



**Figure S5.4** Identification of center of gravity positions of Na1 (blue lines) and Na2-3 (red lines) peaks under the field strength of 20 (**a**), 11.7 (**b**), and 7 T (**c**), respectively.

The <sup>23</sup>Na quadrupolar NMR parameters (**Table 5.1**) that acquired from CASTEP calculations can model Na1 peak very well, however, the simulated static Na2 and Na3 peaks from CASTEP results do not agree with the experimental ones, as shown in **Figure S5.5**. (All the  $\delta_{iso}$  values from **Table S5.3** were adjusted accordingly by setting the  $\delta_{iso}$  of Na1 at -5.30 ppm because it can best describe the Na1, where  $\delta_{iso}$  for Na2 and Na3 were adjusted to -5.16 and -30.89 ppm, respectively).



**Figure S5.5** Simulated <sup>23</sup>Na MAS NMR spectra using the quadrupolar parameters from CASTEP calculations, under the field strengths of (**a**) 20 T and (**b**) 7 T.

**Table S5.2** Summary of the calculated Euler angles from the CASTEP calculation (Euler angles found using MagresView<sup>44</sup> 2.0) based on the phase crystal structure, and the set of Euler angles that can best describe the experimental <sup>23</sup>Na line shapes. ZYZ convention<sup>23, 44</sup> was used for the Euler angle expression. The EFG shielding tensor of Na1 is set as the principal axes frame (PAF) with the Euler angles of (0, 0, 0). The adjacent Na2 and Na3 sites were found relatively to the PAF. The Euler angles extracted from the CASTEP calculation were not completely agree with those that can best describe the Na2-3 line shapes with EXPRESS, this could be due to the inaccuracies from the CASTEP calculation as mentioned in the main paper.

Sites	Sources	α	β	γ
Na2	CASTEP	136.49	158.26	-108.35
	EXPRESS	98	74	65
Na3	CASTEP	23.63	77.18	-55
	EXPRESS	0	61	20

**Table S5.3** Summary The range of parameters attempted for the EXPRESS simulation is provided, with the increment sizes of stepping shown in the parentheses. In practice, a relatively large increment size was attempted first for a specific parameter to obtain a general trend, then the corresponding parameter was fine-tuned with a smaller size increment, separated by comma.

Parameters	Na2	Na3
$\delta_{iso}$ (ppm)	0-10(1,0.1)	-1525 (1, 0.1)
$C_Q$ (MHz)	2.00 - 4.00 (0.1, 0.01)	3.00 - 5.00 (0.1, 0.01)
$\eta_Q$	0-1 (0.1)	0-1 (0.1)
α (°)	-180 - 180 (6, 1)	-180 - 180 (1)
β (°)	0-240 (6, 1)	10-170 (10,1)
γ (°)	-180 – 180 (10, 1)	-130 - 80 (10, 1)
Rate (Hz)	$1-10^7$ (incremented loga	rithmically over 30 steps)



**Figure S5.6** Simulations of Na2-3 line shapes at 20 T field under different Na2-3 exchange rates with EXPRESS. The rate of ~  $2 \times 10^5$  Hz shows the best agreement with the experimental spectrum.

#### DFT Calculations of <sup>23</sup>Na Quadrupolar NMR Parameters

In order to establish the relationship between calculated and experimental <sup>23</sup>Na NMR parameters, the experimental <sup>23</sup>Na NMR parameters reported by Koller et al <sup>17</sup> for a variety of compounds with sodium ions coordinated by oxygen atoms were used. DFT calculations of <sup>23</sup>Na NMR parameters were performed on the reported crystal structures (without DFT optimization) referred to in the paper by Koller et al and compared to the reported experimental results. Data for the three sodalite structures and the NaI·3DMF structure were not used, while DFT calculations were performed on a subsequently reported crystal structure for NaAlO<sub>2</sub>.<sup>45</sup> The NMR data for NaH<sub>2</sub>PO<sub>4</sub> are those reported by Yon & Massiot<sup>46</sup> and the calculations were performed on the crystal structure reported by Choudhary et al.<sup>47</sup> Since Koller et al<sup>17</sup> reported the isotropic <sup>23</sup>Na chemical shifts with respect to solid NaCl at 0 ppm, these experimental chemical shifts were adjusted by +7.21 ppm to be consistent with the <sup>23</sup>Na spectra reported in this work which was referenced to a 1M aqueous solution of NaCl at 0 ppm.<sup>26</sup>

Plotting the DFT-calculated isotropic <sup>23</sup>Na shielding values against the experimental isotropic <sup>23</sup>Na chemical shifts (**Figure S5.7a**) reveals a decent correlation ( $r^2 = 0.84$ ) with the linear relationship shown in **Equation [S5.1a]**:

$$\sigma_{iso}^{(calc)} = -0.9673 \,\delta_{iso}^{(exp)} + 558.77$$
 [S5.1a]

In order to compare calculated values to experimental values, this equation can be rearranged into **Equation [S5.1b]**:

$$\delta_{iso}^{(exp)} = \frac{\sigma_{iso}^{(calc)} - 558.77}{-0.9673} = -1.034 \,\sigma_{iso}^{(calc)} + 577.66$$
 [S5.1b]

When this equation is used to convert calculated shieldings into chemical shifts, the root mean square deviation (RMSD) between calculated and experimental <sup>23</sup>Na isotropic chemical shifts is 5.0 ppm and the mean absolute error (MAE) is 3.7 ppm.

For the quadrupolar coupling constant ( $C_Q$ ), a plot of the DFT-calculated value against the experimental values (**Figure S5.7b**) reveals a decent correlation ( $r^2 = 0.74$ ) with calculated  $C_Q$  slightly overestimating the experimental values:

$$C_Q^{(calc)} = 1.104 \ C_Q^{(exp)}$$
 [S5.2a]

In order to compare calculated values to experimental values, this equation can be rearranged to

$$C_Q^{(exp)} = \frac{c_Q^{(calc)}}{1.104} = 0.9058 C_Q^{(calc)}$$
 [S5.2b]

When this equation is used to convert calculated  $C_Q$  parameters for comparison to the experimental values, the RMSD between calculated and experimental values is 0.36 Hz and the MAE is 0.24 MHz.

Finally, a comparison of the calculated and experimental  $\eta_Q$  values (Figure S5.7c) reveals a fair correlation with the RMSD between calculated and experimental  $\eta_Q$  values being 0.23, while the MAE is 0.17. All the data referred to here is summarized in Table S5.4.



**Figure S5.7** Correlations between (**a**) DFT-calculated <sup>23</sup>Na isotropic chemical shieldings  $(\delta_{iso}^{(calc)})$  and experimental chemical shifts  $(\delta_{iso}^{(exp)})$ , (**b**) DFT-calculated and experimental

<sup>23</sup>Na quadrupolar coupling constants ( $C_Q$ ), (c) DFT-calculated and experimental quadrupolar asymmetry parameters ( $\eta_Q$ ). See **Table S5.4** for data.

**Table S5.4** Summary of experimental and calculated <sup>23</sup>Na NMR parameters, mostly based on the experimental NMR data and crystal structures reported in Table of 1 of Koller et al.<sup>17</sup>

		Experimental		DFT Calculated			Calculated from correlation			
Compound	Site	δ <sub>iso</sub> (ppm) <sup>a</sup>	C <sub>Q</sub> (MHz)	$\eta_Q$	δ <sub>iso</sub> (ppm)	C <sub>Q</sub> (MHz)	$\eta_Q$	$\delta_{iso} \ ({ m ppm})^b$	С <sub>Q</sub> (MHz) <sup>c</sup>	$\eta_Q$
Silicates										
Na <sub>2</sub> SiO <sub>2</sub> (OH) <sub>2</sub> .8H <sub>2</sub> O		3.54	1.14	0.50	542.38	1.32	0.38	16.94	1.20	0.38
Na <sub>2</sub> SiO <sub>2</sub> (OH) <sub>2</sub> .7H <sub>2</sub> O	Na1	6.27	2.56	0.59	553.54	3.13	0.42	5.41	2.84	0.42
	Na2	6.47	0.81	0.77	552.08	0.89	0.80	6.92	0.81	0.80
Na <sub>2</sub> SiO <sub>2</sub> (OH) <sub>2</sub> .5H <sub>2</sub> O	Na1	5.71	1.35	0.45	552.99	1.85	0.25	5.97	1.68	0.25
	Na2	0.01	2.01	0.70	558.53	2.55	0.83	0.25	2.31	0.83
Na <sub>2</sub> SiO <sub>2</sub> (OH) <sub>2</sub> .4H <sub>2</sub> O	Na1	9.01	1.80	0.75	546.86	1.95	0.78	12.31	1.77	0.78
	Na2	9.51	2.83	0.17	545.04	3.15	0.19	14.20	2.85	0.19
Na <sub>2</sub> SiO <sub>3</sub>		22.66	1.46	0.71	532.75	1.52	0.62	26.90	1.37	0.62
$\alpha$ -Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>		24.61	1.82	1.00	542.12	1.94	0.56	17.21	1.76	0.56
$\beta$ -Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	Na1	27.61	2.50	0.00	543.91	2.52	0.62	15.36	2.28	0.62
	Na2	15.51	2.22	0.55	550.86	2.07	0.83	8.17	1.87	0.83
Phosphates										
Na <sub>3</sub> P <sub>3</sub> O <sub>9</sub>	Na1	-7.59	2.20	0.70	567.54	2.38	0.59	-9.06	2.16	0.59
	Na2	1.61	1.57	0.55	556.27	1.76	0.52	2.58	1.59	0.52
NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O		2.41	1.19	0.46	556.15	1.29	0.36	2.71	1.16	0.36
NaH <sub>2</sub> PO <sub>4</sub> .H <sub>2</sub> O		-3.48	1.22	0.26	558.20	1.54	0.08	0.59	1.40	0.08
$NaH_2PO_4^d$	Na1	-2.1	1.57	0.47	564.20	1.84	0.54	-5.61	1.66	0.54
	Na2	-6.0	2.36	0.95	568.88	2.90	0.91	-10.45	2.63	0.91
Other compounds										
Na <sub>2</sub> SO <sub>4</sub>		-1.29	2.60	0.58	561.48	3.16	0.23	-2.81	2.86	0.23
NaAlO <sub>2</sub> <sup>e</sup>		26.21	2.15	0.60	530.54	2.50	0.46	29.18	2.27	0.46
NaOH		19.41	3.50	0.00	534.39	2.53	0.01	25.21	2.29	0.01
Na <sub>2</sub> CrO <sub>4</sub>	Na1	-12.79	2.78	0.57	578.02	3.64	0.50	-19.90	3.30	0.50
	Na2	-6.69	0.50	0.00	566.25	0.93	0.43	-7.74	0.85	0.43
NaClO <sub>4</sub>		-18.29	0.80	0.35	578.58	1.22	0.65	-20.48	1.10	0.65
NaClO <sub>4</sub> .H <sub>2</sub> O	Na1	-4.49	1.71	0.20	563.28	1.69	0.40	-4.67	1.53	0.40
	Na2	-5.19	1.48	0.10	565.57	1.51	0.27	-7.03	1.37	0.27

NaCl		7.21	0	0	545.71	0.00	0.00	13.50	0.00	0.00
Na <sub>2</sub> C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> .H <sub>2</sub> O	Na1	-2.39	1.30	0.82	559.22	1.90	0.77	-0.47	1.72	0.77
	Na2	1.11	0.77	0.77	555.48	1.88	0.31	3.40	1.70	0.31
$Na_4Sn_2Ge_5O_{16}^f$	Na1	-5.59	2.24	0.44	553.05	2.41	0.45	5.91	2.18	0.45
	Na2				552.92	5.36	0.25	6.05	4.85	0.25
	Na3				577.81	2.49	0.33	-19.68	2.26	0.33

<sup>*a*</sup> The <sup>23</sup>Na isotropic chemical shifts reported in Koller et al were adjusted by +7.21 ppm so that 0 ppm = 1M solution of NaCl

<sup>b</sup> These calculated <sup>23</sup>Na chemical shifts were converted from DFT-calculated chemical shieldings using **Equation [S5.1b]** 

 $^{c}$  These "corrected" calculated C<sub>Q</sub> values were converted from the DFT-calculated C<sub>Q</sub> values using **Equation [S5.2b]** 

<sup>*d*</sup> Experimental NMR data from Yon & Massiot 2020; Crystal structure from Choudhary et al 1981

<sup>e</sup> Crystal structure from Kaduc & Pei, 1995

<sup>f</sup> This work



**Figure S5.8** <sup>119</sup>Sn ssNMR spectra at 20 T (MAS = 25 kHz), the Sb-doped sample exhibits a broader <sup>119</sup>Sn line shape due to the local structural disorder.

**Figure S5.8** shows the <sup>119</sup>Sn ( $I = \frac{1}{2}$ , natural abundance of 8.59%) ssNMR spectra collected at 7 T. For both the pristine and the Sb-doped (x = 0.20) phases, there is only one major peak can be seen on the ssNMR spectra, the chemical shift of the Sb-doped phase at -628.3 ppm, exhibits nearly no change relative to pristine phase at -627.2 ppm. Nevertheless, the Sb-phase shows a significant broaden peak width of 3.33 kHz, whereas the pristine phase is only 1.36 kHz. The almost doubling of peak width for the Sb-doped phase indicates that there are more local disorder Sn<sup>4+</sup> environments created from the partial substitution of Sb<sup>5+</sup> at the 8d position.



Figure S5.9  $^{23}$ Na ssNMR spectra at 20 T (MAS = 25 kHz).



**Figure S5.10**  $^{23}$ Na ssNMR spectra at 7 T (MAS = 10 kHz). Spinning sidebands are labeled with asterisks.

The comparison of <sup>23</sup>Na ssNMR spectra for both the pristine and Sb-doped (x = 0.20) phases are shown in **Figure S5.9** and **S5.10**, recorded at 20 and 7 T, respectively. After doping with Sb<sup>5+</sup>, the peak shapes of both Na1 and Na2-3 changes, it's also noticed that the Na2-3 peak shifts toward to higher frequency. Under the field strength of 7 T, the resolution is completely lost between the Na1 and Na2-3 peaks, but the Na1 still remains at a similar position and potentially exhibits a quadrupolar lineshape (with different parameters). Two dominant peaks can be partially resolved at 20 T (**Figure S5.9**), both peaks exhibit Gaussian-like features. Based on their positions, it is reasonable to assign the

peak at higher frequency to "new Na1", and the one at lower frequency to "new Na2-3", upon Sb-doping. These results suggests that there are local structural disorders generated by partially substitution of Sb<sup>5+</sup>, this is consistent with the observation on the <sup>119</sup>Sn ssNMR. Furthermore, the loss of resolution between the Na1 and Na2-3 peaks could indicate an increase in Na<sup>+</sup> dynamics, with Na1 potentially also participating in this process. Replacing Sn<sup>4+</sup> with Sb<sup>5+</sup> creates vacancies for Na<sup>+</sup> to preserve the charge balance, which can facilitate the Na<sup>+</sup> transportation through vacancy migration mechanism.<sup>48</sup> Previously, it was believed that the Na<sup>+</sup> vacancies were created stoichiometrically.<sup>14</sup> Thus, it is possible that vacancies were also produced at the Na1 sites and resulting in the Na<sup>+</sup> mobility at all the Na crystallography sites, leading to a set of much more complicated <sup>23</sup>Na ssNMR to analyze. Hence, collecting the <sup>23</sup>Na spectrum for this sample at other field (such as 11.7 T) is necessary in our follow-up explement. This could provide valuable insights into the Na<sup>+</sup> conduction mechanisms in this class of material.

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# Chapter 6 – Stack Pressure Effects on Interfacial Li Morphologies for HE-Based Li Metal Batteries Using *In Situ* <sup>7</sup>Li Imaging

This chapter demonstrates the current progress of the *in situ* studies on the Li interfacial morphologies under the influence of stack pressure effects. The ideas for this project were generated from discussion with Prof. Goward as we moved from a focus on *operando* measurements of liquid electrolytes toward investigations of solid-state electrolytes. The modifications of pencil cell to include pressure sensitivity and control were achieved by the author. Data collections and analyses were performed by the author. C. A. Gurwell conducted the sample preparation and pressure calibration parts, he also contributed to the prototype design for the new pencil cell. K. J. Sanders contributed to the MRI pulse developments and training. Both K. J. Sanders and G. R. Goward participated in the discussions and provided suggestions along the way with this project.

This chapter investigates an interesting phenomenon regarding how the applied stack pressure affects the Li morphology in ASSBs using Li metal and during the stripping and plating of Li metal. By utilizing *in situ* <sup>7</sup>Li NMR spectroscopy, the Li morphological changes were detected for the cells prepared at lower stack pressures, indicated by newly formed Li microstructures. These microstructures were further located at the interfaces of the plated Li metal foil after cycling, using the CSI technique. The results demonstrate that the stack pressure strongly influences the interfacial microstructual Li formation during galvanostatic cycling, which provides insight into the overall mechanical stability and performance of ASSBs.

## **6.1 Introduction**

Since the commercialization of Li-ion batteries (LIBs) in the 90s, consumers have witnessed enormous developments in portable electronics and electric vehicles (EVs). It is recognized that there is a growing demand for higher energy density from the booming LIB industry. Li metal batteries (LMBs) are highly favored in battery research because Li metal has a high theoretical gravimetric and volumetric capacities of 3860 mA h g<sup>-1</sup> and the lowest standard reduction potential of -3.04 V vs S.H.E., making it one of ultimate anodic candidate materials.<sup>1</sup> However, the implementation of Li metal in combination with traditional (liquid electrolytes) LEs can easily induce dendritic Li growth, which poses significant safety risks, preventing the further development of LMB since the unsuccessful attempt by Moil energy, which dates back to the late 1980s.<sup>2</sup> The rapid development of solid crystalline electrolyte (SCE) materials<sup>3-5</sup> in the recent decades has significantly advanced the possibility of using Li metal as anode. The SCEs received considerable attention because they are much more thermally stable than the traditional LEs. Nevertheless, sluggish Li<sup>+</sup> transport at the grain boundaries (GBs) and electrode-electrolyte interfaces hinders the practical utilization of SCEs. Therefore, improving ion transport at the interfaces is crucial for enhancing the large-scale application of ASSBs.

Different strategies have been explored to address the above mentioned problem. The first strategy is to use hybrid electrolytes (HEs) that combines SCE and ionic liquids (ILs). They can be considered as better alternatives, due to the good chemical and electrochemical stability of ILs,<sup>6</sup> which improves interfacial Li<sup>+</sup> transport<sup>6, 7</sup> and creates the uniform Li deposition supressing the dendritic Li growth.<sup>6, 8</sup> The second strategy is to apply stack pressure to the SCEs, which differs from the fabrication pressure presented previously in Chapter 4. Stack pressure refers to the uniaxial mechanical force applied to the sandwiched ASSB during the battery operation, to ensure intimate contact between the electrolyte and electrode components. Wang et al. studied the effects of active stack pressure on the electrochemical performances of a symmetric Li cell, using garnet Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>O<sub>12</sub> (LLZO) as the SCE. It was reported that a higher stack pressure can prevent void formation, under which the symmetric cell can be cycled at a higher current density.<sup>9</sup> Hayashi et al. also suggested good conductivity can be achieved for a sulfide glass SE with higher stack pressure, due to the low interfacial resistances.<sup>10</sup> Doux et al., previously demonstrated that a moderate stack pressure of 5 MPa can be effective when cycling the argyrodite Li<sub>6</sub>PS<sub>5</sub>Cl (LPSC) against Li metal, but higher pressure up to 25 – 75 MPa could cause Li metal to creep through the GBs due to the low yield strength of Li metal (0.8 MPa), inducing mechanical short-circuiting.<sup>11</sup> Ning et al. reported similar findings for the LPSC, with a cycling rate in between 4 mA cm<sup>-2</sup> and 50  $\mu$ A cm<sup>-2</sup>, the Li filaments can propagate through the SCE and short the cell, promoted by even a moderate pressure of 7 MPa.<sup>12</sup>

Currently, there is very limited information regarding how the stack pressure can affect the microstructual Li behaviours in the LMBs that utilize HEs.<sup>13</sup> Apparently, mixing different electrolyte phases can significantly alternate their mechanical properties.<sup>14, 15</sup> Additionally, most of the electrochemical data presented in the above-mentioned studies were later analyzed with scanning electron microscopy (SEM) and X-ray computed tomography (XCT) to provide spatial Li microstructural information. Nevertheless, Li metal microstructures cannot be easily detected by X-ray based techniques due to its low

scattering efficiency in comparison to the SSEs.<sup>11</sup> Distinguishing them from voids within the SSE body can be challenging. Previously, Marbella et al.<sup>16</sup> demonstrated an *in situ* <sup>7</sup>Li NMR and chemical shift imaging (CSI) study on a garnet-type LLZO electrolyte. The robustness of utilizing <sup>7</sup>Li NMR is because the <sup>7</sup>Li Knight shift appears in an unique range of 240 - 280 ppm,<sup>17, 18</sup> making it distinguishable from the other Li-containing species (e.g. electrolytes at ~ 0 ppm). In addition, the Knight shift of the microstructural Li has an orientational dependency relative to the external magnetic field, which has been well documented before and can be explained by the bulk magnetic susceptibility effects.<sup>18-21</sup> In their report, the early stage of dendritic Li microstructure was detected based on the spectroscopic information. The growth of the dendritic Li during galvanostatic cycling were clearly illustrated, based on the spatial information from CSI.<sup>16</sup> Similar design of the *in situ* cell and the 1D imaging experiments were also conducted by our group before for other cell chemistries using LEs.<sup>22, 23</sup>

Here we present our study that examines the impact of stack pressure on the interfacial Li microstructures formation for the HE-based symmetric Li cell, with the *in situ* NMR setup that similar to the works mentioned above. In this study, a combination of Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP) SCE and Pyr<sub>14</sub>-TFSI LiTFSI was employed, as both materials have excellent thermal and electrochemical stabilities.<sup>5, 24, 25</sup> We utilized *in situ* <sup>7</sup>Li NMR and MRI to probe the interfacial Li morphological change at the Li-electrolyte interfaces, under various stack pressures and correlated them to the electrochemical charging characteristics of the cells. This contribution potentially increases the feasibility of understanding the engineering of the LMB by employing *in situ* MR techniques.

## 6.2 Methods

#### 6.2.1 Cell Preparation and Stack Pressure Calibration

The LAGP nano-powder was purchased from Toshima manufacturing Ltd (Japan) without further purification. Inside an MBraun Ar-filled glovebox, the HE mixtures were prepared by grinding LAGP and Pyr<sub>14</sub>-TFSI : LiTFSI 9:1 (mol.) (IL, Solvionic, France) in a gravimetric ratio of 80% : 20% with a mortar and pestle. Then the HE mixtures were transferred into a 4 mm die set, and then compressed under the axial pressure of 110 MPa, utilizing a YLJ-15L laboratory hydraulic press (MTI Corporation, USA), forming the HE pellets with the thickness of around 3.5 - 4 mm. For each cell, Li ribbon (99.9%, Sigma-Aldrich) with the thickness of 1.5 mm was firstly rolled into the thickness of ~ 0.1 – 0.2 mm, then cut into two circular foils with the diameter of 4 mm. The two piece of Li foils were further adhered on two Cu current collectors. The compressed HE pellets were then sandwiched by the two Li foils within the *in situ* NMR cell (referred as "pencil cell"), which is made of polyether ether ketone (PEEK) rod, forming the symmetric Li/LAGP-IL/Li cell. The design of the cell has been previously published,<sup>23</sup> and the schematic diagram of the cell geometry is shown in **Figure S6.1**.

The HE pellets were sandwiched in between the two Li foil with a controlled stack pressure in the cell body were applied *via* inducing torque to the threaded HPLC ferrules (referred as "nuts" in the following context) on the PEEK cell. To correlate the torque when tightening the nuts with the internal stack pressures, Fujifilm *Prescale*® pressure sensor films were purchased from Sensor Products Inc (SPI, USA) to calibrate the stack pressures,

the detailed discussion of the calibration is described in the Section 6.6 and Figure S6.2. Once the cell is assembled inside the glovebox, epoxy was applied to seal the cell, preventing sample degradation during the *in situ* experiments. Three stack pressures were studied here  $-21 (\pm 3)$ ,  $12 (\pm 1)$ , and  $6 (\pm 1)$  MPa. For convenience, these cells are referred to as 20, 10, and 5 MPa in the following discussion. In our experiments, three cells were prepared for each pressure separately, instead of running a continuous experiment for one cell under the same current density as Wang et al. reported.<sup>9</sup> This is due to the different cell setups. Wang et al. used a compression testing unit inside an Ar-filled glovebox, which provides dynamically controlled axial stack pressures.<sup>9</sup> In contrast, the stack pressures applied in the *in situ* cells in this study were achieved by tightening the nuts, changing the stack pressure requires taking the cell out of the magnet and readjusting the torque values. In such way, the Li-electrolyte interfaces will be destroyed due to the unavoidable shearing forces when unscrewing the nuts. Therefore, we prepared three separate cells and studied the stack pressure effects by comparing their electrochemical and *in situ* NMR/MRI results.

### 6.2.2 In Situ NMR Setup and Electrochemical Cycling

The pencil cell was placed in an 8 mm  ${}^{7}\text{Li}/{}^{19}\text{F}$  double resonance coil inserted in a Bruker Diff50 diffusion probe, positioning vertically inside the RF coil, aligning with the external field  $B_0$ . This orientation guarantees the  $B_1$  field is parallel to the electrode surfaces, so that metallic Li and Cu current collectors do not block the RF penetration. Coaxial cables were extended through the bore of the magnet and connected to the potentiostat externally (**Figure 6.1**). All experiments were performed on a Bruker Avance 300 spectrometer (7 T). 1D <sup>7</sup>Li NMR spectra were collected with a pulse power of  $8 - 9 \mu s$  at the power levels of 60 W. The spectral deconvolutions and analyses were performed using ssNake v1.3.2.<sup>26</sup> The error bars for integral intensity of Li microstructures were calculated statistically based on the intensity differences of each point between the experimental spectra and the fits within the range of 250 – 350 ppm, averaged by number of data points and scan numbers.

Galvanostatic charging cycle was performed on each cell prepared under variable stack pressures, using a constant current of 6.2  $\mu$ A (corresponding to 50  $\mu$ A cm<sup>-2</sup>) for a set duration of 2 hours, with the sampling rate of 1 point s<sup>-1</sup>. A 30 min open-circuit voltage (OCV) period was applied prior to the 1<sup>st</sup> charging allowing the cell to reach its stabilization voltage. The current direction was chosen to strip the bottom Li metal foil and plate the top Li metal foil, as shown in **Figure 6.1**. The charging protocol were applied using Gamry Interface 1000 analyzer (potentiostat), with the maximum cutoff voltage of 5 V for each charging cycle. The NMR and MRI experiments were collected before and after the 1<sup>st</sup> charging cycle for each cell. In this work, the maximum thickness of stripped (plated) Li is estimated to be 0.5  $\mu$ m. See calculations in **Equation [S6.1]** – **[S6.3]**.



Figure 6.1 A schematic diagram of the *in situ* NMR setup used in this work. The pencil cell is positioned vertically, aligning with  $B_0$ . Coaxial wires are connected externally to the potentiostat for electrochemical cycling.

### 6.2.3 <sup>7</sup>Li MRI Experiments

We performed two types of MRI experiments for the *in situ* pencil cells prepared at different stack pressures. An imaging echo sequence (shown in **Figure 2.21a**) was utilized to provide initial <sup>7</sup>Li diagnostic images, in order to reveal the spatial distributions of the bulk HE pellets and the Li metals as the cell was installed. For the electrolyte region, the transmitter frequency offset (O1) was set to 0 Hz to capture the diamagnetic region, with the excitation power of 28600 Hz. A square-wave frequency-encoding gradient was employed, with the gradient strength of 30 G cm<sup>-1</sup> (aligns  $B_0$ ). The sampling rate (dwell time) was set to 8  $\mu$ s, and the total *n* of 512 points, total signal was averaged over 32 scans, resulting in a signal-to-noise ratio (SNR) of 93. For the metallic Li region, the O1 was set to 28000 Hz, corresponding to ~ 240 ppm shift of <sup>7</sup>Li at 7 T ( $v_0 = 116.7$  MHz). To avoid

excitation of the dominant electrolyte signal, a Gaussian shape selective pulse with the power of 1250 Hz was used for excitation of metallic Li signal only. The maximum frequency-encoding gradient was set to  $150 \text{ G cm}^{-1}$  to account the coherence loss of metallic <sup>7</sup>Li signal due to the fast  $T_2$  relaxation of ~  $500 - 800 \ \mu$ s. The sampling rate was set to 0.6  $\mu$ s to account for the loss of FOV due to high gradient, with the total *n* of 512 points. The number of scans were set to 4096 due to the severe signal decay from the fast  $T_2$  relaxation, with the final SNR of 35. A waiting period of at least 100  $\mu$ s is applied before reaching the maximum echo intensity to ensure the gradient power has stabilized at a constant value for all the imaging echo experiments. Aqueous 1M LiCl solution was used as the chemical shift reference at 0 ppm for the <sup>7</sup>Li NMR spectra.

The second type of experiment is chemical shift imaging (CSI), the pulse sequence used in this work is shown in **Figure 2.22**. The O1 was set to 14000 Hz (~ 120 ppm) to capture the signals from both electrolyte and metallic Li region on the NMR spectra, with the excitation pulse power of 28600 Hz The power of phase-encoding gradient pulse was varied from -120 to + 120 G cm<sup>-1</sup> linearly over 64 steps in the indirect dimension, with the pulse duration of 256  $\mu$ s. The smooth square shaped pulse employed to minimize the artifacts induced by high gradient power. The total number of scans were set to either 512 or 1024 (accounts for the phase cycling of 8) to ensure good signal intensity of the metallic Li metal. The two dimensional spectra were processed using Bruker Topspin 4.1.0. In the 2D <sup>7</sup>Li CSI spectra, the signals of Li foils were enhanced by different magnification relative to the dominant signals from HE pellets.

## **6.3 Results and Discussions**

#### 6.3.1 Electrochemical Analyses of the Cell Performances

In order to investigate the effect of stack pressure on the voltage behavior for the symmetric Li/LAGP-IL/Li, the unidirectional constant current with the density of 50  $\mu$ A cm<sup>-2</sup> was applied to three cells prepared under different stack pressures of 20, 10, and 5 MPa. Figure 6.2a and 6.2b show the voltage and current curves as a function of charging time of each cell. The 20 MPa cell exhibits a relatively flat voltage curve, remaining at nearly 0 V throughout the entire charging process, which indicates that the internal resistance within the 20 MPa cell is minimal.<sup>9, 27</sup> In contrast, the cells prepared at 10 and 5 MPa both show unstable voltage curves. At the beginning the charging, the 10 MPa cell exhibits an increase in overpotential of 0.28 V within 8 mins, then stabilized at  $\sim 0.3 - 0.4$ V for the rest of the charging time, until the charging duration reaches 56 mins. After this point, the cell experienced significant polarization, ending the test abruptly as the cutoff voltage was reached. The 5 MPa cell experienced a nearly constant increase in the voltage throughout the entire charging process, reaching a significant polarization at the charging time of 48 mins. In addition, Figure 6.2b shows that the current curve of the 5 MPa cell experiences significant noises in comparison to the other two. This unstable input current may be attributed to reduced stability of the control amplifier on the potentiostat, which is a result of the increased cell resistance. The higher input current density alternated by the control amplifier also suggests a corresponding increase in resistance due to Ohm's law.


**Figure 6.2 (a)** The voltage response to a galvanostatic charging at 50  $\mu$ A cm<sup>-2</sup> under variable stack pressures. The measured voltage from the working electrode (E<sub>w</sub>) is corrected to the initial voltage (E<sub>0</sub>) at the beginning of constant current charging. (b) The current curve during the 1<sup>st</sup> hour of charging cycle.

The increase in cell resistance or polarization that is observed during the ASSBs cycling can typically be correlated with two main factors. The first factor is the formation

of decomposed products at the unstable electrolyte-electrode interfaces, which leads to ionblocking phases and ultimately increases the total cell resistance, causing cell voltage to polarize.<sup>27, 28</sup> The second factor can be correlated to the loss of contact between the electrolyte-electrode interface during cycling, thus increase the interfacial resistance across the cell.<sup>9, 29, 30</sup> The "void-induced polarization" mechanism was previously introduced by Wang and co-authors.<sup>9, 30</sup> Briefly, if the rate of Li stripping is too fast while the low mechanical pressure cannot provide sufficient contacts, an uneven "Li<sup>+</sup> flux" at the Lielectrolyte interfaces can occur during the stripping processes. The uneven stripping of Li metal further causes Li microstructures formation, as well as contact loses at the interfaces. This leads to a decrease in contact areas, which in turns results in significant cell polarization.<sup>9</sup>

Here, the Pyr<sub>14</sub>TFSI-LiTFSI was used as the IL, which possess a stable electrochemical window up to 5 ~ 5.5 V vs (Li/Li<sup>+</sup>).<sup>24, 25</sup> In addition, LAGP is known to exhibit extraordinary electrochemical stability against Li up to 6 V, outperforming its LATP analog.<sup>5</sup> Therefore, we hypothesize that the observed polarization phenomena for the low pressure cells is mainly attributed to the poor interfacial contact under variable stack pressures, and can be explained by the void-induced polarization. Furthermore, Wang et al. also introduced the concept of "critical stack pressure",<sup>9</sup> which is the minimum stack pressure required to maintain intimate contact between the Li-electrolyte interface under a fixed current density without causing cell failure.<sup>9</sup> Conversely, the term "critical current density" can be defined as the maximum current density that can be applied to a cell without failure, under a fixed stack pressure.<sup>9, 29</sup> In this study, since all the cells were tested at a low

current density of 50  $\mu$ A cm<sup>-2</sup> in comparison to the other studies in this field,<sup>9, 10, 13, 16, 27, 31, <sup>32</sup> we ensured all the cells prepared at even lower stack pressure would not undergo immediate polarization upon charging. Thus, we have designed the study such that the effect of critical stack pressure is more closely associated with the electrochemical phenomena. In short, the combination of low current density and variable stack pressure provides the possibility for us to investigate any interfacial changes.</sup>

#### 6.3.2 Revealing Li Interfacial Morphology Changes under Stack Pressures

1D <sup>7</sup>Li NMR spectra were collected for three different cells prepared at three different stack pressures as shown in **Figure 6.3**. Spectra were collected before and after the 1<sup>st</sup> galvanostatic charging for each cell, and the resulting spectra were superimposed together in the range of -20 - 320 ppm. For all cells, the dominant peak is attributed to the HE pellets at ~ 0 ppm. Although the IL signal is expected to appear at -1.4 ppm (**Figure S6.3**), it is not observable in these spectra here due to the overwhelming signal from the LAGP, which dominates the entire diamagnetic region. This observation is consistent with the calculated of Li signals based on the HE composition, where the Li content ratio between LAGP and IL is approximately 50:1. The one of the satellite transitions (ST+) horns of LAGP can be observed at ~ 100 ppm. These signals do not undergo any detectable changes before and after the charging.

Across all three cells, the <sup>7</sup>Li signals at around 240 - 280 ppm are corresponding to the <sup>7</sup>Li Knight shift, which arises from the interaction between nuclei and conductive

electrons within the metallic Li component. Two distinct types of Li metal peaks can be identified. The first type, in the range of 245 - 250 ppm, corresponding to the bulk Li foil positioning perpendicular to  $B_0$ . The second type of peak, appearing in the range of 250 - 280 ppm, can be correlated with the Li filaments or Li stripes with other different orientations. <sup>18-21</sup> The orientational dependence of the metallic <sup>7</sup>Li signal can be explained by the bulk magnetic susceptibility effects. <sup>18-21</sup> The formation of Li microstructures or dendrites during cycling is often linked with the appearance of new <sup>7</sup>Li signal in a different shift region in *in situ* NMR, <sup>16, 17, 33</sup> reflecting the morphological changes of Li metal. In our case, since the cells were positioned such that the pristine Li metal foil is perpendicular to  $B_0$ , we can assign the peaks in 245 – 250 ppm to be the pristine foils, and the formation of new peaks within the 250 – 280 ppm range corresponded to Li microstructures induced by stripping/plating.

**Figure 6.3a** presents the <sup>7</sup>Li spectra of the 20 MPa cell, the main peak at 245 ppm is the pristine Li foil. However, a notable shoulder appears at approximately 254 ppm even before the charging cycle starts. This observation can be related to the mechanical deformation of Li metal due to the application of 20 MPa of stack pressure, as Li metal has a very low yield strength of 0.8 MPa and can be easily deformed by mechanical forces.<sup>11</sup> This deformation is further confirmed by the 1D imaging echo and post-experiment cell inspection (**Figure 6.4**), as well as in the 2D-CSI image (**Figure 86.4**). As shown, in addition to the deformed Li metal, the HE pellet was also deformed at the top edge. Nevertheless, the 20 MPa cell exhibits a nearly unchanged Li morphology. Since the 20 MPa cell demonstrates the best electrochemical performance during the charging, it is not

surprising that the interfaces between the Li and HE pellet remain stable throughout the charging process.



**Figure 6.3** 1D <sup>7</sup>Li NMR spectra collected for the pencil cells before (black solid lines) and after (red dash lines) the galvanostatic charging at 50  $\mu$ A cm<sup>-2</sup>, these cells were prepared with the stack pressures of (**a**) 20 MPa (**b**) 10 MPa and (**c**) 5 MPa, respectively.



**Figure 6.4** 1D <sup>7</sup>Li NMR image recorded for the 20 MPa cell. (**a**) and (**b**) shows the MR images of HE region and metallic region, respectively. (**c**) and (**d**) shows the photos of the corresponding regions, taken when the pencil cell was disassembled after the *in situ* experiments.

As for the cell prepared at 10 MPa, a noticeable change in the Li morphology was detected, with a new <sup>7</sup>Li signal showed up at around 268 ppm in addition to the pristine Li foil at ~ 241 ppm. As discussed earlier, this indicates the formation of new microstructural Li. As shown in **Figure 6.2a**, the 10 MPa cell exhibited a smooth charging curve for about 56 mins, but began to experience polarization afterwards, which ended the charging cycle prematurely. Hence, the formation of new <sup>7</sup>Li peak at 268 ppm can be correlated with new microstructure Li formation. However, the 1D <sup>7</sup>Li NMR spectra alone cannot distinguish

whether the newly formed microstructural Li is interfacial or dendritic,<sup>16, 20</sup> because it does not provide spatial information across the cell. Thus, CSI of the 10 MPa cell was recorded to probe the location of the microstructural peak, shown in **Figure 6.5**.



**Figure 6.5** <sup>7</sup>Li CSI for the 10 MPa cell after polarization of the cell. With two slices of spectra extracted for each of the top and bottom Li foils at the position of -2.64, -2.53, 1.54, and 1.65 mm. The direction of  $Li^+$  plating is indicated with the arrow. The signal of Li metal signal at ~ 250 ppm is magnified by 20 times compared to the signal of the HE pellet.

In the 2D CSI image, no visible dendritic Li grow was observed after polarization of the 10 MPa cell. Previously, Marbella et al. reported a study on the LLZO SCE using similar *in situ* experimental setup.<sup>16</sup> In their study, dendritic Li formation and growth was observed after cycling at 500  $\mu$ A cm<sup>-2</sup> for 4 – 12 hours (under 8 MPa), which eventually shorted the cell.<sup>16</sup> However, in our case, the polarization was applied in only one direction, thus the short charging time and limited number of cycles was not sufficient for dendritic Li to build up. To further investigate the locations of new microstructual Li, two slices of spectra were extracted for each Li foil overlaid with the 2D CSI in **Figure 6.5**. It is notable that the plated Li foil (at the top) exhibits a more asymmetrical peak shape, with the shoulder in the range of ~ 260 - 275 ppm. Upon closer inspection, the Li metal region at the interface (1.54 mm) shows a notable microstructural peak centered at around 260 ppm. This evidence suggests that the major Li microstructures in the 10 MPa cell formed primarily at the interface of the *plated* Li foil, instead of the *stripped* Li foil, as proposed by Wang et al.<sup>9</sup> In addition, Chang et al.<sup>17</sup> used the similar *in situ* MR setup to investigate the microstructual Li grow for a LLZO SCE, they noticed that only the plated Li foil exhibits a significant microstructure Li upon one-directional platting,<sup>17</sup> our experimental results agree well with their observations.

In **Figure 6.3c**, the 5 MPa cell also shows the appearance of new Li microstructures in the range of 253 – 270 ppm in the <sup>7</sup>Li spectrum. Again, this observation is consistent with our hypothesis that the polarization of the cells prepared at low stack pressures resulted from unstable interfacial contacts during plating and stripping of Li metals, indicated by the Li microstructure formations. CSI was also performed before and after the cell polarization to reveal the spatial locations of the Li microstructures, the example of after polarization is shown in **Figure S6.5**. To closely inspect the peak shapes at the Li region, the interfacial Li metal peaks were extracted from two CSI images, representing the Li change before and after the charging, shown in **Figure S6.6**.

The differences between the <sup>7</sup>Li signals before and after the charging process are not clearly evident for the 5 MPa cell (**Figure S6.6**). In the CSI experiment, the metallic Li

signals were phase-encoded by gradient in the xy-plane,<sup>34</sup> in our experiment the encoding (and decoding) time was set to 1 ms. Since the <sup>7</sup>Li peak of metallic Li has a short  $T_2$ relaxation time of ~ 800  $\mu$ s, this could result in significant signal loses even with 1024 scans. Nevertheless, CSI provides the spatial resolution of the microstructural Li, indicating that these microstructures were formed at the interface, rather than dendritic Li growth. To better quantify the microstructures, spectral deconvolutions were performed on the 1D <sup>7</sup>Li NMR. This allows for a more detailed analyses of the interfacial Li morphological change as a function of stack pressure, presented in the following section.

#### 6.3.3 Quantifying the Interfacial Li Microstructures at Different Stack Pressures

The follow-up quantification of interfacial Li microstructure formation was conducted on the 1D <sup>7</sup>Li NMR spectra. Briefly, spectral deconvolution was performed for each cell before and after cycling. For the spectra recorded before cycling, the positions of the main metallic Li peaks were fixed within a tolerance of 1 ppm of fluctuation, representing the bulk Li foil at 245 or 240 ppm. Additionally, the positions of any peaks appearing in between 250 - 270 ppm due to the mechanical deformation or titled cell were constrained as well. Following this, the fittings were performed for the spectra after charging. By subtracting the peak intensities in 250 - 270 ppm before and after charging, we can obtain the increase in microstructual Li content after charging. The relative integral intensity changes of microstructual Li and the deconvolution of spectra are shown in **Table 6.1** and **Figure S6.7**. The preceding analyses of the correlation between microstructual Li

formation as a function of stack pressure, the data was plotted in **Figure 6.6**. It is important to note that the excitation of RF shielding effects from the metallic Li,<sup>19</sup> only the Li signals at around the interface of 14.7  $\mu$ m ("skin depth")<sup>19</sup> were excited. The integral intensity percentage of the Li foil, derived from the spectral deconvolution, should not be treated as the total intensity of the entire Li foil. Instead, it represents only a small amount of interfacial Li. Nevertheless, by the relative signal enhancement (in %) of the microstructural Li across all three cells, it is evident that these values are notably different.



**Figure 6.6** Correlating the relative signal enhancement of microstructual Li in the <sup>7</sup>Li 1D spectra as a function of stack pressure for HE cells.

Therefore, result presented here demonstrates a correlation between the microstructural Li, stack pressure, and cell polarization. As the stack pressure increases, the relative integral intensity of microstructural Li decreases, accompanied by more stable

charging performance. By examining the NMR and MRI results and in conjunction with the electrochemical data, the cell polarization can be strongly correlated with the interfacial Li morphological changes. Specifically, when the stack pressure reaches a sufficiently high level at around 20 MPa, no detectable interfacial Li morphological change was observed after 2 hours of stripping and platting at the current density of 50  $\mu$ A cm<sup>-2</sup>, demonstrated by <sup>7</sup>Li NMR.

For the 10 and 5 MPa cells, detectable amounts of microstructural Li implies that their unstable charging behaviours at 50  $\mu$ A cm<sup>-2</sup> can be attributed to the unstable interface, which is illustrated by the observation of interfacial microstructures from <sup>7</sup>Li spectra and CSI. Additionally, the 5 MPa cell shows a slightly higher amount of microstructures than the 10 MPa, agrees with its steeper polarization curve during cycling. As previously mentioned, the void-induced polarization can be used to explain the unstable charging behavior at lower pressures.<sup>9</sup> If the stack pressure is high (e.g. at 20 MPa), the homogenous plating on the Li foil can be achieved, owing to the sufficient face-to-face contacts. Under a low stack pressure, Li can only deposit at these contact points due to the presence of voids. This causes high resistance and subsequentially polarizes the cell. In addition, the inhomogeneous plating of Li triggers the formation of Li microstructure. While Wang et al.<sup>9</sup> hypothesized that the microstructure formation is mainly attributed to the unstable interface between the striped Li foil and electrolyte, our study suggests that the plated Li foil exhibits a more pronounced morphological change (Figure 6.5 and S6.5). Our findings are more consistent with the study by Marbella et al.<sup>16</sup> and Chang et al.<sup>17</sup>, where the plated Li foil shows a higher accumulation of microstructural Li under unidirectional charging. The microstructural Li eventually triggering the dendritic Li growth and leading to final short-circuiting of the cell.<sup>16</sup>

**Table 6.1** Summary of the relative integral intensity of bulk and microstructural Li from deconvolution of <sup>7</sup>Li NMR spectra of three cells prepared at various stack pressures.

Pressure	Before charging		After charging		Differences
	Bulk Li foil	Microstructual Li	Bulk Li foil	Microstructual Li	
	(240 – 245 ppm)	(250 – 270 ppm)	(240 – 245 ppm)	(250 – 270 ppm)	
20 MPa	54%	46%	53%	47%	< 1%
10 MPa	100%	0%	84%	16%	16%
5 MPa	91%	9%	69%	31%	22%

#### 6.4 Summary

This study aims to understand the effects of stack pressure on Li morphologies during cycling in the HE-based LMBs that use LAGP and Pyr<sub>14</sub>-TFSI LiFSI as the electrolyte materials. Three symmetric Li cells were prepared with the stack pressures of 20, 10, and 5 MPa. Galvanostatic charging was performed at a current density of 50  $\mu$ A cm<sup>-2</sup>. By correlating the electrochemical characteristics with <sup>7</sup>Li NMR spectra for three cells, we linked the unstable cycling behaviours of the lower pressure cells (5 and 10 MPa) to Li-electrolyte contact loss, which arises insufficient contacts due to low stack pressure. This hypothesis is supported by the direct evidence observed from <sup>7</sup>Li NMR spectra, judging by the increase in microstructual Li. The application of <sup>7</sup>Li CSI further provides spatial information of these microstructures, confirming they are located at the plated Li

interfaces. This work bridges the gap in the information provided by Wang's results,<sup>9</sup> and this combination of techniques allows for a more comprehensive understanding of how Li morphology influenced by stack pressure, which ultimately governs the electrochemical performance of ASSBs.

## **6.5 Challenges**

This work shows a very intriguing trend in how the mechanical stack pressure alters the interfacial Li morphology during the stripping/platting tests against metallic Li electrode. However, several challenges remained and need to be addressed for improved experimental accuracy and practical implementation:

First, the original cell design was intended to provide sufficient active volume to observe the Li<sup>+</sup> concentration gradient within the pencil cell,<sup>23</sup> the active volume was set to 2.5 - 3 mm in thickness. Adapting this design for HE pellets requires a minimum thickness of 3.5 mm to ensure adequate contact. Hence, significant Ohmic resistance is expected for this type of cell, considering that ion transport in SCE suffers from poor particle-particle contacts and GBs effects. The utilization of thicker HE pellets limits the maximum current density can be applied, marking the design less practical compared to other studies (thickness of 1 - 1.3 mm).<sup>9, 35-37</sup> In addition, the limited size of the RF coil constrains the size of the pellet to 4 mm diameter in this work, in comparison to 10 - 20 mm with other publications.<sup>9, 11, 29, 35-38</sup> Both factors mentioned above lead to high cell resistance.

The second challenge is the definition of "stack pressure" in this study. While the "stack pressure" was applied by tightening one of the nuts on the pencil cell during the assembly. At this side of Li-electrolyte contact, we only referred the effect of "uniaxial stack pressure". Nevertheless, tightening the nut could induce shearing force between the HE pellets and Li metal. The effect of shearing force is still unclear in this work due to the lack of studies on this aspect. A new prototype of the pencil cell that only applies the uniaxial pressure that tighten by compression was recently designed as shown in **Figure S6.8**, but it has not yet been utilized due to the narrow timeframe of this work. Nonetheless, it is certainly a promising device that can replace the current pencil cell.

Finally, the elastic behaviour of PEEK material (Young's modulus of ~ 4 GPa)<sup>39</sup> could introduce inconsistent pressure overtime. If the pencil cell was used under a high stack pressure, the PEEK cell body could be deformed and expanded due to the high stress. For example, a torque of around 0.2 N m is required to achieve 20 MPa for a fresh cell (**Figure S6.2**). However, we noticed that after months of experiments and testing, only 0.07 – 0.10 N m can achieve the same pressure, indicating the decrease friction between the threads due to the cell volume expansion. In summary, follow-up cell designs and experiment design with fresh cells are necessary to address the above-mentioned issues.



## **6.6 Supplementary Information**

**Figure S6.1** Schematic diagram of the pencil cell geometry used in this work. The HE pellet is sandwiched between the two Li metals supported by two Cu current collectors, forming a symmetric cell. The stack pressures were applied by tightening the nuts at one end of the cell with a controlled torque, which is calibrated with Fujifilm pressure sensor beforehand.

All the stack pressure calibrations were carried out using a FIRSTINFO torque screwdriver with a 5 mm socket attached. The *Prescale* film was placed in between two 2 mm acrylic spacers, which were used to simulate the spacing of the electrolyte pellet and provide smooth surfaces, ensuring the most accurate representation of the stack pressure within the cell.

Upon the application of pressure, the microcapsules on the *Prescale* film rupture, releasing the ink contained inside in the capsules onto the surface of the color developing layer. The ink then reacts with the developer layer and result in an instantaneous and

permanent "color map", visually representing the variation in mechanical pressure across the contact areas. To quantitatively analyze the stack pressure, the compressed *Prescale* films were taken out from the pencil cell and scanned in colour mode using a Xerox Multifunction Printer, at a maximum resolution of 600 DPI (maximum resolution). The colour data was further analyzed using Adobe Illustrator, where the average intensity from three random spots on the *Prescale* film was recorded, these values were further compared to the colour calibration sheet provided by SPI to quantify the stack pressure.

By correlating the final stack pressure with the torque applied to the nuts, an approximate linear relationship is observed at ~ 0 - 30 MPa, corresponding to the torque values between 0.01 to 0.25 N m, as shown in **Figure S6.2**.



**Figure S6.2** Calibration curve of the stack pressure as a function of applied torque on the nuts for the pencil cell.

The following equations calculate the thickness of stripped/platted Li metal:<sup>40</sup>

$$\Delta V = \int_{n(Li)1}^{n(Li)2} \bar{V}_m \, dn(Li) = \bar{V}_m \cdot I \cdot t \cdot C^{-1}$$
[S6.1]

$$\Delta L = \Delta V / A_{electrode}$$
[S6.2]

where  $n(Li)^2$  and  $(Li)^2$  corresponds to the number of mol of Li consumed/created at the electrode.  $\Delta V$  and  $\Delta L$  is the changes of one Li foil volume and length during stripping and plating, respectively.  $\bar{V}_m$  is the partial molar volume of Li (12.97 cm<sup>3</sup> mol<sup>-1</sup>) at room temperature. *I*, *t*, and *C* are current, charging time, and Faraday constant, respectively. This calculation assumes that the stripping and plating of Li is homogeneous across the Li foil surface with the area of  $A_{electrode}$ .



**Figure S6.3** 1D <sup>7</sup>Li NMR spectrum for the IL, Pyr<sub>14</sub>-TFSI : LiTFSI 1:9 (mol.), with the chemical shift value of -1.4 ppm (referenced to aqueous 1M LiCl solution).



**Figure S6.4** <sup>7</sup>Li CSI for the 20 MPa cell, before charging. The deformed top Li foil has a signal intensity that shows up above the top Li foil, indicating some Li metal creeped upwards due to the high stack pressure. The top edge of the HE pellet shows a stronger intensity in the 2D contour plot. Those are consistent with the observations in **Figure 6.4**. Additionally, small amounts of Li from the top Li foil seemed to be penetrated into the top edge of the HE pellet under the high pressure. The signals appear at 0 mm slice of the cell body are attributed to the artifact due to the DC offset at 0 frequency. The signal of Li metal signal at ~ 250 ppm is magnified by 8 times compared to the signal of the HE pellet.



**Figure S6.5** <sup>7</sup>Li CSI for the 5 MPa cell after polarization of the cell. One slice of spectrum extracted for each of the top and bottom Li foils at the position of -1.10 and 2.53 mm, respectively, representing the interfacial Li of each foil. A dash line of 245 ppm provides guide to the eye to highlight the position of 245 ppm. The direction of Li<sup>+</sup> plating is indicated with the arrow.



**Figure S6.6** Extracted <sup>7</sup>Li spectra from 2D CSI for the 5 MPa cell before (black lines) and after (red lines) the charging process. The two peaks on top are the interfacial <sup>7</sup>Li signal of the top foil, and the peaks at the bottom correspond to the bottom Li foil, respectively.



**Figure S6.7** <sup>7</sup>Li spectral deconvolution of the metallic Li regions for the cell prepared before and after charging.



**Figure S6.8** New prototype for the pencil cell. Instead of applying stack pressure by torque, which might induce shearing force between the Li-electrolyte interface. In this prototype,

the stack pressure is applied by uniaxially compress the top smooth plunger into the cell body, then tightened the screw on the screw portion of the cell body, securing the plunger by lateral frictional force.

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# Chapter 7 – Conclusions and Outlooks 7.1 Concluding Summary

In this thesis, ion dynamics were explored for various SSE materials quantitatively and comprehensively from atomic level ion dynamics to bulk scale diffusion with various ssNMR techniques. MRI methods were utilized to explore the interfacial stability between the hybrid solid electrolyte and the Li metal. The summary of each part is provided in this chapter. ASSBs using thermally stable SSEs are considered as the promising candidates for the next generation of LIBs and NIBs. However, the sluggish ion transport in these materials remains a significant challenge for their practical applications. Furthermore, characterizing ion transport is non-trivial, as conventional electrochemical methods such as EIS cannot provide the resolution required to probe ion dynamics at various scales. The motivation of this thesis is to gain a deeper understanding of ion dynamics under various conditions, with the help of ssNMR, which can provide accurate and quantitative data at different length scales, enabling a comprehensive understanding of ion transport in the SSEs.

In **Chapter 3**, the <sup>7</sup>Li dynamics of a series of copolymers modified from PEO were quantified using NMR diffusometry, in collaboration with Professor J. P. Claverie's group at University of Sherbrooke. The main challenge of the PEO-based SPEs are the high crystallinity contents in the PEO at RT, by copolymerizing the PEO with different monomers (10 mol%), the crystallinities in the copolymers were significantly supressed, accompanied with the enhancement of ion conductivities. NMR diffusometry revealed that the <sup>7</sup>Li diffusivity of the TO-modified copolymer exhibits a 4-fold enhancement compared

to the pristine PEO, where the PO- and BO-modified copolymers are around 2 - 3 times higher. These results demonstrate the substantial improvement in ion dynamics achieved through copolymerization.

**Chapter 4** presents a series of very intriguing dynamic studies of the Li<sup>+</sup> conductor LSnPS after treated with high mechanical pressures. In the past, numerous studies showed conductivity enhancements of the SCE pellets after the pressure treatments (measured by EIS), indicating a better interfacial contacts achieved between the particles. However, in this publication, we determined that the Li<sup>+</sup> migration decreases at the micrometer level using NMR diffusometry, as well as the slower local Li<sup>+</sup> dynamics using the NMR relaxometry. By examining the microstructures of the LSnPS using PXRD, it was found that there is microstrain imparted to the LSnPS structures from mechanical pressure, distorting the crystal lattice and impeding the Li<sup>+</sup> transports. The oxide LAPG phase does not exhibit the same behaviour due to its high mechanical strength. This work demonstrates that dynamic NMR studies can be sensitive and quantitative to the Li<sup>+</sup> dynamics even after modest mechanical modification.

In **Chapter 5**, Na<sup>+</sup> dynamics at the atomic level were studied for a novel Na<sup>+</sup> conductor Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> *via* <sup>23</sup>Na quadrupolar NMR. Due to the 2<sup>nd</sup>-order quadrupolar effects and the rapid chemical exchange of the Na2 and Na3 sites in this structure, <sup>23</sup>Na ssNMR cannot completely resolved these sites under available conditions. To confirm the dynamics, <sup>23</sup>Na NMR relaxometry was evaluated on each of the Na1 and Na2-3 lineshapes, revealing that the Na2-3 is highly dynamic, judging by the strong temperature- and field-dependencies of their relaxation. To simulate the lineshapes of Na2-3 under the influence

of chemical exchange, follow-up experimental characterizations were carried out. By analyzing the 1D and 2D-3QMAS <sup>23</sup>Na NMR spectra under multiple fields, a series of constraints were quantified and further applied in the EXPRESS simulation to model the Na2-3 lineshapes. A set of quadrupolar parameters for Na2 and Na3 was found to fit the experimental lineshapes reasonably well, and is within a consistent range of the constraints, including the quadrupolar parameters derived from CASTEP calculations. These experimental results strongly suggest that the Na2 and Na3 are under rapid chemical exchange, whereas the Na1 is more stationary within the structure of Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub>.

**Chapter 6** presents an ambitious *in situ* <sup>7</sup>Li NMR study aimed to investigate the effect of active stack pressure in ASSBs symmetric LMBs using both <sup>7</sup>Li spectroscopy and chemical shift imaging. Previous studies indicated that the high stack pressure can be beneficial for LMB cycling as it provides better contact between the electrode and electrolyte, therefore contributing to a better cyclability. A low stack pressure can lead to void-induced polarization and therefore interfacial Li microstructures, due to the insufficient contacts. In this study, the interfacial stability between the HE and the Li metals were studied using MRI, by evaluating the interfacial microstructural Li metal formation before and after the galvanostatic charging at a current density of 50  $\mu$ A cm<sup>-2</sup>. With increasing stack pressure, the symmetric cell can cycle much more stable. By correlating the relative signal enhancement of the microstructural Li, it is evident that the more microstructure can form for the lower stack pressure cell. This study bridges the gap in the interpretations provided for previous XCT studies, showing that the early stage of Li microstructures could form at the Li-electrolyte interfaces if the stack pressure is

insufficient for a HE-LMB system. Here, our combination of techniques allows for a more comprehensive understanding of how Li morphology influenced by stack pressure, which ultimately governs the electrochemical performance of ASSBs.

#### 7.2 Future Outlooks

This thesis demonstrates the robustness of ssNMR and MRI on studying various aspects for SSE materials, addressing complicated questions regarding the ion dynamics as well as the electrode-electrolyte interfacial stabilities. Improvements and further explorations are still needed to fully assess these materials and gain a deeper understanding of their various properties, to practically apply them in the ASSBs.

In **Chapter 4**, a possible extension of these experiments is to perform a series of multi-nuclear ssNMR experiments to reveal the local structural change of the materials, under much higher pressure (~ few GPa). Very recently, Faka et al. reported a similar study (*JACS*, 2024, *146*(2), 1710-1721) on the sulfide argyrodite LPSC with the maximum fabrication pressure of up to 10 GPa, inducing ~ 2.4% of strain. The significant strain allows them to observe structural differences from the <sup>31</sup>P MAS-NMR, whereas we did not see any notable differences in **Table S4.5** and **Figure S4.12**. It is also interesting to conduct a series of parallel experiments for the oxide materials as well, in order to compare the different responses from these two representative materials from the sulfide and oxide classes.

For the Na ssNMR project presented in **Chapter 5**, we had only conducted the detailed investigations on the Na<sup>+</sup> dynamics for the undoped pristine Na<sub>4</sub>Sn<sub>2</sub>Ge<sub>5</sub>O<sub>16</sub> phase, but not for the most conductive Na<sub>4-x</sub>Sn<sub>2-x</sub>Sb<sub>x</sub>Ge<sub>5</sub>O<sub>16</sub> (x = 0.20). An 1D <sup>23</sup>Na MAS-NMR spectrum of this phase was collected at 20 T (**Figure S5.9**). Apparently, the doping of Sb<sup>5+</sup> fundamentally alter the structure of material, judging by the more Gaussian lineshapes of both "Na1" and "Na2-3" which lost their quadrupolar characteristics. Additionally, all the peaks shift progressively toward higher frequency after doping. The loss of the characteristic quadrupolar lineshape of Na1 and the coalesced quadrupolar shape of the Na2-3 peak could suggest faster Na<sup>+</sup> dynamics, increased local disorder, or a combination of both factors. Thus, the Na<sup>+</sup> conduction mechanism in Sb-doped series is still not well-understood and requires detailed investigations, potentially by combining <sup>23</sup>Na ssNMR and computational methods as demonstrated in **Chapter 5**.

As discussed in **Chapter 6**, several challenges remained that need to be addressed for improved experimental accuracy and practical implementations. First, the *in situ* cell has too much active volume for the electrolyte region, leading to significant increase in the Ohmic resistance. Second, the tightening of the cell nuts introduces shearing forces, which making them not solely dependent on stack pressure. A new *in situ* cell prototype is shown in **Figure S6.8** can be used in the future, coupled with thinner HE pellets. Additionally, it might be possible to perform controllable stack pressure measurements with this prototype. This requires a custom NMR setup with pressure capability, such as a custom copperberyllium high-pressure NMR probe, which utilizes pressurized fluid and can provide up to 250 MPa active pressure (*ECS*, 2017, *164*(8), H5189-H5196). This setup certainly makes *operando* stack pressure controlling and monitoring feasible for the *in situ* NMR and MRI measurements.