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Understanding the Formation of Solid Electrolyte Interphase (SEI) and Sodium Ion Solvation within Novel Electrolyte Systems via NMR Spectroscopy for Battery Applications

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*Do what you think is interesting, do something
that you think is fun and worthwhile, because
otherwise you won't do it well anyway.*

Brian W. Kernighan

*To those who have been affected by Cyclone
Chido and to the inhabitants of the island of
Mayotte.*

*À ceux qui ont été touchés par le cyclone
Chido et aux habitants de Mayotte.*

ABSTRACT

Sodium-ion and sodium-metal batteries are emerging as more sustainable alternatives to current lithium-based systems. These technologies have the potential to deliver high energy density at lower cost. However, their development requires the design of safe and stable electrolytes capable of facilitating the transport of sodium ions within the electrolyte. One of the main challenges lies in the high reactivity of metallic sodium, which can pose safety concerns, reduce battery lifespan, and lead to the formation of undesirable interfacial layers between the electrolyte and the electrode, commonly referred to as the Solid Electrolyte Interphase (SEI) layer.

In this thesis, we investigated novel solid and liquid electrolytes using solid-state Nuclear Magnetic Resonance (NMR) spectroscopy, a powerful technique that provides detailed atomic-level insights into material structure and dynamics. We focused on two types of solid electrolytes: block copolymers containing polymerized ions and zwitterionic plastic crystals, both doped with sodium salts to enhance their ionic conductivity. We also analysed the various phases present in the SEI layer when metallic sodium is employed as the electrode in combination with ionic liquid-based electrolytes.

Our results indicate that the molecular structure, as well as the interactions between the different conformations adopted by the electrolyte solvent and sodium ions, significantly influence the conductivity of our electrolytes. For example, one solvent conformation facilitates ion transport due to its higher dynamics, whereas another exhibits very low mobility, promoting particularly strong interactions between this conformation and the sodium ions. Furthermore, at high concentrations of sodium salt mixed with the zwitterion, sodium ions bind excessively to their local environment, thereby reducing their effective mobility. Although the zwitterion exhibits local disorder, this effect is mitigated by the high concentration of sodium salt. Additionally, we identified key compounds in the SEI layer, such as sodium fluoride and various sulfur- and oxygen-based species. Some of these compounds are known to be highly stable and thus beneficial for the SEI, while others are entirely novel, raising new questions regarding the electrolyte decomposition mechanism during battery operation.

This work improved understanding of local structure, solvation, and sodium-ion interactions, achieved through advanced solid-state NMR spectroscopy, will guide the design of new electrolytes based on ionic liquids, zwitterions, and ion-containing polymers, with the goal of achieving even higher performance.

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Abbreviations and Acronyms

FSI	Bis(fluorosulfonyl)imide
TFSI	Bis(trifluoromethylsulfonyl)imide
C ₃ mpyrFSI	N-Propyl-N-methylpyrrolidinium Bis(fluorosulfonyl)imide
C ₂ mpyr	N-methyl-N-ethylpyrrolidinium
Zwitterion	N-methyl-N-ethylpyrrolidinium boron trifluoride
P _{111i4} FSI	Trimethyl-isobutylphosphonium Bis(fluorosulfonyl)imide
P ₁₄₄₄ FSI	Tributylmethylphosphonium bis(fluorosulfonyl)imide
NaFSI	Sodium Bis(fluorosulfonyl)imide
NaTFSI	Sodium Bis(trifluoromethylsulfonyl)imide
PS	Polystyrene
PEO	Poly(ethylene oxide)
FS-b-PEO	Polystyrene-block-polyethylene oxide
SEI	Solid Electrolyte Interphase
OIPC	Organic Ionic plastic Crystal
ZPC	Zwitterionic Plastic Crystals
PIL–Block copolymer	Polymerized ionic liquid block copolymer
NMR	Nuclear Magnetic Resonance
1D	One-dimensional
2D	Two-dimensional
MAS	Magic Angle Spinning
CPMAS	Cross Polarization Magic Angle Spinning
NOESY	Nuclear Overhauser Effect Spectroscopy

EXSY	Exchange Spectroscopy
HETCOR	Heteronuclear Correlation Spectroscopy
CSA	Chemical Shift Anisotropy
MAS	Magic Angle Spinning
RF	Radio-Frequency
T_1	Spin-lattice relaxation time (longitudinal)
T_2	Spin-spin relaxation time (transversal)
δ_{iso}	Isotropic chemical shift
σ_{iso}	Isotropic shielding constant
C_Q	Quadrupolar coupling constant
ν_Q	Quadrupolar frequency
η_Q	Asymmetry parameter

Résumé en français

Introduction

Les batteries sont essentielles au fonctionnement des appareils électroniques modernes, tels que les ordinateurs, les smartphones et les voitures électriques. Les batteries lithium-ion dominent actuellement le marché des systèmes de stockage électrochimique d'énergie à haute densité. Toutefois, la quantité limitée de ressource de lithium dans le globe terrestre soulève des inquiétudes concernant l'utilisation de cette technologie à long terme. Le sodium, quant à lui, est abondant et facilement accessible. Il représente une alternative prometteuse due à ses propriétés physico-chimiques similaires à celles des électrodes négatives en lithium métallique.¹ Cependant, les batteries sodium-ion ne sont pas encore capables de rivaliser avec les batteries lithium-ion à cause des particularités électrochimiques du sodium, notamment ses interactions dans les systèmes électrolytiques et à l'interface électrolyte-électrode. De plus, les électrolytes liquides classiques comportent des risques de sécurité majeurs, notamment leur tendance à fuir des batteries et leur forte inflammabilité.

Pour surmonter ces défis, les recherches actuelles ont révélé que des matériaux tels que les liquides ioniques, les copolymères de liquides ioniques polymérisés, ainsi que les cristaux plastiques ioniques organiques présentent un fort potentiel pour les applications dans le domaine des batteries. De plus, les électrolytes solides, tels que les Copolymères de Liquides Ioniques Polymérisés (CLIP) et les Cristaux Plastiques Ioniques Organiques (CPIO), offrent sécurité et stabilité.²⁻⁴ Cependant, la formation de la couche d'interphase électrolyte-solide (SEI, pour *Solid Electrolyte Interface*), résultant des réactions redox entre l'électrolyte et l'électrode de sodium métallique, reste un facteur limitant pour les performances et la durée de vie des batteries. Leur conductivité ionique reste également insuffisante.

Pour l'améliorer, ces électrolytes sont dopés avec des sels de sodium, ce qui augmente la concentration en sodium et la viscosité.⁵ Afin d'optimiser les performances globales des batteries sodium-ion, il est essentiel de comprendre les interactions entre les cations et les anions dans les systèmes électrolytiques, ainsi que les phases formées à l'interface électrode-électrolyte.

Dans le cadre de ces travaux de recherche, la Résonance Magnétique Nucléaire (RMN) à l'état solide a été choisie comme méthode de caractérisation privilégiée, car c'est une technique sélective et efficace pour étudier les interactions au sein des systèmes électrolytiques et pour identifier les phases formées à l'interface électrode-électrolyte. Les chapitres suivants présentent une revue approfondie des batteries, abordent les principes fondamentaux de la spectroscopie RMN et discutent des résultats obtenus par RMN sur deux systèmes électrolytiques, ainsi que de l'identification des phases présentes dans la couche de SEI d'une pile symétrique (Na||Na).

Chapitre 1

Les batteries sont des dispositifs permettant de stocker de l'énergie électrique de manière réversible sous forme chimique. Elles sont composées d'une électrode négative, d'une électrode positive et d'un électrolyte. Lors de leur fonctionnement, par exemple lorsqu'elles se déchargent, l'électrode négative subit une oxydation, libérant des électrons qui réduisent l'électrode positive. Ce processus redox est régi par la différence de potentiel chimique (V_0) entre les deux électrodes. L'énergie de chaque électron dépend de cette différence de potentiel et, pour maintenir la neutralité de charge, des cations migrent simultanément de l'électrode négative vers la positive à travers l'électrolyte. Pour inverser la réaction, typiquement lors de la charge, une tension externe est nécessaire, modifiant ainsi le potentiel électrochimique.

Les électrodes négatives sont reconnues pour leur légèreté, leur caractère électronégatif et leur densité énergétique élevée. L'électrode négative en lithium métallique est celle qui présente le plus bas potentiel (-3.04 V par rapport à l'électrode normale à hydrogène) et la capacité théorique ($3829 \text{ mAh} \cdot \text{g}^{-1}$) la plus élevée.⁶⁻⁸ Cependant, les électrodes négatives métalliques, telles que celles en sodium métallique, posent des problèmes de sécurité liés à la formation de dendrites lors de l'électrodéposition, ce qui peut affecter leur durabilité.⁹ Les cathodes, quant à elles, sont généralement composées d'oxydes de métaux de transition (tels que Li_xMO_2). Elles se distinguent par leur capacité à intercaler de manière réversible

des ions Li^+ dans leur structure. Cette idée a été initialement proposée par John B. Goodenough¹⁰ et a révolutionné le domaine des cathodes en doublant le potentiel énergétique des batteries.¹¹ Bien que les oxydes de métaux de transition offrent un fort potentiel, des améliorations sont nécessaires pour réduire les coûts et accroître leur stabilité mécanique et électrochimique.

Les électrolytes assurent le transfert des ions entre les électrodes mais doivent bloquer les électrons. Ils doivent être stables, non toxiques et hautement conducteurs ioniques. Les électrolytes liquides offrent la meilleure conductivité, mais leur solvant est très inflammable. Les électrolytes solides sont généralement plus stables et offrent une meilleure sécurité, mais souffrent d'une conductivité ionique plus faible. Ce problème peut être résolu en combinant des électrolytes solides avec des sels de sodium ou de lithium, ainsi qu'avec des polymères ioniques agissant comme plastifiants. Idéalement, les ions alcalins (par exemple, Li^+ ou Na^+) doivent être les seuls contributeurs à la conduction ionique dans l'électrolyte d'une batterie Li-ion ou Na-ion. Un électrolyte est caractérisé par un nombre de transfert t_+ des cations dans l'électrolyte (voir la définition Equation (1.6) pour un électrolyte solide), dont la valeur est comprise entre 0 et 1. Plus t_+ se rapproche de 1, meilleur est l'électrolyte pour une batterie Li-ion ou Na-ion, et inversement.

Les recherches récentes dans le domaine des batteries sodium-ion, en particulier l'utilisation de liquides ioniques contenant des sels de sodium superconcentrés, ont montré une amélioration significative des performances électrochimiques de ces batteries.^{2,12} Cette amélioration s'explique par le fait que les sels superconcentrés favorisent une formation uniforme et homogène de la couche IES à la surface de l'électrode métallique. De plus, les recherches sur les électrolytes solides ont montré que certains matériaux, notamment les polymères ainsi que les cristaux plastiques ioniques organiques, sont prometteurs pour la prochaine génération de batteries.^{4,5,13} Les copolymères blocs ioniques polymérisés sont structurés de manière à présenter différentes phases au sein du polymère. Ils possèdent un bloc de polystyrène, qui renforce l'intégrité mécanique, et un bloc ionique, qui facilite le transport des ions. Les cristaux plastiques ioniques organiques subissent une transition de phase solide-solide entre 25 et 75 °C. Dans cette phase, un désordre structurel se manifeste, où les molécules effectuent des rotations sur elles-mêmes au sein du réseau, ce qui facilite le déplacement des ions à travers celui-ci.

Ces travaux de thèse sont réalisés en collaboration entre le CEMHTI et l'IFM. Les collègues de l'IFM testent et caractérisent des matériaux à l'aide de différentes techniques telles que la *Differential scanning calorimetry* (DSC), *Electrochemical impedance spectroscopy* (EIS), Spectroscopie Raman, ect. Sur cette

thèse, nous nous focalisons particulièrement sur l'étude par spectroscopie RMN avancée. Des noyaux tels que ^1H , ^{11}B , ^{13}C , ^{19}F , ^{23}Na , et ^{31}P , actifs en RMN, fournissent des informations sur les phases formées sur la couche de SEI et sur les interactions ioniques au sein des électrolytes. L'objectif final est de comprendre ce que la RMN avancée peut révéler sur la formation de l'interface électrolyte-solide ainsi que sur les environnements de solvation des ions dans les batteries au sodium.

Chapitre 2

La Résonance Magnétique Nucléaire est une méthode analytique puissante et polyvalente, largement utilisée en science des matériaux pour étudier l'environnement local des atomes. Contrairement à la diffraction des rayons X, qui est particulièrement efficace pour analyser les structures cristallines, la RMN permet d'examiner une grande variété de matériaux, qu'ils soient organiques ou inorganiques, cristallins ou amorphe, solides ou liquides.

Le principe de la RMN repose sur l'interaction des noyaux atomiques possédant un spin nucléaire non nul, tels que ^1H ou ^{13}C , avec un champ magnétique externe. Dans sa modélisation classique, l'application d'un champ magnétique externe (B_0) provoque une levée de la dégénérescence des niveaux d'énergie du moment magnétique associé au spin nucléaire, séparés par $\Delta E = \gamma \hbar B_0$, où γ représente le rapport gyromagnétique du noyau. Les moments magnétiques peuvent s'aligner soit parallèlement (état de basse énergie), soit antiparallèlement (état de haute énergie) au champ B_0 . Cette séparation des niveaux d'énergie peut être mise en évidence par l'absorption d'un champ radiofréquence (RF) à une fréquence précise, appelée fréquence de Larmor ($\nu_L = \Delta E/h = \gamma B_0/2\pi$). Le signal d'absorption dépend également de l'environnement des atomes, ce qui fait de la RMN un outil puissant pour sonder l'état de la matière. À température ambiante, la différence de population entre les deux niveaux d'énergie suit la statistique de Maxwell-Boltzmann. Le niveau d'énergie le plus bas présente un léger excès de population, ce qui engendre une faible aimantation nucléaire macroscopique (M).

Aujourd'hui, la méthode dite de « RMN pulsée » est la plus couramment utilisée. Elle consiste à appliquer un champ magnétique oscillant et résonant à la fréquence de Larmor du noyau, située dans le domaine des radiofréquences (RF). Ce processus perturbe l'aimantation nucléaire macroscopique M , la sortant de son état d'équilibre. Puis on mesure son retour à l'équilibre. Ce processus génère un signal électrique oscillant, appelé FID (*Free Induction Decay*, signal de décroissance libre), qui décroît

de manière exponentielle. Cette FID est détectée par une bobine, laquelle sert à la fois d'émetteur et de récepteur, et est enregistré dans le domaine temporel. Elle est ensuite transformée dans le domaine fréquentiel par une transformation de Fourier, puis analysée pour obtenir des informations sur l'état du matériau.

Dans les systèmes moléculaires ou ioniques condensés, la présence et le mouvement des noyaux et des électrons voisins engendrent des interactions supplémentaires qui modifient les effets initiaux. Ces interactions incluent le déplacement chimique, le couplage J, l'interaction dipolaire magnétique et l'interaction quadripolaire. La plupart de ces interactions sont anisotropes, c'est-à-dire qu'elles dépendent de l'orientation du tenseur par rapport au champ magnétique statique externe. Lorsqu'il n'y a qu'un seul site cristallographique, cela ne pose aucun problème pour l'analyse du spectre. Cependant, lorsqu'il existe plusieurs sites cristallographiques pour le même isotope, les formes des raies de ces interactions peuvent se chevaucher, ce qui complique l'analyse du spectre. La rotation à l'angle magique (54.74°) permet d'éliminer les effets de certaines interactions (par exemple, l'interaction dipolaire hétéronucléaire) et de réduire les effets des interactions anisotropes¹⁴. Pour les noyaux quadripolaires (c'est-à-dire les noyaux ayant un spin supérieur à 1/2), il est difficile d'obtenir des spectres à haute résolution avec la technique de rotation à l'angle magique (MAS) lorsque l'interaction quadripolaire est très forte. Cependant, des techniques existent pour améliorer la résolution des spectres de ces noyaux, notamment l'utilisation de champs magnétiques intenses (par exemple 17.6 ou 20.0 Tesla), qui permettent de réduire la largeur des raies dans le spectre.

Par ailleurs, l'investigation des interactions ioniques au sein des électrolytes est réalisée à l'aide de méthodes à une ou deux dimensions, basées sur des corrélations homonucléaires ou hétéronucléaires. Ces méthodes exploitent les interactions dipolaires ou les interactions entre les spins nucléaires et électroniques (par exemple effet Overhauser nucléaire). Ces techniques permettent de détecter les liens entre différents noyaux, qu'ils soient dus à une proximité spatiale ou à des échanges chimiques. Ces techniques seront utilisées dans le cadre des travaux de recherche de cette thèse.

Chapitre 3

Nos collègues de Deakin étudient un système électrolytique basé sur un copolymère en blocs de liquide ionique (PIL-Block, pour Polymer Ionic Liquid). Ils ont mélangé ce polymère avec un sel de sodium

(NaFSI) dans un ratio molaire de 1:2.5. Ce système présente une séparation de phases, caractérisée par des températures de transition vitreuse (T_g) distinctes pour chaque bloc du copolymère. De plus, l'incorporation du sel entraîne une diminution de la T_g du composant polymère PIL, tandis que la T_g du polystyrène reste stable autour de 100 °C. Ce phénomène révèle un effet plastifiant localisé. Cet effet favorise une augmentation du mouvement segmentaire et de la dynamique ionique, améliorant ainsi la conductivité ionique au sein du PIL-Block. De plus lorsqu'on ajoute de liquide ionique C₃mpyrFSI à la formulation électrolytique augmente encore la conductivité ionique, en réduisant davantage le T_g du système, ce qui accentue l'effet plastifiant.

La spectroscopie RMN nous a permis de mieux comprendre les phénomènes se produisant à l'intérieur de ces systèmes. Notamment, la spectroscopie par polarisation croisée (CP MAS), avec transfert de polarisation du ¹H vers le ¹³C, et les techniques d'excitation directe du ¹³C permettent de différencier le bloc moins mobile de la partie plus dynamique de l'électrolyte polymère. La méthode CP MAS détecte le bloc rigide grâce à un transfert de polarisation efficace, tandis que l'excitation directe met en évidence la composante ionique mobile, caractérisée par des pics plus fins et des temps de relaxation plus courts. Les analyses des spectres de polarisation croisée ¹³C-¹⁹F et HETCOR ¹H-¹⁹F, qui explorent les interactions polymère-anion, indiquent des interactions minimales, voire inexistantes. En effet, l'absence de pics de résonance dans le spectre ¹³C-¹⁹F et la faible résonance observée pour l'anion TFSI suggèrent un couplage limité entre le polymère et les molécules de NaFSI et NaTFSI. Cependant, l'expérience d'échange (EXSY) du ¹⁹F révèle l'existence de conformations cis et trans du TFSI dans le système électrolytique. Le spectre HETCOR ²³Na-¹⁹F met en évidence une coordination significative des anions TFSI en conformation cis avec les ions sodium, tandis que les anions en conformation trans présentent une plus grande mobilité. De plus, l'ajout du liquide ionique C₃mpyrFSI améliore la mobilité des espèces ioniques et modifie l'équilibre des conformations de l'anion TFSI, en augmentant significativement la proportion d'anions en conformation trans. Cela explique l'augmentation de la conductivité ionique, favorisant également le transport des ions sodium au sein de l'électrolyte, les TFSI trans interagissant faiblement avec les Na⁺.

Chapitre 4

Récemment, nos collègues de Deakin ont introduit un nouveau type de matériau, appelé cristal

plastique zwitterionique (ZPC, pour *Zwitterionic Plastic Crystal*). Ce matériau partage certaines caractéristiques structurales avec les CPIO, notamment une structure cristalline marquée par un désordre local intrinsèque (rotation de la matrice sur elle-même à l'intérieur du réseau) et la capacité à subir une transition de phase solide-solide. Cependant, il se distingue par le fait que ses cations et anions sont liés de manière covalente (Figure. 1). Charulakshmi Thiruvuravishankar, l'une de mes collègues à Deakin, étudie les mélanges binaires du zwitterion $[C_2\text{mpyr}][\text{BF}_3]$ avec deux sels de sodium (NaTFSI et NaFSI) à différentes concentrations (10, 20 et 50 mol%). Elle observe qu'à faible concentration (10 et 20 mol%), la conductivité ionique du zwitterion augmente de manière significative, atteignant jusqu'à cinq fois celle du zwitterion pur. Cependant, à une concentration plus élevée (50 mol%), la conductivité ionique diminue. Par ailleurs, pour le mélange contenant 50 mol% de NaTFSI , un état métastable due à une cristallisation partielle lente, provoque une légère augmentation de la conductivité par rapport au système NaFSI -zwitterion. Les analyses thermiques révèlent des changements structuraux en fonction de la concentration en sel de sodium, quel que soit le sel utilisé.

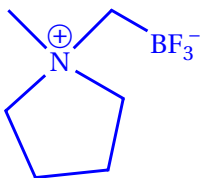


Figure 1. Structure de la molécule d'un cristal plastique zwitterionique $[C_2\text{mpyr}][\text{BF}_3]$

Ces observations sont confirmées par la spectroscopie RMN. Les expériences 2D HETCOR $^{23}\text{Na}-\{^{19}\text{F}\}$ montrent que les cations Na^+ interagissent exclusivement avec les groupes BF_3 des ZPC, tandis que les anions FSI et TFSI compensent leurs charges en interagissant avec les anneaux $[C_2\text{mpyr}]^+$ des ZPC. De plus, l'EXSY ^{19}F révèle qu'à faibles concentrations de sel (10 à 20 mol%), il existe une séparation de phases. Il y a une phase qui correspond au ZPC pur résiduel, tandis que l'autre résulte des interactions entre les cations Na^+ et les groupes BF_3 des ZPC. Ces interactions entre le sel et la matrice pyrrolidinium semblent induire un équilibre complexe entre ordre et désordre dans le réseau cristallin du matériau. En particulier, elles favorisent un désordre rotatoire où les ZPC peuvent tourner autour de leur propre axe. Ce mouvement de rotation perturbe les interactions entre les cations Na^+ et les ZPC. Ce désordre favorise une amélioration de la conductivité ionique en facilitant le mouvement des ions à travers le réseau. Cependant, à des concentrations élevées (50 mol%), une phase homogène unique émerge. Cette phase présente des

environnements chimiquement complexes pour les cations de sodium et les anions. Quel que soit le type de sel utilisé, à cette concentration, deux sites distincts de sodium sont identifiés. Ces deux sites interagissent fortement avec les groupes BF_3 des ZPC, empêchant toute rotation des groupes BF_3 autour de l'axe C–B ainsi que celle de la molécule de ZPC dans son ensemble. Cela réduit la mobilité ionique, entraînant ainsi une baisse de la conductivité. En outre, avec 50 mol% de NaTFSI, le spectre EXSY ^{19}F met en évidence un échange rapide entre les conformations cis et trans des anions TFSI. Ces alternances influencent la dynamique des ions et pourraient expliquer pourquoi, à cette concentration, la conductivité est meilleure avec NaTFSI qu'avec NaFSI.

Ces observations soulignent l'importance d'un ajustement équilibré entre la concentration en sel et la structure des ZPC pour améliorer les performances électrolytiques. Pour atteindre une efficacité optimale dans ce système, il serait probablement nécessaire de limiter la concentration en sel à moins de 50 mol%, afin d'éviter des interactions trop fortes entre les Na^+ et les ZPC.

Chapitre 5

Les électrolytes à base de liquides ioniques, comprenant des cations pyrrolidinium et phosphonium, ont démontré leur capacité à former une couche SEI stable sur la surface des électrodes de sodium. Selon la littérature, la concentration en sels de sodium, tels que le NaFSI, influence favorablement la formation de cette couche SEI. Plus précisément, la combinaison de cations pyrrolidinium et phosphonium avec un sel de sodium surconcentré favorise la formation d'une couche SEI homogène et uniforme. Cependant, les recherches récentes sur la morphologie et la composition de cette SEI ont fourni des informations limitées. En particulier, le manque de résolution des spectres de ^{23}Na empêche d'obtenir des données fiables sur la composition de la SEI. Cette limitation est due au fait que les spectres de sodium ont été acquis sur des spectromètres opérant à des champs magnétiques faibles ou intermédiaires.

Les cellules de batteries symétriques analysées dans cette thèse ont été assemblées en utilisant deux électrodes en sodium métallique et un séparateur Solupor imprégné d'un électrolyte composé des liquides ioniques $\text{P}_{1114}\text{FSI}$ et $\text{C}_3\text{mpyrFSI}$, ainsi que d'un sel de NaFSI surconcentré (42 mol%). Après cyclage, ces cellules ont été ouvertes afin de récupérer la SEI en vue d'une analyse par RMN. L'analyse par RMN MAS à l'état solide, réalisée à des champs élevés et intermédiaires, a confirmé la présence de phases déjà décrites dans la littérature, tout en mettant en évidence la formation de nouvelles phases

issues de la dégradation de l'anion $[\text{FSI}]^-$. En particulier, l'analyse des spectres ^{19}F a permis d'identifier NaF , un composé bien connu pour son rôle dans la formation de la couche SEI, ainsi que de détecter des phases supplémentaires telles que $[\text{FSI}]^-$, $[\text{SO}_2\text{F}]^-$ et CF_2H_2 . Bien que l'identification de CF_2H_2 demeure hypothétique, son déplacement chimique ($\delta_{\text{iso}} = -143.6$ ppm) pourrait correspondre à un produit de dégradation secondaire de $[\text{FSI}]^-$, potentiellement $[\text{N}(\text{SO}_2)_2\text{F}]^-$ ou $[\text{N}-\text{SO}_2\text{F}]^-$. L'analyse des spectres ^{23}Na , basée sur un ajustement de spectres à deux champs magnétiques (9.4 T et 20.0 T), a permis d'identifier des phases telles que Na_2O , NaF , ainsi que des complexes de sodium, comme $\text{Na}_2[\text{SO}_2-\text{N}-\text{SO}_2\text{F}]$, tel qu'il est rapporté dans les travaux de Ferdousi et ses collègues. Cette approche a également révélé la présence de composés supplémentaires dans la couche SEI, notamment NaH et NaOH , vraisemblablement formés par la réaction du sodium avec l'eau résiduelle présente dans l'électrolyte. En outre, de nouvelles phases, telles que $\text{Na}[\text{SO}_2\text{F}]$, $\text{Na}[\text{N}(\text{SO}_2)_2\text{F}]$ ou $\text{Na}[\text{N}-\text{SO}_2\text{F}]$, pourraient résulter d'une dégradation secondaire de l'anion FSI qui interagit avec les ions sodium.

Conclusions

Ces travaux de recherche ont utilisé la RMN avancée à l'état solide pour étudier la formation de la couche SEI et l'environnement des ions dans les batteries et électrolytes sodium. La RMN uni- et bi-dimensionnelle a montré que, lors du mélange du CLIP avec le sel NaFSI , il y a coexistence de conformations cis et trans du TFSI faisant partie du bloc ionique du CLIP. Les anions de TFSI cis interagissent davantage avec Na^+ . L'ajout du liquide ionique $\text{C}_3\text{mpyrFSI}$ augmente la mobilité ionique et favorise la conformation trans, améliorant ainsi la conductivité et le transport des ions sodium. Les expériences ^{19}F EXSY sur les ZPC mélangés avec de faibles concentrations de sel (10–20 mol%) de NaFSI ou NaTFSI a révélé qu'il y a une séparation de phases. Une phase correspond à la phase résiduelle de ZPC pur, et une autre correspond à l'interaction de certaines molécules de ZPC avec les cations Na^+ . Cette configuration permet un désordre rotatif, ce qui facilite le transport des cations Na^+ . À plus forte concentration (50 mol%), une phase homogène se forme, empêchant cette mobilité. L'analyse de la couche SEI montre la présence de NaF , ainsi que de phases supplémentaires comme $[\text{FSI}]^-$ et $[\text{SO}_2\text{F}]^-$. Les spectres ^{23}Na , analysés à deux champs magnétiques (9.4 T et 20.0 T), ont permis d'identifier des phases telles que Na_2O , NaF , et des complexes comme $\text{Na}_2[\text{SO}_2-\text{N}-\text{SO}_2\text{F}]$, en plus de composés comme NaH et NaOH , probablement formés par réaction avec l'eau résiduelle de l'électrolyte. Des

phases supplémentaires, telles que $\text{Na}[\text{SO}_2\text{F}]$, $\text{Na}[\text{N}(\text{SO}_2)_2\text{F}]$ ou $\text{Na}[\text{N}-\text{SO}_2\text{F}]$, pourraient résulter de la dégradation secondaire de l'anion FSI interagissant avec les ions sodium.

Pour les perspectives, afin de compléter notre compréhension des électrolytes à base de ZPC, il serait pertinent d'utiliser des techniques telles que la diffraction des rayons X et des calculs DFT. Ces méthodes permettraient d'approfondir l'analyse des structures locales et des interactions dans les mélanges. De plus, l'utilisation de champs magnétiques très intenses, tels que 1.2 GHz et 1.7 GHz, améliorerait considérablement la résolution des spectres ^{23}Na . Enfin, des calculs DFT pourraient être utilisés pour vérifier les hypothèses concernant les phases identifiées dans la couche SEI.

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General introduction

High-energy-density energy storage systems, characterized by high efficiency, enhanced safety, and cost-effectiveness, are essential for powering modern electronic systems such as portable electronic devices and electric vehicles. Currently, lithium-ion batteries are widely used in numerous applications, but lithium itself is a limited resource,¹ rendering these devices less sustainable. In contrast, sodium represents an abundant and virtually inexhaustible resource (e.g., seawater).² Furthermore, sodium metal anodes exhibit a potential (-2.7 V) and a capacity ($1160 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$) comparable to those of lithium metal anodes.^{3–5} Therefore, sodium batteries are an alternative technology for high-energy density and less expensive storage devices. Although sodium is an excellent candidate, currently, no commercial sodium-based device can rival the performance of the best lithium technologies. This is attributed, in part, to the distinct electrochemical properties of sodium compared to lithium and its differing coordination within the electrolyte. Conventional liquid electrolytes present significant safety concerns, particularly due to their potential to leak from batteries and their highly flammable nature. The decomposition of the liquid electrolyte at the surface of metallic sodium leads to the formation of a non-uniform and thick solid electrolyte interface (SEI) layer, as well as electrolyte depletion.^{6,7} An uneven SEI layer can result in uneven sodium stripping/plating, dendrite growth, and short circuits.^{8,9} From this perspective, sodium and lithium share common issues. To address these challenges, it is crucial to develop new advanced electrolyte materials. Ionic liquids (ILs) are considered promising candidates for the formulation of safe and stable electrolytes.^{10–12} These compounds offer several advantages, including high ionic conductivity, excellent thermal stability, low vapor pressure, and reduced flammability compared to traditional electrolytes. These attractive properties have led many researchers to explore their use in energy storage devices, such as lithium-ion and sodium-ion batteries.^{13,14}

However, during battery operation, the development of the SEI layer, resulting from the redox reaction between the electrolyte and the metal electrode, is a key factor and a potential limiting point for the device's performance. The composition and morphology of this interface are still not well understood. Furthermore, solid electrolytes can offer additional advantages, such as enhanced safety, reduced leakage risks, better stability, and extended lifespan.¹⁵ In this context, Polymerized Ionic Liquid Block (PIL Block) Copolymers and Organic Ionic Plastic Crystals (OIPC) emerge as promising solid electrolytes for sodium and lithium batteries.^{16–19} The unique structure of these materials promotes short-range molecular motions, whether orientational or rotational, significantly facilitating ionic transport within the electrolyte. Although these materials are intrinsically ionic conductors, their ionic conductivity remains insufficient. As a result, they are often doped with sodium or lithium salts in combination with ILs to promote rapid migration of the targeted ions and enhance ionic conductivity. However, the specific interaction mechanisms between cations and anions within these electrolyte systems, particularly when doped with salts, are not yet well understood.

Among the available characterization methods, solid-state Nuclear Magnetic Resonance (ss-NMR) stands out as a key technique for studying the structural composition of the SEI layer and for understanding the structure, dynamics, and solvation of the Na^+ ion within solid electrolyte systems.^{20,21} Indeed, several species present in the SEI and solid electrolyte systems contain isotopes detectable by NMR, such as ^1H , ^{11}B , ^{13}C , ^{19}F , or ^{23}Na . The application of advanced techniques, both in one-dimensional and two-dimensional NMR, offers a promising approach to address the challenges outlined earlier. In this context, the work presented here has employed the latest NMR spectroscopy techniques to investigate the formation of the SEI and the solvation environments of ions in sodium batteries and solid electrolytes.

This manuscript is structured into five chapters. In the first chapter, we will address the differences between lithium-ion and sodium-ion batteries, explore fundamental definitions, and examine the main components of a battery. We will also present a literature review on recent advances in electrolytes for sodium-ion batteries, identifying key gaps in current research and proposing an approach to address these challenges. In the second chapter, we will present the fundamental principles of Nuclear Magnetic Resonance spectroscopy, the interactions involved, as well as the specific characteristics of NMR in solids. We will also discuss the techniques used to enhance sensitivity, along with the various acquisition methods employed in this work. In the third chapter, we will analyze the structure and dynamics of

PIL block copolymers using NMR, to better understand the interactions of Na^+ ions with the other components of the copolymer, particularly the various anionic species present. We will focus on the PIL + NaFSI system with a molar ratio of 1:2.5, as well as the PIL + NaFSI + $\text{C}_3\text{mpyrFSI}$ system with a molar ratio of 1:2.5:1, as these two systems exhibit the best performance in terms of conductivity. In Chapter Four, we will analyse zwitterionic plastic crystal systems by MAS NMR to deepen our understanding of their structure and examine the interactions of the Na^+ ion with other species present in a solid electrolyte composed of the zwitterion and a sodium salt. We will also focus on the influence of salt concentration on the zwitterion structure in order to better understand the reasons for the decrease in conductivity at higher concentrations. Finally, in the last chapter, we will examine the composition of the SEI layer on a metallic sodium electrode using NMR spectroscopy. We will assess the impact of combining pyrrolidinium and phosphonium ionic liquids at different molar ratios, in the presence of 42 mol% NaFSI, on the formation of the SEI layer on a metallic sodium electrode.

Literature review

1.1 Introduction

In general, energy production involves the conversion of a specific form of energy, such as photons or chemical reactions, into an electric current. To date, various technologies have been developed for this purpose, including fuel cells, solar or photovoltaic cells, and thermoelectric cells. Batteries, or accumulators, which are central to this project, are commonly used technologies for storing and releasing electrical energy using chemical energy. There are different types of batteries. The main categories include lithium-ion batteries (LIBs), lead-acid batteries, flow batteries, and sodium-ion batteries (NIBs).¹ LIBs have an edge over other types of batteries due to their unbeatable electrochemical performance. However, other types of batteries such as NIBs are becoming serious competitors. This chapter discusses why NIBs represent a promising alternative to conventional LIBs. It also explains what a battery is, how it works, and the role of each of its components. Finally, it provides an overview of current advancements, identifies key research gaps, and proposes a method to address these issues.

1.2 Success of lithium-ion batteries

Currently, the energy storage market is dominated by rechargeable lithium-ion batteries. This success is partly attributed to the historical development of this technology, as well as its rich and versatile chemistry and light weight, which has led to a wide range of attractive electrode materials compared to other rechargeable batteries. Initially, the discovery of lithium in 1817 and its isolation in 1821 paved

1.3. Why sodium batteries ?

the way for research into its electrochemical properties. In the 1950s, studies revealed the formation of a passivation layer on lithium, leading to investigations into its stability and interest in primary lithium-ion batteries.² However, the history of LIBs began in 1970 when Stanley Whittingham proposed the concept of lithium-ion batteries, discovering intercalation electrodes using titanium disulfide (TiS_2) and molybdenum disulfide (MoS_2) as cathodes, and metallic lithium as the anode.^{2,3} In the 1980s, John B. Goodenough suggested using lithium cobalt oxide (LiCoO_2) as a cathode instead of titanium disulfide.³ This innovation revolutionized the field of cathodes by doubling the energy potential of the batteries. A major turning point occurred with the commercialization of LiCoO_2 batteries by Sony in 1991, leading to the rapid adoption of lithium-ion batteries.² Today, these batteries are widely used in electronic devices such as smartphones and electric vehicles. Although lithium-ion batteries are predominant, the increasing energy demands and contemporary societal needs call for batteries with higher energy density, greater capacity, enhanced safety, optimized performance, and reduced cost. Thus, other types of batteries need to be developed to meet these requirements and address the growing demands.

1.3 Why sodium batteries ?

Sodium-ion batteries were developed based on the initial research and advancements made on LIBs. However, NIBs have limitations compared to LIBs. The intercalation materials used as cathodes, such as layered metal oxides,⁴ are much more efficient for lithium due to its chemistry. Consequently, from the mid-1980s, lithium electrodes demonstrated better performance, making sodium batteries less popular. The commercialization of the first lithium-ion batteries by Sony reinforced this trend. However, over the past fifteen years, the increasing demand for electric vehicles and portable electronic devices has rekindled researchers' interest in sodium-ion batteries for several compelling reasons.

There are concerns regarding the availability of lithium resources being raised. The majority of the world's lithium reserves are concentrated in a limited number of countries, primarily in South America, Australia, and China.⁵ For example, 70% of the world's reserves are located in South America (see Table 1.1). This specific geographical distribution can pose significant supply challenges and create dependency on these nations. Additionally, only a fraction of lithium reserves is economically exploitable, as many are located in remote or politically sensitive areas. For instance, there are 20 ppm of lithium in the Earth's crust, which is difficult to exploit. Consequently, this could lead to supply

challenges and increased costs.

Table 1.1. Comparison of the physical properties of lithium and sodium relevant to their use in rechargeable batteries.^{4,6}

Characteristics	Chemistry	
	¹¹ Na	³ Li
Atomic weight [$\text{g} \cdot \text{mol}^{-1}$]	23	6.94
Mass to electron ratio	23	6.94
Ionic volume [$\text{\AA}^3$]	4.44	1.84
Shannon's ionic radius [$\text{\AA}$]	0.76	1.02
Melting point [$^{\circ}\text{C}$]	98	182
Voltage [V] vs SHE	−2.71	−3.04
Ratio of reserves (ppm in the earth crust)	2830	6.5
Distribution	Everywhere	70% in S. America ⁵
Material abundance in earth's crust [ppm]	23 000	20
Material abundance in water [$\text{mg} \cdot \text{L}^{-1}$]	11 000	0.18
Price of carbonates [\$ per ton]	150	10 000 (fluctuates) ^{5,7}
Price of anode current collector [\$ per metric ton]	1885 (Al)	5719 (Cu)
Metal electrode theoretical capacity [$\text{mAh} \cdot \text{g}^{-1}$]	1165	3829
Metal electrode theoretical capacity [$\text{mAh} \cdot \text{cm}^{-3}$]	1131	2062
Desolvation energy [$\text{kJ} \cdot \text{mol}^{-1}$] in	$\approx -70 \text{ kJ} \cdot \text{mol}^{-1}$ higher than Li	
Coordination preference	Octahedral and prismatic	Octahedral and tetrahedral
Reactivity/flammability of the metal	Highly flammable	Less reactive

Over the past two decades, the price of lithium carbonate (Li_2CO_3) has evolved significantly and has recently been very high. In 2011, the price of Li_2CO_3 was \$5 000 per ton. Today, in 2024, the price is around \$11 600 per ton. Thus, the price has more than doubled. However, between 2010 and 2024, several factors have greatly impacted the price of Li_2CO_3 . The first factor is undoubtedly the sudden rise in popularity of Tesla Model 3, S, and X electric vehicles. This popularity is likely due to environmental regulations aimed at reducing CO_2 emissions as well as government policies favoring electric vehicles. This surge in demand for Li_2CO_3 raw material has affected its price. Figure. 1.1 shows that in December 2017, the price was about \$23,600 per ton, which was already the highest price ever reached at the time before it declined. The second factor is related to the COVID–19 crisis, which caused a spike in prices due to an unexpected demand for batteries to power electronic devices. The price then soared from \$5 192 to \$82 309 per ton, its highest historical level, before decreasing to pre–COVID–19 crisis levels. However, it is important to note that the price of lithium carbonate has been steadily increasing since the 2000s and remains very high.^{5,7} Given the abundance of lithium, it is possible that the price will remain high if demand continues to grow. Therefore, for the production of less expensive batteries, an abundant

1.3. Why sodium batteries ?

resource material with interesting physicochemical properties, such as sodium, is needed.

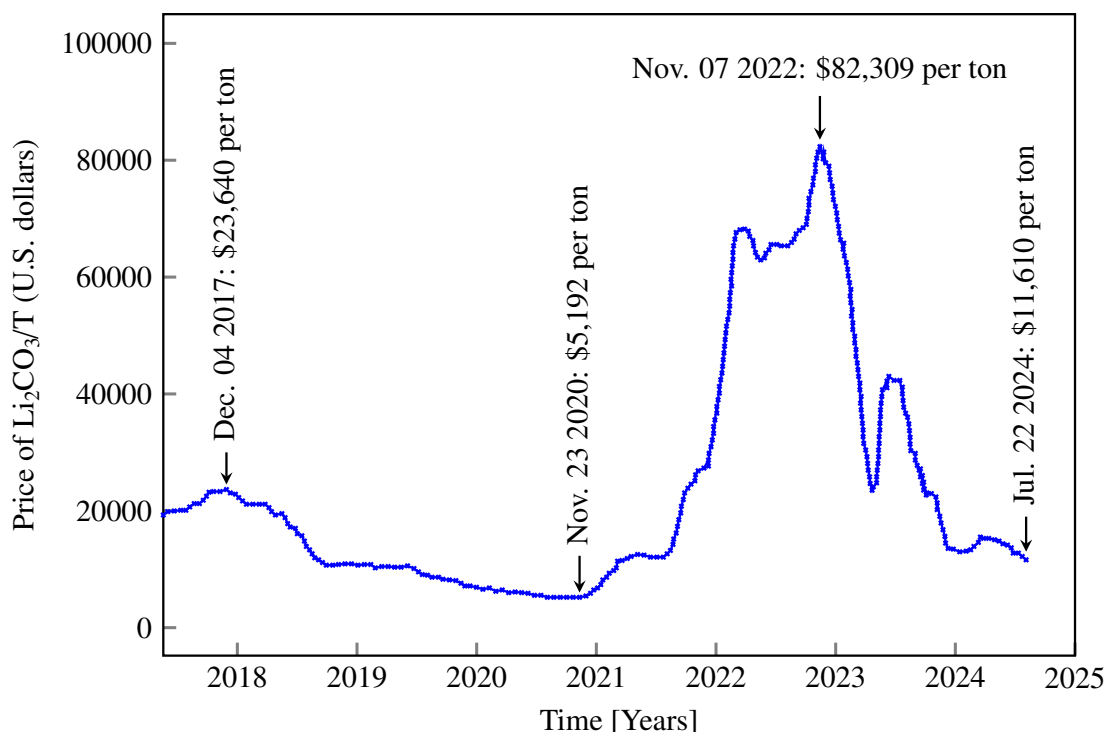


Figure 1.1. The evolution of the price of battery-grade lithium carbonate per metric ton in U.S. dollars over the past seven years. The data comes from the website *tradingeconomics.com*.

The use of sodium instead of lithium in batteries could economically mitigate the potential shortage of lithium. The advantage of sodium over other alkali elements lies in the fact that the position of the chemical element sodium in the periodic table is directly below that of lithium, indicating that they share very similar physicochemical properties. The standard potentials and theoretical capacities of sodium and lithium are quite comparable. As indicated in Table 1.1, the metallic sodium electrode has a standard reduction potential (V_0) of -2.7 V relative to the standard hydrogen electrode, and a charge capacity (Q) of $1165 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. In comparison, for lithium, these values are -3.04 V and $3860 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, respectively.⁸⁻¹³ Although the theoretical capacity of lithium is approximately three times higher than that of sodium, the capacity of sodium is nevertheless very satisfactory, especially when weight is not an issue. Studies reported^{8,10} in the literature on the voltage, stability, and diffusion barrier of Na-ion materials indicate that they can be excellent. In addition, another significant advantage of sodium lies in its abundant availability and low cost. For example, sodium is found in large quantities in seawater

(11,000 mg · L⁻¹ compared to 0.18 mg · L⁻¹ for lithium). According to Table 1.1, a ton of lithium carbonate costs around \$10,000, while that of sodium costs only \$150. The same observation applies to the price of the anode. Thus, the production cost of sodium-ion batteries is lower than that of their lithium-ion counterparts. Consequently, sodium-based batteries are emerging as good candidates for the development of more affordable energy storage solutions.

1.4 Overview of batteries

A battery of accumulators, commonly referred to as a "battery", is a set of electrical accumulators that allows for the reversible storage of electrical energy in chemical form. It is composed of an anode, a cathode, and an electrolyte, as illustrated in Figure. 1.2a.

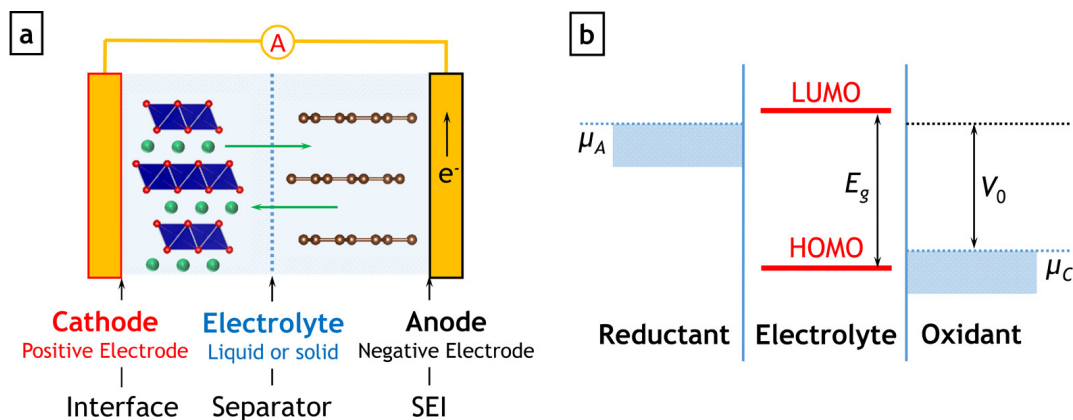


Figure 1.2. Diagram explaining the functioning of a battery. (a) A battery is a multi-component device with a cathode, an anode, an electrolyte, and interfaces between the components. (b) Relative energies of the electrolyte window E_g and the electrochemical potentials of the anode μ_A and cathode μ_C representing the stability of the electrodes concerning the electronic energy levels of the electrolyte. Copyright 2016 American Chemical Society.¹⁴

1.4.1 How do batteries work ?

During the discharge process, the anode (with a chemical potential μ_A) undergoes oxidation as electrons flow through the external circuit, ultimately reducing the cathode (with a chemical potential μ_C). This redox reaction is facilitated by the change in Gibbs free energy (ΔG) expressed as the difference in chemical potential between the two materials forming the redox couple. Consequently, the energy of

1.4. Overview of batteries

each electron is determined by the difference between the anodic and cathodic potentials, represented as $\mu_A - \mu_C = V_0$ (as illustrated in Figure. 1.2b). To maintain charge neutrality, the transfer of electrons involves the simultaneous migration of cations (e.g., Li^+ or Na^+) from the anode, which subsequently intercalate into the cathode. To reverse the reaction, an applied voltage is necessary, and the relevant thermodynamic quantity becomes $\bar{\mu} = \mu + q\mathcal{F}\phi$ where q represents the ionic charge, $\mathcal{F}$ is the Faraday constant, and ϕ corresponds to the applied potential. It is worth noting that in the absence of an applied voltage, the chemical potential μ and the electrochemical potential $\bar{\mu}$ are identical. The reversibility of the redox reaction enables the electrochemical system to undergo multiple cycles.

1.4.2 Components in batteries

The cathode functions by releasing electrons during the electrochemical reaction process (reduction). The opposite process occurs at the anode (oxidation). Typically, the redox reaction occurring at a metallic negative electrode during charge is given by Equation (1.1), where M denotes a metal.



The electrode that enables the design of high energy density storage systems is lithium metal, as it is the most electropositive (-3.04 V relative to the standard hydrogen electrode (SHE)) and the lightest (equivalent mass $M = 6.94 \text{ g} \cdot \text{mol}^{-1}$ and specific density $\rho = 0.53 \text{ g} \cdot \text{cm}^{-3}$).^{13,15} The performance of lithium batteries is optimized when lithium metal is used as an electrode and intercalation materials are used for the positive electrode, as mentioned in Section 1.2. For example, the use of lithium metal anodes in Li-LMO (lithium transition metal oxide) cells allows for a specific energy of about $440 \text{ Wh} \cdot \text{kg}^{-1}$. For Li-S and Li-air systems, this specific energy can reach up to $650 \text{ Wh} \cdot \text{kg}^{-1}$ and $950 \text{ Wh} \cdot \text{kg}^{-1}$ respectively, far surpassing that of traditional Li-ion cells.¹² Although lithium metal electrodes offer promising advantages, they also have significant drawbacks, particularly in terms of safety. One of the main challenges associated with these electrodes is the formation of dendrites.¹² These structures can develop during battery charging and cross the electrolyte, potentially causing internal short circuits and a local increase of temperature, with in extreme cases, risks of fire or explosion. Additionally, these electrodes can encounter durability issues. Repeated charge and discharge cycles can lead to the degradation of the electrode material, thereby reducing the overall lifespan of the battery. Therefore,

to address these drawbacks, researchers are now exploring alternative materials for negative electrodes, such as silicon-additive anodes,¹⁶ among others.

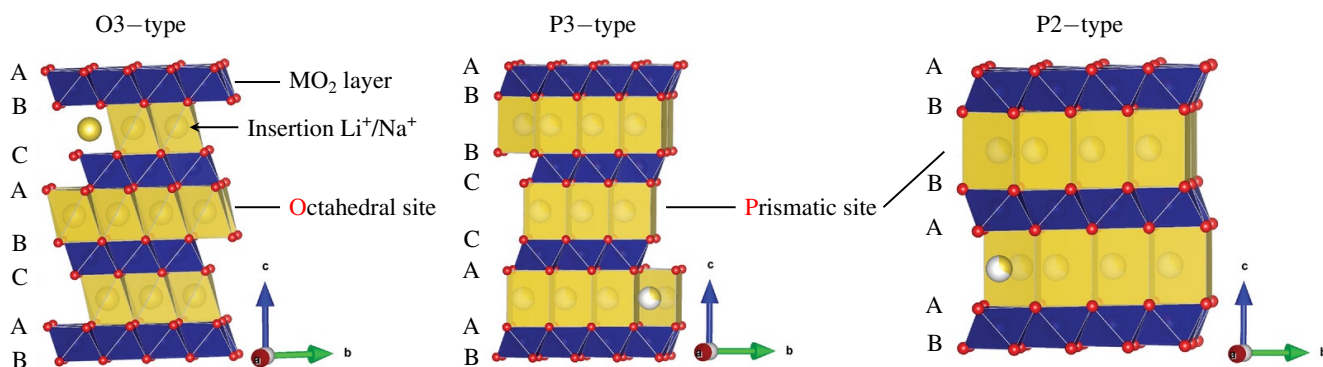


Figure 1.3. Crystal structures of metal oxides with O3–, P3–, and P2– types configurations. In the O3– configuration, alkali ions can be inserted into octahedral voids. In the P2– or P3– configurations, they can be inserted into trigonal prismatic voids.

Most positive electrodes possess the capability to reversibly insert alkali ions into their crystalline structure at a high redox potential. To ensure optimal cycling performance of cells, it is essential that these materials exhibit minimal volumetric expansion during the processes of ion intercalation and deintercalation.⁷ Oxides have proven to be the most suitable materials for serving as positive electrodes in liquid-state batteries.¹⁷ John B. Goodenough was the first to propose the use of these materials as electrodes, which earned him the Nobel Prize in Chemistry in 2019, shared with Stanley Whittingham and Akira Yoshino. These oxides are classified into three families: layered oxides, spinel oxides, and polyanion oxides.¹⁸ Among these three categories, layered oxides (Li_xMO_2 or Na_xMO_2 , where M represents one or more 3d ions with different oxidation states, often cobalt) stand out as the most promising candidates due to their high intercalation potentials (relative to Li^+/Li), leading to high gravimetric and volumetric energy density.^{19,20} The structure of layered oxides (Figure. 1.3) consists of oxygen octahedra centered on transition metals (MO_6), which share edges, allowing alkali ions to be inserted either into trigonal prismatic (P) or octahedral (O) voids. For example, during discharge, the stoichiometric composition of the electrode gradually changes from Na_yMO_2 to $\text{Na}_{x+y}\text{MO}_2$ as sodium ions are integrated into the crystal structure.



1.4. Overview of batteries

Insertion reactions are fundamentally reversible (provided that the number of inserted ions does not change too much) because they do not require the formation or breaking of covalent bonds. In the case of Na_xMO_2 , for example, sodium atoms simply diffuse between layers of oxygen atoms, where they are stabilized by Van der Waals forces, resulting in a negligible change to the host crystal structure. Although layered oxides are promising for lithium-ion or sodium-ion battery cathodes, significant efforts are needed to overcome challenges related to cost, durability, and electrochemical and mechanical stability. Strategies such as reducing cobalt content, exploring new alkali-rich materials, and optimizing electrolytes are promising avenues for improving the performance of layered cathodes.¹⁸

Electrolytes transport ions from one electrode to another and are essential for the design of the "ideal" battery. The electrolyte must be chemically compatible with the electrode materials and include electrochemical and chemical stability under operational conditions. Additionally, electrolytes should exhibit low toxicity, low vapor pressure, non-flammability, and ease of manufacture and implementation. Most importantly, the electrolyte must possess high ionic conductivity and negligible electronic conductivity. Ideally, the only mobile charge carriers should be Li^+ or Na^+ ions. Therefore, a good electrolyte is characterized by its transference number t_i , mathematically described in the paper by Bruce and Vincent.²¹ This transference number is defined by the fraction of the total electric current carried in an electrolyte by a given ionic species i . The sum of the transference numbers for all the ions in solution always equals unity. Conventional batteries use liquid electrolytes for their high conductivity, low viscosity, and good transference number for the alkali cation (e.g., $t_+ \approx 0.7$).²² However, these electrolytes also present significant safety challenges. Indeed, some solvents used in liquid electrolytes are very volatile and flammable, which can lead to leaks and increase the risk of explosion. Current research is focusing on the development of solid electrolytes by exploring a range of materials such as ceramics²³ and polymers.²⁴ These electrolytes offer several advantages, particularly in terms of safety, as they are non-volatile and cannot leak out of the battery. These properties significantly reduce the risks compared to conventional liquid electrolytes. However, a major disadvantage of solid electrolytes is their low ionic conductivity. This drawback can be mitigated by mixing these materials with additives.²⁴

1.4.3 Solid electrolyte interphase

The solid-electrolyte interphase (SEI), refers to a thin layer that forms on the surface of electrodes within batteries, as illustrated in Figure. 1.4. This layer typically forms during the initial charging phase of

the battery as a result of the redox reaction between the electrolyte and the solid electrode. A good passivating SEI functions as a barrier between the electrolyte and the solid electrode, which plays an important role in ensuring the long-term stability and durability of the battery. It facilitates the movement of ions while blocking the electron flow, thus establishing a fundamental basis for the battery's operation. However, in real-world conditions, when the battery undergoes charge and discharge cycles, ions undergo back-and-forth movements between the anode and the cathode.²⁵ During the charging process, ions originating from the positive electrode migrate towards the negative electrode. Under favorable conditions, certain lithium or sodium ions can accumulate on the surface of the negative electrode and get reduced, initiating the formation of minuscule particles known as nuclei.²⁶ These nuclei could potentially promote the growth of dendrites, tree-like structures that can cause short circuits, leading to the formation of "dead sodium"—sodium rendered electrochemically inactive due to its isolation from the battery's conductive network. These dendritic formations lead to diminished capacity and result in a decrease in Coulombic efficiency during cycles.²⁶ Thus, the SEI can potentially restrict or prevent dendrite growth.

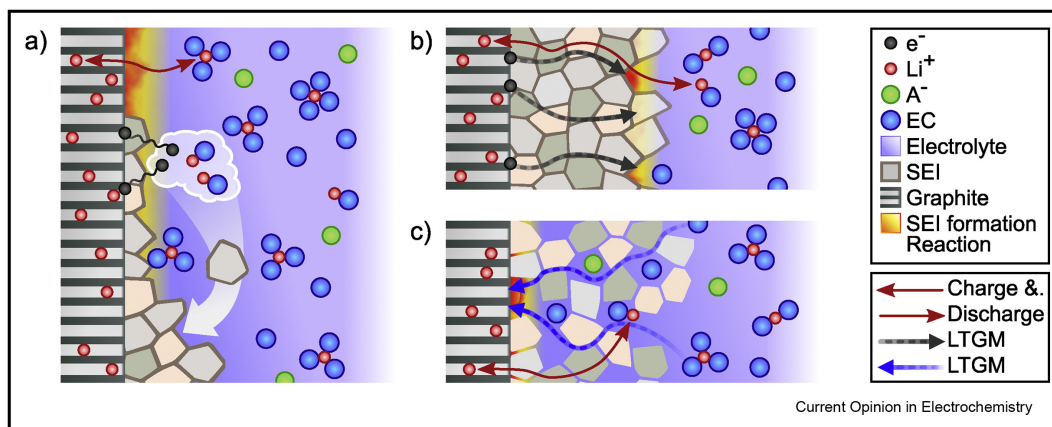


Figure 1.4. Cross-sectional cut through the negative electrode, the SEI, and the electrolyte. The solvent, Li^+ and electrons are mobile species and move as indicated by the corresponding arrows. (a) Initial formation of the SEI: electrons tunnel, the electrolyte undergoes reduction, and the reduction products precipitate as a solid film. (b) Long-term growth of the SEI occurs through a mechanism that transports the negative charge towards the SEI/electrolyte interface. (c) Alternatively, the long-term growth of the SEI is driven by the diffusion of the electrolyte towards the electrode/SEI interface. Copy from [25]²⁵

Sodium electrodes react spontaneously with the electrolyte, resulting in the formation of a fragile SEI on their surface.²⁷ This SEI often exhibits structural heterogeneity, which compromises the cyclic stability of the electrodes.^{27–30} To address these issues, one strategy involves regulating the electrolyte

1.5. Molecular interactions and solvation

components to construct a robust SEI. Reports have indicated that the SEI consists of various organic and inorganic components.²⁷ The most commonly identified components are Na_2CO_3 , Na_2O , and NaF .^{28–30} Among these, NaF exerts a particularly favorable influence on the SEI.²⁷ Indeed, the electronic insulation properties of NaF can promote a more uniform sodium deposition, thereby reducing the formation of dendrites and "dead sodium". To obtain a NaF -rich SEI on sodium electrodes, two strategies have been adopted. The first method involves adding fluorine-containing additives or solvents, such as bisfluoroacetamide. The second method involves enhancing the coordination of fluorinated anions (e.g., $[\text{FSI}]^-$ or $[\text{TFSI}]^-$, these anions will be discussed in the next sections) through strategies such as the use of highly concentrated electrolytes, localized highly concentrated electrolytes, or anion-aggregated solvation shells induced by additives.^{28,31} In this way, the degradation of the anions contributes to the formation of an NaF -rich SEI.

1.5 Molecular interactions and solvation

The solvation of Na^+ ions in the electrolyte plays a crucial role in ionic transport through the electrolytic medium. Indeed, the mobility of solvated ions is directly influenced by the interactions between these ions and the solvent molecules, which affects the ionic conductivity of the electrolyte. Moreover, the desolvation process of Na^+ ions has a significant impact on phenomena occurring at the electrode surface, including the formation of the SEI layer, as well as intercalation and plating processes. The following sections address the typical interactions between electrolyte components and the solvation phenomenon.

1.5.1 Interactions between electrolyte components

Molecular interactions play an important role in the stability and efficiency of electrolytes. Among these interactions, coordination bonds, hydrogen bonds, and van der Waals forces (Figure. 1.5) are particularly important for understanding the solvation and electrochemical properties of electrolytes.

Coordination bonding is a short-range interaction between an ion and solvent molecules. It is characterised by a dative covalent bond where the electrons come from a single atom, similar to a classic covalent bond in terms of strength. The strength of this bond depends on the solvent's ability to provide free electron pairs, which is influenced by their nature as Lewis bases. Cations like Na^+ have empty orbitals ready to accept electrons from donors such as adiponitrile ($\text{C}_6\text{H}_8\text{N}_2$). Anions such as

bis(fluorosulfonyl)imide (FSI^-) in sodium salts can also form coordination bonds, and the strength of these bonds can be altered by the presence of electron-withdrawing groups in the anion that affect the electron distribution of the anions.

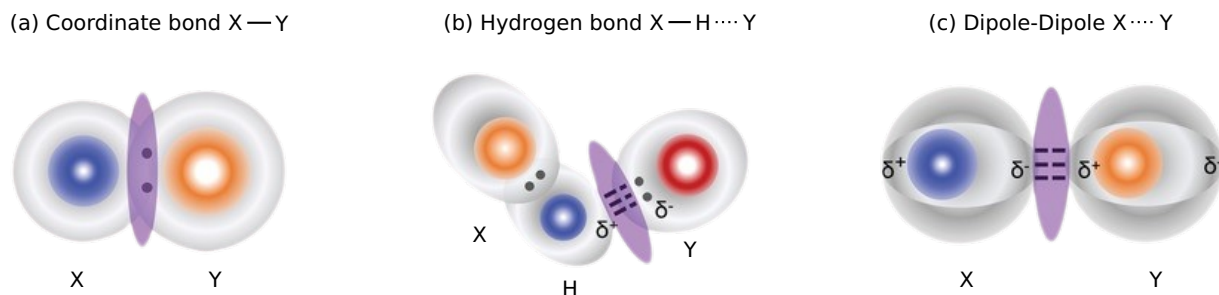


Figure 1.5. Diagram showing the types of interactions and bonding in the electrolyte. a) Coordination bond. b) Hydrogen bond. c) Dipole-dipole interaction (the gray shading represents the electron cloud of the atoms). Adapted from [32]³² (CC BY 4.0).

Hydrogen bonding is a short-range interaction, though it is weaker than coordination bonding. It involves electrostatic attraction between a hydrogen atom covalently bonded to an electronegative atom (X) and another electronegative atom (Y) carrying a pair of free electrons. This type of interaction can be observed between the anions of sodium salts and solvent molecules, as well as between solvent molecules and additives. Consequently, it influences the solvation structure and electrochemical performance.

Van der Waals forces, which are weaker than coordination bonds, encompass various electrostatic interactions present in electrolytes. These include:

Dipole-dipole forces, arising from permanent dipoles between polar molecules.

$$U_{ion-ion} = -\frac{z_1 z_2 e^2}{4\pi\epsilon_0 r} \quad (1.3)$$

Induced dipole forces, occurring when a permanent dipole induces a dipole in a nearby molecule.

$$U_{ion-dipole} = -\frac{ze\mu \cos \theta}{4\pi\epsilon_0 r} \quad (1.4)$$

Dispersion forces, found between all atoms and molecules due to instantaneous dipoles created by uneven

1.5. Molecular interactions and solvation

electron distribution.

$$U_{dipole-dipole} = -2 \left(\frac{\mu_1 \mu_2}{4\pi\epsilon_0} \right)^2 \left(\frac{1}{r^6} \right) \left(\frac{1}{3k_B T} \right) \quad (1.5)$$

where U is the electrostatic potential energy, ϵ_0 is the dielectric constant, ze is the charge of the ion, and r is the distance between the two molecules or atoms. μ represents the dipole moment of the solvent molecules, θ is the angle of the dipole relative to the line joining the ion and the dipole center, k_B is the Boltzmann constant, and T is the absolute temperature. These forces are influenced by several factors such as the dipole moment, ionization energy, and molecular deformability of the solvent molecules. Electrostatic interactions in electrolytes, exemplified by interactions between a negatively charged oxygen atom and a positively charged Na^+ ion, are essential for the solvation process. These interactions can be modulated by adjusting the dipole effect of the molecules or the distance between solvent molecules and Na^+ ions.

1.5.2 Ion solvation

Solvation is a process involving interactions between a solvent and dissolved molecules, characterised by significant interactions between both ionised and non-charged molecules with the solvent. This phenomenon decisively influences the properties of both the solute and the solvent. When the attractive forces between the solvent molecules and the solute particles exceed the forces holding the solute particles together, the solvent molecules organise around the solute particles, leading to their dispersion in the solution. This reorganisation of solvent molecules into solvation complexes results in changes in the vicinity of the solute, and the closest ones form what is referred to as the "first solvation shell". It can involve the formation of various types of bonds, including coordination bonds, hydrogen bonds, and van der Waals forces. In addition to this first shell, some solvation structure models introduce the concept of a "second solvation shell".³² This second shell is generally less dense than the first and contains solvent molecules that are partially bound to the solute particles, as well as anions attracted to these particles. It may also include ion pairs and solvent molecules, as well as free anions.

To explain how solvent molecules organize around an ion, two main parameters are used. The first is the coordination number, which indicates how many solvent molecules surround the central ion in the closest layer. The second is the average bond length, which measures the distance between the sodium

ion and the donating atom of the solvent molecules. According to research by Fard et al., as reported by Tian et al., the solvation geometries of the Na^+ ion vary depending on the solvents used.^{32,33} For example, in EC (ethylene carbonate) solvents, five molecules surround each Na^+ ion, while in VC (vinyl carbonate) solvents, three molecules do so due to the larger size of VC molecules. The bond length between Na^+ and O decreases as steric hindrance is reduced. Steric hindrance is caused by repulsion between neighboring solvent molecules (see Figure. 1.6). This hindrance is more significant with large solvents or a high number of solvent molecules surrounding the ion. Additionally, simulations show that adding EC to other solvents like PC (propylene carbonate) or DMC (dimethyl carbonate) alters the solvation structure, which has varying effects on the average bond length depending on the size of the solvent molecules.

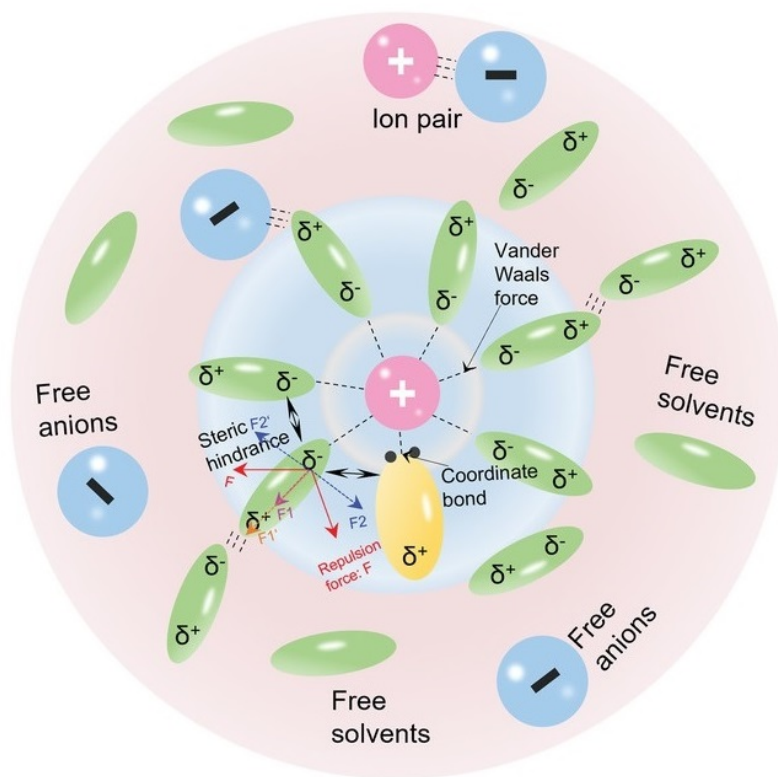


Figure 1.6. A model illustrating the solvation structure of cations within a battery electrolyte. The light blue area represents the first solvation shell, and the light red area represents the second solvation shell. Adapted from [32]³² (CC BY 4.0).

The shuttling of sodium ions in a battery can be divided into three distinct stages: the dissolution and solvation of sodium ions (stage I), the migration of sodium ions (stage II), and the desolvation of sodium ions at the electrolyte-electrode interface (stage III). The interactions between cations, solvent molecules,

1.6. Recent advancements in electrolytes for sodium-ion batteries

and anions are crucial, determining the lattice energy of the salts and the solvation energy.³² To improve solubility, sodium salts with weakly coordinated anions have been developed, and solvents with a high donor number have been studied. They will be discussed in the following sections.

1.6 Recent advancements in electrolytes for sodium-ion batteries

Current research on the development of materials for electrodes and electrolytes aims to enhance the performance and stability of batteries. On one hand, the use of conventional liquid electrolytes with a sodium metal electrode presents significant challenges. For example, the anode reacts spontaneously with the electrolyte, leading to the formation of dendrites on the anode surface, which can result in battery failure,²⁵ as explained in Section 1.4.3. To promote more homogeneous formation and improved cycling stability, one approach is to utilise highly concentrated ionic liquids.^{28,29} On the other hand, the development of sodium-ion based cathode and anode materials, such as transition metal oxides layered (Li_xMO_2) and polyanionic ($\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$) compounds, has improved battery performance and stability.¹⁸ However, research on sodium electrolytes has received less attention. In efforts to replace the flammable solvent-based liquid electrolytes, research on solid-state electrolytes (SSEs) has intensified. Among various types of SSEs, solid polymer electrolytes^{34,35} (SPEs) and organic ionic plastic crystals³⁶ (OIPCs) stand out due to their low cost, ease of fabrication, and high flexibility. Moreover, their thermal and chemical stability makes them suitable for high-temperature battery applications. However, despite their promising properties, these solid-state electrolytes exhibit low ionic conductivity, ranging from 10^{-7} to $10^{-5} \text{ S} \cdot \text{cm}^{-1}$.^{37–39} Several strategies have been adopted to improve their ionic conductivity. One approach involves doping SSEs with ionic liquids as plasticizers, thereby improving their ionic conductivity without compromising safety. The following sections provide a comprehensive overview of the current advancements in ionic liquid, polymer, and plastic crystal electrolytes for sodium batteries.

1.6.1 Ionic liquids

Room temperature ionic liquids (RTIL) constitute a category of molten salts (which is why there is no solvent) characterized by a melting point below 373 K (100 °C) and are generally liquid at room temperature. They are typically formed by the combination of large organic cations and anions with delocalized charges. RTILs are distinguished by their high conductivity and great thermal stability.

Additionally, they exhibit low vapor pressure and are less flammable than traditional electrolytes. Furthermore, being primarily composed of organic ions, they offer a high level of structural flexibility, allowing their properties to be adjusted according to specific needs.¹⁰ In this context, RTILs are considered as potential safe and stable candidates to be used in electrolyte formulation.⁴⁰

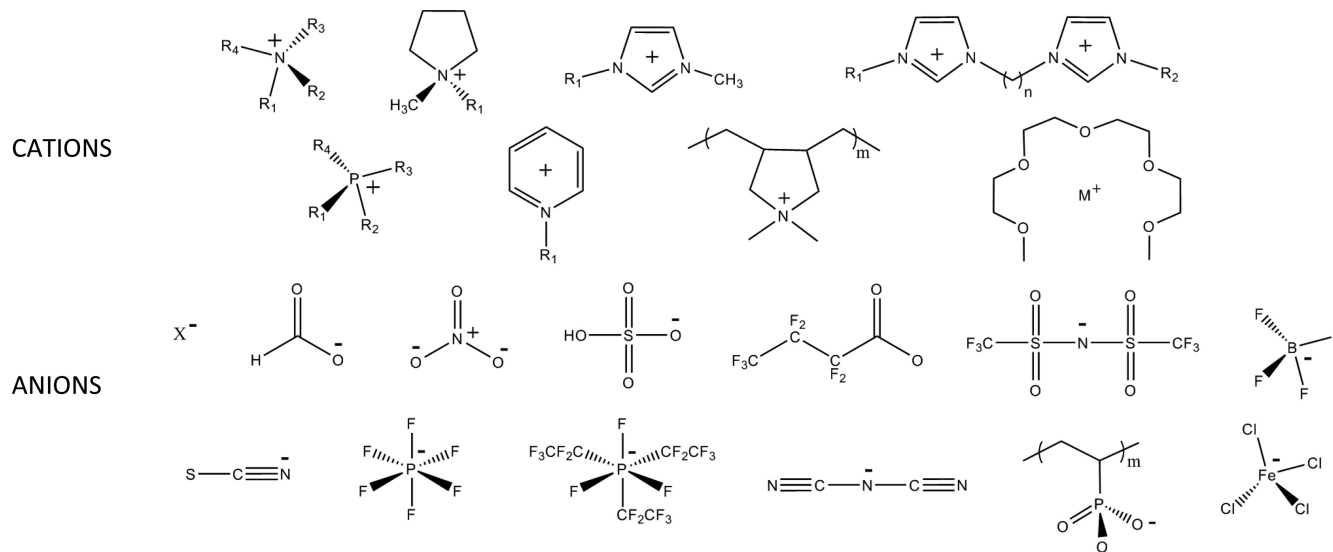


Figure 1.7. Here are several chemical structures of cations and anions commonly used in ionic liquids, such as protic, aprotic, dicationic, polymeric, magnetic, and solvate ionic liquids. Copy from [41]⁴¹

Numerous subclasses of Ionic Liquids (ILs) have been reported in the article by Haye et al.,⁴¹ based on specific structural characteristics. There are protic and aprotic ILs, based on the well-established division between proton-donating (protic) and non-proton-donating (aprotic) molecular solvents. There are also ILs with a chiral center (chiral ILs), a paramagnetic atom or group (magnetic ILs), a divalent ion (divalent ILs), a polymeric or polymerisable ion (polymeric ILs), a fluorocarbon moiety (fluorous ILs), or a coordinated ion (solvate ILs). Figure. 1.7 displays the cations and anions commonly used in various types of ionic liquids. Several combinations of organic cations such as imidazolium ($C_3H_4N_2^+$), pyridinium ($C_5H_5NH^+$), and anions such as hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), bis[(trifluoromethyl)sulfonyl]imide ($TFSI^-$), or bis[fluorosulfonyl]imide (FSI^-) have been utilised to create ILs with good ionic conductivity.⁴⁰ Among these ILs, those containing the anions FSI^- and $TFSI^-$ exhibit higher conductivities. Interestingly, FSI^- shows better diffusivity compared to its $TFSI^-$ -based counterparts.⁴² This is attributed to its low rotational barrier around the N–S bonds, which prevents crystallization and enhances the fluidity of the solutions in which it is present. FSI^- displays a

1.6. Recent advancements in electrolytes for sodium-ion batteries

more diffuse ionic charge, which also makes it less prone to form ion pairs and bond to cations or solvent molecule, helping it diffuse faster.⁴⁰ Thus, the anions FSI⁻ and TFSI⁻ are generating increasing interest as potential components for next-generation battery electrolytes.^{40,43}

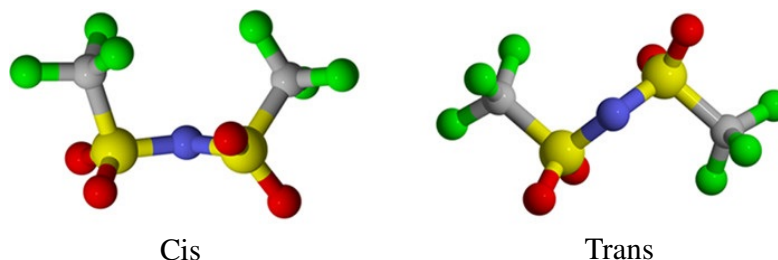


Figure 1.8. Projections of the structure of TFSI⁻ in the *cis* and *trans* conformers. Atom color scheme: carbon = gray; nitrogen = blue; oxygen = red; fluorine = green; sulfur = yellow. Copy from [44]⁴⁴

The anion TFSI⁻ is a weakly coordinating anion widely used in ionic liquid used as solvents. Studies on multivalent batteries reported in the literature show that Mg(TFSI)₂ possesses remarkable electrochemical properties, including high stability and high ionic conductivity.⁴⁰ These properties are attributed to the conformational flexibility and delocalized negative charge of TFSI anions. Research indicates the presence of two conformers (*cis* and *trans*, see Figure. 1.8) in TFSI-containing solutions and in solids.^{45,46} However, the *cis* conformer is preferred for coordinating with multivalent metal ions due to its higher dipole moment, with a value of $\mu = 5.42\text{D}$ for the *cis* conformer compared to $\mu = 0.67\text{D}$ for the *trans* conformer. These structural variations influence battery performance, particularly ion transfer between the electrode and the electrolyte. In addition to the *cis* and *trans* conformers, TFSI anions can also form mono- and bidentate coordinations through their sulfonyl oxygens and cations in the solvation structures of electrolytes.

The anion FSI⁻, which is structurally similar to TFSI⁻, is recognized for its advantageous properties. It is frequently used in combination with Li⁺ or Na⁺ to form a salt. When incorporated into an ionic liquid, this salt notably increases the viscosity, as the dissolved salt tends to thicken the liquid by enhancing ionic interactions. Furthermore, the presence of this salt elevates ionic conductivity by supplying additional ions that facilitate improved charge transport within the electrolyte. In addition, the high concentration of lithium or sodium salt in the electrolytes has a significant impact on the quality and characteristics of the SEI layers that form on lithium or sodium metal anodes.^{29,47} Indeed, recent research has highlighted the effective role of the [FSI]⁻ anion in enhancing the passivation of anode materials in sodium-ion

batteries. For example, Ferdousi and co-workers^{28,29} investigated IL electrolyte mixtures composed of pyrrolidinium cations ($C_3\text{mpyrFSI}$, see Figure. 1.9) and NaFSI, as well as electrolytes composed of phosphonium cations ($P_{111i4}\text{FSI}$, see Figure. 1.9) and NaFSI. According to their findings, the SEI in the dry superconcentrated ionic liquid electrolyte $C_3\text{mpyrFSI}$ mixed with 50 mol% NaFSI is composed of sodium fluoride (NaF), sodium oxide (Na_2O), and a complex unidentified component related to FSI, proposed as $\text{Na}_2[\text{SO}_3-\text{N}-\text{SO}_2\text{F}]$. An example of the ^{23}Na solid-state NMR spectrum indicating these compounds is presented later in Section 1.7.1. When approximately 1000 ppm of water is added (wet electrolyte), it significantly affects the SEI formation, leading to a more active and uniform deposit with higher amounts of reduced SEI species (S, O, F, and N). In the presence of water, the SEI contains the same products but also includes compounds formed by the reaction between FSI anions, water molecules and sodium cations, which contributes to improved stability of charge-discharge cycling.

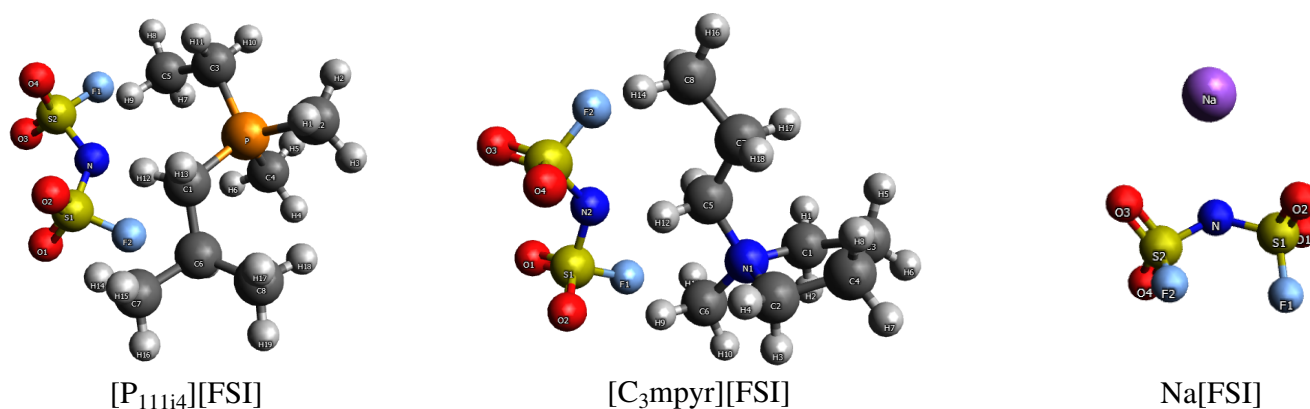


Figure 1.9. Ionic liquid electrolytes based on phosphonium and pyrrolidinium fluoro(sulfonyl)imide and sodium salt

The studies mentioned in the previous paragraph have demonstrated that superconcentrated ionic liquid electrolytes facilitate the formation of a homogeneous and uniform SEI layer, and that water has a beneficial effect on this SEI. However, the nature of the compounds formed at the interface between the electrolyte and the electrode remains not entirely clear in the NMR measurements. This is due to the difficulty of studying the ^{23}Na nucleus, which is quadrupolar, using NMR. The use of high magnetic fields, such as those provided by 750 and 850 MHz spectrometers, can be highly beneficial for the investigation of sodium. In addition, studies have been conducted by mixing salts to obtain both FSI^- and TFSI^- anions in a quasi-solid and solution state.^{48,49} The findings from these studies revealed that this mixture enhances the thermal, transport, and electrochemical properties of the base material. Notably,

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it was observed that Li^+ ions are solvated by TFSI^- and FSI^- anions in solution. However, research on the interaction of TFSI^- and FSI^- with sodium in solid-state electrolytes remains limited. To elucidate the transport properties of sodium, an in-depth investigation of sodium solvation using high-field NMR spectroscopy is necessary.

1.6.2 Polymerized ionic liquid block copolymers

A polymer is a macromolecule composed of repeating small chemical units called monomers. These monomers chemically assemble to form longer and often branched chains. Polymers are also referred to as macromolecules due to their significantly larger molecular size compared to ordinary chemical compounds. Their use as electrolytes dates back to 1973 when Fenton et al. discovered that alkali salts could be dissolved in poly(ethylene oxide) (PEO),⁵⁰ thus laying the foundation for the development of solid polymer electrolytes (SPEs). These electrolytes offer several advantages, particularly in terms of safety, as they are non-volatile, essentially non-flammable and cannot leak out of the battery. These properties significantly reduce the risk of fire or explosion compared to conventional liquid electrolytes, which are known to be flammable. Furthermore, polymer electrolytes can be designed in a multifunctional manner.^{50,51} This design allows for structuring different phases within the polymer, where one phase can provide high mechanical strength (polystyrene or poly(methyl methacrylate) blocks are commonly used), while another phase can facilitate ion conduction (PEO-based blocks are the most frequently used).⁵¹ This capability enables better adaptation to specific application needs, thereby enhancing the overall performance of the electrolyte. Despite their numerous advantageous properties that make them suitable for use as electrolytes, these electrolytes generally exhibit lower conductivity at room temperature, ranging from 10^{-7} to $10^{-5} \text{ S} \cdot \text{cm}^{-1}$, compared to conventional electrolytes.⁵² The transference number in polymers can be calculated using the Bruce-Vincent equation:⁵³

$$t_+ = \frac{I_S(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)} \quad (1.6)$$

Where R_0 and R_S are the impedances before and after polarization, respectively, I_0 and I_S are the initial and final values of the steady-state current variations, respectively, and ΔV is the constant voltage value of 10 mV.

The transport of Li^+ in PEO is determined by the segmental motions (α relaxations) of the ethylene

oxide chains in the amorphous phase, corresponding to the diffusion of conformational states along the polymer chains, which is slow and limits ionic conductivity at temperatures below the melting point of PEO (65 °C).⁵¹ Additionally, the lithium ions are strongly bound to the coordination to oxygen in the ethylene oxide repeating units, which hinders the migration of lithium ions between chains, and results in a relatively low fraction of charge carried by the lithium ion. Such a low lithium transport number will cause strong concentration polarisation in the cell during cycling, leading to the activation of side reactions and the formation of lithium dendrites. Given that lithium and sodium share similar chemistry, sodium will encounter the same issues as lithium with these electrolytes.

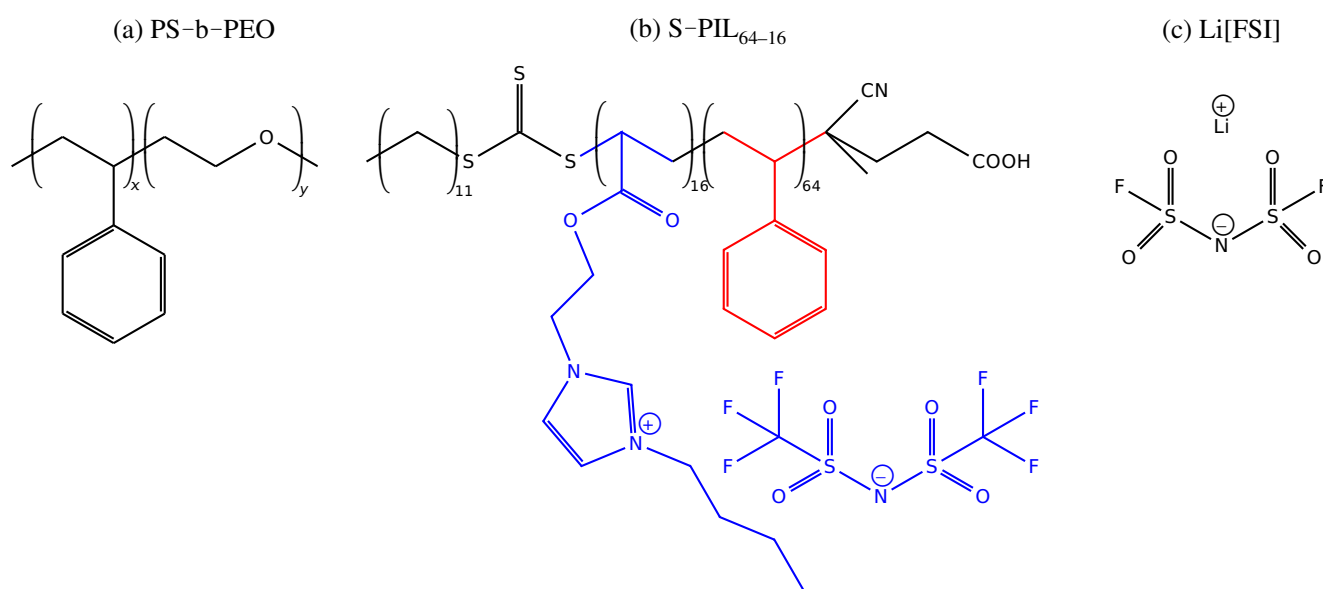


Figure 1.10. (a) PS-b-PEO: polystyrene-block-polyethylene oxide; (b) Structure of polymerized ionic liquid block (PIL block) copolymers: 64 polystyrene blocks (in red) to enhance mechanical integrity, incorporated with 16 ionic imidazolium-derived blocks and [TFSI]⁻ (in blue) to facilitate charge transport (Adapted from⁵¹), (c) Sodium salt Li[FSI] incorporated to increase the Li⁺ concentration.

Fortunately, several approaches have been attempted to improve the ionic conduction and mechanical properties of SPEs, encompassing the introduction of nano-fillers for mechanical reinforcement, the development of novel hybrid materials, the utilization of plasticizers such as ILs to enhance ionic conduction, and a combination of these approaches. Goujon et al.⁵¹ have developed and analyzed a ternary polymer electrolyte system using a sequential PIL block copolymer, where a polystyrene block plays a crucial role in improving mechanical integrity. This system encompasses a sequential copolymer composed of poly(styrene-*b*-1-((2-acryloyloxy)ethyl)-3-butylimidazolium

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bis(trifluoromethanesulfonyl)imide) (refer to Figure. 1.10b), designated as S-PIL₆₄₋₁₆. Furthermore, it incorporates an ionic liquid ([C₃mpyr][FSI]) along with a lithium salt (LiFSI). The study demonstrates that the S-PIL₆₄₋₁₆ electrolyte exhibits high Li⁺ ion conductivity ($4 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 50 °C), stable cycling performance up to 0.20 mA·cm⁻² in a lithium symmetrical cell, and an theoretical discharge capacity of 167 mAh·g⁻¹ almost achieved in the first cycle. Consequently, these materials hold great potential as polymer electrolytes for lithium-metal batteries. Moreover, they could also have significant promise as polymer electrolytes for sodium-metal batteries by replacing lithium with sodium.

However, within this polymer, the precise mechanisms governing interactions between cations and anions remain largely unknown at the current juncture. For instance, the specific anion FSI or TFSI with which a Li⁺ or Na⁺ ion might preferentially interact has yet to be ascertained. According to references,^{48,49} Li⁺ is solvated by both anions in the liquid state. However, it is important to question whether this observation also applies to PIL block copolymers containing Na⁺ ions. To address this issue, experiments correlating sodium with the fluorines present in the anions could provide valuable insights.

1.6.3 Organic ionic and zwitterionic plastic crystals

Plastic crystals constitute a family of solid materials characterised by long-range order while exhibiting short-range disorder, mainly due to the rotational movements of molecules or ions.³⁶ There are three types of materials recognised for displaying plastic crystal behaviour. First, inorganic salts like Li₂SO₄ and α -Na₃PO₄, which can show rotator phases and plastic crystal behavior at high temperatures, allowing cation conduction via a "paddle-wheel" rotation of the anion. Second, molecular species such as succinonitrile, which can offer good ionic conductivity, for example, with an added lithium salt, but have the drawback of volatility, especially above relatively low melting points. Finally, organic ionic plastic crystals (OIPCs), consisting of cations and anions similar to ILs, use a relatively large and symmetrical organic cation in combination with an inorganic anion, which is generally either symmetrical or possesses a diffuse charge.^{36,54}

OIPCs represent an emerging and promising category of materials for use as solid-state electrolytes in sodium⁵⁵ and lithium⁵⁴ batteries. They exhibit one or more solid-solid phase transitions before melting. For example, Jin and collaborators⁵⁶ studied the structural behaviors and ionic transport of the OIPC [P₁₂₂₄][PF₆]. They reported that this material exhibits rich phase behavior and advantageous ionic

conductivities, with three solid-solid phase transitions and a highly "plastic" and conductive final solid phase in which the conductivity reaches $10^{-3} \text{ S} \cdot \text{cm}^{-1}$. Figure. 1.11 illustrates these phase transitions of the material in the DSC curves and shows how the ionic conductivity evolves across the different phases. These transitions are associated with the emergence of rotational or translational movements of ions or molecules, leading to a progressive evolution from an ordered crystalline phase to an increasingly disordered structure, as illustrated in Figure. 1.12. These movements are amplified by an increase in free volume at higher temperatures or by defects,^{36,57} such as vacancies, due to structural disorder. This results in a substantial increase in ionic conductivity and facilitates the rapid transport of added metal ions, such as lithium and sodium. Given the excellent structural behavior and the potential for high conductivity that these materials can achieve, OIPCs are considered promising candidates for solid electrolytes.

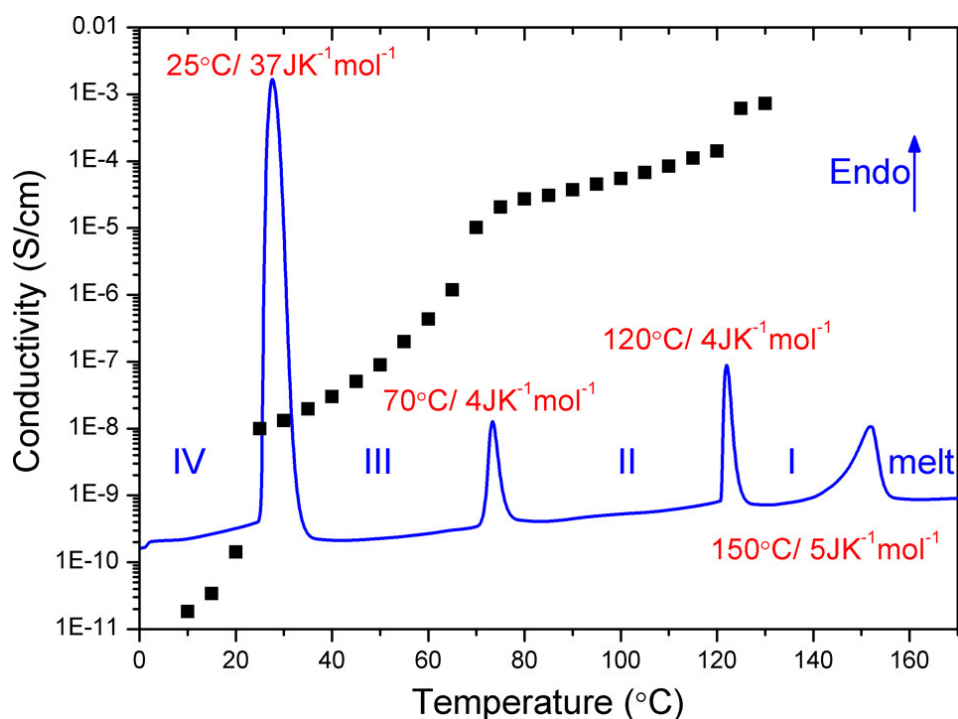


Figure 1.11. The DSC trace of the OIPC $[\text{P}_{1224}][\text{PF}_6]$, as well as the conductivity as a function of temperature. Each solid phase is identified by Roman numerals. Reprinted with permission from Liyu Jin et al. Copyright **2012** American Chemical Society.⁵⁶

Recently, Makhlooghiazad and colleagues⁵⁸ reported a new type of material, zwitterionic plastic crystals (ZPC), which share structural similarities with OIPCs and exhibit rotational disorder in some or all parts of the molecule. However, their cations and anions are covalently bonded, preventing their migration under the influence of an electric field. Like OIPCs, these materials can possess

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intrinsically disordered structures and undergo solid-solid phase transitions. Consequently, these unique materials could provide an optimal ionic environment for the transport of specific ions, such as lithium or sodium, without interference from the ion transport of the matrix material, while also benefiting from the favorable mechanical properties of plastic crystals. For the fabrication of their new material, they selected small heterocyclic molecules to promote rotational disorder, plasticity, and enhanced conductivity. Additionally, they used the BF_3 charge-diffuse group to establish moderate interactions with target ions and ensure robust stability against hydrolysis. The structure of these molecules is illustrated in the Figure. 1.13. The researchers demonstrated that their new materials, zwitterion-based electrolytes, can facilitate efficient transport of target ions, achieving a high ionic conductivity of $1.4 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 30°C . Specifically, these materials can efficiently transport lithium ions and maintain stable cycling of lithium metal cells. Thus, disordered zwitterions emerge as preferred choices due to their potential to enhance the transport of target ions in other batteries based on alkali metals or multivalent ions, while also being adaptable to advancements in both solid and liquid electrolytes.

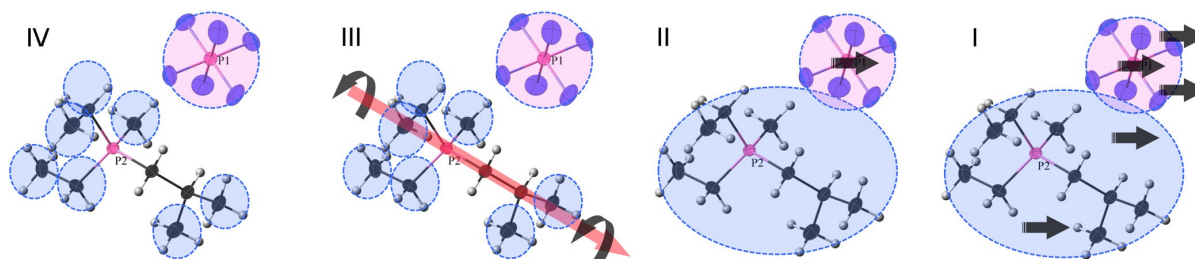


Figure 1.12. Diagram illustrating the molecular motions across the different phases (IV to I) of $[\text{P}_{1224}][\text{PF}_6]$ with increasing temperature. In phase IV, only the methyl and ethyl groups of the cation are rotating, while the anion also rotates; in phase III, the entire cation can rotate around an axis, and the anion continues to rotate; in phase II, the whole cation can rotate freely, and the anion can both rotate and diffuse; finally, in phase I, both the cation and the anion are able to diffuse. Reprinted with permission from Liyu Jin et al. Copyright **2012** American Chemical Society.⁵⁶

Another report by Makhlooghiazad et al.⁵⁹ examines the thermal, ionic, and diffusion properties of new solid $\text{ZPC}^{(1)}$ electrolytes mixed with lithium salts, namely 10 mol% LiFSI and 10 mol% LiBF_4 . It is noted that $\text{ZPC}^{(1)}$ and LiBF_4 mixtures exhibit more complex phase behavior than $\text{ZPC}^{(1)}$ and Li[FSI] mixtures, with additional phase transitions at high concentrations. On the other hand, $\text{ZPC}^{(1)}$

and Li[FSI] mixtures show lower melting points, reduced glass transition temperatures, as well as higher ionic conductivity and diffusivity. The properties of these electrolytes were compared to those of an analogous OIPC, [C₂mpyr][BF₄], showing that ion fixation in the ZPC⁽¹⁾ does not negatively affect ionic conductivity. Additionally, studies were also conducted on symmetric cells with metallic lithium. Electrolytes concentrated to 90 mol% Li[FSI] in ZPC⁽¹⁾ demonstrated remarkable galvanostatic stability up to 1000 cycles with low polarization. These electrolytes also show good performance in full Li|LiFePO₄ cells. However, the mixture of zwitterions with lithium salts results in electrolytes that can be soft solids, quasi-solids, or liquids. Nevertheless, zwitterionic electrolytes offer new perspectives for solid electrolytes. So far, these materials have been primarily combined with lithium salts, but their behavior when combined with sodium salts, such as Na[FSI] and Na[TFSI], remains to be determined. The specific interaction between Na⁺ ions and the zwitterion is a pertinent question, and this question remains unanswered.

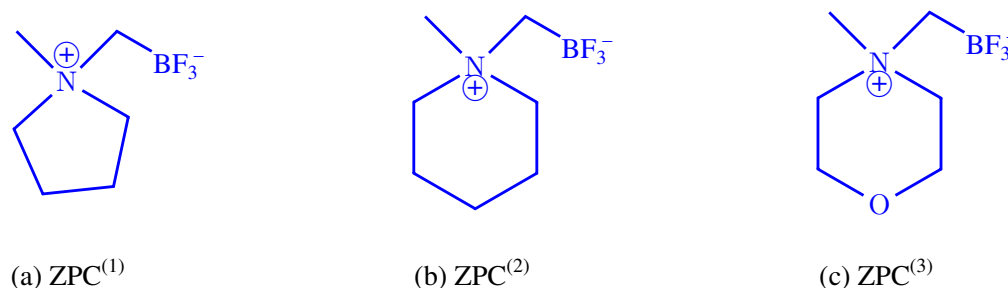


Figure 1.13. Chemical Structures of Zwitterions: (a) Zwitterions can serve as a solid ionic conductor matrix. (b) Zwitterions can be incorporated into composites with functional additives to improve ion transport and mechanical properties. (c) Zwitterions can be combined with lithium salts to form non-volatile liquid electrolytes with enhanced ion transport. Adapted from [58] (Makhlooghiyazad et al.⁵⁸), Copyright © 2021, Nature Materials.

1.7 NMR as a key characterisation technique

Nature Materials. To guide research toward more effective electrolyte formulations, it is crucial to understand the solvation mechanisms of sodium ions within the electrolyte and the formation of the SEI layer. As outlined in Section 1.5.2, the solvation of Na⁺ ions is important because it directly affects their transport through the electrolyte. Moreover, the desolvation process influences the phenomena occurring

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at the electrode surface, including SEI formation and the processes of intercalation or electrodeposition. Therefore, to elucidate these mechanisms in new electrolyte formulations, various characterization techniques can be utilized.

Differential scanning calorimetry (DSC) can be used to examine the thermal properties of materials.⁶⁰ It measures key temperatures such as the liquidus temperature (T_l), the glass transition temperature (T_g), and the crystallization temperature (T_c). In addition to these temperatures, DSC provides information on the energies associated with these transitions, such as the enthalpy of fusion and the enthalpy of crystallization. This technique is particularly useful for assessing the thermal stability of polymer-based electrolytes⁶¹ or ZPC⁵⁸ within the operating temperature range of batteries. However, despite its many advantages, DSC primarily focuses on thermal analysis and provides limited information about the structure and dynamics of electrolyte species. Therefore, for a comprehensive understanding of material properties, it is often necessary to use other methods in conjunction with DSC.

Electrochemical impedance spectroscopy (EIS) can be employed to evaluate the electrochemical properties of materials.⁶² By measuring a system's response to an alternating signal applied at various frequencies, EIS provides precise information on resistance and capacitance. This method is particularly useful for characterizing materials such as electrodes and electrolytes in batteries. For example, the simulation of the Nyquist plot of a lithium-ion battery half-cell system can provide data on several key parameters, such as the bulk resistance of the cell (R_b), which includes the electrolyte, separator, and electrodes; the resistance of the interfacial layer (R_{SEI}); the charge-transfer resistance of the double layer (R_{ct}); as well as the diffusional effects of lithium ions on the host material (W).⁶² However, EIS only provides indications of the resistance of the media traversed by charged species, without explaining the underlying causes of this resistance. Furthermore, the models used to describe the movement of these species do not always capture all the nuances of the phenomenon, which can lead to incorrect interpretations.⁶³ Therefore, just like DSC, EIS should be combined with other techniques to obtain a comprehensive understanding of material properties.

X-ray diffraction (XRD) is an essential method in crystallography for analyzing the atomic structure of crystals. By measuring the angles and intensities of X-rays diffracted by a crystal, this technique allows for the determination of the arrangement of atoms within the crystal lattice. The results provide information on atomic positions, lattice parameters (such as axis lengths and interaxial angles), as well as crystal symmetry, which facilitates the classification of crystals according to their symmetry systems,

such as cubic or orthorhombic.⁶⁴ However, despite its power, XRD has notable limitations. It can only analyze materials with a periodic structure. Therefore, materials with disordered structures generally cannot be resolved by this method. For example, multiphase structures present at the electrolyte-electrode interface often escape detection by XRD. Additionally, solid electrolytes mixed with additives, which are often soft in nature, also pose significant challenges for XRD analysis.

Table 1.2. Table showing the characteristics of the nuclei studied by NMR in this project, including their spin, natural abundance. It also specifies the Larmor frequencies of these nuclei under magnetic fields of 11.75 T and 19.97 T.

Isotope	Spin	Nat. Abundance (%)	γ ($10^6 \cdot \text{rad} \cdot \text{s}^{-1} \cdot \text{T}^{-1}$)	Larmor Frequencies (MHz)	
				11.75 (T)	19.97 (T)
^1H	1/2	99.99	267.522	500.13	850.13
^{11}B	3/2	80.10	85.847	160.46	272.75
^{13}C	1/2	1.07	67.283	125.75	213.76
^{19}F	1/2	100.00	251.815	470.59	799.92
^{23}Na	3/2	100.00	70.808	132.29	224.88
^{31}P	1/2	100.00	108.394	202.46	344.14

Nuclear magnetic resonance (NMR) spectroscopy is a powerful and versatile analytical method, widely used in materials science to analyze the local environment of atoms. Unlike XRD, which is particularly effective for studying crystalline structures, NMR allows for the examination of a wide variety of substances, whether they are organic or inorganic, crystalline or amorphous, solid or liquid. Thus, NMR is particularly well-suited for studying sodium-based batteries and materials used in batteries. Chemical and electrochemical processes within a battery are governed by redox reactions involving various chemical elements, with Na^+ ions often playing an important role. ^{23}Na NMR spectra can differentiate among the various products of these reactions because these spectra are influenced by the electronic structure of the products. Other nuclei, such as ^1H and ^{19}F , can also provide valuable complementary information. However, NMR measurements for some isotopes can be complicated due to their low natural abundance, low gyromagnetic ratio (γ), which can affect the sensitivity and detectability of NMR measurements (see Table 1.2). Therefore, it is necessary to use advanced NMR techniques (described in Chapter 2) to improve sensitivity. While the ^{23}Na nucleus benefits from 100% natural abundance and a broader chemical shift range compared to ^7Li , potentially offering better resolution, it is a quadrupolar nucleus ($I > 1/2$) with a strong quadrupolar coupling. Consequently, ^{23}Na spectra

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generally exhibit distinctive and broad lineshapes. The use of higher magnetic fields, such as the 850 MHz available at CEMHTI, is particularly advantageous for optimizing the resolution and sensitivity of ^{23}Na NMR.

1.7.1 Examples of NMR applications to batteries

There are several NMR-based approaches for analyzing materials used in batteries. Electrolytes can be studied using conventional NMR, either in static mode or under magic angle spinning (MAS), depending on their state—liquid or solid. However, for studying solid interfaces (e.g., SEI), two distinct approaches can be employed.

In situ or *operando* NMR involves placing an entire battery inside an NMR magnet and a radiofrequency coil to perform measurements.⁶⁵ This technique allows real-time observation of changes in battery materials during charge and discharge cycles while preserving the battery's integrity. The technique offers significant advantages. It reduces the effects of self-relaxation processes, enables precise identification of chemical species, whether crystalline or amorphous, and facilitates the monitoring of dynamic processes as well as the detection of metastable phases.¹⁴ For these reasons, it is used to study electrolyte-electrode interfaces in sodium or lithium batteries.^{66–70} For example, Gotoh and his colleagues⁶⁷ investigated the mechanisms of over-lithiation and over-sodiation, as well as delithiation and desodiation in half-cells (hard carbon || Na), using *operando* solid-state NMR spectroscopy observing the ^7Li and ^{23}Na nuclei. During the delithiation process of hard carbon, the authors observed a shrinkage of lithium dendrites and an uneven removal of quasi-metallic clusters. Conversely, over-sodiation of hard carbon led to the formation of metallic sodium and dendrites, detected at approximately 1120 – 1130 ppm in the *operando* ^{23}Na NMR spectra. Although *in situ* NMR experiments are extremely useful for observing structural changes in batteries in real-time, this technique has significant limitations. Specifically, it is conducted under static conditions, meaning without sample rotation. This restriction arises due to the induction of strong eddy currents when metallic components are rotated in a strong magnetic field.⁶⁵ Consequently, this limitation introduces additional challenges, both in terms of spectral resolution and data analysis.

Ex situ NMR is a technique performed outside the usual environment of the studied material. Specifically, it first requires the removal of the relevant part of the battery into a glove box filled with argon to avoid any reaction with moisture or air. This part is then transferred to a sample holder, such

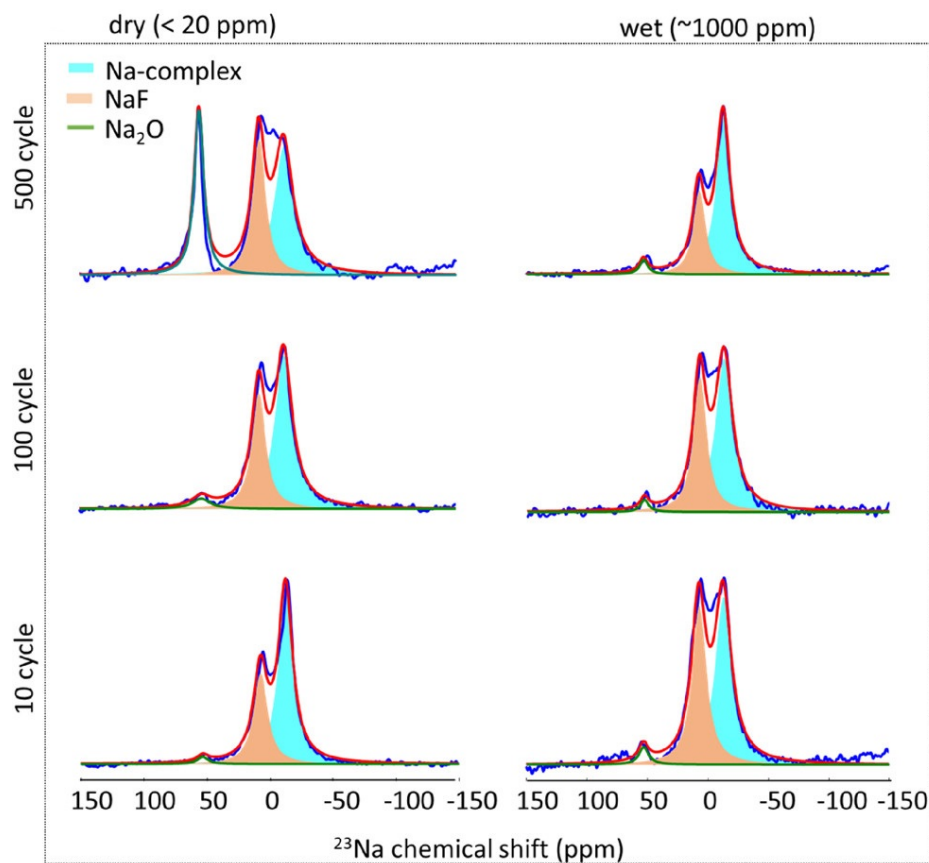


Figure 1.14. The ^{23}Na MAS-NMR spectra (MAS of 20 kHz) of the SEI products on the surface of sodium metal. Reprinted with permission from Ferdousi et al.²⁹ Copyright 2021 American Chemical Society.

as a rotor, for NMR analysis. The measurements are carried out under magic angle spinning (MAS) to improve sensitivity and resolution, which is one of the main advantages of *ex situ* NMR. Traditionally, this method is used to examine global changes in the solid parts of a battery at different states of charge.⁷¹ Let us revisit the example of Ferdousi and colleagues²⁹ mentioned in Section 1.6.1. They used *ex situ* ^{23}Na MAS NMR to analyze the SEI products present on the surface of metallic sodium. The SEI was removed after 100 cycles using a current density of $1 \text{ mA} \cdot \text{cm}^{-2}$ and a polarisation of 1 hour at 50°C . The obtained spectra are presented in Figure. 1.14. The spectral analysis conducted by the authors identified the Na_2O , NaF phases, as well as a Na -complex, as mentioned in Section 1.6.1. This example demonstrates the effectiveness of *ex situ* NMR in identifying these phases. However, due to the quadrupolar nature of the sodium atom, the spectral signatures of different phases can show quadrupolar line shapes resulting in significant peak overlap, which complicates the analysis of ^{23}Na spectra. The

1.7. NMR as a key characterisation technique

use of high-field spectrometers can mitigate the quadrupolar effect in the ^{23}Na spectrum, and/or the application of a technique called multiple quantum magic angle spinning (MQMAS) could improve the resolution.

1.7.2 NMR resonance frequency shift ranges

The MAS NMR spectra of ^{23}Na for several simple sodium compounds exhibit narrow resonances, which are attributed to highly symmetric environments around the sodium atom, with nearly zero quadrupole coupling constants (C_Q). In contrast, other compounds in which sodium is situated in less symmetric environments show quadrupolar line shapes (Table 1.3). The values of isotropic chemical shifts (δ_{iso}) for ^{23}Na compounds span a relatively wide range, suggesting that they could be useful for obtaining structural information. Studies on model sodium compounds have been reported in the literature (see Table 1.3). Some of these compounds have been detected in electrochemical cells. The isotropic chemical shifts (δ_{iso}) of sodium-containing compounds in the electrolyte and the solid electrolyte interphase (SEI) range from -15 to 55 ppm.

Table 1.3. ^{23}Na Isotropic Chemical Shifts (δ_{iso}), Quadrupolar Coupling Constant (C_Q), Asymmetry Parameter of the Electric Field Gradient (η) reported in the literature for various sodium compounds.

Compound	References	δ_{iso} [ppm]	C_Q (MHz)	η
Metallic–Na	Reference ¹⁴	1131.0	0.00	ND
Na_2O	Reference ⁷²	54.0	0.00	ND
NaOH	Reference ^{73,74}	20.0 or 12.2	3.60	0.15
NaH	Reference ⁷⁵	17.8	0.00	0.00
$\text{Na}_2\text{O}_2/\text{Na}_{(\text{site 1})}$	Reference ⁷²	7.0	0.47	0.10
$\text{Na}_2\text{O}_2/\text{Na}_{(\text{site 2})}$	Reference ⁷²	11.8	0.47	0.10
NaF	Reference ²⁹	7.4	0.00	0.00
$\text{Na}_2\text{CO}_3/\text{Na}_{(\text{site 1})}$	Reference ⁷²	7.0	1.20	0.60
$\text{Na}_2\text{CO}_3/\text{Na}_{(\text{site 2})}$	Reference ⁷²	7.5	1.28	0.50
$\text{Na}_2\text{CO}_3/\text{Na}_{(\text{site 3})}$	Reference ⁷²	-4.0	2.48	0.65
NaBr	Reference ⁷⁶	5.2	ND	ND
Na_2SO_4	Reference ⁷⁴	-8.5	2.60	0.53
NaHCO_3	Reference ⁷⁶	-5.4	ND	ND
NaNO_3	Reference ⁷⁶	-7.3	ND	ND
NaO_2	Reference ⁷²	-23.0 to -33.0	0.00	ND
$\text{Na}_2[\text{SO}_3\text{--N--SO}_2\text{F}]$??	Reference ²⁹	-12.6	0.00	ND

Reeve et al.⁷² reported δ_{iso} values for several sodium compounds used in sodium-oxygen (Na--O_2)

cathodes. According to their study, sodium fluoride (NaF) has an δ_{iso} value of 7.4 ppm, while sodium peroxide (Na_2O_2) has a value of 7 ppm. In contrast, sodium superoxide (NaO_2) shows a value of 54 ppm. Additionally, Na_2O_2 has two sodium sites, with a quadrupole coupling constant of 0.47 MHz.

1.8 Research gaps and questions

1.8.1 Research gaps

First of all, it is well established that the formation of the SEI layer results from the decomposition of the electrolyte at the electrode surface. Although the composition of the SEI in electrolyte systems composed of ionic liquids and highly concentrated sodium salts has been extensively studied using various characterization techniques, it remains poorly understood due to its complexity. The challenge of characterising the SEI arises from several factors, such as the small size of the layers, their disordered structure, their sensitivity to atmospheric conditions (especially exposure to air), and the presence of multiple phases. These factors make it challenging to accurately characterize SEI layers. Gaining new insights into their composition and structure could be crucial for developing an optimal and high-performance electrolyte. Furthermore, materials such as PIL block copolymers and ZPC have shown promise as candidates for high-performance solid electrolytes. However, the introduction of a sodium salt into ZPCs and PIL block copolymers raises important questions about the specific interactions between Na^+ ions and the zwitterion, as well as the interactions between Na^+ ions and the ionic block of the PIL block copolymers. These questions remain unanswered. Understanding these fundamental interactions is essential for the development of solid electrolytes capable of conducting Na^+ ions with minimal resistance.

1.8.2 Research questions

NMR spectroscopy proves to be an exceptionally powerful investigative tool for addressing the previously raised questions. It allows for the discernment and evaluation of complex interactions between atomic nuclei, as well as interactions within materials such as PIL block and ZPC. Short-range disorder affects dipole-dipole interactions, whether intramolecular or, to a lesser extent, some intermolecular interactions. These interactions can be effectively detected through single-pulse NMR measurements as well as

1.9. Conclusion

complex two-dimensional techniques, such as exchange experiment. Thus, this project has two main objectives. Firstly, it aims to understand how sodium interacts within zwitterionic and polymeric solid electrolytes. Secondly, it seeks to deepen our understanding of the formation of the SEI in sodium batteries, particularly with IL electrolytes. To achieve these goals, we will employ advanced experimental characterization techniques, primarily focused on NMR spectroscopy. These techniques will include both one-dimensional and two-dimensional measurements for studying solid-state electrolytes, as well as *ex situ* measurements for analyzing the SEI. The fundamental question that this project will attempt to address is:

What can advanced NMR spectroscopy reveal about the formation of the SEI and the solvation environments of ions in sodium batteries and electrolytes ?

This question can be divided into two sub-questions: The first sub-question addresses how Na^+ cations interact with other ionic species in novel sodium-based electrolytes, such as ionic copolymers and zwitterionic solid materials. The second sub-question examines how ionic interactions, ion transport, and the formation of the solid electrolyte interphase in sodium-containing ionic liquid electrolytes are influenced by sodium salt concentration or additives, and how these factors correlate with the cycling performance of cells.

1.9 Conclusion

In this first chapter, we examine the current dominance of lithium-ion batteries in the energy storage market primarily due to their remarkable electrochemical performance. However, in response to the growing demand for more economical, safe, and sustainable energy solutions, sodium-ion batteries are emerging as a promising alternative. Although sodium has certain limitations compared to lithium, its advantages, such as abundance, lower cost, and comparable electrochemical properties, make sodium-ion batteries attractive for future applications.

Recent advances in the field of sodium-ion batteries, particularly the use of ionic liquids with superconcentrated sodium salts, have led to improved performance. Furthermore, research on solid electrolytes, including polymerized ionic liquid copolymers and ionic plastic crystals, suggests that these materials could be promising candidates for the next generation of batteries, especially when combined with additives. However, the understanding of the components that form at the electrolyte-electrode

interface remains limited. Moreover, the solvation mechanisms of sodium ions within polymerized ionic liquid copolymers and ionic plastic crystals are still not well understood. Nuclear Magnetic Resonance spectroscopy represents a valuable tool for elucidating these sodium ion solvation mechanisms within the electrolyte and the formation of the solid electrolyte interphase. This could, in turn, guide research towards more efficient electrolyte formulations.

The next chapter will focus on presenting the fundamental concepts of Nuclear Magnetic Resonance.

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Review of NMR Spectroscopy

Nuclear magnetic resonance was discovered in the 1940s, following advancements in nuclear physics and magnetism. In 1946, physicists Felix Bloch and Edward Purcell made a significant breakthrough by developing techniques to observe the magnetic resonance of atomic nuclei.^{1,2} They demonstrated that these nuclei could absorb and reemit radio waves when subjected to a magnetic field, paving the way for a new method of analysis. For this discovery, Bloch and Purcell were awarded the Nobel Prize in Physics in 1952. During the 1950s and 1960s, NMR was refined to become an important analytical tool in studying molecular structures and chemical compositions, leading to the emergence of NMR spectroscopy. Today, NMR plays an important role in various scientific fields, including chemistry, biology, and medicine, where it is used in applications such as magnetic resonance imaging (MRI). The following sections present the fundamental principles of NMR, the interactions observed in NMR, as well as several essential techniques to improve spectral resolution in solid-state NMR.

2.1 Principle

The fundamental principle of NMR is to observe the magnetic properties of atomic nuclei. Some isotopes have an angular momentum-like property known as nuclear spin. The magnetic moment $\vec{\mu}$ of each nucleus is proportional to this spin. In other words, the relationship between the magnetic moment and the spin can be expressed by the following equation:

$$\vec{\mu} = \gamma \hbar \vec{I} \quad (2.1)$$

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where, γ represents the gyromagnetic ratio, a constant specific to each isotope, $\vec{I}$ is the nuclear spin angular momentum, and $\hbar$ is the reduced Planck constant, defined as $\hbar = \frac{h}{2\pi}$.

The phenomenon of nuclear magnetic resonance can be described in two different ways. The first description is classical in nature and is based on the equations of classical mechanics, as formulated by Felix Bloch¹ to explain the observed phenomenon. The second description is quantum in nature and uses the equations of quantum mechanics, as proposed by Edward M. Purcell.²

2.1.1 Classical Description

The description uses classical electromagnetism theory to explain the movement of a magnetic dipole moment when subjected to a magnetic field. The magnetic moment experiences a torque $\vec{\mu} \times \vec{B}_0$, which is equal to the rate of change of the orientation of its angular momentum³:

$$\hbar \frac{d\vec{I}}{dt} = \vec{\mu} \times \vec{B}_0 \quad (2.2)$$

By combining Equation (2.1) and Equation (2.2), it follows that the motion of a magnetic moment $\vec{\mu}$ in a magnetic field $\vec{B}_0$ is described by the following equation:

$$\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}_0 \quad (2.3)$$

This relation describes the precessional motion of the magnetic moment μ around the magnetic field B_0 at a frequency $\omega_0 = -\gamma B_0$, known as the Larmor frequency, as illustrated in Figure. 2.1.

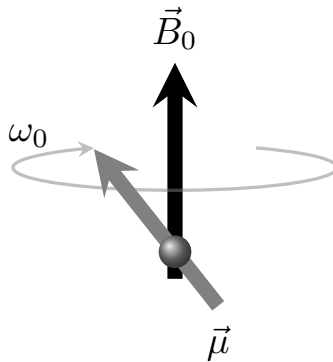


Figure 2.1. Precessional motion of a magnetic moment $\vec{\mu}$ around a static magnetic field $\vec{B}_0$ at the Larmor frequency ω_0 .

Macroscopic magnetization

So far, we have examined the behavior of an isolated magnetic moment. However, in condensed matter where there are multiple nuclei, this magnetic moment is subjected to the influence of thermal agitation, as well as to interactions with the surrounding nuclei and electrons (spin-lattice interaction). A thermal equilibrium tends to be established between the spin system and the lattice through this spin-lattice interaction. Once this equilibrium is reached, a longitudinal macroscopic magnetization M_0 is created, aligned with the magnetic field B_0 , such as:

$$M_0 = \frac{N\gamma^2\hbar^2 I(I+1)B_0}{3kT} \quad (2.4)$$

where N is the number of nuclei in the system, k is the Boltzmann constant, and T is the temperature of the system.

Resonance

This macroscopic magnetization is perturbed from equilibrium by the application of an oscillating electromagnetic field B_1 , which is perpendicular to the static field B_0 . This oscillating field is given by $B_1(t) = 2B_1 \cos(\omega t)$ and can be decomposed into two fields of amplitude B_1 rotating around B_0 at frequencies $\pm\omega$. By adopting a rotating reference frame at frequency ω with the same sign as ω_0 (which depends on the sign of the gyromagnetic ratio of the observed nucleus), the oscillating field B_1 appears as static. Combining this field B_1 with the static field B_0 results in an effective field B_e , around which the macroscopic magnetization precesses. This effective field can be described as follows⁴:

$$B_e = \left(B_0 + \frac{\omega}{\gamma} \right) \vec{k} + B_1 \vec{i} \quad (2.5)$$

where $\vec{k}$ and $\vec{i}$ are the unit vectors along the (Oz) axis, which is parallel to B_0 in the laboratory coordinate system $(Oxyz)$, and the (Ox') axis of the rotating frame $(Ox'y'z')$, respectively. The orientation of the effective field, denoted by the angle θ between the effective field and the static field B_0 , is given by:

$$\tan \theta = \frac{B_1}{B_0 - \left(\frac{\omega}{\gamma} \right)} = \frac{\omega_1}{\omega_0 - \omega} \quad \text{with } \omega_1 = \gamma B_1 \quad (2.6)$$

Since the amplitude of the field B_1 is much smaller than the static field B_0 , it only influences the

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orientation of the effective field when the difference $|\omega - \omega_0|$ is close to ω_1 . This condition is referred to as resonance.

Pulsed Fourier Transform NMR

Nuclear magnetic resonance can be performed using two main methods: scanning NMR and pulsed NMR. Currently, pulsed NMR is the most commonly used method due to its ability to repeatedly apply radiofrequency field pulses and accumulate the signal induced by the precessing magnetization. This technique has improved sensitivity, with gains estimated at a factor of ten or more, and has significantly reduced the time required to achieve a comparable level of sensitivity to that of scanning NMR, with time reductions by a factor of 100⁵.

The experimental setup consists of a static magnetic field B_0 of constant strength. Pulsed radiofrequency fields of short duration are applied to disturb the equilibrium orientation of the macroscopic magnetization. The return of the magnetization to its thermal equilibrium state is described by the Bloch equations:

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1} \quad (2.7)$$

$$\frac{dM_{xy}}{dt} = -\frac{M_{xy}}{T_2} \quad (2.8)$$

In a static magnetic field with a value B_0 , an oscillating magnetic field B_1 at the Larmor frequency of the nucleus is applied for a defined duration τ . This oscillating field perturbs the macroscopic magnetization $\vec{M}$, causing it to deviate by an angle $\theta = \gamma B_1 \tau$ relative to B_0 . This process causes the magnetization to leave its initial equilibrium state. The variations of the longitudinal component M_z and the transverse components M_x and M_y as they return to equilibrium in the laboratory frame are described by the following equations.

$$M_x + iM_y = M_0 \sin(\theta) \exp\left(i\omega_0 t - \frac{t}{T_2}\right) \quad (2.9)$$

$$M_z = M_0 \left[1 - \cos(\theta) \exp\left(-\frac{t}{T_1}\right)\right] \quad (2.10)$$

The precession of the transverse components of the macroscopic magnetization generates an electromotive force that is proportional to the transverse component of the magnetization at the terminals

of a coil placed around the sample and oriented parallel to the (O_x) axis. By recording this electromotive force, one obtains the free induction decay signal, commonly known as FID. This signal can then be analyzed to produce a NMR spectrum through Fourier transformation. Figure. 2.2 shows an example of a pulsed NMR FID with Fourier transform for the nucleus ^{23}Na .

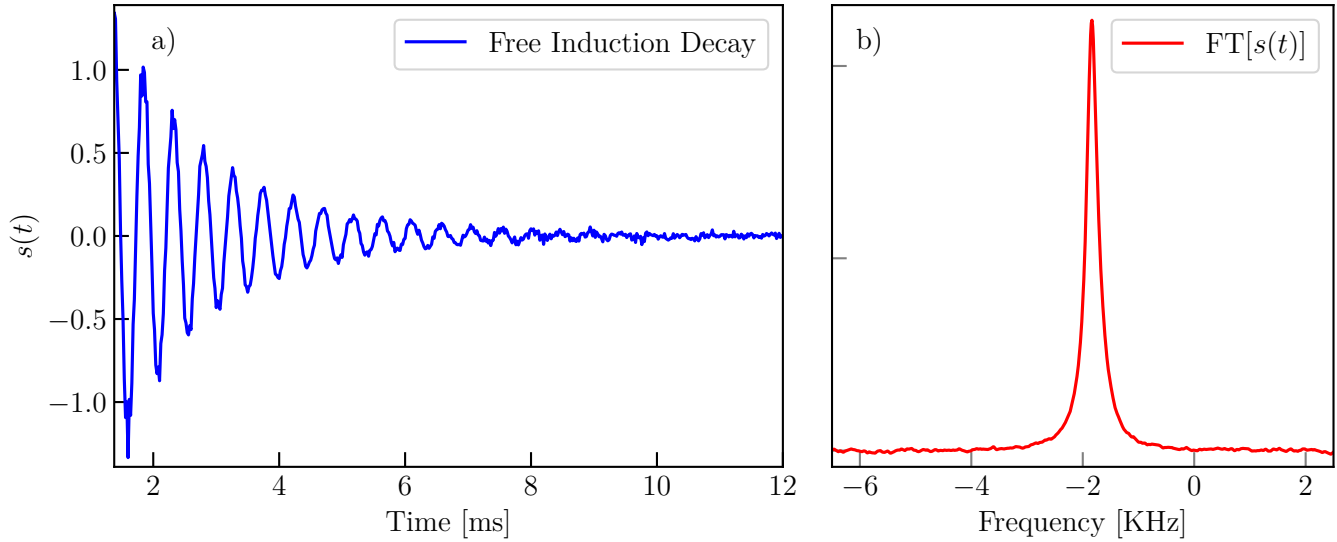


Figure 2.2. Example of pulsed NMR for the ^{23}Na nucleus. (a) Free induction decay signal and (b) its Fourier transform.

It can be observed that the signal acquisition process is divided into two distinct phases. First, an initial delay is noted during which the signal remains at zero. This delay is followed by the actual signal acquisition phase, which begins after a short moment. The period during which the signal is zero is referred to as the "dead time". This dead time corresponds to the duration needed for the sensor to transition from transmitter mode to receiver mode, and it is on the order of a few μs .

2.1.2 Quantum Description

In the quantum framework, the Hamiltonian operator for the Zeeman interaction $\hat{\mathcal{H}}_0$ is defined as:

$$\hat{\mathcal{H}}_0 = -\vec{\mu} \cdot \vec{B}_0 = -\hbar\gamma B_0 \hat{I}_z = -\hbar\omega_0 \hat{I}_z \quad (2.11)$$

where the spin operator $\vec{I}_z$ represents the component along the (O_z) axis of the spin angular momentum I in the laboratory frame $(Oxyz)$, with the (O_z) axis being parallel to the static magnetic field B_0 . In the case of an isolated spin, the total Hamiltonian $\hat{\mathcal{H}}$ reduces to the Zeeman Hamiltonian $\hat{\mathcal{H}}_0$ since the only

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interaction it experiences is that of the static magnetic field B_0 . The eigenvectors of $\hat{\mathcal{H}}$ are the wave functions describing the eigenstates of the isolated spin system in the magnetic field B_0 . These states are denoted as $|I, m\rangle$, where I is the spin quantum number and m is the magnetic quantum number. The magnetic quantum number m can take on $2I + 1$ values ranging from $-I$ to $+I$ in increments of one unit. The eigenvalues of $\hat{\mathcal{H}}$ represent the energies corresponding to the different eigenstates of the magnetic moment. These eigenvalues are determined from the eigenvalue equation:

$$\hat{\mathcal{H}}|I, m\rangle = E_m|I, m\rangle \quad (2.12)$$

where E_m is the energy associated with the state $|I, m\rangle$, and is given by:

$$E_m = -\hbar\omega_0 m \quad (2.13)$$

Here, E_m represents the energy of the state $|I, m\rangle$ and depends on the magnetic quantum number m .

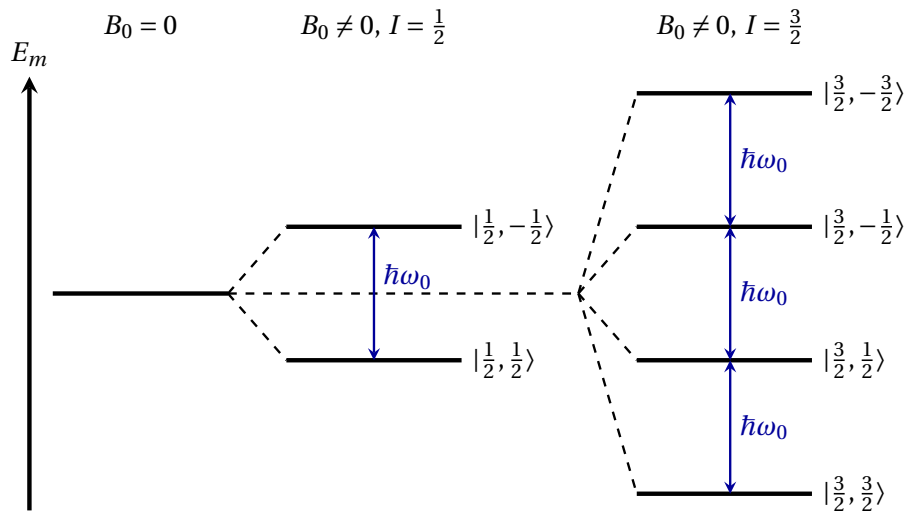


Figure 2.3. Illustration of the Zeeman energy levels for an isolated spin with $I = \frac{1}{2}$ and $I = \frac{3}{2}$ in interaction with a magnetic field B_0 .

The quantum state of an isolated spin magnetic moment can be described by a superposition of multiple quantum states. The wave function $|\psi(t)\rangle$ can be represented in a Hilbert space (a finite-dimensional vector space). In this space, $|\psi(t)\rangle$ can be expressed as a linear combination of state

vectors, such as:

$$|\psi(t)\rangle = \sum_{i=1}^n c_i(t)|i\rangle \quad \text{with} \quad \sum_{i=1}^n |c_i|^2 = 1 \quad (2.14)$$

The superposition coefficients c_i are complex numbers that indicate the probability $|c_i|^2$ of obtaining an eigenvalue E_i when measuring the observable $\hat{H}$. The Hilbert space has a dimension of $n = (2I + 1)^N$, where I represents the spin quantum number and N is the number of nuclei with spin I in the system under consideration. The time variation of the wave function $\psi(t)$ is then reflected in the time variation of the superposition coefficients c_i . For example, for an isolated spin $\frac{1}{2}$, considering the eigenvectors $|\frac{1}{2}, -\frac{1}{2}\rangle = |\alpha\rangle$ and $|\frac{1}{2}, \frac{1}{2}\rangle = |\beta\rangle$, the state function $|\psi(t)\rangle$ can be expressed as a linear combination of these two eigenvectors, as follows:

$$|\psi(t)\rangle = C_\alpha(t)|\alpha\rangle + C_\beta(t)|\beta\rangle \quad (2.15)$$

When dealing with an ensemble of spins, it is preferable to use the density operator rather than the state function to describe the ensemble. The density operator is defined as follows:

$$\rho(t) = \sum_k p_k |\psi_k(t)\rangle \langle \psi_k(t)| = \sum_k p_k \sum_i \sum_j c_i^k c_j^{k*} |i\rangle \langle j| \quad (2.16)$$

where p_k is the probability that the spin system of the ensemble is in one of the possible states $|\psi_k(t)\rangle$, with $\sum p_k = 1$, and $\rho^k = |\psi_k(t)\rangle \langle \psi_k(t)|$ is the density operator of a spin system in the ensemble. This spin density can be expressed as an ensemble average of the operators ρ^k in the following manner:

$$\rho = \sum_i \sum_j \overline{c_i c_j^*} |i\rangle \langle j| \quad (2.17)$$

where the terms $\overline{c_i c_j^*}$ are the elements of the density matrix ρ . For example, for a system of isolated spins $\frac{1}{2}$, with the eigenvectors of the system denoted as $|\alpha\rangle$ and $|\beta\rangle$, the density operator ρ is expressed as follows:

$$\rho = \begin{pmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{pmatrix} = \begin{pmatrix} \overline{c_\alpha c_\alpha^*} & \overline{c_\alpha c_\beta^*} \\ \overline{c_\beta c_\alpha^*} & \overline{c_\beta c_\beta^*} \end{pmatrix} \quad (2.18)$$

The diagonal elements $\rho_{\alpha\alpha}$ and $\rho_{\beta\beta}$ of the density matrix represent the populations of the states

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$|\alpha\rangle$ and $|\beta\rangle$, and their sum is equal to 1, i.e., $Tr[\rho] = 1$. The off-diagonal elements $\rho_{\alpha\beta}$ and $\rho_{\beta\alpha}$ are cross-terms that represent the interference effects between the states $|\alpha\rangle$ and $|\beta\rangle$. These terms are complex numbers that indicate phase coherence between the states when their average is not zero. Therefore, the off-diagonal elements are called coherences.

Let's now examine the density matrix in the context of thermal equilibrium. At a temperature T , when the system is in thermal equilibrium, the density operator for a set of isolated spins subjected to a magnetic field B_0 is described by the following relation⁶:

$$\rho_{eq} = \frac{\exp\left(-\frac{\hbar\mathcal{H}_0}{k_B T}\right)}{Tr\left[\exp\left(-\frac{\hbar\mathcal{H}_0}{k_B T}\right)\right]} \quad (2.19)$$

In the case of high temperatures, the exponential terms can be approximated by their first-order Taylor expansion:

$$\rho_{eq} \approx \frac{\hat{1} - \frac{\hbar\mathcal{H}_0}{k_B T}}{Tr\left[\hat{1} - \frac{\hbar\mathcal{H}_0}{k_B T}\right]} \quad (2.20)$$

Given that the trace of $\mathcal{H}_0$ is zero ($Tr[\mathcal{H}_0] = 0$) and the trace of the identity matrix is equal to $2I + 1$ ($Tr[\hat{1}] = 2I + 1$), Equation (2.20) can be simplified as follow:

$$\rho_{eq} \approx \frac{1 - \hbar\mathcal{H}_0}{(2I + 1)k_B T} \approx \frac{1}{(2I + 1)k_B T} - \frac{\hbar\mathcal{H}_0}{(2I + 1)k_B T} \quad (2.21)$$

Since the identity matrix does not affect the evolution of the system, and by combining this relationship with Equation (2.11), the expression can be simplified further:

$$\rho_{eq} \approx \frac{\hbar^2 \omega_0 \hat{I}_z}{(2I + 1)k_B T} \quad (2.22)$$

Thus, the density operator for a spin system in thermal equilibrium in a magnetic field B_0 is proportional to the operator $\hat{I}_z$. In many textbooks, the factor in front of the $\hat{I}_z$ operator is taken to be 1, therefore the approximation $\rho_{eq} \approx \hat{I}_z$ is often used.

The equation governing the evolution of the density operator is described by the Liouville-Von Neumann differential equation⁶.

$$\frac{d\rho}{dt} = -i \left[\hat{\mathcal{H}}, \rho \right] \quad (2.23)$$

The general solution to this equation is given by:

$$\rho(t) = U(t)\rho(0)U^{-1}(t) \quad (2.24)$$

where $\rho(0) = \rho_{eq} \approx I_z$ and $U(t)$, called the propagator or evolution operator, is a unitary operator. This operator allows us to calculate the density operator at any time t . When the Hamiltonian is time-independent, the propagator $U(t)$ can be expressed explicitly.

$$U = \exp\left(-i\frac{\hat{\mathcal{H}}}{\hbar}t\right) \quad (2.25)$$

These equations indicate that the change in the density operator over a time period t is directly influenced by the Hamiltonian that affects the system during that time. To describe the evolution of the density operator during an NMR experiment, three types of evolution can be distinguished: evolution induced by radiofrequency pulse, free evolution, and evolution due to coupling phenomena.

In a Nuclear Magnetic Resonance (NMR) experiment, the Hamiltonian corresponding to the radiofrequency pulse in the rotating frame is:

$$\hat{\mathcal{H}}_{RF} = -\hbar\gamma B_1 [\cos(\phi_{RF})\hat{I}_x + \sin(\phi_{RF})\hat{I}_y] \quad (2.26)$$

So, the evolution of the density operator under the effect of a radiofrequency pulse of duration τ_p can be expressed as follows.

$$\begin{aligned} \rho(\tau_p) &= \exp\left(-i\frac{\hat{\mathcal{H}}_{RF}}{\hbar}\tau_p\right)\rho(0)\exp\left(i\frac{\hat{\mathcal{H}}_{RF}}{\hbar}\tau_p\right) \\ &= \exp(i\omega_1\tau_p [\cos(\phi_{RF})\hat{I}_x + \sin(\phi_{RF})\hat{I}_y])\hat{I}_z \exp(-i\omega_1\tau_p [\cos(\phi_{RF})\hat{I}_x + \sin(\phi_{RF})\hat{I}_y]) \end{aligned}$$

This expression simplifies as follows:

$$\rho(\tau_p) = \sin(\omega_1\tau_p) [\sin(\phi_{RF})\hat{I}_x - \cos(\phi_{RF})\hat{I}_y] + \cos(\omega_1\tau_p)\hat{I}_z \quad (2.27)$$

If a pulse t_p is such that $\omega\tau_p = \frac{\pi}{2}$, then the longitudinal part of the density matrix is zero, while the transverse part is maximal: $\rho(\tau_p) = \sin(\phi_{RF})\hat{I}_x - \cos(\phi_{RF})\hat{I}_y$. Moreover, if a pulse t_p is such that $\omega\tau_p =$

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π , the density matrix is given by $\rho(\tau_p) = -\hat{I}_z$. These observations are consistent with what is indicated by the Bloch equations.

After the application of the radiofrequency field pulse, the system is only affected by the static field B_0 . The Hamiltonian governing this period of free evolution is given by $\hat{\mathcal{H}}_0 = -\hbar\Omega_0\hat{I}_z$, where $\Omega_0 = \omega_0 - \omega_{RF}$ represents the precession frequency in the rotating frame. By applying the previous reasoning, which involves the Hamiltonian $\hat{\mathcal{H}}_0$, the density operator during the free precession period τ_2 is formulated as follows:

$$\rho(\tau_2) = \frac{\sin(\omega_1 \tau_p)}{2i} \left[-\hat{I}_+ e^{-i(\phi_{RF} + \Omega_0 \tau_2)} + \hat{I}_- e^{i(\phi_{RF} + \Omega_0 \tau_2)} \right] + \cos(\omega_1 \tau_p) \hat{I}_z \quad (2.28)$$

with $\hat{I}_{\pm} = \hat{I}_x \pm i\hat{I}_y$

The signal measured in NMR is a complex signal detected in quadrature during the period τ_2 . It is proportional to the average of the observable $\langle \hat{I}_+ \rangle$.⁷

$$s(\tau_2) \sim 2i\langle \hat{I}_+ \rangle e^{-i\phi_R} \sim 2i\text{Tr}[\hat{I}_+ \rho(\tau_2)] e^{-i\phi_R} \quad (2.29)$$

where ϕ_R is the phase of the receiver. By selecting an impulse duration τ_p such that $\omega\tau_p = \frac{\pi}{2}$, and adjusting the receiver phase ϕ_R to match the phase of the pulse ϕ_{RF} , the expression for the recorded signal simplifies to:

$$s(\tau_2) = s(0)e^{i\Omega_0\tau_2} \quad \text{with} \quad s(0) = \frac{\hbar^2\omega_0}{(2I+1)k_B T} \quad (2.30)$$

The signal $s(\tau_2)$ describes the movement of magnetization, which continuously precesses around the z -axis. However, in reality, this signal decays over time due to relaxation phenomena. This decay occurs because the magnetic spin moments, after being disturbed by a radiofrequency pulse, gradually return to their equilibrium state. This return is influenced by fluctuations in the local fields caused by dynamics. This phenomenon, known as longitudinal relaxation, is denoted as T_1 .

There is also another form of magnetization decay, known as "transverse decay" or transverse relaxation (T_2). This decay is primarily due to two phenomena. First, the loss of coherence between magnetic spin moments, caused by fluctuations in interactions between neighboring spins, leads to variations in the perceived local fields. This results in differences in resonance frequencies. Second, inhomogeneities in the static field B_0 cause variations in precession frequencies depending on spatial positions. These frequency variations lead to a defocusing of magnetic moments, thereby contributing to

the decay of transverse magnetization. This phenomenon is called "apparent" decay and is characterized by a time constant T_2^* , which is inversely proportional to the width of the resonance line:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma\Delta B_0 \quad (2.31)$$

The relaxation phenomenon can be approximated by an exponential damping. This approach allows incorporating this behavior into the signal expression as follows:

$$s(\tau_2) = s(0)e^{i\Omega_0\tau_2 - \frac{\tau_2}{T_2^*}} \quad (2.32)$$

The acquisition of the signal $s(\tau_2)$ allows for the measurement of the FID signal. By applying a Fourier transform to this signal, a frequency spectrum can subsequently be obtained, as illustrated in Figure. 2.2.

2.2 Interactions

In condensed molecular or ionic systems, the presence and movement of nuclei and electrons in these systems give rise to additional interactions that modify the initial effects. These additional interactions include chemical shift, J-coupling, magnetic dipole interaction, and electric quadrupole interaction. Thus, the Hamiltonian for the system is the aggregate of the Hamiltonians for each individual interaction:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{\mathcal{RF}} + \hat{\mathcal{H}}_{\text{CS}} + \hat{\mathcal{H}}_J + \hat{\mathcal{H}}_D + \hat{\mathcal{H}}_Q \quad (2.33)$$

where $\hat{\mathcal{H}}_0$ and $\hat{\mathcal{H}}_{\mathcal{RF}}$ represent the Hamiltonians for the Zeeman interaction with the static magnetic field B_0 and the radiofrequency field B_1 , respectively. $\hat{\mathcal{H}}_{\text{CS}}$ describes the chemical shift interaction. $\hat{\mathcal{H}}_J$ and $\hat{\mathcal{H}}_D$ are the Hamiltonians for the indirect and direct spin-spin coupling interactions, respectively. Finally, $\hat{\mathcal{H}}_Q$ is the Hamiltonian for the electric quadrupole coupling. Since the environment around a nucleus in a molecule is not always spherically symmetric, these interactions can be anisotropic. The anisotropic nature of these interactions is accounted for by expressing them in the Cartesian coordinate system (x, y, z) as a second-rank Cartesian tensor.

In high-field NMR, these interactions are typically much weaker than the Zeeman interaction (Equation (2.11)), and can be viewed as perturbations to the spin system in the presence of the static

2.2. Interactions

field B_0 . Consequently, the Hamiltonian for these interactions can be simplified to first or second order using stationary perturbation theory, depending on their strength, by focusing only on the secular terms that commute with the Zeeman Hamiltonian $\hat{H}_0$. We will discuss these interactions in the sections that follow.

2.2.1 Chemical Shift Interaction

In the presence of an external magnetic field, the orbital motion of electrons around the nucleus generates a local magnetic field, denoted B_{induced} , which can be expressed as $B_{\text{induced}} = -\sigma B_0$, where σ is the shielding constant. The magnetic field locally experienced by the nucleus is then the combination of the main field B_0 and the field induced by the electron movement, given by $B_{\text{local}} = B_0(1 - \sigma)$. Measuring this screening induced by the surrounding electrons provides valuable information about the chemical environment around the nucleus, such as the number of ligands and the nature of the first neighbors. The shielding tensor $\hat{\sigma}$ is a second-rank matrix and can be written in the following form:

$$\hat{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \quad (2.34)$$

The asymmetric part of this tensor has no influence on the NMR spectrum at first order⁸, so there exists a principal reference frame (X, Y, Z) in which this tensor is diagonal. The diagonal tensor can then be expressed in the following form:

$$\hat{\sigma}_d = \begin{pmatrix} \sigma_{XX} & 0 & 0 \\ 0 & \sigma_{YY} & 0 \\ 0 & 0 & \sigma_{ZZ} \end{pmatrix} \quad (2.35)$$

$$\alpha = \beta \quad (2.36)$$

The chemical shift interaction that affects spin I is described by the chemical shift Hamiltonian $\hat{\mathcal{H}}_{\mathcal{CS}}$ as follows:

$$\hat{\mathcal{H}}_{\mathcal{CS}} = -\hbar\gamma B_0 \hat{\sigma} \hat{I} = -\hbar\omega_0 \hat{\sigma} \hat{I} \quad (2.37)$$

Given the application of the static field B_0 along the z -axis, only the secular term of the Hamiltonian

associated with the chemical shift is considered in the (x, y, z) frame. This Hamiltonian is given by the following relation:

$$\hat{\mathcal{H}}_{\mathcal{C}, \mathcal{J}} = -\hbar\omega_0 \hat{\sigma}_{zz} \hat{I}_z \quad (2.38)$$

where σ_{zz} represents the component of the tensor along the z -axis when the field B_0 is aligned with this axis. However, the component $\hat{\sigma}_{zz}$ is expressed in the new principal frame (x', y', z') as follows:

$$\sigma_{zz} = \sigma_{XX} \sin^2(\beta) \cos^2(\alpha) + \sigma_{YY} \sin^2(\beta) \sin^2(\alpha) + \sigma_{ZZ} \cos^2(\beta) \quad (2.39)$$

Where α , β , and γ are the angles that allow the transition between the reference frames (x, y, z) and (X, Y, Z) , known as Euler angles.

The principal values of the shielding tensor can also be represented by three parameters: an isotropic term σ_{iso} , an anisotropic term σ_{CSA} , and an asymmetry parameter η_{CSA} . The Haeberlen convention, used in this document, is described below:

The isotropic term σ_{iso} is the average of the three principal values of the tensor, given by:

$$\sigma_{\text{iso}} = \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ})$$

The principal values of the tensor are ordered such that:

$$|\sigma_{ZZ} - \sigma_{\text{iso}}| \geq |\sigma_{XX} - \sigma_{\text{iso}}| \geq |\sigma_{YY} - \sigma_{\text{iso}}|$$

The anisotropy of the shielding is defined as the largest deviation from the isotropic value:

$$\sigma_{\text{CSA}} = \sigma_{ZZ} - \sigma_{\text{iso}}$$

The asymmetry of the tensor is quantified by the parameter η_{CSA} :

$$\eta_{\text{CSA}} = \frac{\sigma_{YY} - \sigma_{XX}}{\sigma_{ZZ} - \sigma_{\text{iso}}} \quad \text{where} \quad 0 \leq \eta_{\text{CSA}} \leq 1$$

Considering Haeberlen's convention, for any orientation of the shielding tensor, the Hamiltonian

2.2. Interactions

$\hat{\mathcal{H}}_{\mathcal{CS}}$ becomes:

$$\hat{\mathcal{H}}_{\mathcal{CS}} = -\hbar\gamma B_0 \left(\sigma_{\text{iso}} + \frac{\sigma_{\text{CSA}}}{2} [3\cos^2(\beta) - 1 - \eta \sin^2(\beta) \cos(2\alpha)] \right) \hat{I}_z = -\hbar\omega_{\text{CS}}(\alpha, \beta) \hat{I}_z \quad (2.40)$$

It can be observed that the isotropic and anisotropic effects of the interaction are proportional to the magnetic field B_0 . Consequently, the frequency difference between two different environments becomes larger, and the effects of chemical anisotropy are enhanced as B_0 increases. The actual resonance frequency observed is slightly altered by a phenomenon known as the chemical shift. This resonance frequency, denoted ω , is the sum of the Larmor frequency ω_0 and the contribution from the chemical shift $\omega = \omega_0 + \omega_{\text{CS}}$.

Solid-state NMR is often conducted on samples in powder form, where all single crystals are randomly oriented in space. Each crystallite can adopt any orientation Ω with equal probability. Consequently, each crystallite exhibits its own resonance frequency, determined by its orientation in the static field. The sum of contributions from each crystallite leads to a broadening of the resonance lines, reflecting both the distribution of crystallite orientations in the powder and the anisotropy of the interaction responsible for this broadening. The shape of the resonance line obtained for a powder is described by the following equation:

$$S(\omega) = \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^\pi \sin(\beta) d\beta \int_0^{2\pi} S(\omega(\Omega)) d\gamma \quad (2.41)$$

where the angles α , β , and γ convert the principal reference frame of the interaction to the laboratory reference frame through three successive counterclockwise rotations. $S(\omega(\Omega))$ represents the signal associated with a specific crystallite orientation. The Figure. 2.4 illustrates an example of the expected resonance line shapes for a powder spectrum dominated by anisotropic chemical shift interactions.

To compare spectra obtained with spectrometers operating at different static magnetic field intensities, a chemical shift scale δ , expressed in parts per million (ppm), is used, which is independent of the field B_0 . This chemical shift is measured relative to a reference signal.

$$\delta_{\text{iso}} = \left(\frac{\omega_{\text{iso}} - \omega_{\text{ref}}}{\omega_{\text{ref}}} \right) \cdot 10^6 = \left(\frac{\sigma_{\text{ref}} - \sigma_{\text{iso}}}{1 - \sigma_{\text{ref}}} \right) \cdot 10^6 \quad (2.42)$$

Consequently, all NMR spectra presented in this manuscript will be expressed in ppm.

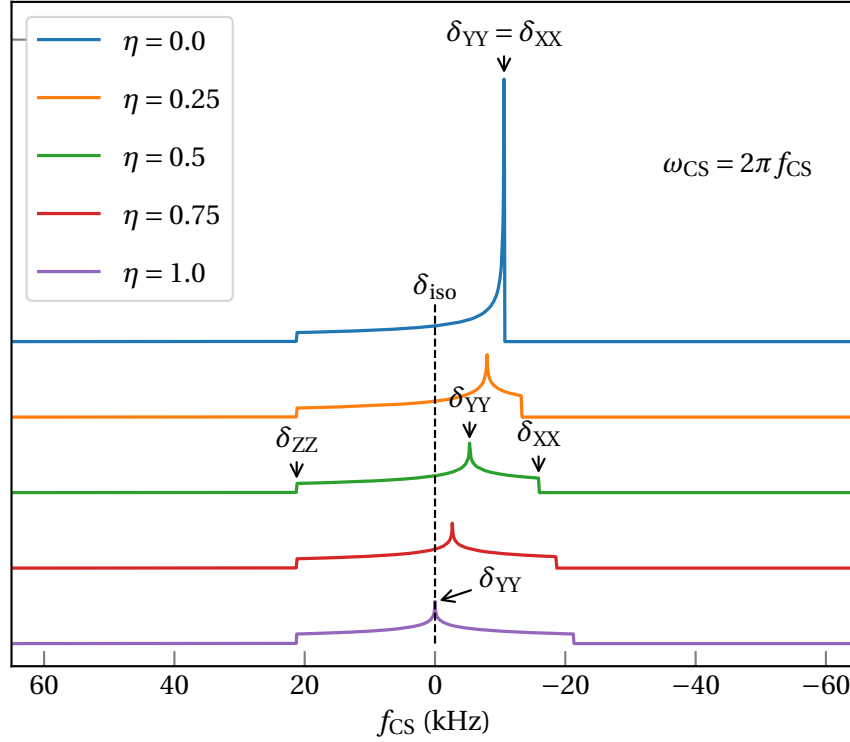


Figure 2.4. An example of simulated powder spectra for protons at 19.97 T, exhibiting a chemical shift anisotropy $\delta_{\text{CSA}} = 25$ kHz.

2.2.2 Indirect spin-spin coupling interactions

Indirect spin-spin coupling, also known as J-coupling, is an interaction that occurs through the bonding electrons between nuclei with non-zero spins that are covalently bonded. The Hamiltonian $\mathcal{H}$ describing this interaction is given by the following form:

$$\mathcal{H}_J = 2\pi \sum_{i < j} \hat{I}_i \cdot J_{ij} \cdot \hat{I}_j \quad (2.43)$$

In this expression, J_{ij} is a second-rank tensor that describes the indirect spin-spin coupling between nuclei I_i and I_j . This tensor is composed of two parts: an isotropic part, denoted J_{ij}^{iso} , and an anisotropic part, denoted J_{ij}^{aniso} . Thus, we can write:

$$J_{ij} = J_{ij}^{\text{iso}} + J_{ij}^{\text{aniso}} \quad (2.44)$$

where J_{ij} represents the indirect spin-spin coupling constant. This constant satisfies the condition that $J_{ij} = \frac{1}{3} \text{Tr}[J_{ij}]$. Furthermore, the anisotropic component J_{ij}^{aniso} is characterized by a trace of zero.

2.2. Interactions

In the case of high-field NMR, In the case of high-field NMR, the Hamiltonian is given by:

$$\mathcal{H}_J = 2\pi J \hat{I}_z \cdot \hat{S}_z \quad (2.45)$$

The anisotropic component of the coupling J is significant only in particular cases, such as strong coupling or anisotropic environments, and is difficult to measure separately from the dipolar coupling due to the similarity of their Hamiltonians. In contrast, the isotropic component, or scalar coupling, is commonly used in NMR to reveal direct connectivities between nuclei with non-zero spin. However, this interaction, being weak (ranging from a few Hertz to several hundred Hertz), is often obscured by other stronger interactions in solid samples.

2.2.3 Dipolar Coupling Interaction

The dipole-dipole interaction refers to a direct coupling that occurs at a distance between the magnetic moments of spin. For a dipole-dipole coupling between two spins, denoted as $\vec{I}$ and $\vec{S}$, the Hamiltonian describing this interaction is given by:

$$\mathcal{H}_D = \frac{\mu_0 \hbar \gamma_I \gamma_S}{4\pi} \left(\frac{\vec{I} \cdot \vec{S}}{r_{IS}^3} - 3 \frac{(\vec{I} \cdot \vec{r}_{IS})(\vec{S} \cdot \vec{r}_{IS})}{r_{IS}^5} \right) \quad (2.46)$$

In the case of a heteronuclear dipole-dipole interaction, the Hamiltonian of the interaction is expressed as follows:

$$\mathcal{H}_D = \frac{\mu_0 \hbar \gamma_I \gamma_S}{4\pi r_{IS}^3} (1 - 3 \cos^2 \theta) \hat{I}_z \hat{S}_z \quad (2.47)$$

In the case of a homonuclear dipole-dipole interaction, the Hamiltonian of the interaction is expressed as follows:

$$\mathcal{H}_D = \frac{\mu_0 \hbar \gamma_I^2}{4\pi r_{I_1 I_2}^3} (1 - 3 \cos^2 \theta) \left[\hat{I}_{1z} \hat{I}_{2z} - \frac{1}{4} (\hat{I}_{1+} \hat{I}_{2-} + \hat{I}_{1-} \hat{I}_{2+}) \right] \quad (2.48)$$

This interaction does not cause a shift in resonance frequencies, but it generally manifests as a homogeneous broadening of the resonance peaks in solid-state NMR.

2.2.4 Quadrupolar Interaction

The quadrupolar interaction occurs only in nuclei with a nuclear spin greater than $\frac{1}{2}$. This interaction arises from the coupling between the nuclear quadrupole moment eQ and the local electric field gradient. The quadrupole moment originates from the non-spherical distribution of electric charges within the nucleus.

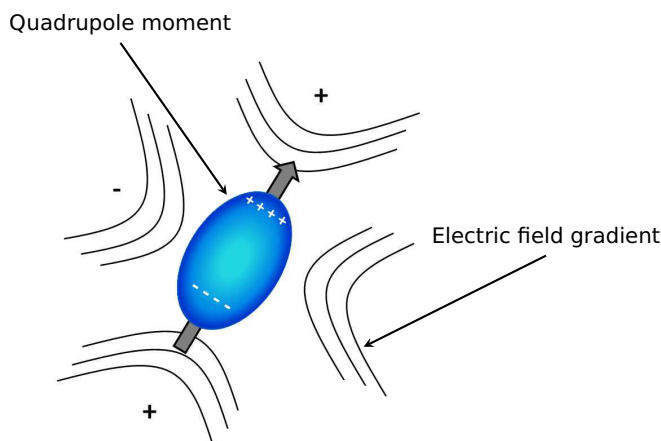


Figure 2.5. Representation of the electric field gradient around a quadrupolar nucleus.

The Hamiltonian describing this interaction takes the following form:

$$\hat{\mathcal{H}}_Q = \frac{eQ}{2I(2I-1)\hbar} \hat{I} \cdot V \cdot \hat{I} \quad (2.49)$$

where V is the electric field gradient tensor. Similar to the shielding tensor σ in chemical shift, there exists a principal reference frame (X, Y, Z) in which V is diagonal and its trace is zero. The diagonal tensor can then be expressed in the following form:

$$\hat{V}_d = \begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix} \quad \text{with} \quad V_{XX} + V_{YY} + V_{ZZ} = 0 \quad (2.50)$$

The principal values of this tensor are represented by two parameters: the quadrupolar coupling constant C_Q and the asymmetry parameter η_Q . The definitions of these parameters are provided below:

2.2. Interactions

According to convention, the principal components of the tensor are arranged in the following order:

$$|V_{ZZ}| \geq |V_{XX}| \geq |V_{YY}| \quad (2.51)$$

The quadrupolar coupling constant C_Q is defined by the equation:

$$C_Q = \frac{e^2 q Q}{h} \quad \text{with} \quad eq = V_{ZZ} \quad (2.52)$$

$$\nu_Q = \frac{V_{YY} - V_{XX}}{V_{ZZ}} \quad \text{with} \quad 0 \leq \nu_Q \leq 1 \quad (2.53)$$

In the interaction's principal frame of reference (X, Y, Z) , the quadrupolar interaction Hamiltonian is expressed by the following relation:

$$\hat{H}_Q = \frac{e^2 q Q}{4I(2I-1)} \left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 - I_-^2) \right] \quad (2.54)$$

Since the quadrupolar interaction is of the same order of magnitude as the Zeeman interaction, it is necessary to consider the second-order approximation of $\hat{H}_Q$. In the case of high-field NMR, when the quadrupolar interaction is weak compared to the Zeeman interaction, a first-order expansion of the interaction is sufficient. However, if the quadrupolar interaction is strong, it is necessary to perform a second-order expansion of the interaction.

A first-order expansion of the interaction in the laboratory frame (x, y, z) leads to the following Hamiltonian:

$$\hat{H}_Q^{(1)} = \frac{e^2 q Q}{8I(2I-1)} (3I_z^2 - I(I+1)) [3\cos^2(\beta) - 1 + \eta \sin^2(\beta) \cos(2\alpha)] \quad (2.55)$$

The characteristic frequency difference between two Zeeman energy levels, m and n , is thus modified by an amount $\omega_{Q,m \leftrightarrow n}^{(1)}$, which is given by:

$$\Delta\omega_{Q,m \leftrightarrow n}^{(1)} = \frac{\omega_Q}{4} (m^2 - n^2) [3\cos^2(\beta) - 1 + \eta \sin^2(\beta) \cos(2\alpha)] \quad \text{with} \quad \omega_Q = \frac{e^2 q Q}{8I(2I-1)} \quad (2.56)$$

Second-order effects of the quadrupolar interaction impact all transitions and are described for the

central transition in the static case by the following expression:

$$\omega_{Q, \frac{1}{2} \leftrightarrow -\frac{1}{2}}^{(2)} = \frac{\omega_Q^2}{6\omega_0} \left(I(I+1) - \frac{3}{4} \right) [A(\eta, \alpha) \cos^4(\beta) + B(\eta, \alpha) \cos^2(\beta) + c(\eta, \alpha)] \quad (2.57)$$

with

$$\begin{aligned} A(\eta, \alpha) &= -\frac{27}{8} - \frac{9\eta \cos(2\alpha)}{4} - \frac{3\eta^2 \cos^2(2\alpha)}{8} \\ B(\eta, \alpha) &= \frac{15}{4} - \frac{\eta^2}{2} + 2\eta \cos(2\alpha) + \frac{3\eta^2 \cos^2(2\alpha)}{4} \\ C(\eta, \alpha) &= -\frac{3}{8} + \frac{\eta^2}{3} + \frac{\eta \cos(2\alpha)}{4} - \frac{3\eta^2 \cos^2(2\alpha)}{8} \end{aligned}$$

Let us note that the second-order effects of the quadrupolar interaction on the Zeeman frequencies are inversely proportional to the main magnetic field ω_0 , and thus to B_0 . Therefore, the stronger the static field, the narrower the central line width. The first- and second-order effects of the quadrupolar interaction on the Zeeman frequencies are illustrated in the Figure. 2.6.

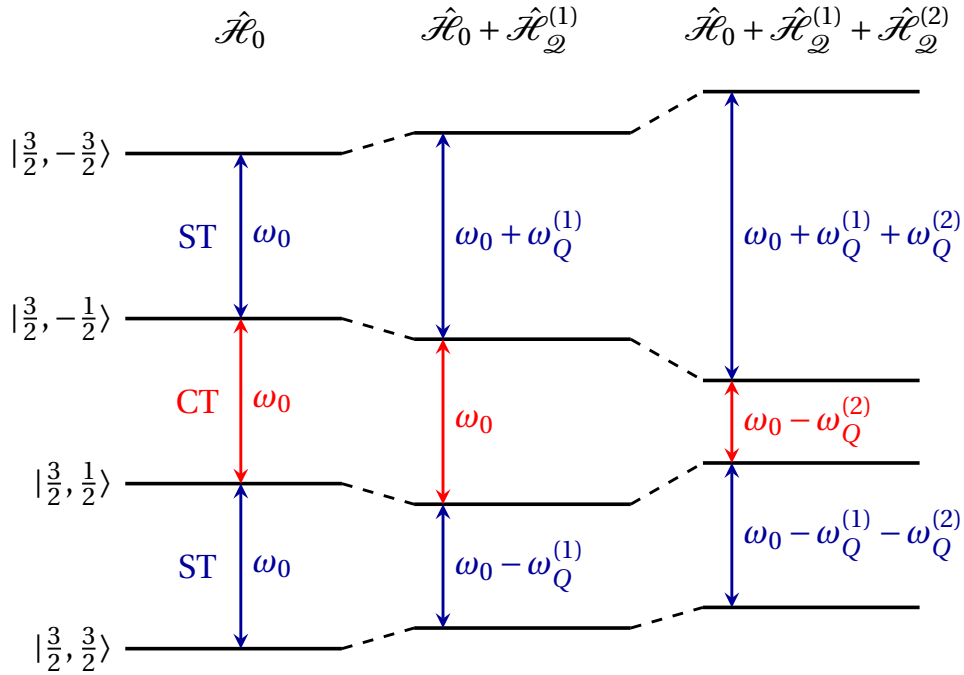


Figure 2.6. First and second-order effects of the quadrupole interaction on the Zeeman energy levels for a spin $\frac{3}{2}$ (CT refers to the central transition and ST to the satellite transitions).

2.2. Interactions

The resonance of a nucleus subjected to a quadrupolar interaction, whether of first or second order, is influenced by the orientation of the electric field gradient tensor relative to the static field. Figure. 2.7 shows the powder spectrum for a nucleus with a spin of $3/2$, where the electric field gradient tensor exhibits axial symmetry. In this example, the quadrupolar coupling constant applied to the nucleus causes a first-order quadrupolar broadening, which affects only the satellite transitions $m \leftrightarrow m - 1$ ($m \neq \frac{1}{2}$).

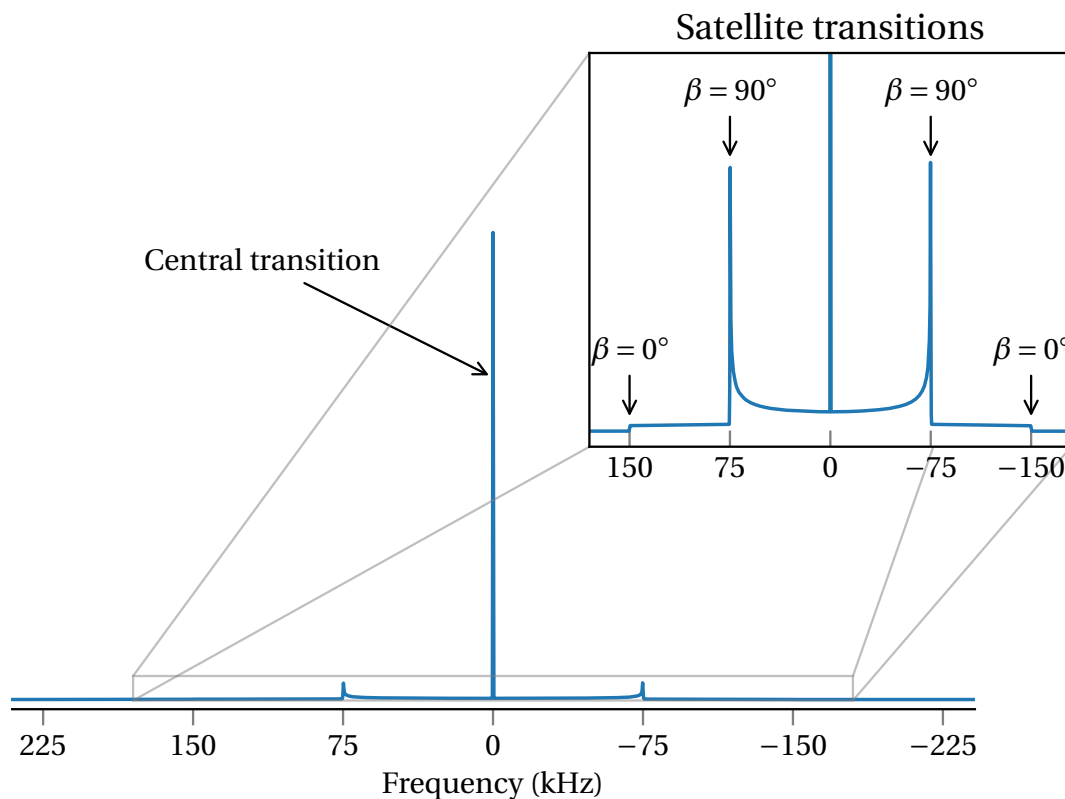


Figure 2.7. Here is an example of simulated powder spectra for a spin- $3/2$ nucleus with an axial symmetry tensor ($\eta = 0$). It illustrates a ^{23}Na NMR spectrum simulated at a field strength of 19.97 T, with a quadrupolar coupling constant $C_Q = 150$ kHz.

It has been seen that when the quadrupolar interaction is strong, all transitions are affected by the second-order effects of this interaction (Equation (2.57)). However, the resonance lines associated with satellite transitions are often too broad to be properly exautocited and observed, and the one associated with the central transition $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ is affected by second-order broadening. The different forms of second-order lines encountered in powder spectra of the central transition for a spin $\frac{3}{2}$ nucleus are illustrated in Figure. 2.8.

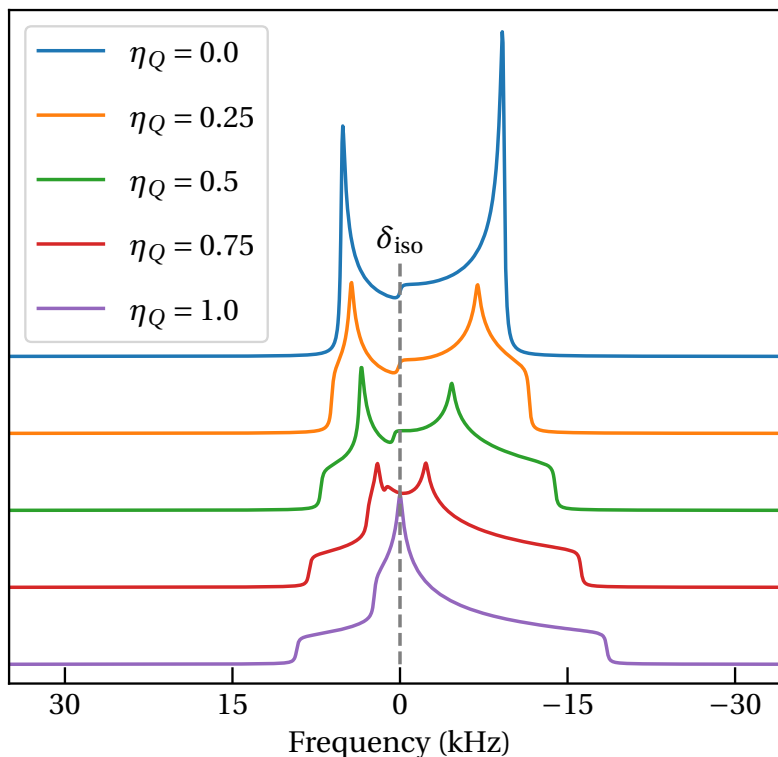


Figure 2.8. Second-order quadrupolar line shapes for the central transition of a spin $\frac{3}{2}$, depending on different values of the asymmetry parameter η_Q . These profiles are derived from ^{23}Na NMR spectra, simulated at a static magnetic field of 19.97 T with a C_Q of 5 MHz.

2.3 High-resolution NMR

The examples presented in the previous sections show that, in the case of powder spectra, significant broadening of the resonance lines is caused by anisotropic interactions (particularly chemical shift and quadrupolar interactions), which depend on the orientation of the tensor relative to the static field. However, when multiple crystallographic sites are present for the same isotope, the resonance lines broadened by these interactions can overlap, complicating the analysis of the obtained spectrum. Fortunately, solutions exist to cancel or reduce this broadening. The following sections present these solutions as well as an effective tool for analyzing the obtained spectra.

2.3.1 Magic Angle Spinning

The idea of rotating the sample at a frequency ω_r around an axis inclined at an angle β_r relative to the magnetic field was proposed by E. R. Andrew⁹ and I. J. Lowe¹⁰. They demonstrated that this

2.3. High-resolution NMR

approach makes the orientation of the interaction tensor, as well as the orientation of the internuclear vectors, time-dependent. In the case of dipolar interaction, E.R. Andrew demonstrated that the average Hamiltonian varies over the course of a rotation period. It is given by:

$$\mathcal{H}_D(t) = \frac{\mu_0}{4\pi} \frac{\hbar \gamma_I \gamma_S}{r_{IS}^3} \frac{1}{2} (1 - 3 \cos^2 \beta_r) (1 - 3 \cos^2 \beta_{ij}) \hat{I}_z \hat{S}_z \quad (2.58)$$

where β_r is the angle chosen to cancel the term $(1 - 3 \cos^2 \beta_r)$, and $\beta_{ij} = \theta(t) - \beta_r$, as illustrated in Figure. 2.9. Thus, the dipolar interaction is averaged to zero over a rotation period if the rotation frequency is greater than the line width induced by these interactions in a static spectrum. The specific angle that allows for the averaging of the dipolar interaction is referred to as the "magic angle" β_m , which is 54.74° . However, in the development of the time-dependent dipolar Hamiltonian, there are two additional terms that are periodic in ω_r and $2\omega_r$. These terms are responsible for the sidebands (see E. R. Andrew's paper⁹, p. 508).

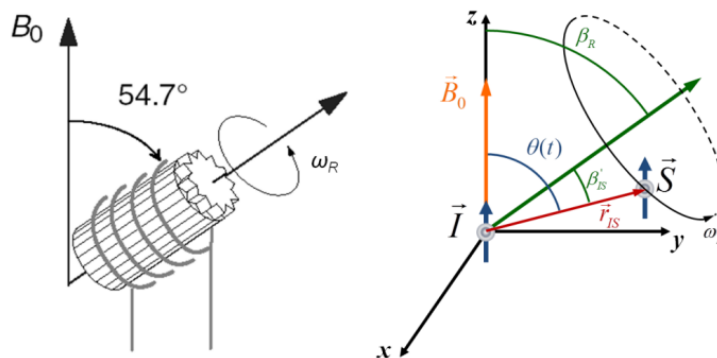


Figure 2.9. Representation of a rotor in rotation at the magic angle, as well as the angles β_r and β_{ij} in the case of a dipolar interaction between two nuclei with spins I and S .

For chemical shift interaction, the term σ_{zz} in the Hamiltonian $\hat{\mathcal{H}}_{CS}$ (2.56) is averaged over one rotation period, leading to the following expression:

$$\sigma_{zz} = \sigma_{iso} + \frac{1}{2} (1 - 3 \cos^2 \beta_r) \frac{\sigma_{CSA}}{2} (3 \cos^2(\beta_r) - 1 - \eta \sin^2(\beta) \cos(2\alpha)) \quad (2.59)$$

When the angle β_r corresponds to the magic angle, that is, $\beta_r = \beta_m$, the σ_{zz} term is reduced to its isotropic value, provided that the rotation frequency is sufficiently high. The averaged Hamiltonian over a rotation

period is then expressed as:

$$\mathcal{H}_{\text{CS}} = -\hbar\omega_0\sigma_{\text{iso}}\hat{I}_z \quad (2.60)$$

In the case of quadrupolar interaction, the first order of this interaction can be averaged to zero if the rotation frequency is sufficiently high. However, the second-order terms of the quadrupolar interaction are influenced by Legendre polynomials of degree 2 and 4. As illustrated in Figure 2.10a, no common angle β_r allows these two polynomials to be simultaneously canceled. Consequently, the degree 2 polynomial can only be canceled by a rapid rotation of the sample around the magic angle, while a broadening of the resonance line persists, induced by the non-averaged degree 4 polynomial, proportional to $P_4(\cos\beta_m) = -0.39$. Thus, the particular nature of quadrupolar interactions is explained, even in the case of magic angle spinning. Figure 2.10b illustrates how the powder spectra of the central transition, shown in Figure 2.8, are affected by magic angle spinning at infinite speed.

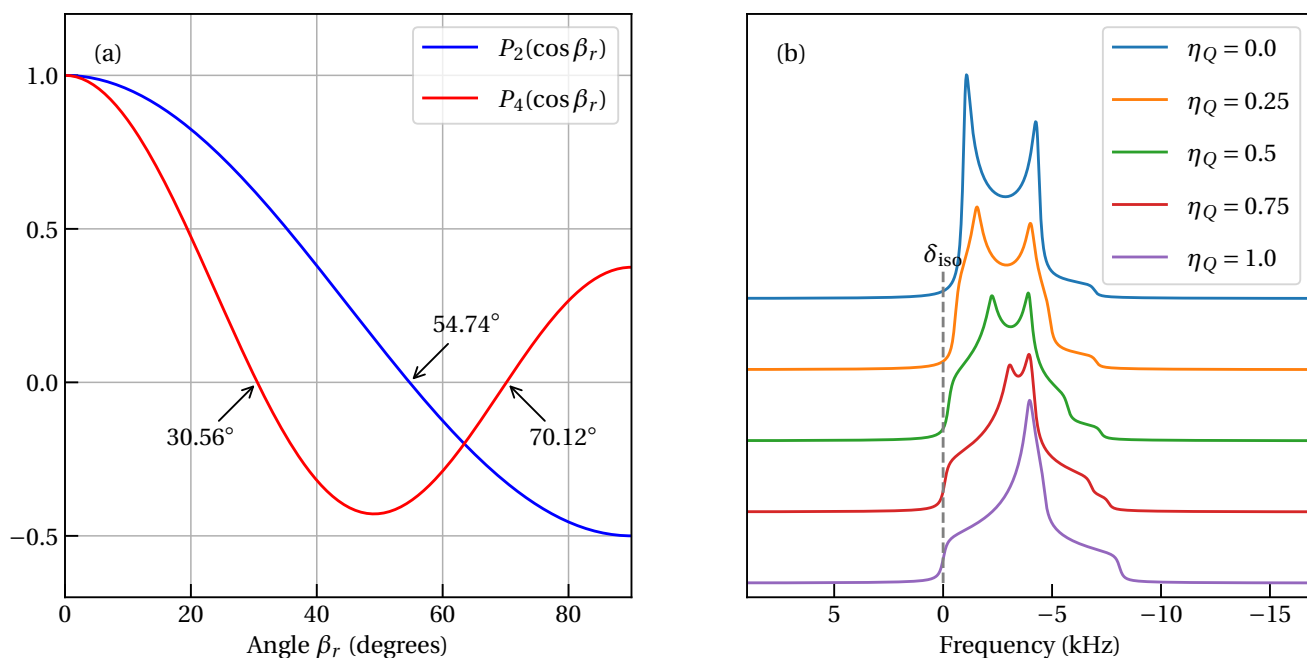


Figure 2.10. (a) Evolution of the Legendre polynomials P_2 and P_4 as a function of the angle β_r . (b) Powder spectra in MAS at infinite speed for the central transition of a spin $\frac{3}{2}$ for different values of η_Q .

The rotation speed is limited by the size of the rotor used. The smaller the rotor, the higher the rotation speed. For example, a maximum speed of 7 kHz can be reached with a rotor of 7 mm in diameter, and over 110 kHz for rotors with a diameter of 0.7 mm. However, these speeds do not always suffice to completely cancel out the effects of dipolar or quadrupolar couplings, which are on the order of several

2.3. High-resolution NMR

tens of kHz and several MHz, respectively. Additionally, the anisotropy of chemical shift, which is directly proportional to the static field B_0 , becomes increasingly difficult to average out by magic angle spinning as the intensity of the magnetic fields increases. Residual interactions are manifested by the appearance of spinning sidebands on either side of the main peak, at frequencies that are multiples of the rotation frequency.

2.3.2 High-resolution quadrupolar nuclei

Due to the difficulty of obtaining high-resolution spectra by magic-angle rotation for quadrupolar nuclei, different methods such as Double Rotation (DOR)^{11,12}, Multiple Quantum Magic Angle Spinning (MQMAS)¹³, and Satellite Transitions Magic Angle Spinning (STMAS)¹⁴ have been proposed to achieve better resolution. However, only the MQMAS method will be discussed in the manuscript, as it is the most commonly used high-resolution method for half-integer quadrupolar nuclei.

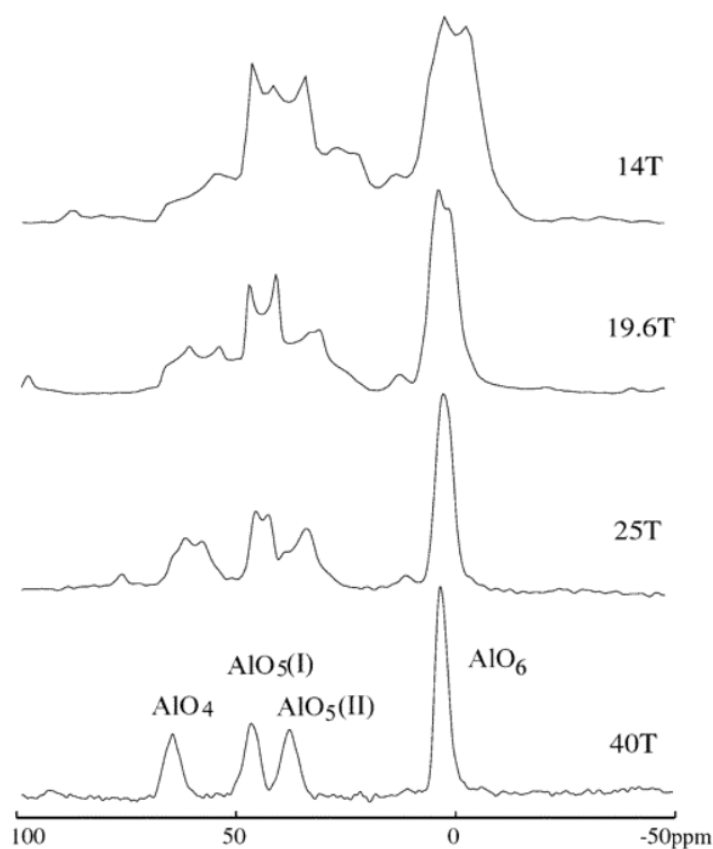


Figure 2.11. ^{27}Al MAS spectra of the A_9B_2 compound obtained at different magnetic fields, ranging from 14 to 40 T.¹⁵

Let us begin by examining the effect of strong magnetic fields on nuclei with very high quadrupolar coupling. It has been noted that the second-order effects of the quadrupolar interaction on the Zeeman frequencies are inversely proportional to the strength of the magnetic field B_0 . Consequently, a stronger static field results in a narrower central line width, and sensitivity increases with the field strength. Figure 2.11 presents the results from Gan et al¹⁵ on the spectra of A_9B_2 obtained at 14, 19.6, 25, and 40 T. It shows that up to 14 T, spectral overlap makes it difficult to analyze the four ^{27}Al sites, and the chemical and quadrupolar parameters cannot be measured precisely. At 19.6 T, the AlO_6 line begins to separate from the others, and at 25 T, the AlO_4 line no longer overlaps with the AlO_5 sites, although these still overlap partially. At 40 T, the second-order quadrupolar effects are nearly eliminated, and the residual line width (about 5 ppm) is due to fluctuations in the main field. The four sites are well resolved, close to their individual chemical shifts, with a nearly Gaussian line shape. At this very high field, the spectra are similar to those of $I = \frac{1}{2}$ spins, allowing for rapid and reliable data acquisition while retaining quantitative accuracy, although the quadrupolar coupling is less apparent.

The MQMAS method, developed by Frydman et al¹⁶, is a two-dimensional technique that allows for the separation of isotropic interactions from anisotropic interactions caused by second-order quadrupole effects. The experiment involves measuring the variation of symmetric multi-quantum coherences (such as 3Q, 5Q, 7Q, or 9Q) in a first dimension. These measurements are then correlated with the evolution of the 1-quantum coherence of the central transition, observed during rotation at the magic angle. This results in an auto-correlation for each site, where the slope depends on the proportionality factor between the second-order broadening of the central transition and that of the observed multi-quantum transition. This factor depends on the observed transition as well as the number of nuclear spins. By performing a shear operation on the obtained two-dimensional map, one can obtain a correlation map between an isotropic dimension and the anisotropic dimension of the central transition. Thus, the C_Q as well as the chemical shift distribution in an MAS NMR spectrum can be precisely determined by this technique.

2.3.3 Quadrupolar nuclei nutation

As mentioned previously, a strong quadrupolar interaction can lead to significant broadening of the resonance lines associated with satellite transitions, making uniform excitation difficult. Thus, during the duration of the radiofrequency pulse, the quadrupolar interaction can no longer be neglected. In this context, quadrupolar nuclei exhibit a specific response to the pulse, which depends on the ratio $\frac{\omega_Q}{\omega_1}$ ^{17–19}.

2.3. High-resolution NMR

Our analysis will concentrate on the intensity of the signal originating from the central transition. The radiofrequency field necessary to exautocite a quadrupolar nucleus can be determined by considering three distinct limiting cases. The response of the central transition after a selective pulse of duration τ_p can be modeled by the following expression:

$$S(\tau_p) = S_0 \frac{\sin \left[\left(I + \frac{1}{2} \right) \omega_1 \tau_p \right]}{I + \frac{1}{2}} \quad (2.61)$$

This equation describes the nutation curve in two limiting regimes. The first limiting regime corresponds to a situation where $\omega_Q \ll \omega_1$, i.e., in the case of a liquid ($C_Q = 0$). In this case, we are in a so-called non-selective regime, where the pulse duration is equivalent to that observed in a liquid, meaning when the spin is equal to $1/2$. The second limiting regime applies when $\omega_Q \gg \omega_1$, which corresponds to a selective regime. The Figure. 2.12 illustrates an example of the nutation curve for spins of $3/2$ and $5/2$, in both non-selective and selective regimes. For a spin $3/2$, the pulse duration required to induce maximum perturbation in a solid with significant quadrupolar interaction, relative to the radiofrequency field, is given by $\tau_{90}(S) = \frac{\tau_{90}(L)}{2}$. Furthermore, for a spin $5/2$, the duration of the selective pulse for the central transition is $\tau_{90}(S) = \frac{\tau_{90}(L)}{3}$.

In general, the duration of the selective pulse for the central transition is determined by:

$$\tau_{90}(S) = \frac{\tau_{90}(L)}{I + \frac{1}{2}} \quad (2.62)$$

In the intermediate regime between these two limiting cases, the evolution of the intensity of the central transition as a function of pulse duration is aperiodic. This regime notably allows for the excitation of multi-quantum transitions. To uniformly and quantitatively exautocite signals from different sites with varying quadrupolar frequencies, it is essential to use short pulses. This ensures that the signal intensity remains independent of the quadrupolar frequency. Quantitative information is obtained when the pulse duration meets the following condition:

$$\tau_p < \frac{\pi}{2(I + \frac{1}{2})} \quad (2.63)$$

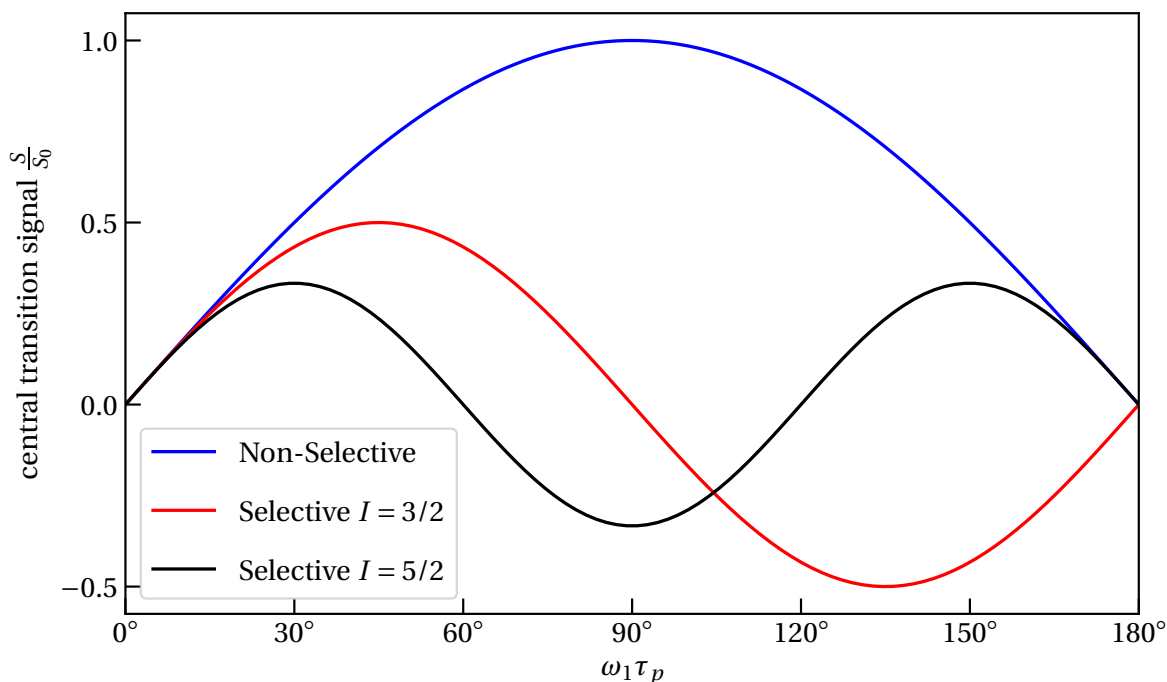


Figure 2.12. The intensity of the central transition signal after excitation by a single RF pulse with a nominal flip angle of $\omega_1 \tau_p$, where τ_p represents the pulse duration, is plotted for the nonselective ($\omega_Q \ll \omega_1$) and selective ($\omega_Q \gg \omega_1$) irradiation limits.

2.4 One-dimensional acquisition methods

Various pulse sequences are employed to excite nuclear energy transitions. These range from single-pulse experiments for general applications to more complex and sophisticated methods. Some sequences are designed to optimize the signal-to-noise ratio, while others aim to minimize acoustic ringing effects, which manifest as vibrations within the probe and become more noticeable when the signal is weak. This section focuses exclusively on the pulse sequences used in the context of this project.

2.4.1 Single pulse

The single pulse or "direct excitation" sequence is primarily used for fundamental experiments due to its ease of implementation. During this sequence, a recycling time, noted as D1, is provided to allow the system to return to its equilibrium state in between each scan. Then, a short-duration radiofrequency (RF) pulse, characterized by a pulse width p_1 and a power PLW1, is applied. Excitation pulses lead to the creation of coherences (i.e., transverse magnetization). Before acquiring the FID signal, a short delay,

2.4. One-dimensional acquisition methods

on the order of a few microseconds, called the "dead time" (DE) in Figure. 2.13, is necessary between the end of the pulse and the start of signal recording. This delay is the time needed for the electronic system of the spectrometer to switch from emission mode to reception mode. The detected NMR signal corresponds to coherences of order $p = -1$ and manifests as a sinusoidal signal that decays over time. The duration of the RF pulses p_1 and the delay between the pulses D1 are frequently determined using this pulse sequence. The typical duration of RF pulses is on the order of a few microseconds, while the delays between the pulses and the duration of the decaying signal can be measured in milliseconds or seconds. For example, the parameter p_1 is measured by recording the nutation curve of a reference sample, on which the reference frequency f_{ref} is also determined. As for D1, it is assessed by measuring the relaxation time T_1 of the sample. To ensure that the maximum signal is obtained in each scan, it is common practice to set D1 to $5 \times T_1$.

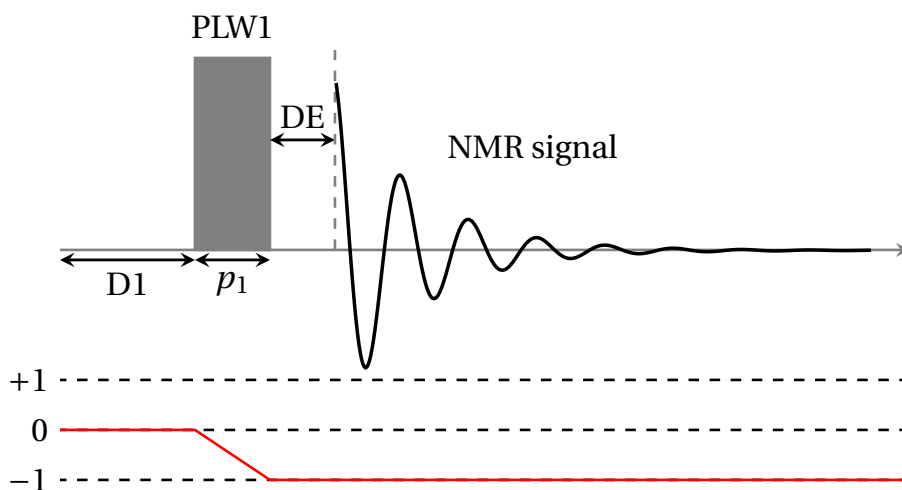


Figure 2.13. Diagram of the single pulse sequence and the coherence pathway for a spin $\frac{1}{2}$.

2.4.2 Hahn echo pulse sequence

In the presence of strong interactions, various broadening mechanisms play a significant role, causing a rapid decay of the free precession signal. Since the same coil is used both to emit radiofrequency pulses and to record the free precession signal, detecting the signal immediately after the pulse becomes impossible. Indeed, during the dead time (DE), the transverse magnetization undergoes a reduction, leading to a partial loss of the signal. This loss can result in significant spectral distortions, particularly when spectral lines are broad, which leads to a rapid defocusing of the transverse magnetization and,

consequently, to a loss of information. The Hahn echo technique²⁰, or "spin echo" helps to recover this signal loss by refocusing magnetic field inhomogeneities and linear interactions relative to the spin I_z operator. This results in a shift of the signal's temporal origin to positive times. An example of a spin echo pulse sequence is illustrated on the Figure. 2.14. The experiment is broken down into seven stages:

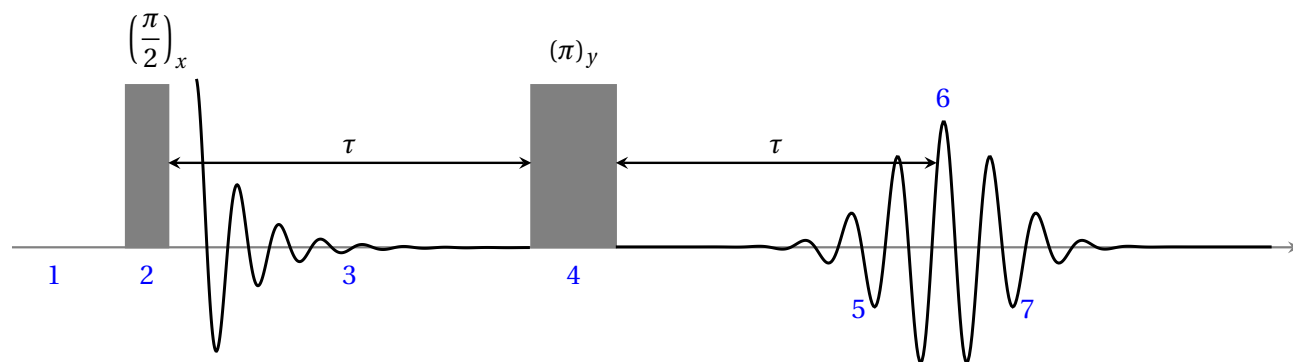


Figure 2.14. Spin Echo Pulse Sequence

1. The density operator, describing the state of the system, is proportional to I_z and is therefore the system is initially in thermal equilibrium, with the magnetization aligned along the z axis.
2. A $\frac{\pi}{2}$ excitation pulse with an x phase tips I_z into the transverse plane, along the $-y$ axis.
3. During free precession, transverse relaxation and B_0 field inhomogeneity cause the operator to locally precess at different speeds, spreading the local magnetization vectors out in the $x - y$ plane.
4. A π refocusing pulse with a y phase rotates all spin states by π around the y axis, reversing the magnetization vectors' relative positions.
5. In the second free precession period, the magnetization vectors continue to locally precess at different speeds but converge due to the refocusing pulse (in the absence of diffusion).
6. A spin echo occurs when all magnetization vectors realign perfectly along the $-y$ axis.
7. Finally, the spins continue to precess freely and desynchronizes once again.

The reorientation of the system's evolution under the effect of the π pulse has allowed the signal to reappear, in the form of a "spin echo". To eliminate the "dead time" problem, it is feasible to start

2.4. One-dimensional acquisition methods

data acquisition at the end of the second delay τ (step 6). By doing so, a Fourier transform applied to the signal from this precise moment, referred to as the "half-echo" in this context, avoids the need to correct the first-order phase, which is usually required when the signal is acquired after the dead time in a single-pulse experiment. In addition, acquiring a complete echo allows for obtaining a pure absorption mode spectrum without distortion. To achieve a Hahn echo in combination with magic angle spinning, it is necessary to synchronize the duration τ with the spinning frequency. In other words, the duration of this delay τ must be a multiple of the spinning period ($\tau = \frac{n}{\nu_r}$).

2.4.3 Acoustic ringing compensation by pulse sequences

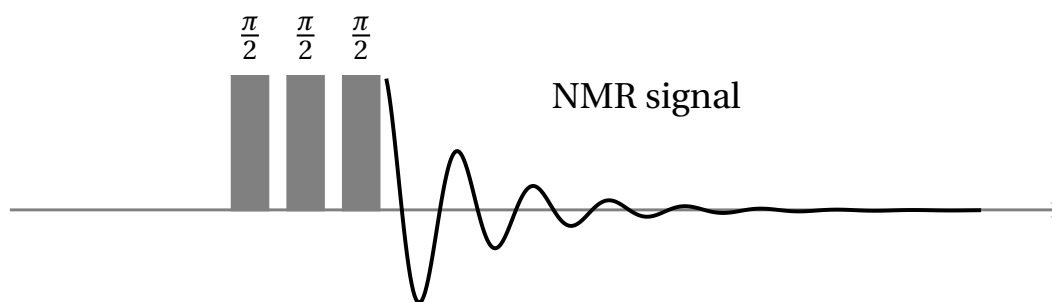


Figure 2.15. Aring Pulse Sequence

When a pulse is applied to a NMR probe in a strong magnetic field, the oscillating radiofrequency current in the circuit induces mechanical (acoustic) vibrations within the probe's metal components. These mechanical vibrations, in turn, generate radiofrequency signals that can be detected by the probe's coil. This phenomenon, known as "acoustic ringing", appears in the FID signal and generally dissipates within tens to hundreds of microseconds after the pulse, depending on the frequency used and the characteristics of the probe. Acoustic ringing is particularly problematic in high magnetic fields and low frequencies, and becomes even more challenging when large spectral widths (i.e., short dwell times) are employed. It can complicate the observation of very broad lines and lead to baseline and phase issues when analyzing sharp lines with large spectral widths. The delay τ applied in the spin-echo pulse sequence helps to attenuate the acoustic resonance induced by the π pulse, so that the difference spectrum primarily reflects the NMR signal. However, if the spin-lattice relaxation time (T_1) is short, it will also decay with τ .²¹ Consequently, this method is particularly effective when T_1 is significantly longer than T_2 . Various pulse techniques can be employed for data collection to reduce acoustic ringing phenomena.

Among these methods, the "aring" pulse sequence stands out as a significant approach. This technique involves applying three $\frac{\pi}{2}$ pulses separated by a very short delay ($1\mu\text{s}$), followed by the acquisition phase of the NMR signal. This sequence is illustrated in the Figure. 2.15. Another pulse sequence, referred to as "aring2", is also used. This sequence consists of an initial $\frac{\pi}{2}$ pulse, followed by a delay greater than $D1$. Subsequently, a second π pulse is applied, followed by a brief delay. Finally, a third $\frac{\pi}{2}$ pulse is delivered before the acquisition phase. Both sequences ultimately lead to the same result.

2.4.4 Cross polarization

The dipolar interaction, although often considered detrimental and thus typically eliminated by MAS, can nevertheless be advantageously exploited for polarization transfer. Specifically, it allows the strong polarization of an abundant nucleus with spin I and a high gyromagnetic ratio (such as the proton ^1H) to be transferred to a nucleus with spin S characterized by lower abundance and/or lower receptivity (such as ^{13}C). This method was initially demonstrated by Hartmann and Hahn²² through a double resonance experiment. The experiment involves the simultaneous application of two radiofrequency fields, B_{1I} and B_{1S} , tuned to the respective Larmor frequencies of the spin I and spin S nuclei. In the rotating frame, a polarization transfer occurs between the two nuclei at a rate that depends on the intensity of the radiofrequency fields B_{1I} and B_{1S} . This transfer is optimized when the Hartmann-Hahn conditions are met, that is to say:

$$\gamma_I B_{1I} = \gamma_S B_{1S} \quad (2.64)$$

Cross-polarization enables a theoretical maximum enhancement, quantified by a factor of η , such that²³:

$$\eta = \frac{\gamma_I}{\gamma_S} (1 + \epsilon)^{-1} \quad \text{with} \quad \epsilon = \frac{S(S+1)N_S}{I(I+1)N_I} \quad (2.65)$$

where N_S and N_I represent the number of nuclei with spin S and I in the system, respectively. When a polarization transfer is made from the proton to a nucleus with low isotopic abundance (e.g, ^{13}C), the value of ϵ is almost zero. The theoretical maximum polarization gain can then be approximated by the ratio of the gyromagnetic ratios of the nuclei with spins I and S ($\eta = \frac{\gamma_I}{\gamma_S}$). Alexander J. Vega demonstrated that, for a half-integer spin quadrupolar nucleus, an efficient polarization transfer from a spin 1/2 nucleus

2.4. One-dimensional acquisition methods

to the central transition of the quadrupolar nucleus must satisfy the following conditions²⁴:

$$\gamma_I B_{1I} = \gamma_S B_{1S} \quad (\omega_Q \ll \omega_{1S}) \quad (2.66)$$

$$\gamma_I B_{1I} = \left(S + \frac{1}{2}\right) \gamma_S B_{1S} \quad (\omega_Q \gg \omega_{1S}) \quad (2.67)$$

For magnetization transfer via cross-polarization in rotation at the magic angle, the transfer dynamics are influenced by the rotation. The Hartmann-Hahn conditions are satisfied when^{24,25}:

$$\gamma_I B_{1I} = \gamma_S B_{1S} \pm n\omega_r \quad \text{with } n \text{ an integer} \quad (2.68)$$

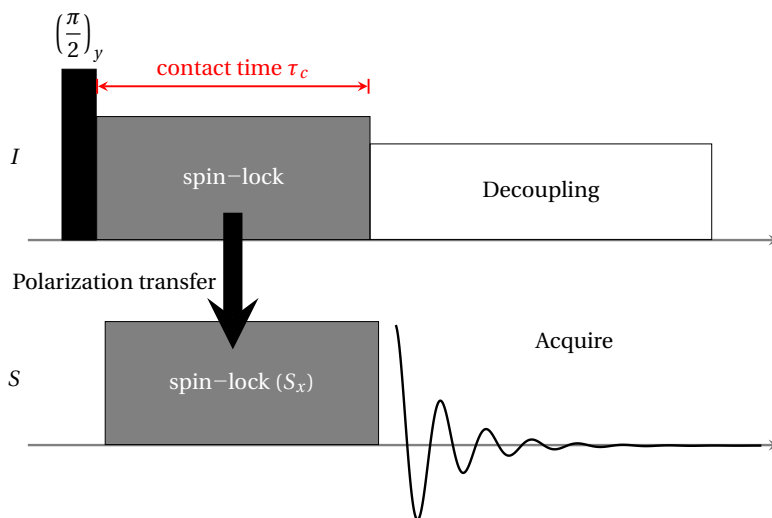


Figure 2.16. Schematic representation of a cross-polarization experiment from a nucleus with spin I to a nucleus with spin S .

The principle of cross polarization relies on the application of a $\frac{\pi}{2}$ pulse on the I spin, followed by the transfer of polarization from the I spins to the S spin over a duration τ_c , known as the contact time. Subsequently, the signal is detected on the S spin, while the I spins are decoupled to avoid undesirable interactions that could interfere with detection. The CP pulse sequence illustrating this process is schematically represented in Figure. 2.16. One of the major advantages of cross-polarization lies in its ability to produce a NMR spectrum with a high signal-to-noise ratio in a significantly reduced time compared to the direct excitation method. Additionally, CP is particularly effective for nuclei with low natural abundance and low gyromagnetic ratios, ^{13}C . For instance, an optimal transfer of polarization

from the ^1H to ^{13}C can enhance the ^{13}C signals by a factor of $\eta = \frac{\gamma_{\text{C}}}{\gamma_{\text{H}}} = 4$. Moreover, this technique allows for the distinction between mobile and immobile nuclear sites, which is particularly beneficial for studying sample dynamics. However, it is important to note that the CP method does not yield quantitative spectra, as the signal intensity is exaggerated compared to that obtained through direct excitation.

2.5 Two-dimensional acquisition methods

Two-dimensional nuclear magnetic resonance (2D NMR) spectroscopy is a technique that allows for the detection of proximity relationships between different nuclei, whether these relationships are spatial or due to chemical bonding. In other words, this method is based on the analysis of correlations between identical (homonuclear) or different (heteronuclear) nuclei. The result is a two-dimensional spectrum that is actually three-dimensional. It includes the chemical shift of nucleus 1 (δ_1), the chemical shift of nucleus 2 (δ_2), and the signal intensity. This spectrum is displayed as a map with contour lines, with the δ_1 and δ_2 axes represented in the plane of the screen. The pulse sequence for a generic two-dimensional experiment is divided into four consecutive steps²⁶:

Preparation–Evolution–Mixing–Detection

The basic pulse sequence (see Figure. 2.17 without the mixing time part) starts with the application of a $\frac{\pi}{2}$ RF pulse, typically on nucleus 1. After this excitation, the spins of nucleus 1 evolve for a time t_1 . Then, "mixing" involves applying pulses and delays to obtain a magnetization transfer from nucleus 1 to nucleus 2. After the transfer, the spins of nucleus 2 continue to evolve for a time t_2 . The signal, which evolves during this t_2 period, is detected to create the first spectrum. The amplitude of the FID observed during t_2 depends on the duration of the evolution period t_1 and the precession that was experienced by the spins of nucleus 1. Thus, a series of experiments conducted with increasing values of delay t_1 produces a modified series of spectra after Fourier transformation on the t_1 dimension. Applying Fourier transformation again on this dimension yields the two-dimensional NMR spectrum. In other words, the two-dimensional experiment results in a set of time-domain data $s(t_1, t_2)$. The Fourier transformation of $s(t_1, t_2)$ along the t_2 dimension gives a modified series of spectra $S(t_1, \delta_2)$. Then, the Fourier transformation of $S(t_1, \delta_2)$ along the t_1 dimension results in the two-dimensional spectrum $S(\delta_1, \delta_2)$.

There are a large number of two-dimensional techniques. However, for the purposes of this project, we will focus exclusively on those that have been employed in this thesis.

2.5.1 Exchange Spectroscopy

The exchange spectroscopy (EXSY) experiment is used to analyze the exchange between nuclei or groups of atoms within a molecule. These exchanges can result from chemical reactions or conformational rearrangements, which refer to changes in the positions of atoms due to chemical transformations or spatial rearrangements within the molecule. EXSY is based on a pulse sequence similar to that used in the Nuclear Overhauser Effect Spectroscopy (NOESY) experiment. The Nuclear Overhauser Effect (NOE) is a phenomenon that transfers nuclear polarization through interactions between neighbouring nuclear spins. The basic sequence of the EXSY/NOESY experiment, illustrated in Figure 2.17, consists of three $\frac{\pi}{2}$ pulses. The first pulse generates transverse spin magnetization. During the evolution time t_1 , which is incremented throughout the 2D experiment, the spins undergo precession. Then, during the mixing time t_m , located between the last two $\frac{\pi}{2}$ pulses, in NOESY experiments, the nuclear spins interact in space via dipolar interactions, but not through scalar coupling. If two nuclei are close enough (within a few Å), their spins can influence each other's relaxation rates, resulting in cross-relaxation and a transfer of polarization between them. In EXSY, the chemical process will transfer the nuclei between different sites with distinct chemical shifts, leading to magnetization transfer and cross-peaks in the 2D spectrum.

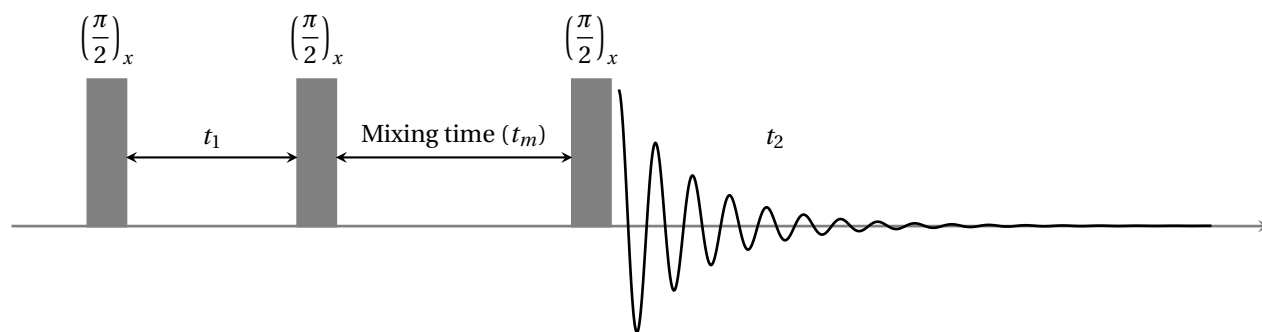


Figure 2.17. The Nuclear Overhauser Effect Spectroscopy pulse sequence.

Although NOESY and EXSY experiments use the same pulse sequence, they differ in the nature of the processes they explore. NOESY is particularly suited for studying large molecules with restricted motion, as these conditions favor the NOE transfer. In contrast, EXSY is optimized for the study of "slow" exchange processes ("slow" meaning that they do not lead average chemical shifts) and requires shorter mixing times to detect the motions of atoms from one environment to another one.²⁷ In both

EXSY and NOESY spectra, peaks appear along the diagonal (i.e. the magnetization stays on the same nucleus during t_1 and t_2). When an exchange or a magnetization transfer occurs between different sites, peaks known as "cross peaks" appear off the diagonal. In our study, this method is particularly useful for examining phase separation within electrolytes as well as the conformational movements of molecules.

2.5.2 Heteronuclear Correlation Spectroscopy

Heteronuclear Correlation (HETCOR) spectroscopy is a double-resonance heteronuclear technique. This method operates similarly to the cross-polarization experiment but is distinguished by the addition of an indirect dimension (t_1). It allows for the revelation of correlations through the dipolar interaction of nuclei located in the first coordination sphere, and potentially in the second coordination sphere, particularly by increasing the contact time. Unlike the EXSY method, HETCOR spectra only display cross-peaks. Furthermore, these spectra do not exhibit symmetry. For instance, the interpretation of a $^{13}\text{C}\{^1\text{H}\}$ HETCOR spectrum can indicate which protons are attached to which carbon atoms in a given molecule. In our case, HETCOR spectroscopy will help us identify less dynamic molecules present in electrolytes, as dynamics hinder polarization transfer by performing a polarization transfer from hydrogen (^1H) to carbon (^{13}C). It will also help us understand the coordination of sodium within the electrolyte by performing a polarization transfer from TFSI/FSI fluorines (^{19}F) to sodium (^{23}Na).

2.6 Simulations of NMR spectra

Experimental NMR spectra often display broad peaks and sometimes overlaps when there are multiple distinct chemical environments, making their interpretation challenging. Therefore, it is frequently necessary to model these spectra using parameterized functions. This approach allows for the extraction of characteristic interaction parameters for each chemical environment. The functions used incorporate parameters such as δ_{iso} , δ_{CSA} , η_{CSA} , C_Q , and η_Q , which are defined in Section 2.2. The fitting of the simulated spectrum to the experimental spectrum is then carried out by optimizing these parameters through a least-squares minimization algorithm to achieve the best match.

There are several software programs for simulating solid-state NMR spectra, which are generally divided into two main categories based on the approach used. The first category includes programs that simulate both the NMR experiments and the resulting spectra. This approach calculates the spin

2.6. Simulations of NMR spectra

dynamics of a predefined system according to a pulse sequence also specified by the user. For example, the SIMPSON²⁸ program allows for this simulation and takes into account experimental imperfections such as finite pulse durations and the effect of radiofrequency field intensity on a specific quadrupolar nucleus. Adjusting a simulated spectrum to match an experimental spectrum is possible by varying the system description, but this process is time-consuming due to the complexity of the simulations. The second category is based on the assumption that excitations and spectral line shapes are idealized. Among these simulation programs are ssNake²⁹, Nmrglue³⁰, and Dmfit³¹. Nmrglue is an open-source Python package used for working with multidimensional data and has been widely employed in this present studies. Dmfit, on the other hand, is a program developed at the CEMHTI laboratory that simulates spectra while accounting for line shape terms of interactions and under various conditions (one or two dimensions, static experiments, MAS at infinite or finite speed). This program has also been extensively used in this project.

Since Dmfit³¹ is primarily designed for solid-state NMR, most adjustment methods focus on powder patterns resulting from either chemical shift anisotropy (CSA) broadening or quadrupolar broadening. When CSA is nearly zero, the model used to simulate the 1D spectrum is the pseudo-Voigt function. For simulating 1D CSA spectra, you can choose between a static spectrum (*CSA stat* model), an infinite MAS, or a finite MAS (*CSA mas* model). Among these options, the static and infinite MAS methods are relatively quick, while the finite MAS method requires more time. For quadrupolar broadening, you can choose to include or exclude satellite transitions, and *Czjzek* distributions can be considered if the sample has a disordered structure. When simulating 1D quadrupolar spectra, it is also possible to choose a static spectrum of the central transition (*Q stat 1/2* model), an infinite MAS (*Quad 1st* and *Q mas 1/2* models for first and second orders transitions), or a finite MAS (*int2QUAD* model). Additionally, Dmfit allows for simulating 2D MQMAS spectra, with or without *Czjzek* distributions.

2.6.1 Example of CSA spinning sidebands

Spinning sidebands play a important role in the quantitative analysis of spectra, as they contribute to the area under the peak curve, which helps estimate the occupancy percentage of each site. For example, consider a MAS NMR spectrum of ¹⁹F, recorded under a magnetic field of 11.7 T (500 MHz) for a ZPC sample mixed with sodium NaFSI salt in a 5:1 molar ratio, with a spinning speed of 20 kHz. This spectrum was fitted using the CSA MAS model, which accounts for spinning sidebands with the Dmfit

program. It is important to note that this model is valid for a nucleus with spin 1/2. The model allows for the precise determination of the isotropic chemical shift, the asymmetry parameter, and an estimate of the anisotropic chemical shift. This leads to a coherent interpretation of the spectrum using a unique set of parameters. The spectra were fitted using two CSA MAS models, with the parameters presented in Figure. 2.18. The calculated isotropic chemical shifts correspond to the resonance frequencies of the FSI molecule in the mixture, with asymmetry parameters of 0.1 and 0.2 for the two respective fluorine sites. It was also observed that the model accounts for the spinning sidebands, each exhibiting a different intensity. This variation in intensity can be attributed to the asymmetry parameter of the chemical shift. Another signal, attributed to the BF_3 group, appears in the frequency range of -130 to -150 ppm. However, this spectrum will be discussed in more detail in Chapter 4.

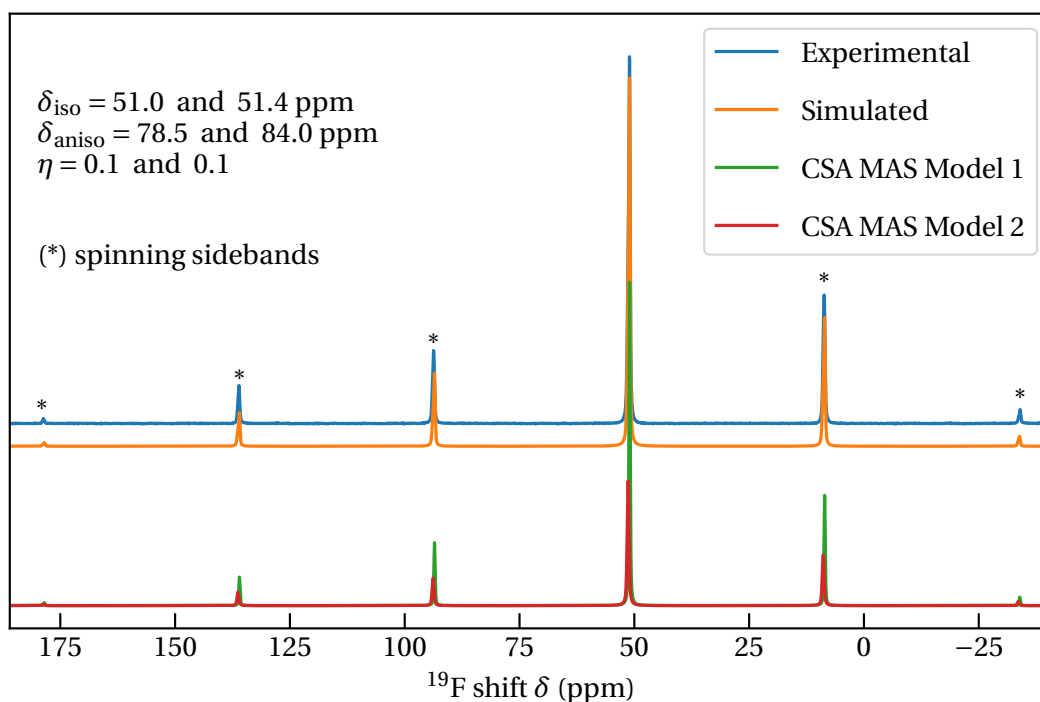


Figure 2.18. ^{19}F spectrum of ZPC mixed with sodium salt NaFSI in a 5:1 ratio, acquired at a spinning frequency of 20 kHz under a magnetic field of 11.7 T, was perfectly fitted using two CSA MAS models.

2.6.2 Example of quadrupolar fitting

Figure. 2.19 illustrates a new example of fitting, this time applied to the spectrum of a quadrupolar nucleus with a spin of 3/2, specifically the isotope ^{23}Na . As in the previous example, the spectrum of

2.6. Simulations of NMR spectra

^{23}Na was acquired under a magnetic field of 11.7 T, but this time with a ZPC sample mixed with sodium salt NaFSI in a 1:1 molar ratio, using a spinning rate of 20 kHz. The spectrum fitting was performed using the Int2QUAD model of Dmfit, while the satellite transitions were excluded from the fit due to their invisibility in the spectrum.

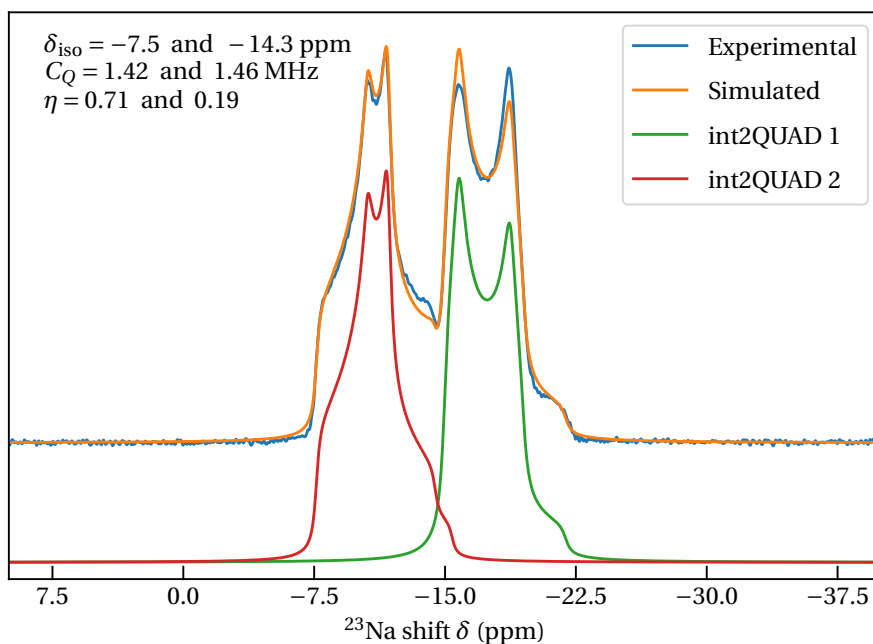


Figure 2.19. The ^{23}Na spectrum of the ZPC, mixed with sodium salt NaFSI in a 1:1 ratio, was acquired using a spectrometer with a magnetic field of 11.7 T and a rotation speed of 20 kHz. The data were fitted using two Int2QUAD models from Dmfit.

As mentioned earlier, the line shapes are idealized, with processing programs assuming uniform excitation across the entire spectral range. However, deviations can be observed between experimental and ideal line shapes, as shown by the spectrum fitting presented in Figure. 2.19. These deviations can be attributed to experimental imperfections, such as B_1 field inhomogeneity and short pulse phase imperfections, among others. Nonetheless, the fitting appears to be appropriate, and the results will be examined in detail in Chapter 4.

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Investigation of Sodium Ion Solvation in Polymerized Ionic Block Co-polymer Electrolytes

3.1 Introduction

In the chapter 1, we highlighted that solid polymer electrolytes offer several advantages: they are inexpensive, easy to synthesize and manufacture, and provide great flexibility in terms of properties. These materials are also distinguished by their thermal and chemical stability, properties that make them

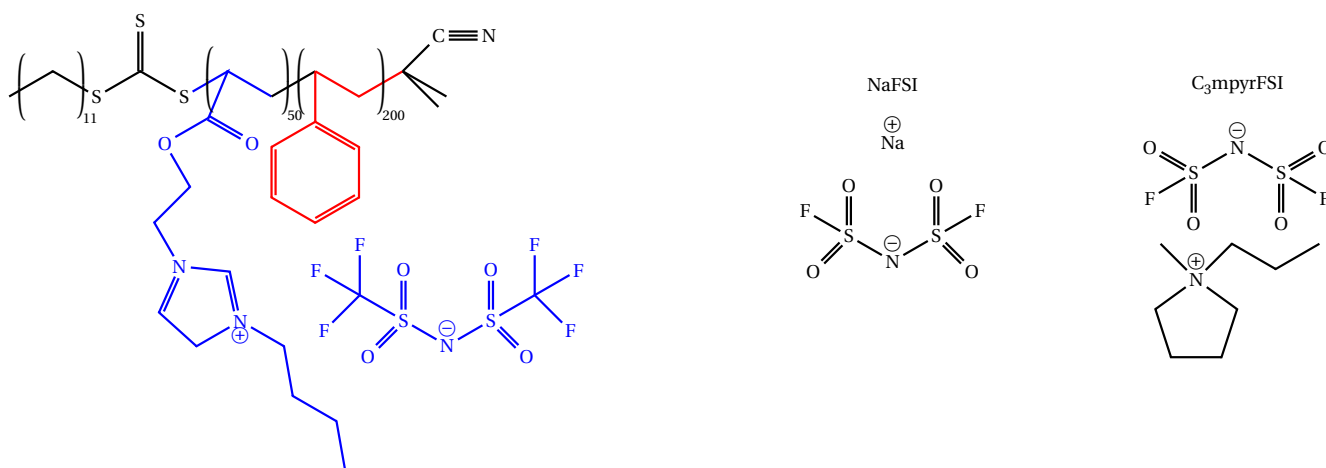


Figure 3.1. Chemical structure of (left) PS-b-PAEBImTFSI (PIL-Block Copolymer), (middle) sodium bis(fluorosulfonyl)imide (NaFSI), and (right) propyl-methylpyrrolidinium bis(fluorosulfonyl)imide (C₃mpyrFSI).

particularly suitable for solid-state battery applications operating at high temperatures. However, despite their promising properties, significant challenges remain for these materials, particularly in achieving

3.1. Introduction

both high ionic conductivity and optimal mechanical strength simultaneously. According to the review by Rollo-Walker et al¹., the introduction of ionic polymers has improved ionic conductivity, while the use of sequenced copolymers has strengthened the mechanical properties of solid polymer electrolytes. Makhlooghiazad and colleagues² examined a similar system in which a Polymerized Ionic Liquid Block (PIL–Block) Copolymer is mixed with sodium salt (NaFSI) and an ionic liquid, namely C₃mpyrFSI. The chemical structures of these materials are illustrated in Figure. 3.1. They conducted an evaluation of the thermal characteristics and ionic conductivity of the PIL–Block copolymer at different concentrations of NaFSI salt. The results obtained from DSC reveal that both the pure polymer and the binary electrolytes (polymer + salt), exhibit phase separation. This separation is manifested by distinct glass transition temperatures (T_g) observed for each block of the copolymer, suggesting incompatibility among the components. Furthermore, it is noted that the incorporation of salt leads to a decrease in the T_g of the PIL polymer component, while the T_g of the polystyrene remains stable at around 100 °C. This phenomenon indicates a localized plasticizing effect. This plasticizing effect promotes an increase in segmental motion and ionic dynamics, resulting in improved ionic conductivity within the PIL. Additionally, adding the ionic liquid C₃mpyrFSI to the electrolytic formulation improves ionic conductivity ($\sigma = 2.8 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 70 °C) and further lowers the T_g of the system to -43°C , as shown in the Table 3.1.

Table 3.1. Comparison of Glass Transition Temperatures (T_g) of the SPEs with Different NaFSI Concentrations and Ionic Liquid and Their Conductivities at 70 °C

PIL:NaFSI:IL molar ratio	T_g (°C) onset	ΔT_g (°C)	σ at 70 °C ($\text{S} \cdot \text{cm}^{-1}$)
1.0 : 0.5 : 0.0	–11	15	1.8×10^{-6}
1.0 : 1.5 : 0.0	–19	16	6.6×10^{-6}
1.0 : 2.0 : 0.0	–19	16	5.3×10^{-6}
1.0 : 2.5 : 0.0	–23	15	2.0×10^{-5}
1.0 : 3.0 : 0.0	–21	14	2.1×10^{-5}
1.0 : 2.5 : 1.0	–43	28	2.8×10^{-4}

These studies have shown that the plasticizing effect is responsible for the improvement in ionic conductivity. However, for sodium battery applications it would be preferable for this ionic conductivity to be primarily mediated by Na⁺ ions. In other words, it is necessary for the Na⁺ transference number t_{Na^+} to be as high as possible. Thus, understanding the interactions between Na⁺ ions and other species present in the electrolyte is essential, as they affect t_{Na^+} as well as impacting the sodium ion conduction mechanism and the desolvation processes that will occur at the electrode surface. Therefore, in this

chapter, we will examine the structure and dynamics within the PIL block copolymer using NMR, in an effort to understand the Na^+ ion interactions with the other species of the PIL block copolymer, such as the different anionic species present. We will focus in particular on the PIL + NaFSI system with a molar ratio of 1:2.5 (Solid Polymer Electrolyte I), and on the PIL + NaFSI + $\text{C}_3\text{mpyrFSI}$ system with a molar proportion of 1:2.5:1 (Solid Polymer Electrolyte II), as these are the systems that exhibit the best conductivity.

3.2 Experimental NMR section

3.2.1 One-Dimensional NMR Experiments

The samples were prepared by our collaborator from Deakin IFM, Dr. Gregory Rollo-Walker. All samples were placed in 1.3 mm Bruker NMR rotors inside a glove box under a controlled atmosphere with argon to avoid any water or oxygen contamination. The solid-state MAS NMR spectra of ^{13}C , ^{19}F , and ^{23}Na were acquired using a Bruker Avance III spectrometer operating at a magnetic field strength of 850 MHz (20.0 T) and with a sample rotation speed of 50 kHz. Measurements were performed with a 1.3 mm MAS Venturi probe (quadrupole resonance probe HFXV), which has separate channels for ^1H and ^{19}F . The duration of the 90° pulse was $3.5\ \mu\text{s}$ at 50 W for ^{13}C and $2.6\ \mu\text{s}$ at 25 W for ^{19}F . For the ^{23}Na isotope, the duration of the selective excitation pulse of type $\pi/4$, selective of the central transition, was measured to be $2.25\ \mu\text{s}$ at a power of 50 W. The spectra of ^{13}C were obtained by direct excitation as well as by cross-polarization (from ^1H to ^{13}C), with a contact time of 2 ms, followed by proton ^1H decoupling. The recycle time used in the experiment was 5 seconds, and a total of 20 000 scans were performed. The spectra of ^{19}F and ^{23}Na were obtained by single pulse excitation, with 16 and 400 scans respectively, and a recycle delay of 5 s for quantitative comparison for ^{19}F , as the measured relaxation time was 400 ms. The spin-lattice relaxation times (T_1) of ^{19}F were measured using the inversion-recovery method ($180^\circ - \tau_{\text{delay}} - 90^\circ - \text{acquisition}$). The isotropic chemical shifts of these three isotopes were calibrated relative to the resonance frequency of TMS for ^{13}C , fluoroacetophenone for ^{19}F , and a 1M NaCl solution for ^{23}Na .

3.2.2 Two-Dimensional NMR Experiments

The two-dimensional ^{19}F – ^{19}F EXSY (NOESY) experiments were performed using the pulse sequence implemented by R. J. Messinger at CEMHTI, integrated into Bruker's Topspin software. The chosen

3.3. NMR Investigation of the Solid Polymer Electrolyte I

spectral width was 25 000 Hz in the direct dimension (ω_2) and 9 408 Hz in the indirect dimension (ω_1). A total of 200 increments was used, with 8 scans per spectrum. Several mixing times were explored, namely 12.8, 25.6, 51.2, and 102.4 ms. The carrier frequency (O1) was centered on the TFSI signal. Two-dimensional heteronuclear correlation spectra ^{19}F – ^{23}Na were recorded at a spinning frequency of 50 kHz, applying a ramped polarization transfer with contact times ranging from 200 μs to 2 ms. The spectral width was set to 50 kHz for the ^{23}Na dimension and 10 kHz for the ^{19}F dimension. A total of 200 increments were acquired, with 280 scans per spectrum. The carrier frequency (O1) was successively centred on the TFSI signal, followed by the FSI signal.

3.3 NMR Investigation of the Solid Polymer Electrolyte I

3.3.1 Distinction Between Ionic and Rigid Blocks in the PIL Block

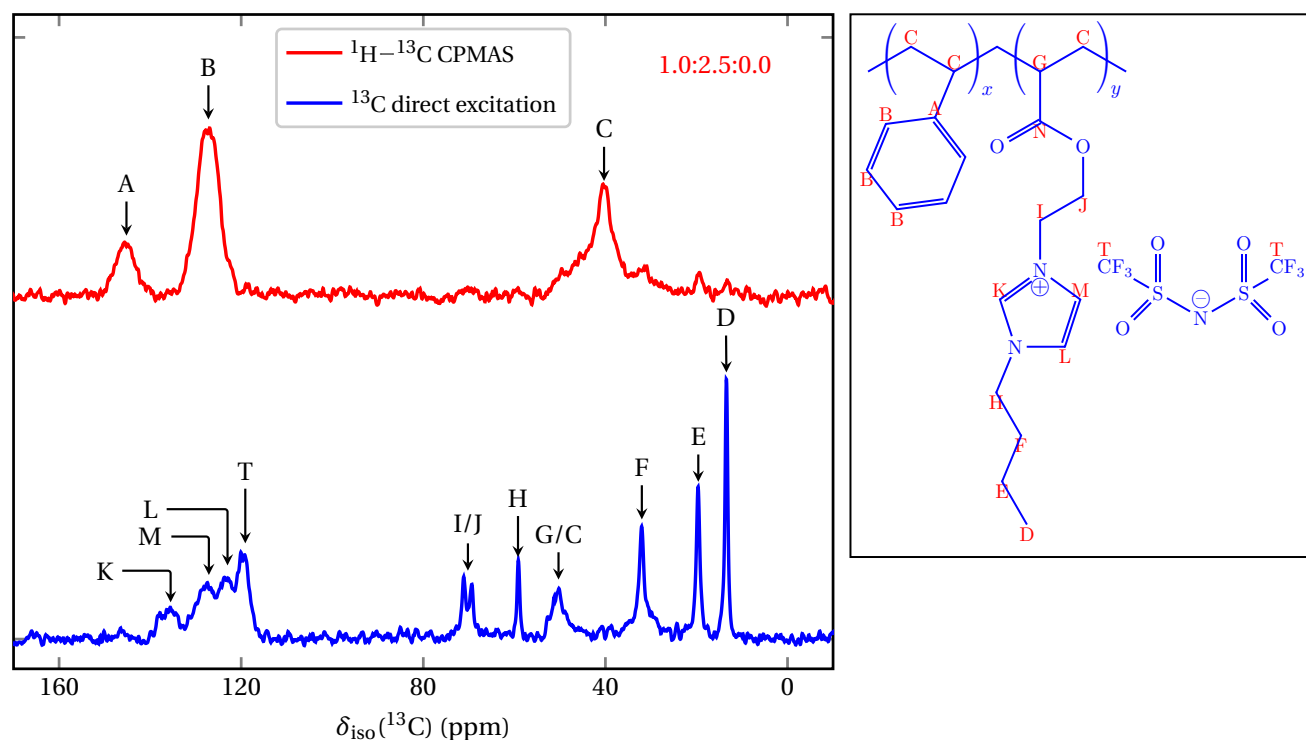


Figure 3.2. High-field MAS NMR spectra: (red line) cross-polarization ^1H – ^{13}C and (blue line) ^{13}C direct excitation. The peak assignments, based on previous work,^{3,4} are indicated with the structure shown in the inset.

Figure. 3.2 shows the comparison between the ^{13}C spectrum acquired by direct excitation (blue line) and

the spectrum obtained by cross-polarization (CPMAS) with transfer of polarization from ^1H to ^{13}C . The CPMAS spectrum reveals only the resonance frequencies of the carbon sites (A, B, and C) in the rigid part of the polymer, namely the polystyrene block. The rigid nature of this component allows efficient ^1H to ^{13}C polarisation transfer, while the dynamics present within the ionic component average away the dipolar couplings between the protons and the carbons ($^1\text{H}-^{13}\text{C}$), preventing cross-polarization from occurring. This is why the carbons present in the ionic component are not detected, as the ionic block features more inherent dynamics. In contrast, the direct excitation spectrum highlights only the dynamic ionic component, where the movements reduce the ^{13}C relaxation times T_1 compared to those of the rigid component, also resulting in a reduction of the ^{13}C line widths. This explains why the peaks in the direct excitation spectrum are narrower, particularly those from the alkyl chain on the ionic group, reflecting the polymer mobility rather than crystallinity. Therefore, these two experiments allow for the distinction between the two components of the electrolyte, namely the rigid part and the ionic part, based on the differences in the local dynamics present.

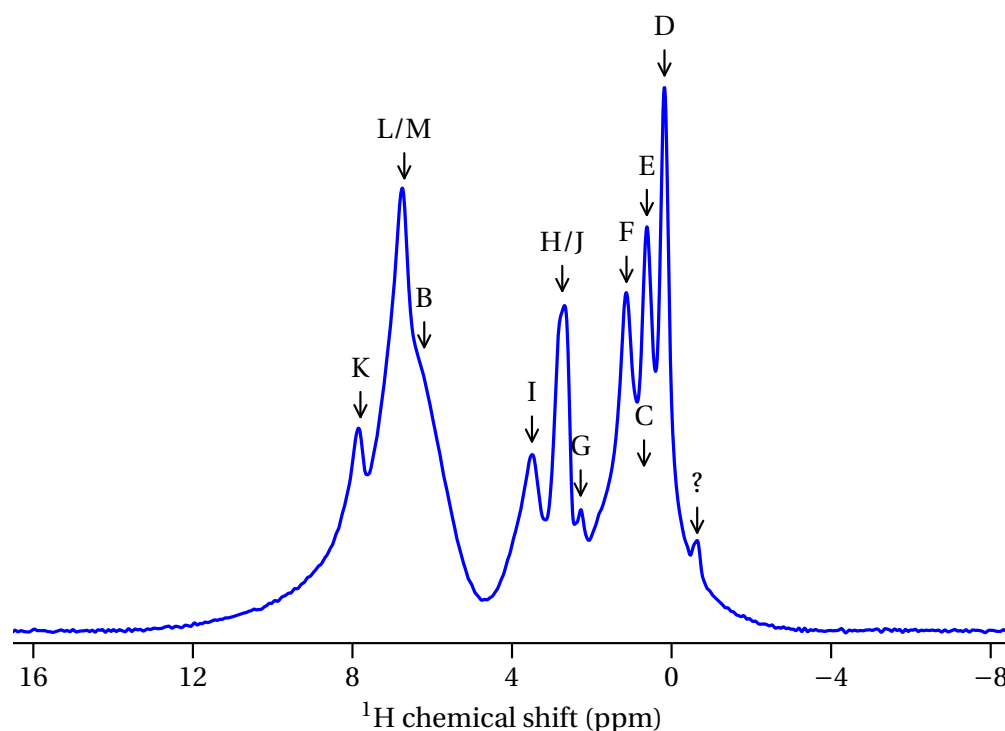


Figure 3.3. ^1H MAS NMR spectrum of Solid Polymer Electrolyte I. The peak assignment is based on the work of Joseph *et al.*⁴ and Bouchmella *et al.*³

The proton resonance spectrum, shown in Figure. 3.3, displays broad peaks that can be attributed to

3.3. NMR Investigation of the Solid Polymer Electrolyte I

the rigid segment of the polymer. This spectrum also reveals fine signals corresponding to the ionic chain. Additionally, an unidentified peak, marked with a question mark, is observed and may be associated with the presence of an impurity.

3.3.2 Interactions polymer-anions

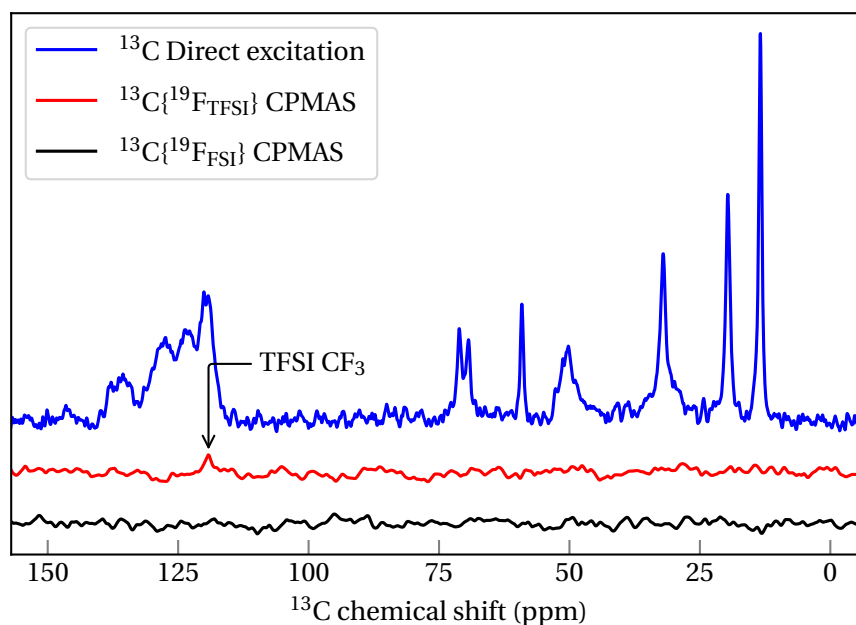


Figure 3.4. Comparison of the ^{13}C Spectrum by Direct Excitation and Polarization Transfer from $^{19}\text{F}_{\text{FSI}}$ and $^{19}\text{F}_{\text{TFSI}}$ to ^{13}C .

In this section, we examine the interaction between the polymer and the anions. Given that the anions are fluorinated and the polymer chains are carbon-based, we employed the $^{13}\text{C}\{^{19}\text{F}\}$ cross-polarization technique, enabling polarization transfer from ^{19}F to ^{13}C . This method was implemented in two steps: first, by setting the carrier frequency on the FSI signal, and second, by setting it on the TFSI signal. The results, illustrated in Figure 3.4, reveal that no resonance peak is observed in the spectrum when the carrier frequency is positioned on the FSI signal. In contrast, a single weak resonance signal is detected when the carrier frequency is positioned on the TFSI signal. This peak can be attributed to the CF_3 carbon of the TFSI anion, which has strong couplings to its three covalently bonded fluorines. The absence of peaks from the polymer suggests that the anion interactions with the polymer are either absent, weak or short-lived. To further investigate, we attempted a HETCOR experiment between ^1H and ^{19}F , using a 1.3 mm MAS Venturi probe equipped with separate ^1H and ^{19}F channels, available at the

CEMHTI laboratory. However, the results indicate that no correlation between the ^1H and ^{19}F signals was observed.

3.3.3 ^{19}F NMR and ^{19}F – ^{19}F Exchange Spectroscopy

Figure 3.5 presents the ^{19}F MAS NMR spectrum of solid polymer electrolyte I, obtained under a high magnetic field with a rotation speed of 50 kHz. This spectrum reveals the presence of two types of signals from fluorine atoms, associated with the anions FSI and TFSI, as illustrated in Figure 3.5 (a) and (b). The first signal, visible in Figure 3.5a, is characterized by a unique isotropic chemical shift

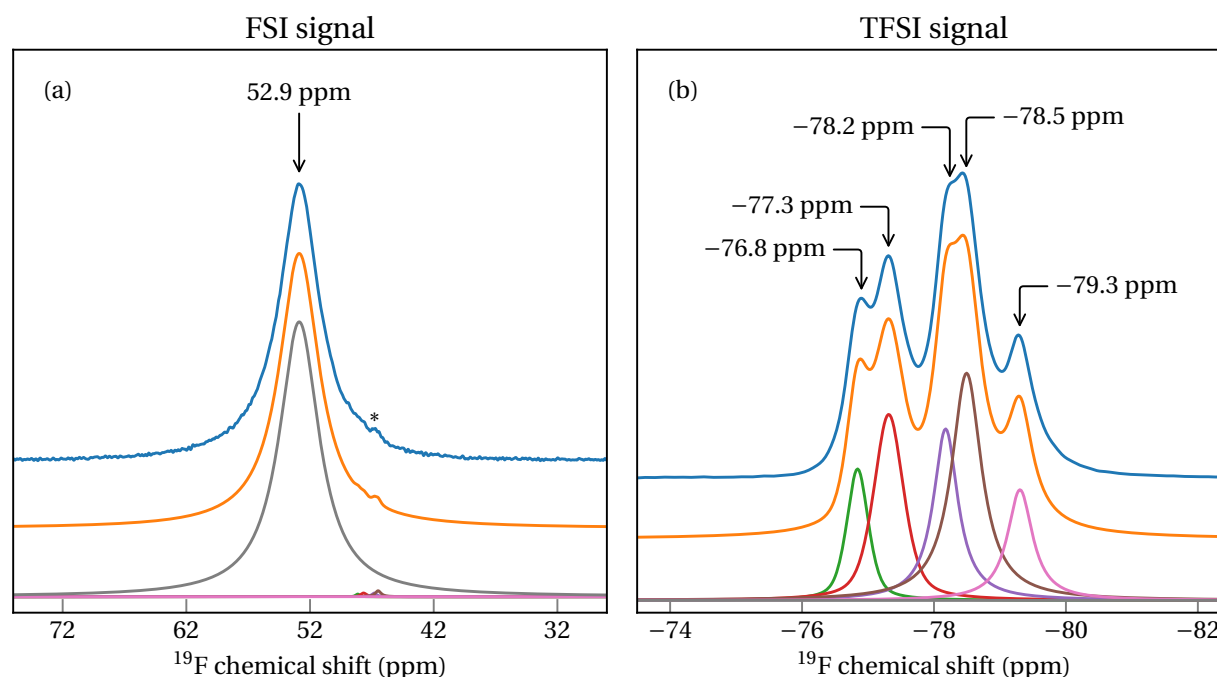


Figure 3.5. Experimental solid-state ^{19}F MAS (50 kHz) NMR spectrum of the electrolytic system (in light blue), fitted (in orange) with six lines. (a) corresponds to the signal of the FSI molecule, and (b) to the signals of the TFSI molecules. The asterisk indicates the spinning sidebands associated with the TFSI signals.

of 52.9 ppm, attributed to the FSI anions derived from sodium salt NaFSI. It is noted that this signal is overlapped by less intense peaks, which actually correspond to the spinning sidebands associated with the TFSI signals. The signals presented in Figure 3.5b are associated with the CF_3 groups of the TFSI molecule, the counter-anion from the cationic block of the polymer. Interestingly, a thorough analysis of these TFSI signals reveals five distinct peaks, displaying isotropic chemical shifts of -76.8 , -77.3 ,

3.3. NMR Investigation of the Solid Polymer Electrolyte I

−78.2, −78.5, and −79.3 ppm, respectively. The first four peaks show similarities with the ^{19}F NMR spectrum obtained from pure NaTFSI salts, while the peak at −79.3 ppm corresponds to the ^{19}F spectrum obtained from pure LiTFSI salts, as reported by Chen and colleagues⁵. In their study, they examined the conformational states of TFSI in the crystalline structures of the aforementioned salts. In pure NaTFSI salt, TFSI molecules adopt *cis* conformations, while in pure LiTFSI salt, TFSI molecules adopt *trans* conformations. Based on this research, we can attribute the four peaks with resonance frequencies of −76.8, −77.3, −78.2, and −78.5 ppm to TFSI anions adopting a *cis* conformation, while the peak with a resonance frequency of −79.3 ppm is associated with TFSI anions adopting a *trans* conformation.

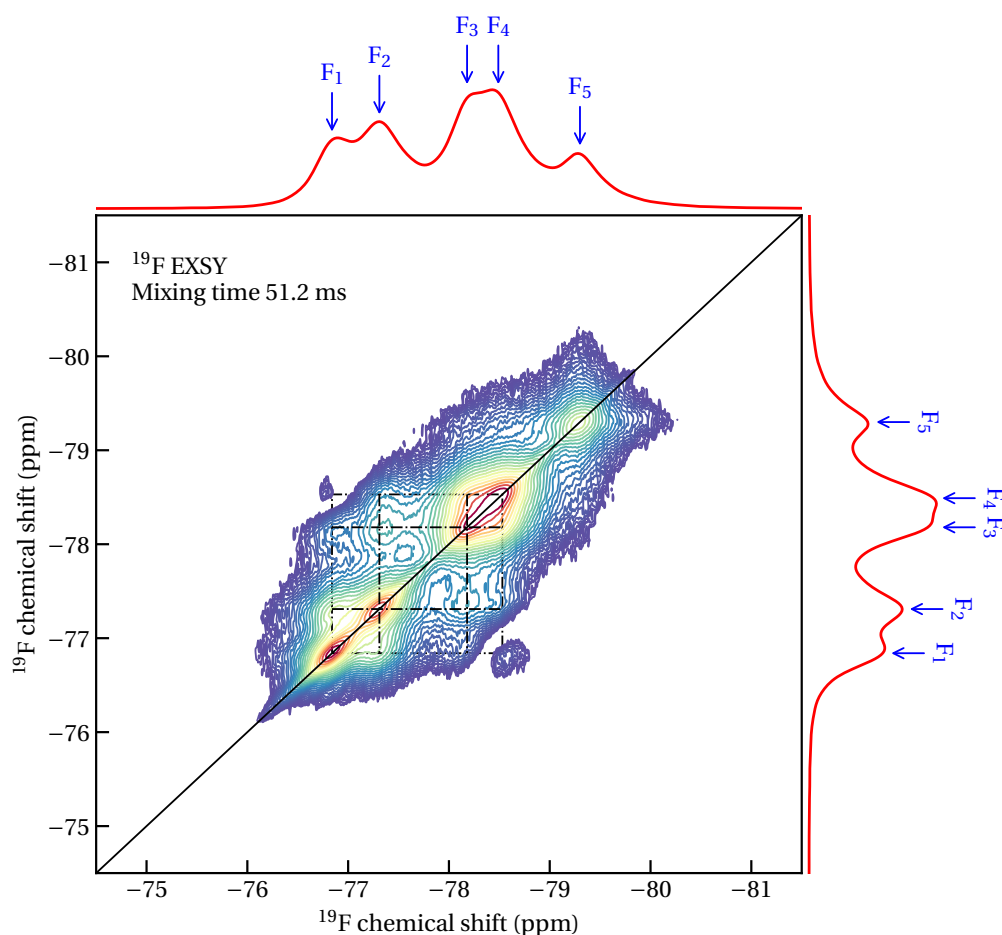


Figure 3.6. 2D EXSY $^{19}\text{F} - \{^{19}\text{F}\}$ spectrum of Solid Polymer Electrolyte I acquired at 20T with a spinning speed of 50 kHz and a mixing time of 51.2 ms. The carrier frequency (O1) was set on the TFSI signal. The experimental time for the measurements is 21 minutes.

To corroborate this hypothesis, a $^{19}\text{F} - \{^{19}\text{F}\}$ two-dimensional exchange spectroscopy (EXSY) experiment was conducted, with a mixing time of 51.2 ms. Cross peaks present in such spectra

indicate either chemical or conformational exchanges, or spatial proximity between the different fluorine environments. The results of the EXSY spectrum (Figure. 3.6) clearly show cross peaks. In particular, the four TFSI peaks with resonance frequencies of -78.5 ppm (F_4), -78.2 ppm (F_3), -77.3 ppm (F_2) and -76.8 ppm (F_1) exchange magnetization with one another. This observation suggests that the CF_3 groups undergo exchange processes and/or are in close proximity to each other. Therefore, these peaks could indeed correspond to molecules adopting a *cis* conformation, as the two CF_3 groups will be spatially closer to each other. The four distinct peaks can then be assigned to two *cis* conformation TFSI anions solvating a sodium cation, where the four CF_3 groups have distinct local environments and chemical shifts. This structure is remarkably similar to the pure NaTFSI salt are reported by Chen and colleagues⁵. In contrast, the fifth TFSI peak, showing a particularly low chemical shift of -79.3 ppm (F_5), does not appear to exchange magnetization significantly with the other four peaks, indicating that this TFSI anion is spatially far apart from the others. According to its chemical shift, this peak corresponds to TFSI adopting a *trans* conformation, and we assign it to TFSI anions interacting with the cationic group of the ionic polymer. In addition, a exchange EXSY experiment was conducted over the entire fluorine spectrum, with the carrier frequency positioned in the middle, between the FSI and TFSI signals, using a prolonged mixing time of 102.4 ms. This mixing time was intended to promote spin diffusion over longer distances. However, no detectable exchange was observed between the FSI signal and those of TFSI, suggesting a significant distance between the FSI and TFSI species. This observation may indicate that there is a phase separation between these two species, however, rapid dynamics (e.g. diffusion) of the FSI species could also hinder the polarisation transfer and prevent cross peaks from appearing.

3.3.4 Sodium-Anion Interactions

To further understand the interactions of the Na^+ ions in the polymer electrolyte system, a 2D heteronuclear correlation $^{19}F - \{^{23}Na\}$ (HETCOR) experiment was performed with a contact time of 2 ms. The ^{23}Na spectrum reveals a single chemical environment for the sodium ions. The HETCOR spectrum (Figure. 3.7) shows no cross peak between Na^+ ions and FSI^- anions. This does not necessarily mean that there is no close interaction between the Na^+ and FSI^- ions present, as such an interaction would be expected. It does mean that the dipolar coupling interaction between Na^+ and FSI^- fluorine nuclei is too weak to be detected by NMR, and this may be due to a weaker Na-FSI interaction, faster FSI dynamics, or a combination thereof. Regarding the $TFSI^-$ anions, the HETCOR spectrum reveals strong

3.3. NMR Investigation of the Solid Polymer Electrolyte I

coordination of Na^+ ions with these species. As a result, FSI^- anions are more mobile than TFSI^- anions. Furthermore, a more detailed analysis shows that only the signals from TFSI^- in the cis conformation correlate with the sodium ions, while those from TFSI^- in the trans conformation do not correlate with Na^+ ions. This confirms the solvation of the sodium cations by two distinct (cis) TFSI^- anions, and indicates that those in the trans conformation are either not interacting closely with the sodium or have (like the FSI^- anions) significantly higher mobility.

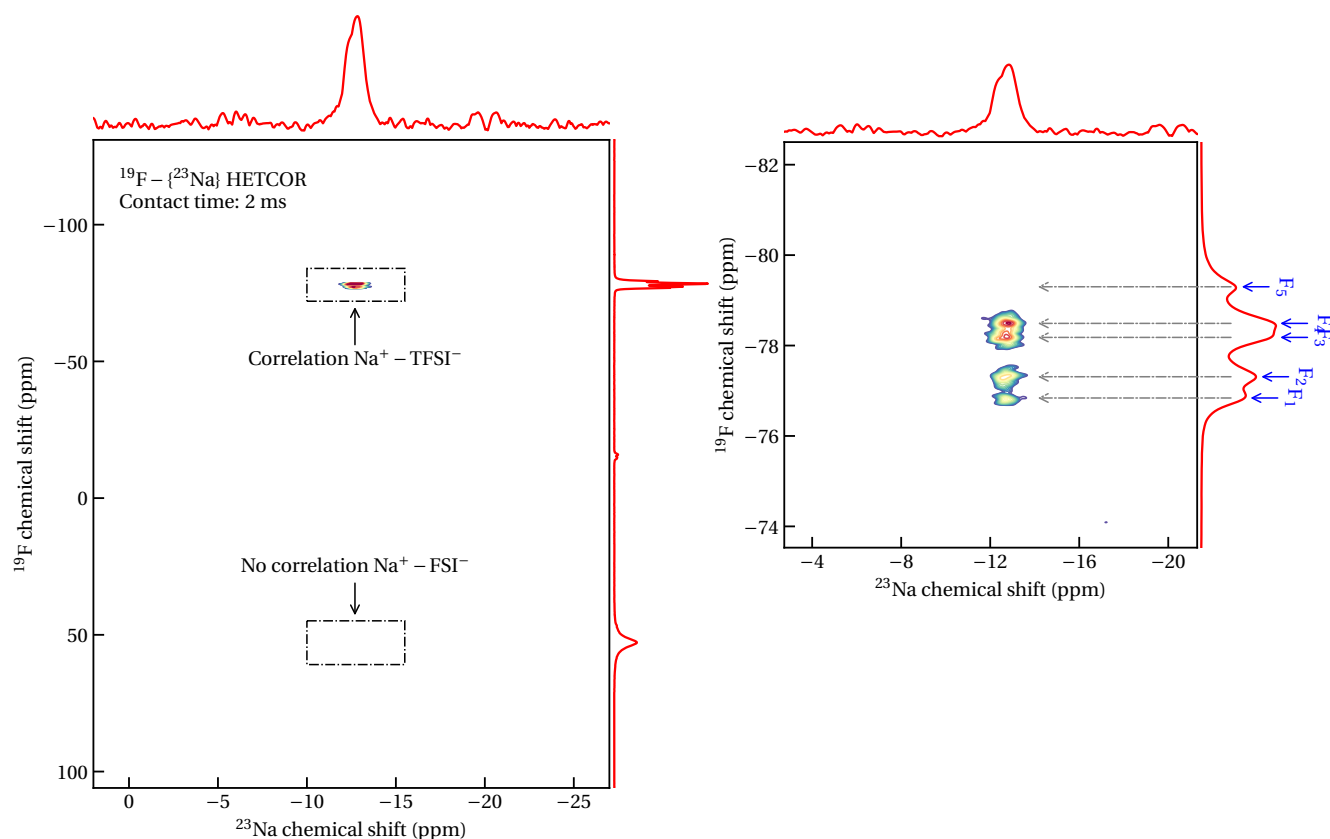


Figure 3.7. 2D HETCOR $^{19}\text{F} - \{^{23}\text{Na}\}$ spectrum of Solid Polymer Electrolyte I acquired at 20T with a spinning speed of 50 kHz and a contact time of 2 ms. The figure on the right shows the complete HETCOR spectrum, and the figure on the left shows a zoom into the frequency domain of the TFSI. The experimental time for the measurements is 12.82 hours.

Structurally, the close interaction between the Na^+ ions and the oxygen (O) atoms of two TFSI^- molecules, leads the anions to adopt a cis conformation. In the NaTFSI salt structure, the cis TFSI^- molecules stack into layers, with two Na^+ ions located between them, and the very similar fluorine chemical shifts observed here suggest a similar arrangement occurs in this polymer electrolyte. In

this arrangement, the TFSI⁻ molecules are less mobile, and their four CF₃ groups are inequivalent, which explains why, in the ¹⁹F spectra, there are four resonance frequencies associated with the TFSI⁻ molecules in the cis conformation. On the other hand, in the case of the TFSI⁻ molecules in the trans conformation, interactions with neighbouring cations (the Na⁺ ions or the cationic group of the polymer) are not sufficient to hinder anion rotations and so the resonance frequencies of the fluorine nuclei are averaged into one. Such dynamics explain why only a single peak is observed for the TFSI⁻ in the trans conformation, and also why no correlations of this peak with other sites are observed.

3.4 NMR Investigation of the Solid Polymer Electrolyte II

3.4.1 Effects of Ionic Liquid Incorporation

The experiments were repeated in the PIL-Block ternary system with the addition of the ionic liquid C₃mpyrFSI. When comparing the spectra of the two solid polymer electrolytes (Solid Polymer Electrolyte I and II), similarities in terms of chemical shifts are observed, along with some notable differences. In

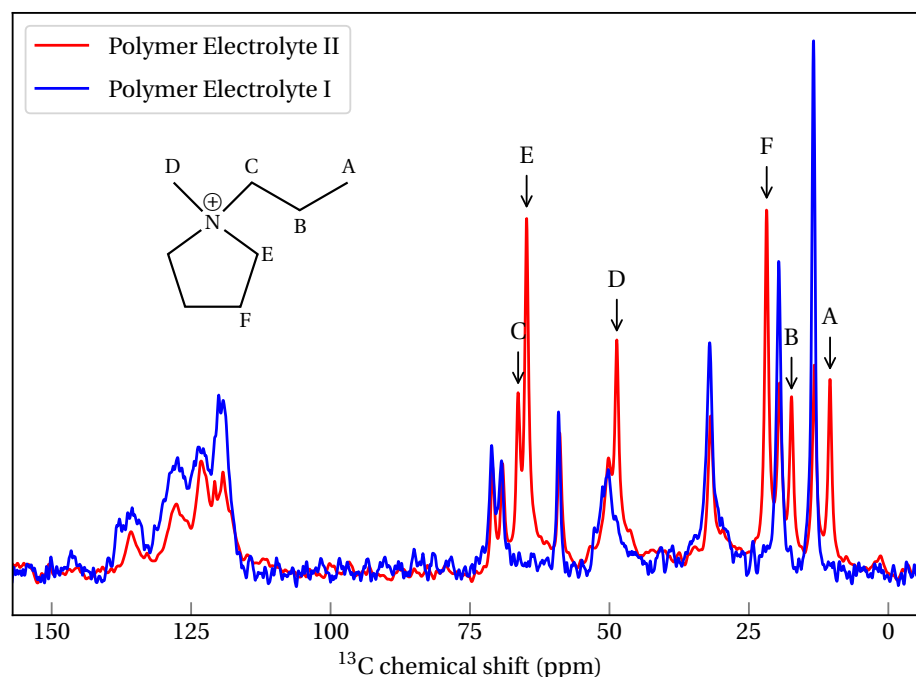


Figure 3.8. Comparison of the ¹³C spectrum by direct excitation of polymerized ionic block copolymer electrolytes, with and without the addition of extra IL.

particular, the fluorine signals (Figure. 3.10) from the FSI and TFSI anions exhibit sharper peaks after the

3.4. NMR Investigation of the Solid Polymer Electrolyte II

introduction of the ionic liquid $C_3\text{mpyrFSI}$. This indicates that the addition of $C_3\text{mpyrFSI}$ makes the ionic species in the system more dynamic. Furthermore, the ^{13}C spectrum obtained by direct excitation reveals even sharper peaks originating from the ionic polymer compound. Additionally, the addition of extra ionic liquid induces the appearance of new peaks, attributed to the carbon sites of the $[C_3\text{mpyr}]^+$ cation. This finding is consistent with the work of Makhlooghiyazad et al.², who explain that this plasticizing effect promotes increased segmental motion and ionic dynamics, leading to improved ionic conductivity. This plasticizing effect results from the reduced interaction between the FSI and the polycation through co-coordination with a metal cation, thereby causing a decrease in the glass transition temperature (T_g).

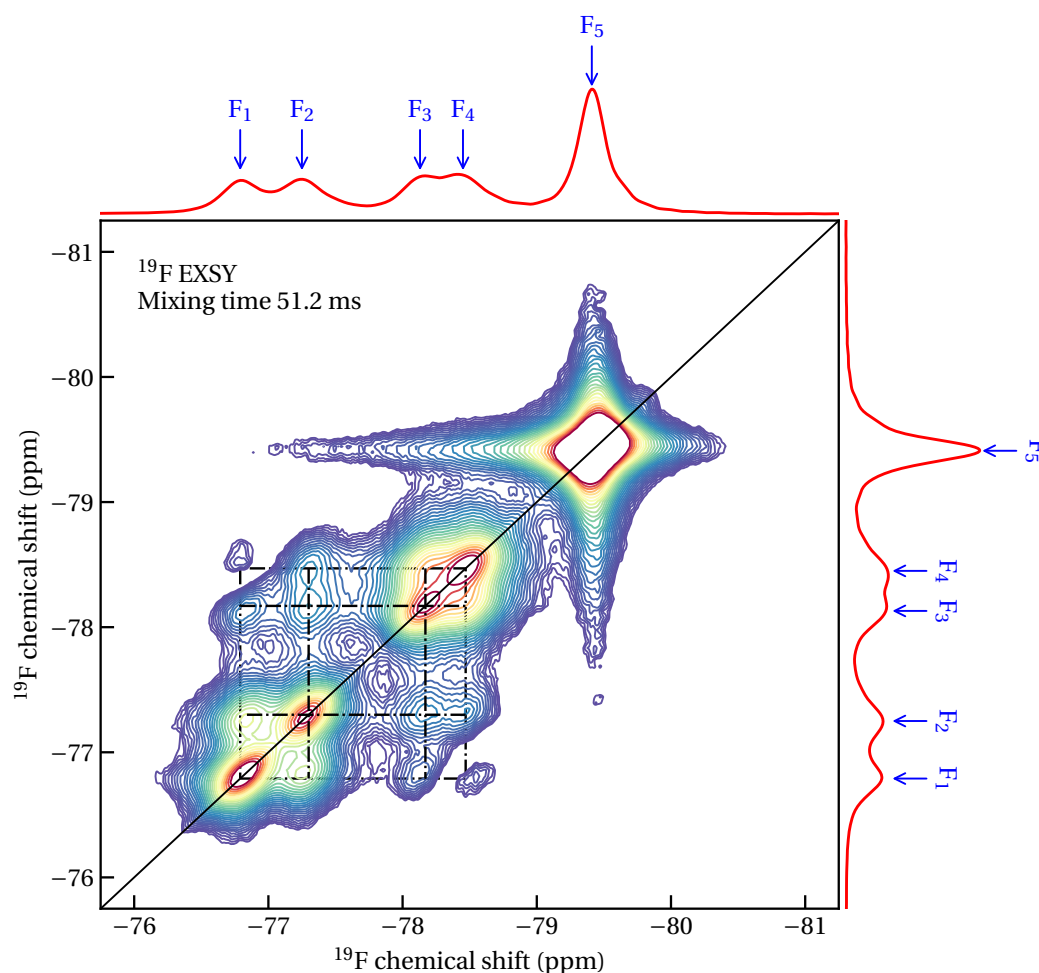


Figure 3.9. 2D EXSY $^{19}\text{F} - \{^{19}\text{F}\}$ spectrum of Solid Polymer Electrolyte II acquired at 20T with a spinning speed of 50 kHz and a mixing time of 51.2 ms.

Moreover, even the TFSI molecules in the cis conformation become more dynamic with the addition of the ionic liquid. This is also visible in the EXSY spectrum (Figure. 3.9). In the ^{19}F EXSY spectrum

of Solid Polymer Electrolyte I, the intensity of the cross-correlation peaks is almost at the noise level. In particular, the cross peaks (F_1 , F_4), (F_1 , F_3), (F_2 , F_4), and (F_2 , F_3) are less intense. In contrast, the ^{19}F EXSY spectrum of Solid Polymer Electrolyte II shows that all the cross-correlation peaks are more intense. This combination of increased dynamics and more efficient polarisation transfer may be due to a faster exchange between different sites resulting from the plasticizing effect of the added ionic liquid. Additionally, it is worth noting that the base of the peaks attributed to the TFSI molecules in the *trans* conformation shows a tailing effect extending towards the F_1 and F_2 peaks. This does not mean that the F_5 site has exchanged with or is spatially close to the other sites. Instead, this is explained by the high intensity of the F_5 peak, which has a Lorentzian shape, and the observed tailing corresponds to the base of the F_5 peak.

3.4.2 Increase in the number of TFSI anions in the *trans* conformation

A detailed analysis of the ^{19}F spectrum, depicted in Figure 3.10, allows for estimating the percentages of FSI and TFSI molecules in our electrolytic system. The addition of C_3mpyFSI increases the number of anions by 1.3 compared to the system without the addition of IL. Interestingly, the addition of IL reduces the number of molecules in the *cis* conformation while increasing those in the *trans* conformation. In fact, in the Solid Polymer Electrolyte I system, the ^{19}F spectrum shows that 87.7% of the TFSI molecules are in the *cis* conformation and 12.3% in the *trans* conformation. With the addition of the extra ionic liquid, the proportion of TFSI in the *cis* conformation decreases from 87.7% to 58.9%, while the proportion of molecules in the *trans* conformation increases from 12.3% to 41.1%. This means that the number of TFSI molecules in the *trans* conformation has been multiplied by approximately 3.3. It is important to note that C_3mpyFSI does not contain any TFSI molecules, meaning that the total number of TFSI molecules remains the same in both electrolytic systems. The addition of C_3mpyFSI enhances the plasticizing effect, which in turn increases segmental motion and ionic dynamics, as Makhlooghiazad et al. have stated. Since Na^+ is strongly coordinated (with a coordination number of 6 oxygens) to the TFSI in the *cis* conformation, the increased ionic dynamics (from C_3mpyFSI and the ionic block) break these Na^+-O bonds and more Na -FSI interactions will occur. The TFSI molecules that no longer solvate the sodium cations will then automatically adopt the *trans* conformation, explaining the increase in the number of TFSI molecules in the *trans* conformation. Furthermore, it is known that TFSI molecules in the *trans* conformation are more mobile than those in the *cis* conformation. TFSI molecules in the *cis*

3.5. Conclusion

conformation interact strongly with Na^+ , effectively trapping the Na^+ ions and reducing their contribution to ionic conduction. In contrast, FSI and TFSI molecules in the trans conformation, due to their high mobility, will better enable the Na^+ ions to move through the PIL block, thereby enhancing the sodium contribution to the ionic conductivity.

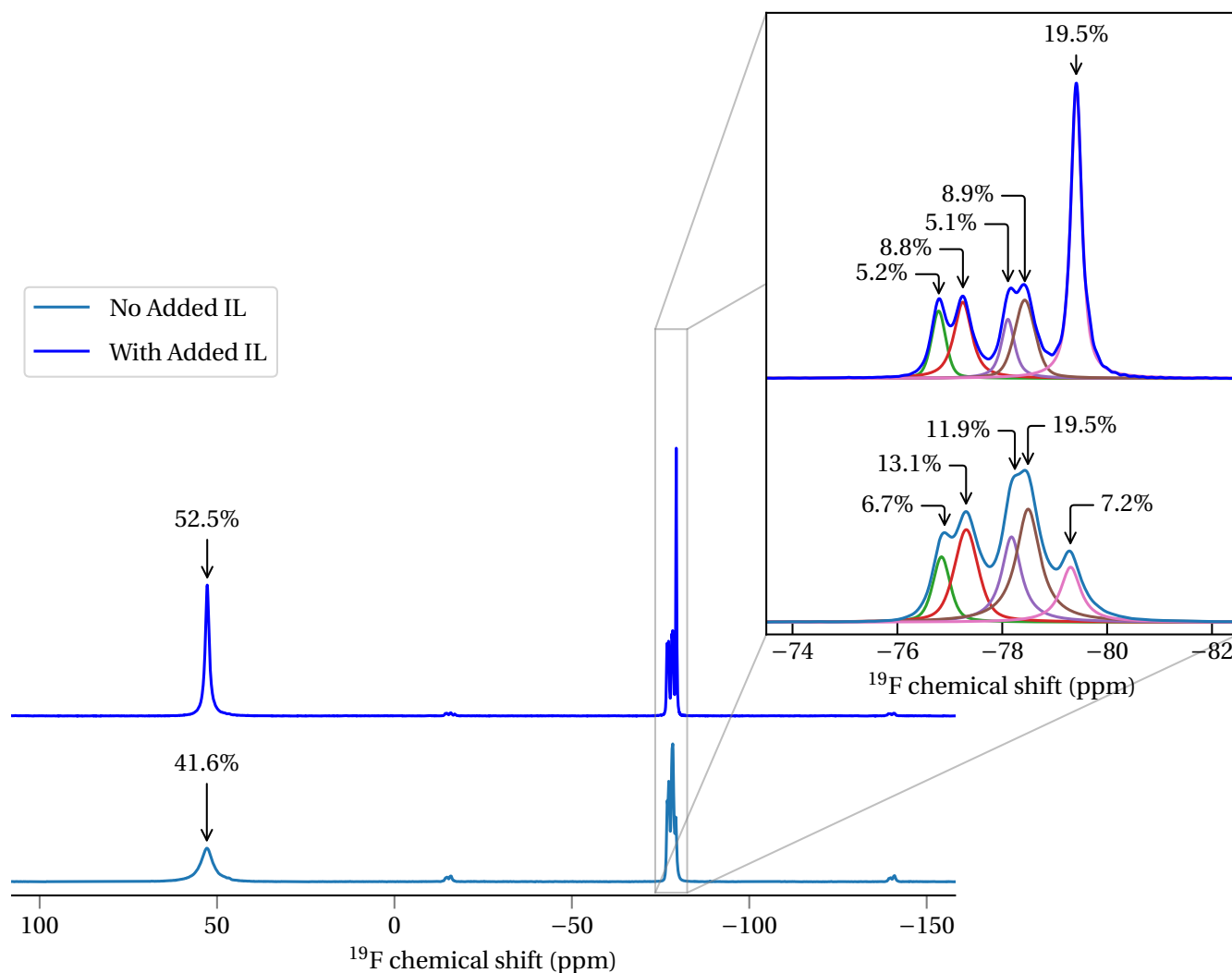


Figure 3.10. Comparison of the ^{19}F spectrum of Solid Polymer Electrolytes I and II and the contribution percentages of fluorine sites with and without the addition of Ionic Liquid.

3.5 Conclusion

In conclusion, CPMAS spectroscopy and direct excitation techniques effectively differentiate the rigid polystyrene block from the dynamic ionic component of the polymer electrolyte. CPMAS detects the

rigid fraction through efficient polarization transfer, while direct excitation highlights the mobile ionic component with narrower peaks and shorter relaxation times. Cross-polarization $^{13}\text{C}-^{19}\text{F}$ and HETCOR $^1\text{H}-^{19}\text{F}$ analyses of polymer-anion interactions indicate minimal, if any, interactions. The absence of resonance peaks in the $^{13}\text{C}-^{19}\text{F}$ spectrum and the weak resonance observed for the TFSI anion suggest limited coupling between the species. However, the EXSY ^{19}F experiment reveals the existence of cis and trans TFSI conformations in the electrolyte system. The $^{23}\text{Na}-^{19}\text{F}$ spectrum demonstrates significant coordination of TFSI anions in the cis conformation with sodium ions, while trans-conformation anions exhibit greater mobility. Furthermore, the addition of the ionic liquid $\text{C}_3\text{mpyrFSI}$ enhances the mobility of ionic species and shifts the equilibrium of TFSI anion conformations, significantly increasing the proportion of trans anions, thereby promoting sodium ion transport.

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Investigation of Sodium Ion Solvation within a Zwitterionic Plastic Crystal Doped with Sodium Salt

4.1 Introduction

In Chapter 1, we examined the work of Makhlooghiyazad and their collaborators¹, who introduced a new type of material called zwitterionic plastic crystals (ZPCs). These materials share structural characteristics with organic ionic plastic crystals but are distinguished by the fact that their cations and anions are covalently bonded (see Figure. 4.1a), resulting in a net neutral molecular charge and thus preventing their migration under an electric field. They also exhibit crystal structures featuring inherent local disorder and can undergo solid-solid phase transitions. These properties offer potential

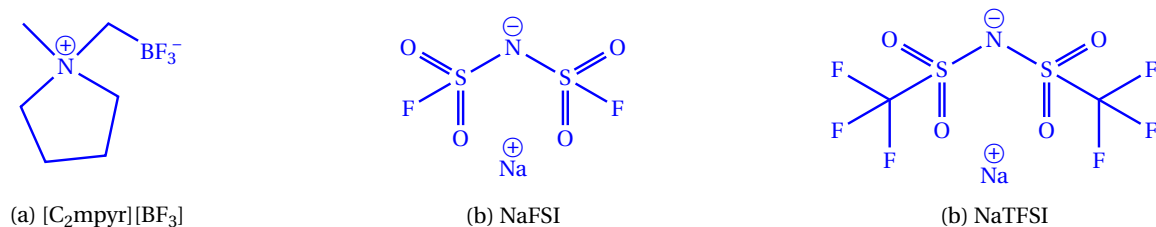


Figure 4.1. Structures: (a) Zwitterion $[C_2mpyr][BF_3]$, (b) NaFSI Salt, and (c) NaTFSI Salt

for improving the transport of specific ions, such as sodium, without interference from the matrix material, while also demonstrating favorable mechanical properties, making these materials particularly

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attractive for applications in solid-state batteries as solid electrolytes. Like many solid electrolytes, relatively low ionic conductivity is one of the weaknesses of these materials. However, the introduction of sodium salts, such as NaFSI and NaTFSI, with zwitterionic plastic crystals could help increase the overall conductivity of the solid electrolyte system. Charulakshmi Thiruvuravishankar, one of my colleagues at the Institute for Frontier Materials, has conducted in-depth research on binary mixtures of the zwitterion $[C_2\text{mpyr}][\text{BF}_3]$ (molecular structure shown in Figure. 4.1a) with one of two sodium salts (NaTFSI and NaFSI) at different concentrations (10, 20, and 50 mol%). She employed differential scanning calorimetry to analyse the thermal properties and phase behaviour of these systems and measured ionic conductivity as a function of temperature (see Table 4.1). Her results show an increase

Table 4.1. Ionic conductivity values at 30 °C and 50 °C for binary mixtures of the pure zwitterion with 10 mol% and 50 mol% sodium salts NaTFSI and NaFSI.

Sample	σ at 30 °C ($\text{S} \cdot \text{cm}^{-1}$)	σ at 80 °C ($\text{S} \cdot \text{cm}^{-1}$)
10 mol% NaFSI	2.92×10^{-8}	4.24×10^{-6}
50 mol% NaFSI	3.25×10^{-6}	1.05×10^{-4}
10 mol% NaTFSI	3.32×10^{-5}	3.91×10^{-4}
50 mol% NaTFSI	3.84×10^{-6}	2.15×10^{-4}

in ionic conductivity with temperature across all mixtures, with no phase transitions detected. At a low concentration (10 mol% of NaTFSI), the ionic conductivity of the zwitterion increases significantly, reaching up to five orders of magnitude above that of the pure zwitterion, due to an increase in charge carriers and enhanced ionic dynamics. However, at higher concentrations (50 mol%), conductivity decreases. Furthermore, for the mixture at 50 mol% NaTFSI, a metastable state allows a slight increase in conductivity compared to the NaFSI-zwitterion system, attributed to slow partial crystallization. In this chapter, we will analyse these systems by MAS NMR to gain insights into their structure as well as probing the interactions of the Na^+ ion with other species present in the zwitterion-sodium salt solid electrolyte. We will study the impact of the salt concentration on the zwitterion structure to try to understand the decrease in conductivity at the higher concentration.

4.2 Thermal properties

The thermograms presented in Figure. 4.2 illustrate the thermal behaviour of the pure zwitterion as well as binary mixtures composed of the zwitterion and NaTFSI and NaFSI salts at molar proportions of

10%, 20%, and 50%. As observed for other OIPCs in various previous studies², the ZPC undergoes a single solid-solid phase transition at 61 °C before remaining in phase 1 until its melting point at 104 °C. This solid-solid phase transition is associated with rotational and orientational rearrangements of the zwitterion's constituent ions over a given temperature range.

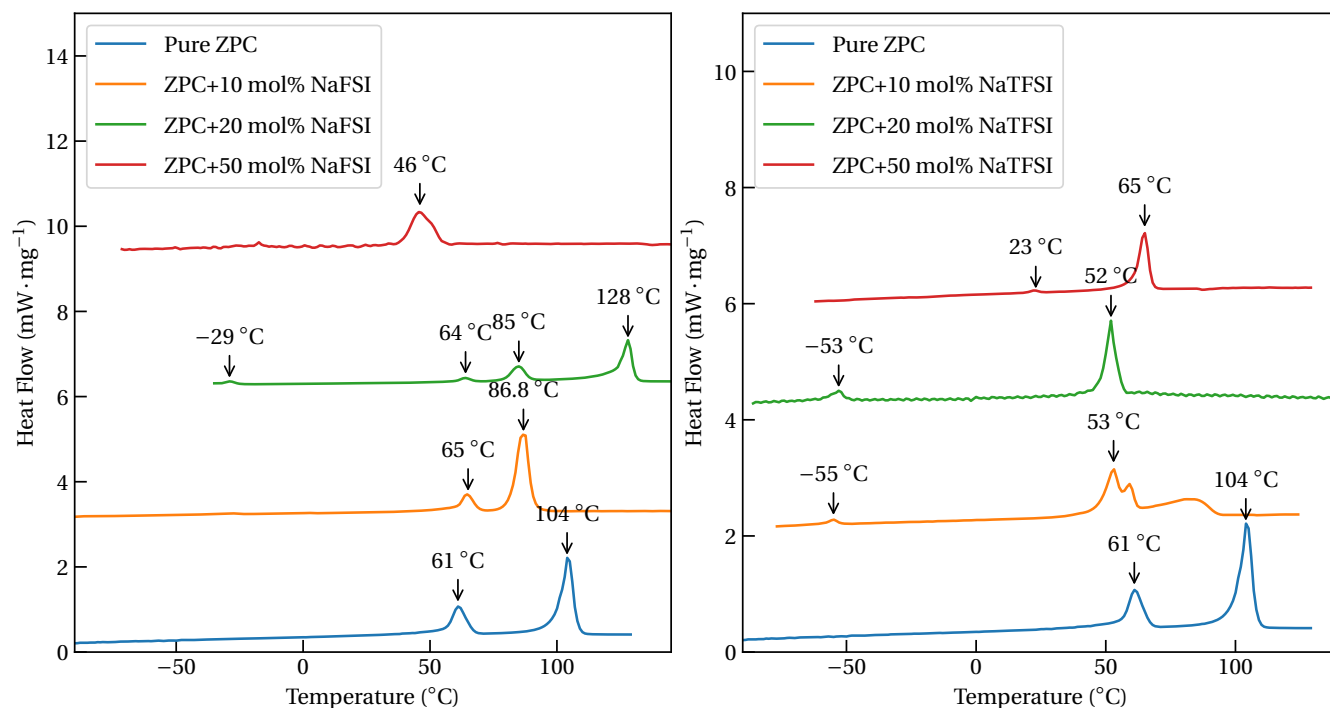


Figure 4.2. DSC thermograms of 10, 20 and 50 mol% NaFSI and NaTFSI-ZPC binary mixtures

ZPC mixtures containing sodium salts remain solid over a wider temperature range, as illustrated in Figure. 4.2, in contrast to the ZPC and lithium salt mixtures^{1,3,4}. The addition of 10 mol% NaTFSI leads to a broadening and a shift of the melting peak to a lower temperature, reaching 86 °C. Notably, a new peak appears at 52 °C in the sample containing 10 mol% NaTFSI. This peak becomes more intense in the sample containing 20 mol% NaTFSI, and during a heating cycle with a slower scanning rate, a shoulder associated with the melting peak at 50 °C becomes visible. These observations suggest the presence of a eutectic transition for a composition close to 20 mol% NaTFSI. The mixture containing 50 mol% NaTFSI exhibits characteristics of a metastable solid, with a symmetric and well-defined melting peak at approximately 65 °C, indicating the existence of a single phase for this binary mixture. At this salt concentration, a metastable behaviour is observed during the second heating cycle, resulting in the formation of a supercooled liquid due to the slow kinetics of nucleation and growth of the solid phase. This slow kinetics prevents the mixture from crystallising and reaching its thermodynamically stable

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state. Consequently, no melting peak is detected in subsequent heating cycles.

In mixtures containing 10 mol% NaFSI, the addition of salt causes a shift in the melting peak to a lower temperature, reaching 85 °C, while reducing the enthalpy of fusion. This behaviour is consistent with previous observations in mixtures of OIPC with sodium or lithium salts, as well as in mixtures of ZPC with lithium salts³, suggesting the presence of a eutectic phase. When the NaFSI concentration is increased to 20 mol%, the melting peak shifts to a higher temperature, accompanied by the appearance of two additional peaks at 64 °C and 85 °C. These results indicate the possible existence of a eutectic phase at a lower NaFSI concentration, around 20 mol%. A further increase in salt concentration at this level could lead to the appearance of a peritectic phase, where the temperature associated with this transition coincides with the solid-solid transition in ZPC. Such peritectic transitions, characterized by the combination of two solid phases into a single phase, have already been reported in mixtures of P_{111i4}TFSI/NaTFSI¹. At a concentration of 50 mol% NaFSI, a single melting peak around 50 °C was observed, suggesting the formation of a stable compound at this composition. However, during the second heating cycle, the binary ZPC—50 mol% NaFSI mixture showed no melting peak, indicating the formation of a supercooled liquid. This phenomenon aligns with a trend reported in various electrolyte phase diagrams, where the crystallization of materials is often challenging—a typical behavior observed in mixtures of lithium and sodium salts with OIPC.

The phase behavior of these binary mixtures is highly complex, requiring further analyses, such as NMR spectroscopy, to comprehensively characterize the behavior of this system.

4.3 Experimental NMR section

The samples were synthesised and prepared by collaborators at Deakin University. All zwitterion-based electrolyte system samples were placed in 1.3 mm and 2.5 mm Bruker NMR rotors within a glove box under a controlled argon atmosphere. These samples were then analysed under different magnetic fields (11.7 T, 17.6 T, and 20 T). The thermogram obtained by DSC indicates that the zwitterionic plastic crystal material undergoes a phase transition within a temperature range of 52 to 65 °C, which could pose an issue during these experiments, as fast magic angle spinning of the rotor can lead to an increase in the sample temperature, potentially reaching these critical values and risking a phase transition. To prevent this transition, the sample was cooled by a jet of cold nitrogen gas, with a temperature varying between

0 °C and –20 °C. This approach allowed the average temperature of the sample within the rotor to be maintained between 15 and –20 °C. For the spectra recorded at 20 T, the same NMR parameters used for the polymerized ionic copolymer system were applied, with only slight variations in the spinning frequency and number of scans. We used the same reference samples to measure the radiofrequency fields and calibrate the isotropic chemical shifts.

4.4 ZPC mixed with NaFSI salt

4.4.1 Fluorine spectra of the binary system

The ensemble of ^{19}F solid-state MAS NMR spectra obtained from mixtures of the zwitterion with proportions of 10%, 20%, and 50% in moles of sodium salt (NaFSI) is presented in Figure. 4.3. The spectrum of ZPC in its pure state reveals the presence of a single isotropic signal at a resonance frequency of –139 ppm, attributed to the $\text{C}-\text{BF}_3$ group, where the three fluorine sites are equivalent presumably due to rotational dynamics. However, upon analysis of the spectra from the ZPC mixtures associated with proportions of 10% and 20% in moles of sodium salt, a significant evolution is observed. In these contexts, two distinct sets of isotropic signals are detected in each spectrum. One of these signals is associated with the fluorine of the FSI anions, while the other originates from the $\text{C}-\text{BF}_3$ groups. A more in-depth analysis of the signal attributed to the FSI anions in the 10 and 20 mol% systems reveals a notable asymmetry. Spectrum reconstruction then indicates the presence of two distinct FSI environments, observed at chemical shifts of 51.0 ppm and 51.3 ppm. Furthermore, the signal from the BF_3 group also exhibits two distinct peaks, indicating the presence of two unique structural environments for the BF_3 groups. One of these peaks, located at –139 ppm, corresponds to the BF_3 sites in the crystal structure of the pure zwitterion, while the other, located at –146, corresponds to the BF_3 sites in a distinct phase that incorporates the NaFSI salt and in which the anionic BF_3 group is presumably interacting with the Na cations (see later).

It should be noted that as the molar percentage of NaFSI increases, the relative amount of the pure zwitterion phase gradually decreases, while the $\text{C}-\text{BF}_3 \cdots \text{Na}$ sites increase, as expected. However, there is a limit in terms of the molar percentage of sodium salt mixed with ZPC beyond which a phase change occurs. This limit lies between 20% and 50% moles of NaFSI, as shown in Figure. 4.3. Indeed, the ^{19}F spectrum of the zwitterion mixture with a molar proportion of 50% NaFSI reveals that the pure ZPC

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phase is absent, leaving only the $\text{C}-\text{BF}_3 \cdots \text{Na}$ sites visible, and four new distinct isotropic $\text{C}-\text{BF}_3$ signals at resonance frequencies of -147 , -148 , -149 , and -152 ppm, as well as a very complex set of peaks in the FSI region. These new signals must be due to a set of $\text{C}-\text{BF}_3$ fluorine sites in a new phase with a larger number of surrounding Na cations, leading to multiple different chemical environments. Furthermore, a complex set of peaks is observed in the FSI region. These signals almost seem to form a symmetric multiplet, although the splittings (400 Hz) are too large to be explained by J-couplings. These complex peaks are likely due to different configurations of the FSI around the positively charged region of the zwitterionic structure. The number of FSI configurations is related to the number of surrounding Na^+ cations around the $\text{C}-\text{BF}_3$ group.

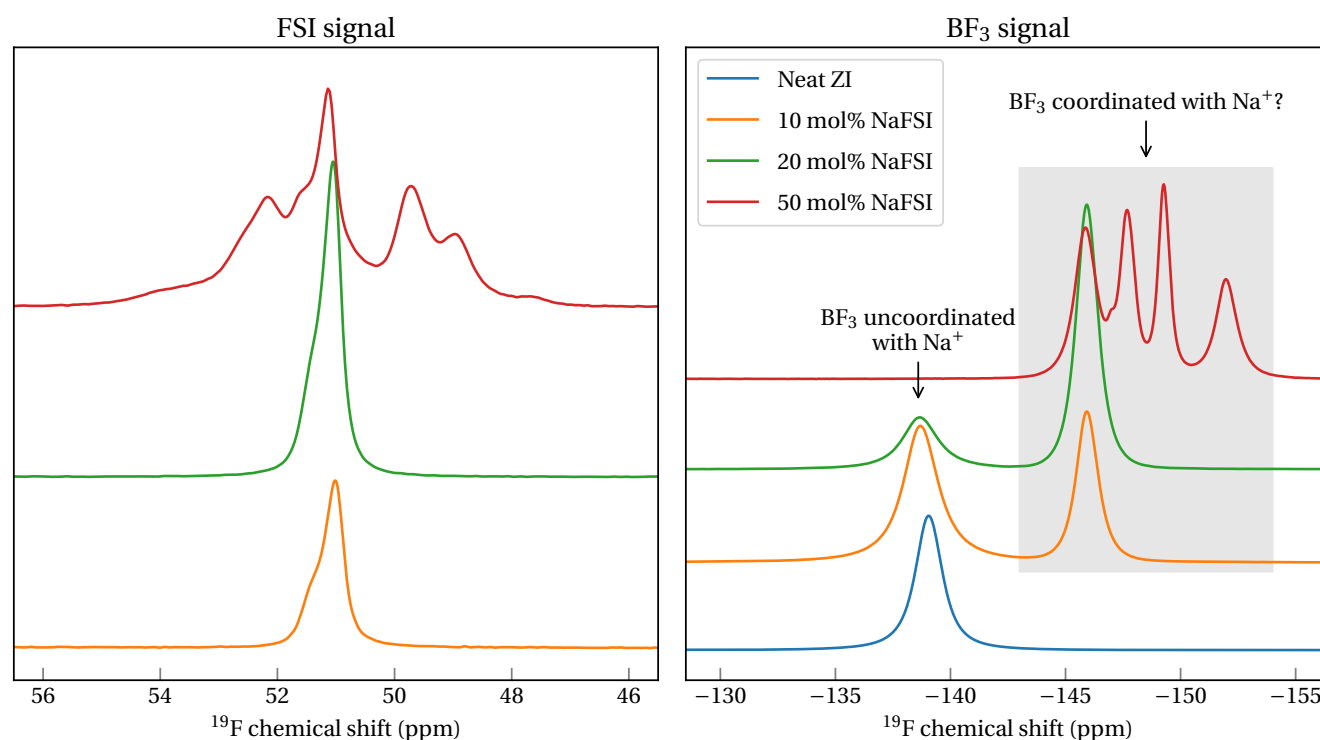


Figure 4.3. Solid-state ^{19}F MAS NMR spectra obtained from mixtures of the zwitterion system with molar proportions of 10%, 20%, and 50% sodium salt (NaFSI). The signals for FSI species are observed on the left, while those for BF_3 species appear on the right.

4.4.2 Exchange Spectroscopy

The 2D $^{19}\text{F}-\{^{19}\text{F}\}$ exchange spectroscopy (EXSY) experiment was conducted to reveal chemical or conformational exchange, or to determine the spatial proximity between fluorine atoms. The observed

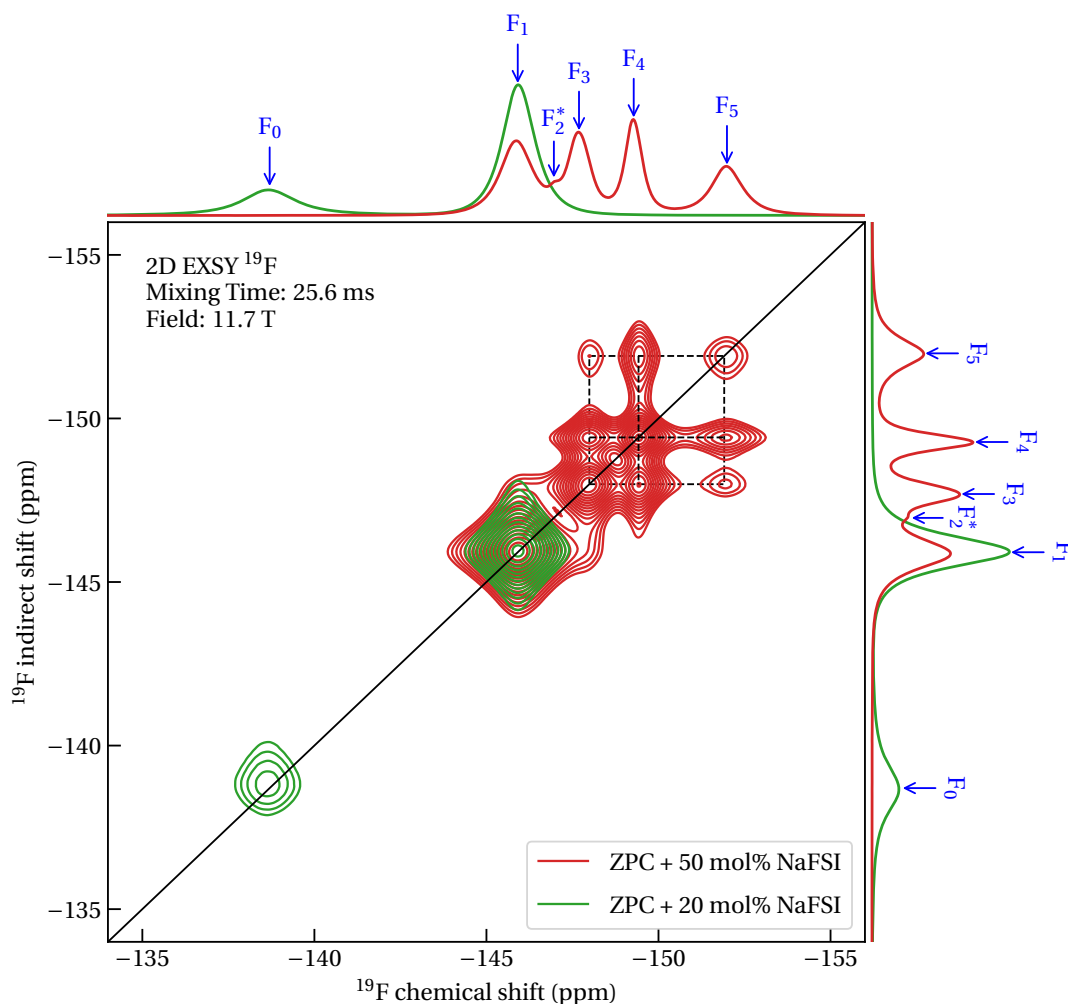


Figure 4.4. 2D EXSY ^{19}F NMR spectrum with a mixing time of 25.6 ms, focusing on the BF_3^- region of zwitterion mixture samples containing NaFSI mole fractions of 20% and 50%. The 1D spectra of the zwitterion mixed with 20% mole NaFSI (green line) and the zwitterion mixed with 50% mole NaFSI (burgundy line) for ^{19}F are displayed on the vertical and horizontal projections.

results do not reveal significant cross-peaks between the $\text{C}-\text{BF}_3$ groups in the ZPC system mixed with 20% NaFSI, as shown in the green line contour in Figure. 4.4. This observation is consistent with a phase separation between the pure ZPC component and the phase containing the Na salt. However, for the ZPC mixed with 50 mol% NaFSI, exchange peaks are clearly observed between certain peaks as illustrated in Figure. 4.4, burgundy line. The fluorines F_3 , F_4 , and F_5 exchange among themselves, indicating a potential positional exchange where each mentioned fluorine can swap positions with another, or that they are very close spatially. The fact that these three peaks are all of approximately equal intensity may indicate that this high salt content phase contains a $\text{C}-\text{BF}_3$ group in which the rotation of the group is

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slow enough (frequency on the order of 10 Hz according to the EXSY spectrum) that the three fluorine sites are no longer equivalent and thus three distinct isotropic shifts are observed. This slowed rotation may be due to steric hindrance in the crystal structure and/or strong interactions of this group with sodium cations. Fluorine F_1 does not participate in these exchanges with the other fluorines. Regarding fluorine F_2 , no deformation of line contours is observed for the chosen mixing time (51.2 ms), indicating that there is also no spatial proximity with the other fluorines. Unexpectedly, there also appears to be some cross peak intensity between F_1 and F_3 which may suggest that the peaks F_1 to F_5 are all co-existing in the same phase rather than two separate phases as one might expect based on Figure. 4.3. Another potential explanation is that this may be an artifact arising from the close proximity of these peaks and the Lorentzian tail of the intense F_1 peak. This is discussed further below.

4.4.3 Sodium spectra of the binary mixtures

Figure. 4.5 shows the ^{23}Na spectra for the zwitterion, mixed with proportions of 10, 20, and 50% NaFSI. The sodium spectra of the zwitterionic systems containing 10 and 20 mol% NaFSI display similar chemical shifts. Spectrum fitting indicates that sodium ions in these systems are distributed between two distinct chemical environments. The first environment is characterized by a sharp peak with a chemical shift of 13.4 ppm and no observable sidebands, indicating a near-zero quadrupolar constant C_Q according to the in2QUAD fitting model. This peak is attributed to dynamic sodium sites, likely associated with FSI ions. The second environment shows a slightly broader peak with a chemical shift of 13.6 ppm. This peak generates sidebands, according to the in2QUAD model, which calculates a $C_Q = 0.075$ MHz. This peak is attributed to less dynamic sodium sites, likely corresponding to sodium ions interacting with the BF_3 group of the zwitterion.

In the zwitterion-NaFSI mixture at a 1:1 molar ratio (50% zwitterion and 50% NaFSI), the ^{23}Na NMR spectrum was acquired under two different magnetic fields, 11.7 T and 17.6 T. At 11.7 T, the spectrum lacks resolution, making interpretation complex due to the presence of multiple overlapping sodium sites. However, the spectrum indicates the existence of a sodium site characterized by strong quadrupolar coupling. To improve spectral resolution, an acquisition was performed at a higher magnetic field of 17.6 T. The fitting of the resulting spectrum (Figure. 4.5c) reveals two distinct sodium sites. The first site (Na1) has a chemical shift of $\delta = -13.8$ ppm and is attributed to sodium ions interacting with the zwitterion's BF_3 group, as observed in mixtures containing 10% and 20% NaFSI. The second sodium

site (Na2), on the other hand, is characterized by a chemical shift $\delta = -15.1$ ppm, a $C_Q = 1.06$ MHz, and an asymmetry parameter $\eta = 0.8$. This site likely corresponds to a second sodium ion stabilized by two BF_3 groups from zwitterion molecules, held together by electrostatic interactions between BF_3^- and Na^+ . This sodium spectrum corroborates the differences observed in the fluorine NMR spectra, where a new series of chemical environments for the FSI^- species and the zwitterion's BF_3^- group are present at this molar ratio (50% zwitterion and 50% NaFSI), indicating the existence of a Na-rich phase. These results also indicate less overall dynamics in this phase, consistent with the observed lower ionic conductivity of the 50 mol% NaFSI sample.

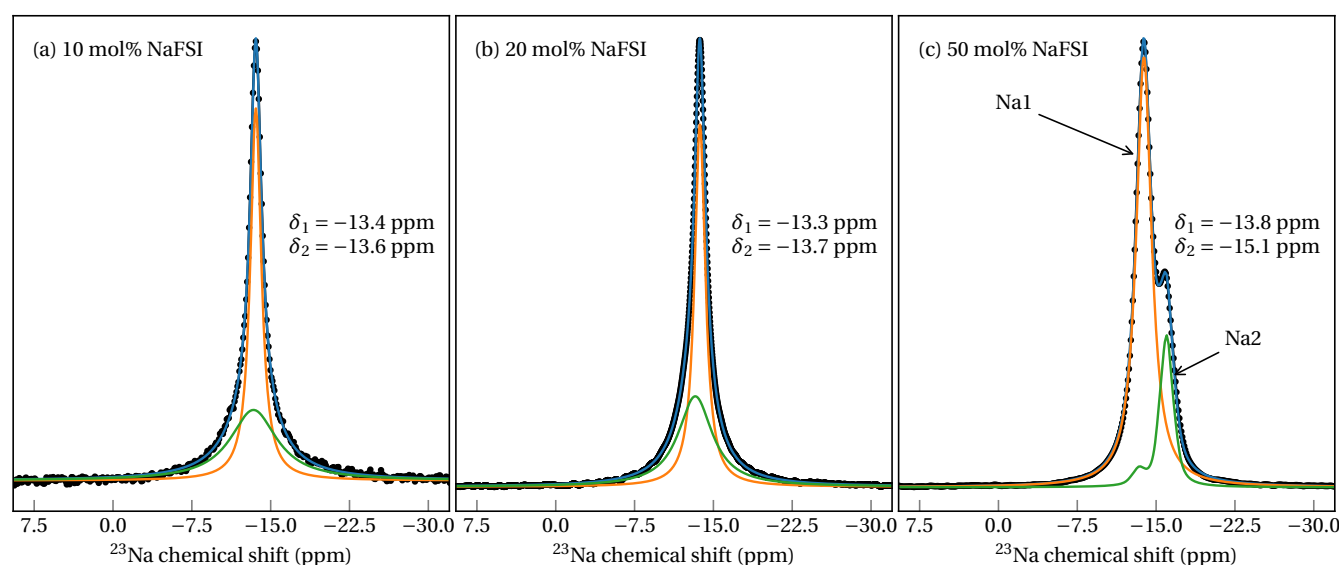


Figure 4.5. ^{23}Na MAS spectra of zwitterion samples mixed with 10, 20, and 50 mol% NaFSI. The spectra in Figures (a) and (b) were obtained under a field of 11.7 T with MAS at 20 kHz at 0 ° C. The spectrum in Figure (c) was obtained under a field of 17.6 T with MAS at 40 kHz at 0 ° C.

4.4.4 Sodium-Anion Interactions

The 2D $^{23}\text{Na} - \{^{19}\text{F}\}$ HETCOR experiment was conducted to observe proximities of fluorine and sodium sites within the 10% and 50% salt systems. The results of the HETCOR experiments reveal the presence of sodium exchange peaks associated with $-\text{BF}_3$ anions, while no sodium exchange peaks with FSI^- anions (not shown in the figure) are observed across the various systems studied. This discrepancy suggests a stronger interaction between the $-\text{BF}_3$ anions and sodium ions, as illustrated in Figure. 4.6. Interactions between FSI^- and Na^+ ions may still be present but may have short lifetimes on the timescale

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of NMR experiments, hindering their detection. In contrast, the robust interaction between BF_3 groups and Na^+ is likely attributed to a more localized negative charge on the BF_3 groups compared to the FSI^- species. Focusing on the correlation between Na^+ and $-\text{BF}_3$ (see Figure. 4.6), for the zwitterion plastic crystal material mixed with 20 mol% NaFSI, the exchange peak aligns solely with one of the two BF_3 peaks, specifically the peak with a chemical shift of -146 ppm. This confirms that this $\text{C}-\text{BF}_3$ moiety interacts strongly with the Na^+ ions, corresponding to the chemical environment $\text{C}-\text{BF}_3 \cdots \text{Na}^+$, while the other $\text{C}-\text{BF}_3$ group corresponds to the (phase separated) pure ZPC phase in which no sodium is present.

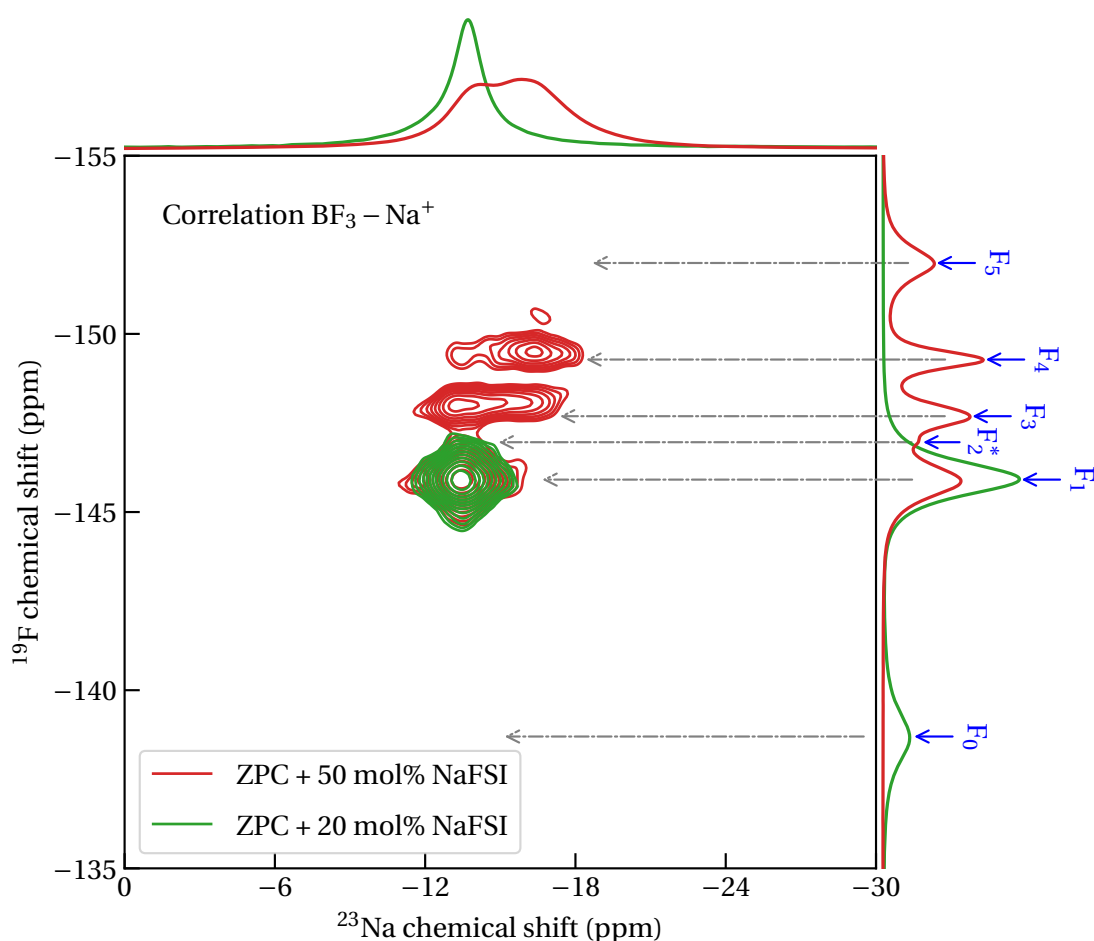


Figure 4.6. 2D HETCOR spectra with polarization transfer from ^{19}F to ^{23}Na were used to investigate the correlations between sodium sites and BF_3^- ions in zwitterionic plastic crystal mixtures containing 20% and 50% NaFSI mole fractions, with a contact time of 2 ms. The ^{23}Na and ^{19}F spectra are projected onto the horizontal and vertical dimensions, respectively.

In the case of the zwitterionic plastic crystal material mixed with 50 mol% NaFSI, the HETCOR

spectrum shows that the fluorine site F_1 is only correlated with the sodium site Na1. In contrast, the fluorine site F_3 is correlated with both sodium sites (Na1 and Na2), as indicated by cross-peaks distributed between these two sites. Fluorine F_4 appears to be exclusively correlated with the sodium site Na2. This suggests that the F_1 sites are very close to Na1, the F_3 sites are close to both Na1 and Na2, while the F_4 sites are located near Na2. Finally, the F_5 and F_1 sites seem to be distant from the sodium sites. Again, these data suggest that there is only a single sodium-containing phase present at 50 mol% salt concentration with a crystal structure that incorporates features seen in the 20 mol% sample, rather than two distinct and separate sodium containing phases. This would be consistent with the cross peaks observed between fluorine sites F_1 and F_3 discussed above. The EXSY spectrum indicates spatial proximity and/or chemical exchange among the F_3 , F_4 , and F_5 sites. It would therefore be logical that if the F_3 and F_4 sites are correlated with the sodium sites, the F_5 sites would also be correlated with at least one sodium site. This may be due to the fact that the F_5 and F_2 sites are highly mobile (rotating on themselves), which makes polarization transfer inefficient. Another possible explanation could be related to the configuration of the sodium sites. One of these sites is likely located between a carbon and a fluorine, while the other is positioned between two fluorine atoms. In this configuration, the two sodium sites could be spatially very distant from the F_2 and F_5 sites. The 2 ms contact time used in this experiment (which enables correlations over a limited distance) might therefore be insufficient to observe correlations between the F_1 and F_5 sites. The dynamics of cross-polarization, particularly through increasing the contact time, could have provided insights into evaluating the distances between fluorine atoms F_2 and F_5 and sodium sites Na1 and Na2.

4.4.5 Local Structure with NaFSI

Based on information obtained through NMR spectroscopy results, we propose a local structural model for zwitterionic systems mixed with 10, 20, and 50 mol% NaFSI. The structure of the ZPC electrolyte with 10 mol% NaFSI is similar to that of ZPC with 20 mol% NaFSI, as indicated by the ^{19}F NMR spectrum. With the addition of 10 and 20 mol% NaFSI, phase separation on the NMR lengthscale was observed. One phase consists of pure zwitterion, while a second phase forms. This second phase results from interactions between ZPC and sodium via the $[\text{BF}_3]^-$ group, as well as interactions between ZPC and FSI through the $[\text{C}_2\text{mpyr}]^+$ ring, as illustrated in Figure. 4.7a. These interactions are represented by arrows in Figure. 4.7. When NaFSI is added, Na^+ ions break their bond with the FSI anion to form a

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complex with the $[\text{BF}_3]^-$ group of ZPC. Within this complex, the Na^+ ion positions itself between two $[\text{BF}_3]^-$ groups belonging to the ZPC molecule. The fluorine atoms involved in this complexation are equivalent, which results in a single resonance peak for the $[\text{BF}_3]^-$ group in the ^{19}F NMR spectrum. As for the FSI^- anion, it preferentially interacts with the $[\text{C}_2\text{mpyr}]^+$ ring, as shown in Figure. 4.7a.

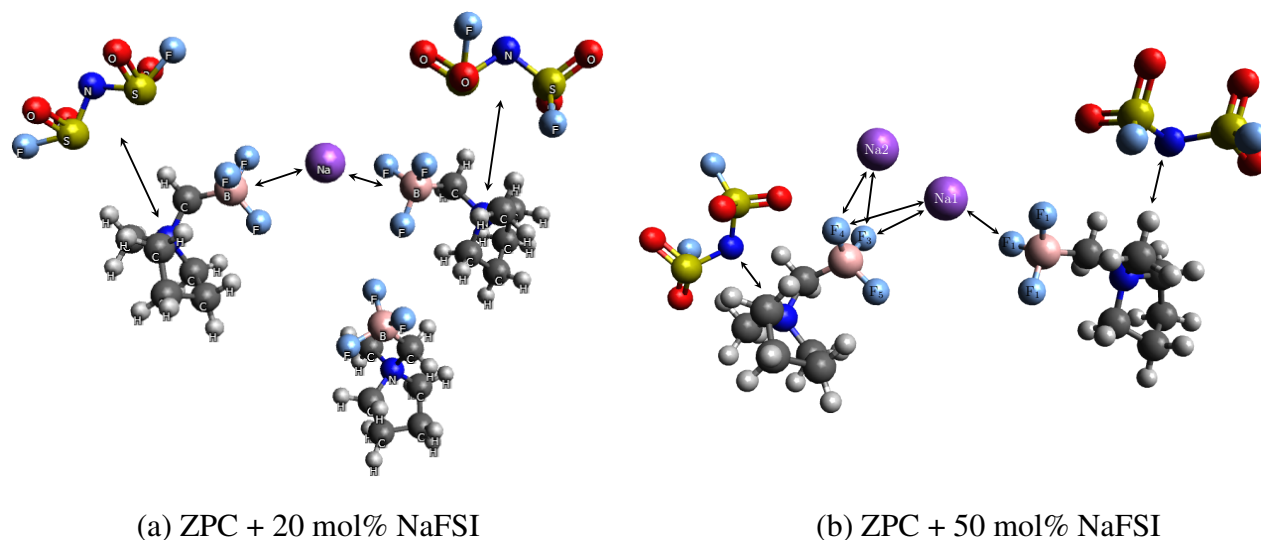


Figure 4.7. Visualization of local structural changes with increasing NaFSI salt concentration.

When the concentration of NaFSI is increased to 50 mol%, the pure ZPC phase disappears. As with the previous concentrations, all Na^+ ions break their bond with the FSI^- anion to form a complex with the BF_3 group of the ZPC phase. However, this time, two distinct sites for the Na^+ ions emerge. One of these sites, labeled Na2, is spatially close to the fluorine atoms F_3 and F_4 , while being distant from the Na1 site (see the ^{23}Na EXSY spectrum in the appendix). Meanwhile, the Na1 site shows spatial proximity to the fluorines F_1 , F_3 , and F_4 . Thus, the two sodium sites are spatially organized in a manner consistent with previous observations, as illustrated in Figure. 4.7b. The spatial proximity between the F_3 and F_4 sites and the Na1 and Na2 sites restricts rotation around the $\text{C}-\text{B}$ axis. In contrast, the proximity between Na1 and F_1 does not hinder this rotation, suggesting that the two Na^+ ions interact with two distinct ZPC molecules, as illustrated in Figure. 4.7b. Additionally, the $[\text{FSI}]^-$ anion preferentially interacts with the $[\text{C}_2\text{mpyr}]^+$ ring, as shown in Figure. 4.7b. However, the shape of the ^{19}F spectrum suggests the probable existence of multiple configurations of the FSI^- anion around the $[\text{C}_2\text{mpyr}]^+$ ring, which appears to attract at least two FSI^- molecules (not shown in the figure).

4.5 ZPC mixed with NaTFSI salt

4.5.1 Impact of Concentration on TFSI and BF_3 Groups

For the zwitterion-NaTFSI mixture at a molar ratio of 4:1 (80% zwitterion and 20% NaTFSI), the ^{19}F spectrum analysis (Figure. 4.8) reveals a well-defined isotropic peak at -80.2 ppm, characteristic of the TFSI molecule signal. As noted in the previous chapter on polymerized ionic liquid block copolymer systems, TFSI can adopt various conformations.⁵ TFSI molecules that are strongly coordinated with sodium cations in a cis conformation may exhibit up to four distinct ^{19}F signals, while those in a trans conformation produce only a single signal. Based on this, the peak at -80.2 ppm can be attributed to the CF_3 group of the TFSI molecules in a trans conformation, likely interacting with the cationic group of the zwitterion $[\text{C}_2\text{mpyr}]^+$ cation rather than with the $[\text{BF}_3]^-$ group, and this suggests that Na-TFSI interactions are relatively weak in this sample. Additionally, the fluorine spectrum shows three other well-defined isotropic peaks at -137.4 , -142.9 , and -143.8 ppm, labeled as F_0 , F_1 , and F_2 , respectively, in the figure. These peaks correspond to signals from the $[\text{BF}_3]^-$ group in zwitterionic molecules. The peak at -139 ppm is associated with zwitterionic molecules that are unaffected by sodium ions, that is, free zwitterionic species, similar to those observed with the addition of 20% mol NaFSI. In contrast, the other two peaks likely stem from zwitterionic molecules influenced by sodium ions. In the previous case, the 20% NaFSI mixture presented only one environment for ^{19}F . Here, however, we observe two distinct environments for fluorine, indicating that the two salts, NaFSI and NaTFSI, exert different effects on the zwitterion.

Interestingly, by increasing the zwitterion-NaTFSI molar ratio to 1:1, the ^{19}F NMR spectrum undergoes a significant change, resulting in new structural environments for both TFSI and BF_3 groups. The ^{19}F spectrum presented in Figure. 4.9 shows four peaks in the TFSI spectral region, while two sharp peaks, which overlap in the BF_3 spectral region, are observed. In the BF_3 spectral region, the chemical shifts attributed to the free zwitterions disappear, suggesting the formation of a new single phase that incorporates both the zwitterions and salt ions. Moreover, the two overlapping BF_3 peaks are significantly shifted compared to the BF_3 peaks measured from the 20% mol NaTFSI ZPC system. The chemical shifts of the peaks measured in the spectral domain of the TFSI molecule are -78.8 (F_a), -79.3 (F_c), -80.4 (F_b), -81.2 (F_d) ppm. These shifts do not correspond to the typical values for TFSI molecules

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in cis conformation coordinated with sodium cations. According to the research by Chen et al⁵., these chemical shift values would correspond to the simultaneous presence of both cis and trans conformations of TFSI. Based on their studies, we can assign the F_c and F_d resonances to TFSI molecules in the trans conformation, while the F_a and F_b resonances correspond to those in the cis conformation. In general, the cis conformer is relatively more coordinating than its trans counterpart, which is less coordinating and more dynamic. Increasing the concentration of NaTFSI salt does not favor either of these conformers.

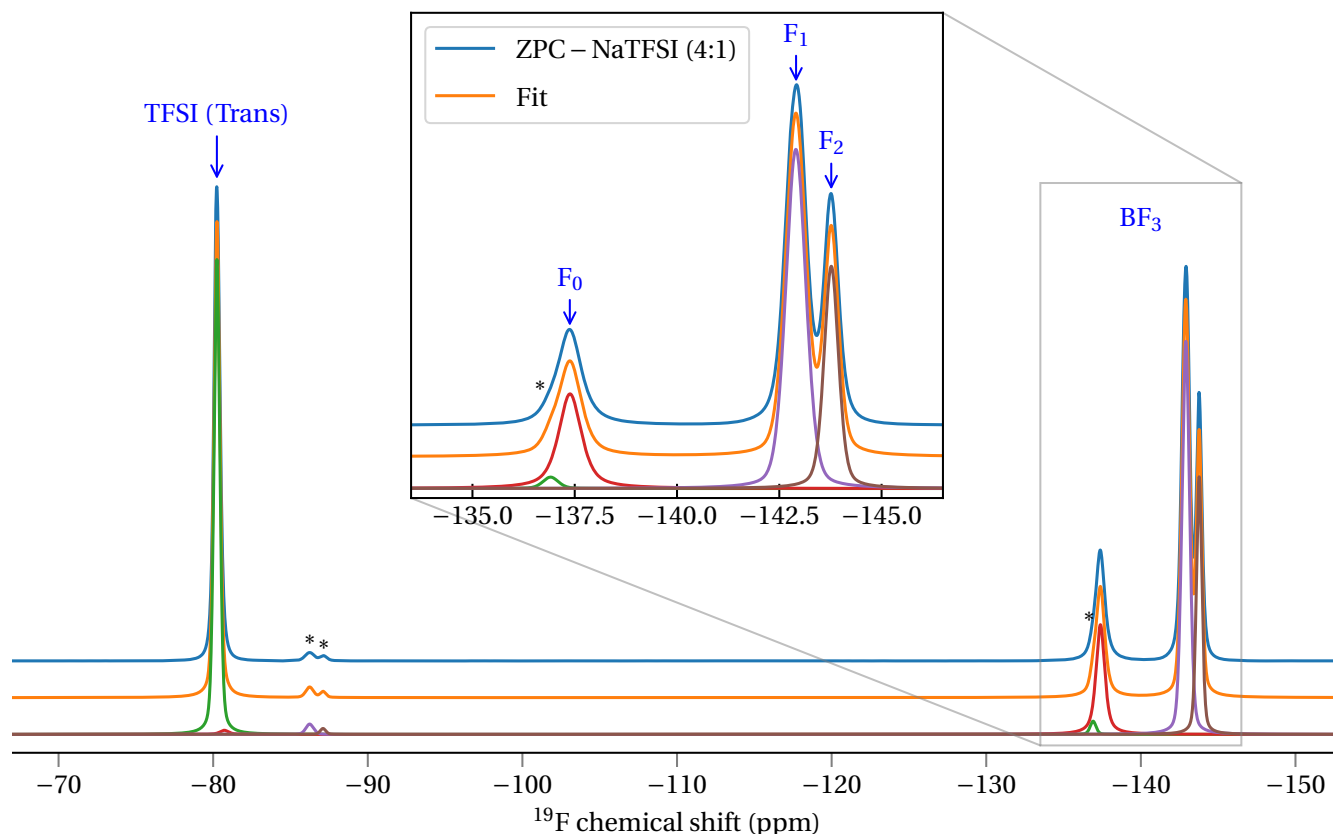


Figure 4.8. ^{19}F NMR MAS spectrum of the zwitterion-NaTFSI mixture with a molar ratio of 4:1. The spectrum was acquired under a 17.6 T magnetic field with MAS at 40 kHz at 0 °C. The CSA MAS model was used to fit the spectrum. The TFSI signal shows a chemical shift of $\delta_{\text{iso}} = -80.2$ ppm with a CSA of -36 kHz, while the signals from BF_3 have chemical shifts of $\delta_{\text{iso}_0} = -137.4$ ppm, $\delta_{\text{iso}_1} = -142.9$ ppm, and $\delta_{\text{iso}_2} = -143.8$ ppm. The anisotropic chemical shifts are $\delta_{\text{CSA}_0} = 21.5$ kHz, $\delta_{\text{CSA}_1} = 24.5$ kHz, and $\delta_{\text{CSA}_2} = -31$ kHz, respectively.

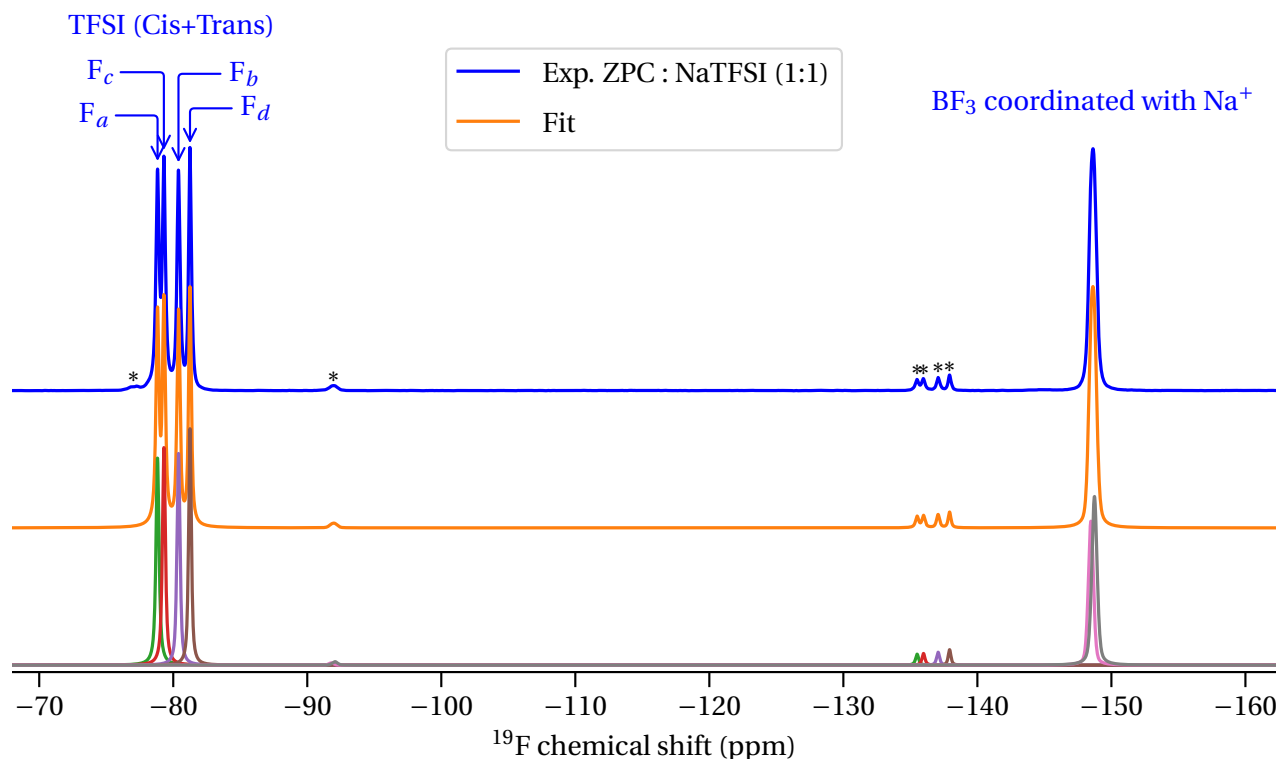


Figure 4.9. ^{19}F NMR MAS spectrum of the zwitterion- NaTFSI mixture with a molar ratio of 1:1. The spectrum was acquired under a 17.6 T magnetic field with MAS at 40 kHz at 0 °C. The CSA MAS model with Gaussian-Lorentzian lineshape was used to reconstruct the spectrum. The chemical shifts calculated for the signals emanating from TFSI are $\delta_1 = -78.8$, $\delta_2 = -79.3$, $\delta_3 = -80.4$, and $\delta_4 = -81.2$ ppm, with respective anisotropic chemical shifts of $\delta_{\text{CSA}_1} = 44.7$, $\delta_{\text{CSA}_2} = 45.6$, $\delta_{\text{CSA}_3} = 48.9$, and $\delta_{\text{CSA}_4} = 50.8$ kHz. The chemical shifts calculated for the signals emanating from BF_3 are $\delta_{b_1} = -148.5$ and $\delta_{b_2} = -148.7$, with $\delta_{\text{CSA},b_1} = -27$ and $\delta_{\text{CSA},b_2} = -30.8$ kHz.

4.5.2 Exchange Spectroscopy

Figure. 4.10 shows the 2D ^{19}F EXSY NMR spectrum of the 20% NaTFSI ZPC. The carrier frequency was set to the resonance region of the BF_3 group, with a spectral excitation window of 20 kHz in the direct dimension and 10 kHz in the indirect dimension. The spectrum reveals that site F_0 does not exhibit any cross peaks with sites F_1 or F_2 . This absence of correlation indicates that there is neither chemical exchange nor spin diffusion between F_0 and the other sites, suggesting a significant spatial separation between F_0 and sites F_1 and F_2 . Additionally, the three fluorine atoms rotate around the C–B axis, resulting in a single averaged F_0 resonance frequency. This observation is consistent with the 1D ^{19}F

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spectrum assignment, where the F_0 sites correspond to the fluorine atoms of unbound zwitterions. In contrast, the EXSY spectrum shows cross peaks between fluorine sites F_1 and F_2 , indicating a correlation between these two sites. This suggests that F_1 and F_2 are either undergoing chemical exchange or are spatially close. The introduction of NaTFSI salt into the mixture alters the local structure of the zwitterionic matrix, the Na^+ ions appear to position themselves in regions of high electron density within the BF_3 group, likely between the boron atom and one of the fluorine atoms. This positioning mechanically restricts the rotation of the three fluorine atoms around the C–B axis. Consequently, F_1 and F_2 sites represent the fluorine atoms of zwitterions bound to Na^+ ions. This same mechanism is observed with the addition of NaFSI salt.

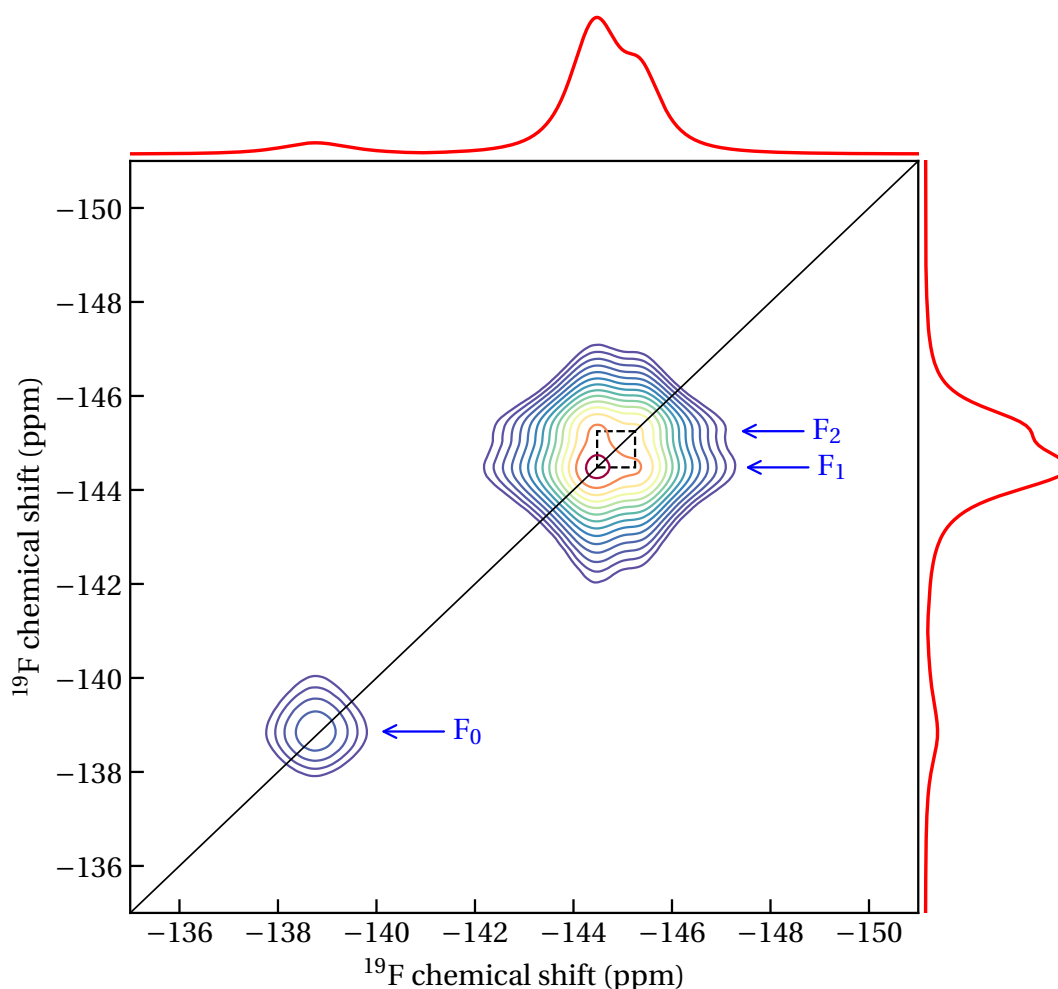


Figure 4.10. 2D EXSY ^{19}F NMR spectrum of a zwitterion-NaTFSI mixture at a 4:1 ratio. The spectrum was acquired under a magnetic field strength of 11.7 T at 0 °C, with the carrier frequency centered on the BF_3 signal.

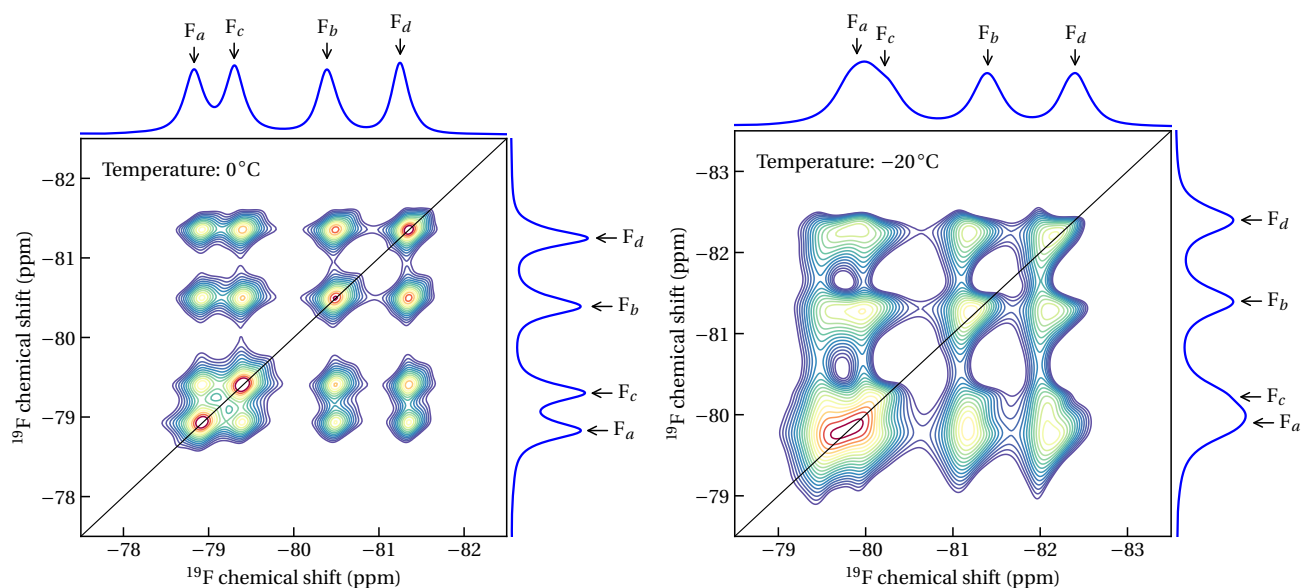


Figure 4.11. 2D EXSY ^{19}F NMR spectrum for a zwitterion/NaTFSI mixture in a 1:1 ratio. The spectrum was acquired under a magnetic field of 17.6 T with a MAS rate of 40 kHz, at temperatures of 0°C and -20°C . The carrier frequency is centered on the TFSI signal.

In the ZPC mixture containing 50% NaTFSI, the two fluorine sites from BF_3 are spatially very close. Interestingly, when focusing the analysis on TFSI and setting the carrier frequency within the resonance range of TFSI, the EXSY spectrum obtained at 0°C (Figure. 4.11) reveals cross-peaks for each of the four resonances. These cross-peaks are relatively intense and sharp, however, these observations do not allow us to determine whether the peak intensity results from a rapid exchange between cis and trans TFSI conformations or from a spin diffusion process between these conformations. Typically, rapid exchanges are favored at higher temperatures, while spin diffusion is more likely at lower temperatures due to increased dynamics at high temperatures and reduced dynamics at low temperatures. To test this further, we cooled the sample temperature from 0°C to -20°C . The EXSY spectrum recorded at -20°C shows that all peaks remain correlated. It is established that the cis conformation is less mobile than the trans conformation due to its greater coordinating ability. Consequently, at -20°C , one would expect the cross-peaks associated with the cis conformation to be more intense than those of the trans conformation. However, no notable difference in cross-peak intensity was observed. The variations observed between the spectra include a 1 ppm shift in all resonances relative to the spectrum recorded at 0°C , as well as a broadening of peaks in the 1D spectrum, confirming reduced dynamics at -20°C compared to 0°C . These observations therefore suggest that the origin of the cross-peaks may be attributable to a rapid

exchange between the cis and trans conformations of TFSI.

4.5.3 Sodium spectra

Figure. 4.12 presents the ^{23}Na MAS NMR spectra for the ZPC mixtures containing 20 mol% NaTFSI (Figure. 4.12a), as well as the 50 mol% NaTFSI system (Figure. 4.12b). The fitting of the spectrum for the system with 20 mol% NaTFSI reveals the presence of a single chemical environment, characterized by a sharp peak at a chemical shift of -14.20 ppm. In this case, a single lineshape was sufficient to achieve an optimal fit, in contrast to the zwitterionic system mixed with NaFSI salt in the same proportions, where two lineshapes were required to accurately fit the sodium spectrum.

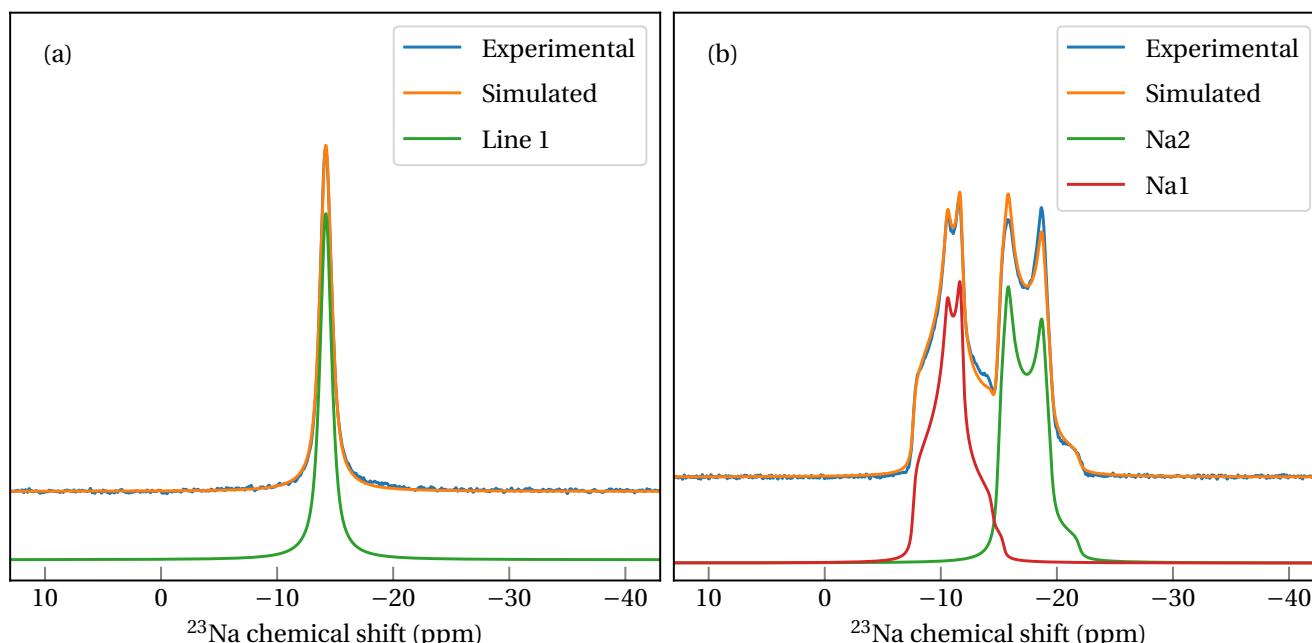


Figure 4.12. MAS spectra of ^{23}Na from zwitterionic plastic crystal samples mixed with (a) 20 mol% NaTFSI and (b) 50 mol% NaTFSI. The spectrum was acquired under a magnetic field of 11.7 T with MAS at 20 kHz at 0° C. The models (a) Lorentzian and (b) in2QUAD were used to reconstruct the spectrum.

In the mixture containing 50% NaFSI, spectral analysis (Figure. 4.12b) reveals the presence of two distinct sodium sites, each exhibiting significant quadrupolar coupling. The first site, designated as Na1, is characterized by a chemical shift of $\delta_1 = -7.5$ ppm, a quadrupolar coupling $C_Q = 1.42$ MHz, and an asymmetry parameter $\eta = 0.71$. The second sodium site, labeled Na2, shows a chemical shift of $\delta_2 = -14.3$ ppm, a quadrupolar coupling $C_Q = 1.46$ MHz, and an asymmetry parameter $\eta = 0.2$.

The chemical shift associated with the Na2 site generally corresponds to that observed during the complexation of Na^+ ions in environments where these ions are located near the delocalized electron cloud of the $[\text{BF}_3]^-$ group. In contrast, the Na1 site, though also complexed with the $[\text{BF}_3]^-$ group, is likely situated slightly further from this group compared to the Na2 site. Similar to the addition of NaFSI in the zwitterionic plastic crystal, the incorporation of this salt alters all the chemical environments present. In particular, the sodium environment changes from a single environment, observed at low NaTFSI concentrations, to two distinct chemical environments at higher salt concentrations, and the relatively large quadrupolar coupling constants indicate that these sodium species are immobile and exist within asymmetric coordination environments. The accurate fitting of these line shapes also suggests a relatively ordered crystalline environment with crystallographic sodium sites that are quite well defined. This reorganization of the sodium sites also influences the chemical environments of the TFSI^- species and the $[\text{BF}_3]^-$ group of the zwitterion, thereby inducing rearrangements in the local structure.

4.5.4 Sodium-Anion Interactions

In the case of the mixture containing 20 mol% NaTFSI, the HETCOR spectrum, shown in Figure. 4.13a, reveals the absence of correlation peaks between Na^+ ions and TFSI anions adopting the trans conformation. This suggests high mobility of the TFSI anions in the trans conformation within this system. The reason for this lack of correlation with Na^+ ions is similar to that observed in the previous case with the addition of sodium salt NaFSI, with any complexes formed between trans- TFSI^- ions and Na^+ ions having very short lifetimes on the timescale of NMR experiments, making them difficult to detect. However, a significant interaction is observed between the BF_3 groups and the Na^+ ions. This correlation, however, is not generalized to all fluorine sites of the BF_3 group, only the F_1 and F_2 sites show correlation with Na^+ ions, while the F_0 site does not. This experiment confirms the assignment made to the F_0 site in the ^{19}F 1D spectrum, indicating that it corresponds to zwitterion molecules not associated with any sodium ions, due to a low availability of free Na^+ ions. Zwitterions interacting with sodium ions have the Na^+ positioned close to regions of higher electron density, likely at an intermediate distance between two fluorine atoms in the BF_3 group.

In the case of the zwitterionic plastic crystal material containing 50 mol% NaTFSI, the HETCOR spectrum reveals the absence of a correlation peak between TFSI^- anions and Na^+ cations, whereas clear correlations are observed between BF_3^- groups and Na^+ cations. A correlation between the cis

4.5. ZPC mixed with NaTFSI salt

conformations of TFSI[−] and the Na⁺ ions may have been expected, as was observed in the polymerized ionic liquid block co-polymer electrolyte systems. However, no such interaction is observed in the present electrolyte system. The absence of correlation between TFSI[−] anions and Na⁺ cations suggests that TFSI[−] anions compensate their charge through preferential interaction with the cationic group of the zwitterion, i.e., the [C₂mpyr]⁺ ring, while all Na⁺ ions are exclusively coordinated with the more charge-localised BF₃[−] groups. Zooming in on the BF₃ spectral domain, illustrated in Figure. 4.14, reveals that each of the two sodium sites correlates with both fluorine sites within the BF₃[−] group. This observation suggests that the Na1 and Na2 sites are spatially close to the fluorine sites of BF₃, indicating a structural configuration in which sodium ions are stabilized by electrostatic interactions with BF₃[−] groups.

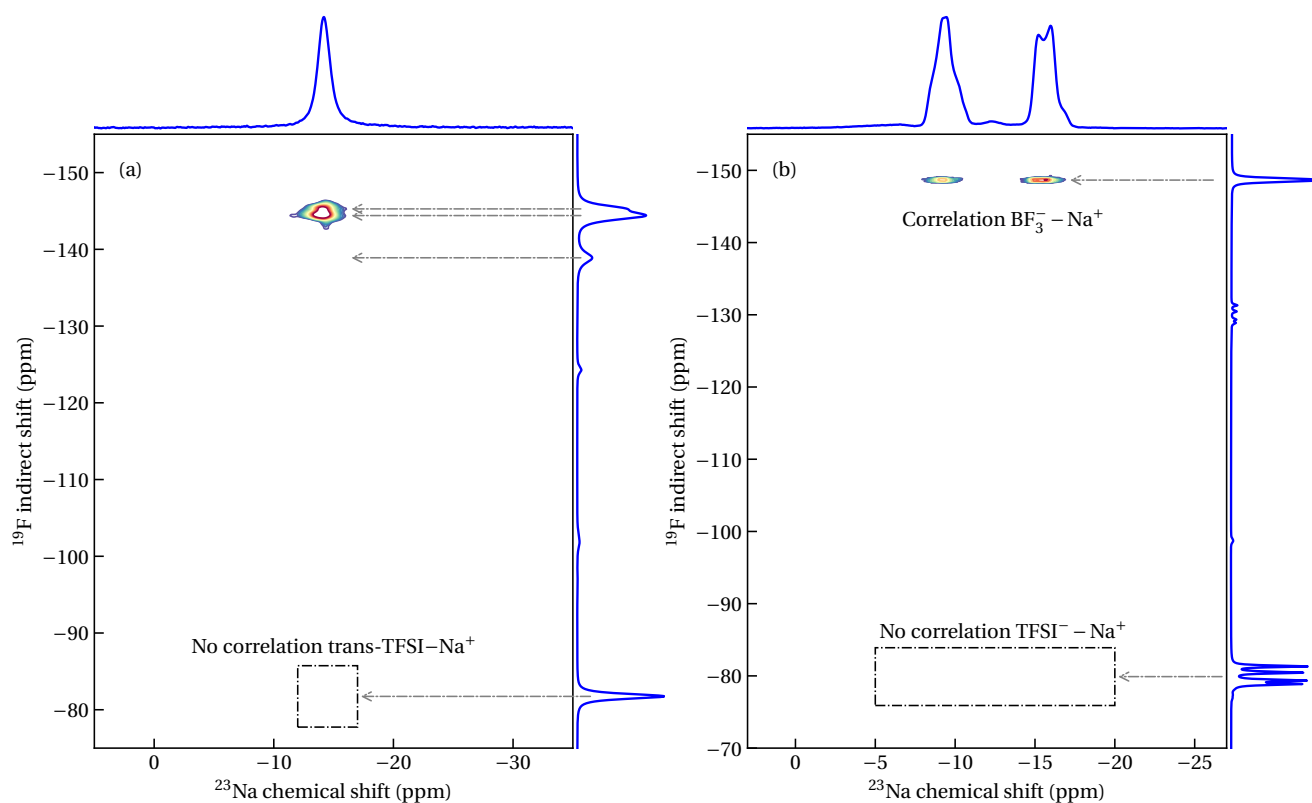


Figure 4.13. 2D HETCOR spectra with polarization transfer from ¹⁹F to ²³Na to investigate the sodium-anion interactions within zwitterionic plastic crystal mixtures containing (a) 20% and (b) 50% NaTFSI mole fractions systems. The ²³Na and ¹⁹F spectra are projected onto the horizontal and vertical dimensions, respectively.

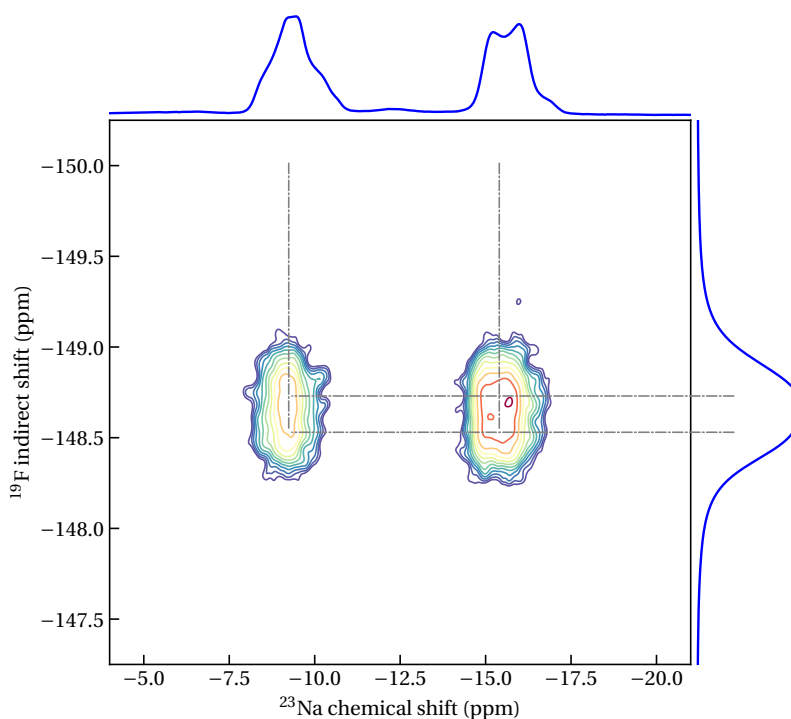


Figure 4.14. 2D HETCOR spectrum of the zwitterionic plastic crystal mixed with 50% NaTFSI, with a zoom on the BF_3 group region.

4.5.5 Local Structure with NaTFSI

We observed that zwitterions containing 10% and 20% molar fractions of NaTFSI salt exhibit an identical structure. Similar to mixtures containing NaFSI salt in the same proportions, the addition of 10% and 20% molar fractions of NaTFSI induces phase separation. One phase consists of pure zwitterions, while a second phase forms. This new phase results from the interaction between the BF_3 group of the zwitterions and Na^+ ions, as evidenced by the HETCOR spectra (Figure. 4.13). Phase separation is confirmed by the ^{19}F EXSY spectrum, which shows that cross-peaks correlate only among the fluorine atoms of the newly formed phase, whereas the fluorine atoms of the pure zwitterion do not interact with this new phase. Based on the NMR spectra obtained for the zwitterionic system containing 20 mol% of NaTFSI, we propose a structure illustrated in Figure. 4.15. In this structure, the phase of pure zwitterions is represented by the F_0 sites, spatially distant from other zwitterions and Na^+ cations. The Na^+ cations position themselves around the BF_3 group, being close to the F_2 sites while slightly farther from the F_1 sites, though sufficiently close to detect a $\text{Na}-\text{F}_1$ correlation. Finally, the $[\text{TFSI}]^-$ anions, after dissociating from Na^+ , balance the charges by interacting with the $[\text{C}_2\text{mpyr}]^+$ rings of the zwitterions,

4.5. ZPC mixed with NaTFSI salt

adopting a trans conformation.

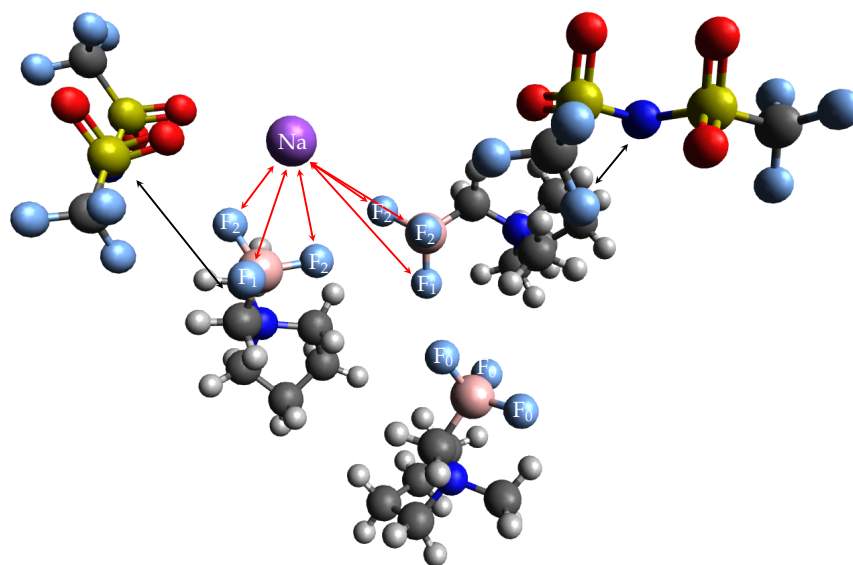


Figure 4.15. Visualization of local structural changes in the zwitterionic electrolyte system mixed with 20 mol% NaTFSI. The red arrows indicate the spatial proximity between sodium and the fluorine atoms. The black arrows indicate the interaction of the TFSI anion with the $[C_2\text{mpyr}]$ ring.

In the electrolyte system composed of ZPC mixed with 50 mol% NaTFSI, the pure ZPC phase completely disappears. A single phase is observed, as has also been observed for mixtures containing 50 mol% NaFSI. NMR results reveal that this single phase contains two distinct sites for Na (Na1 and Na2). These sites are spatially distant from each other, but each site is in close proximity to the fluorine atoms of the BF_3 group. Furthermore, within the BF_3 group, two fluorine atoms exhibit a similar chemical environment, as confirmed by the HETCOR spectrum (Figure. 4.14). A schematic representation based on the NMR analyses is shown in the Figure. 4.16. Red arrows illustrate the interactions between the BF_3 group and the Na^+ cations, while a black arrow represents the interactions between the TFSI^- anions and the C_2mpyr rings. As in previous case, the Na^+ cations dissociate from the TFSI^- anions to preferentially interact with the BF_3 groups. The TFSI^- anions, in turn, balance their charges by interacting with the $[\text{C}_2\text{mpyr}]^+$ rings, as shown in the Figure. 4.16. The arrangement of TFSI^- anions around the $[\text{C}_2\text{mpyr}]^+$ rings is unique, as these anions rapidly alternate between cis and trans conformations. This dynamic behavior is corroborated by the ^{19}F EXSY spectrum (Figure. 4.11).

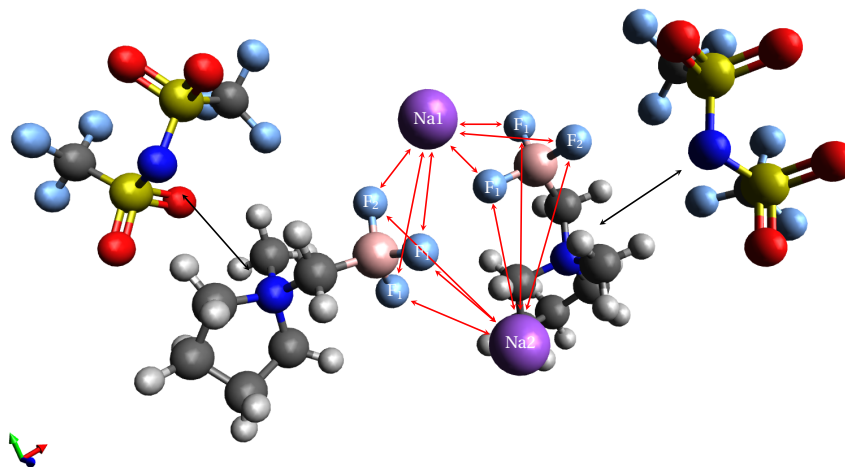


Figure 4.16. Visualization of local structural changes in the zwitterionic electrolyte system mixed with 50 mol% NaTFSI.

4.6 Conclusion

In this chapter, we studied the structural properties and interactions in ZPCs doped with sodium salts, particularly NaFSI and NaTFSI. Thermal analyses and NMR spectroscopy reveal significant structural changes depending on the concentration of sodium salt. The NMR spectra, especially the 2D HETCOR experiments $^{23}\text{Na}-\{^{19}\text{F}\}$, showed that Na^+ cations exclusively interact with the BF_3 groups of the ZPCs, while the FSI and TFSI anions compensate for their charges by interacting with the $[\text{C}_2\text{mpyr}]^+$ rings of the ZPCs. Furthermore, the ^{19}F EXSY demonstrated that at low salt concentrations (10 to 20 mol%), phase separation occurs on the NMR lengthscale. One phase consists of pure ZPC, while the other results from interactions between Na^+ cations and the BF_3 groups of the ZPCs. The interactions between the salt and the pyrrolidinium matrix appear to induce a complex balance between order and disorder in the crystalline lattice of the material. Notably, they promote rotational disorder, where the ZPCs can rotate on their own axis. This rotational motion can disrupt the interactions between Na^+ cations and the ZPCs. Consequently, this disorder leads to an improvement in ionic conductivity by facilitating the movement of ions through the lattice. However, at high concentrations (50 mol%), a single homogeneous phase emerges. This phase exhibits chemically complex environments for sodium cations and the anions. Regardless of the salt type, at this concentration, there are two sodium sites. These two sodium sites strongly interact with the BF_3 groups of the ZPCs, preventing any rotation of BF_3 around the C–B axis as well as of the ZPC molecule itself, resulting in reduced ionic mobility and, therefore, lower

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conductivity. Additionally, with 50 mol% NaTFSI, the ^{19}F EXSY spectrum revealed rapid exchange between cis and trans conformations. This indicates that the TFSI anions alternate between cis and trans conformations, influencing the dynamics of the ions. This likely explains why, at a given concentration, the conductivity is better with NaTFSI than with NaFSI. These observations highlight the crucial role of achieving a balanced adjustment between salt concentration and the structure of the ZPCs to enhance electrolytic performance. To achieve optimal efficiency in this system, it is likely necessary to limit the salt concentration to less than 50 mol% to avoid excessively strong interactions between Na^+ and the ZPCs.

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References

NMR study of SEI on sodium metal in a super-concentrated ionic liquid

5.1 Introduction

Ionic liquid-based electrolytes, including pyrrolidinium and phosphonium cations, have demonstrated their ability to form a stable SEI layer on a sodium metal anode¹. In the first chapter, we have seen that the concentration of sodium salts, such as NaFSI, favorably influences the formation of this SEI layer^{2,3}. More specifically, the combination of pyrrolidinium and phosphonium cations with a superconcentrated sodium salt promotes the formation of a homogeneous and uniform SEI layer. However, recent research on the morphology and composition of the SEI has provided limited information. For example, the ^{23}Na MAS NMR data reported by Ferdousi and collaborators are of good quality. However, the Gaussian-Lorentzian model used for fitting the ^{23}Na spectrum may not always be suitable for this nucleus due to its quadrupolar nature. Consequently, this model does not account for sites exhibiting strong or weak quadrupolar interactions that may be present in the spectrum. In this chapter, we continue this research by conducting a more detailed investigation into the composition of the SEI layer using NMR spectroscopy. We will examine the impact of combining the ionic liquids $\text{C}_3\text{mpyrFSI}$ (pyrrolidinium) and $\text{P}_{1114}\text{FSI}$ (phosphonium) at different molar ratios, associated with 42 mol% NaFSI, on the formation of the SEI layer on a sodium metal anode. In addition to ^{23}Na NMR, we will extend our analysis to other nuclei, such as ^{19}F and ^{31}P , to obtain complementary information on the composition of the SEI. Prior to using NMR spectroscopy, other methods, such as the galvanostatic charge-discharge technique, will be

employed to evaluate the cycle behavior during the charge and discharge phases.

5.2 Methods section

5.2.1 Electrolytes preparation

The electrolytes were prepared by Lixu Huang, a PhD student within the Electromaterials research group I collaborated with at the Institute for Frontier Materials, Deakin University. The ionic liquids P_{111i4} FSI and C_3 mpyrFSI were purchased from Boron Molecular with a certified purity of 99.9%. The sodium bis(fluorosulfonyl)imide salt (NaFSI), also with a purity of 99.9%, was supplied by Solvionic. To minimize the impact of residual moisture, the two ionic liquids were subjected to vacuum drying at 50 °C for 48 hours. This procedure reduced the water content to less than 50 ppm, as confirmed by Karl Fischer titration using a Karl Fischer 831 coulometer with Hydranal® Coulomat AG reagent. Subsequently, the ionic liquids C_3 mpyrFSI and P_{111i4} FSI were mixed in different ratios, and a fixed concentration of NaFSI (42 mol%) was added, according to the compositions specified in Table 5.1. All experimental procedures were conducted in an argon-filled glove box, ensuring an inert environment. Finally, all the prepared electrolytes were vacuum-sealed and stored in hermetically sealed vials under argon atmosphere within the glove box to preserve their purity and physicochemical properties.

Table 5.1. Electrolyte composition with 42 mol% NaFSI system

Expt. No.	Electrolyte composition (mol%)		IL composition (mol%)	
	NaFSI salt	ILs	C_3 mpyrFSI	P_{111i4} FSI
1	42	58	100	0
2	42	58	80	20
3	42	58	50	50
4	42	58	20	80
5	42	58	0	100

5.2.2 Coin cells assembling

The fabrication of symmetrical coin cells was performed using two metallic sodium electrodes, which were carefully prepared and cut into discs with a radius of 2 mm. A Solupor separator, impregnated with electrolyte, was placed between the two electrodes, serving as a porous barrier between the electrodes

with the electrolyte penetrating it. The electrolytes used are those described in the previous section. The assembly, consisting of the electrodes and the separator, was mounted in a standard coin cell configuration, as illustrated in Figure. 5.1. The electrolyte was added before the cell was hermetically sealed using a hydraulic crimping machine in a glove box under a controlled atmosphere. After assembly, the cells underwent charge-discharge cycles at a current density of $1\text{mA}\cdot\text{cm}^{-2}/1\text{mAh}\cdot\text{cm}^{-2}$ for 20 cycles at a temperature of 50°C . The electrochemical measurements were performed using a Bio-Logic instrument controlled by EC-Lab software.

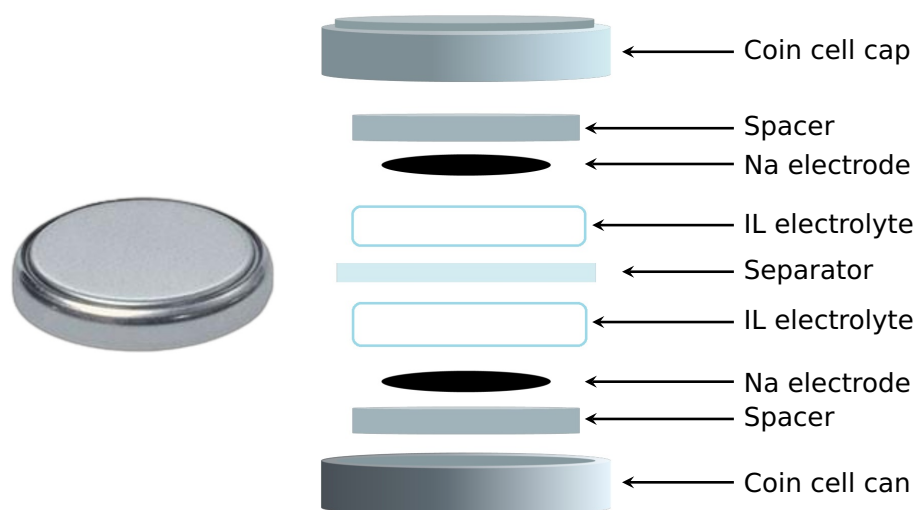


Figure 5.1. Structural Overview of the Sodium Symmetric Coin Cell Battery Components.

5.2.3 Sample preparation for NMR

After cycling, the coin cells were placed in an argon-filled glove box to prevent contamination. All manipulations described were performed in the glove box. The coin cells were then disassembled using a coin cell disassembler. The SEI products present on the surface of the sodium metal electrodes were scraped off using a stainless steel spatula. Although some researchers clean the surface of the metal electrode with dimethyl carbonate (DMC) before scraping the SEI products, we chose not to wash our samples to avoid any potential loss of material. Furthermore, during scraping, metallic sodium is also removed. Since metallic sodium is an electronic conductor, this poses a problem during MAS

5.2. Methods section

NMR measurements. Indeed, a high concentration of metallic sodium can hinder sample rotation due to the Foucault currents induced during rotation, which disrupt the rotational movement. To mitigate these conductivity issues, our samples were diluted in boron nitride (BN), which helps reduce overall conductivity. The choice of boron nitride (BN) is justified by its ability to mix homogeneously with our samples without generating unwanted signals in the spectra. In contrast, potassium bromide (KBr) exhibits resonance frequencies for the isotopes ^{79}Br and ^{81}Br that are very close to that of ^{23}Na , which could lead to spurious signals in the spectra. The mixture was then ground in a mortar until a homogeneous consistency was achieved, and subsequently placed into 2.5 mm cylindrical zirconia (ZrO_2) MAS rotors.

5.2.4 NMR Experimental parameters

The magic angle spinning NMR spectra were recorded on two Bruker Avance III spectrometers with magnetic field strengths of 500 MHz (11.7 T) and 850 MHz (20.0 T), corresponding to Larmor frequencies of 470 MHz and 800 MHz, respectively, for the ^{19}F isotope. The measurements were carried out using a 2.5 mm double-resonance MAS probe for both magnetic fields. The ^{19}F spectra were acquired by applying a radiofrequency pulse with a $t_{\frac{\pi}{2}}$ duration of 1.5 μs for the 500 MHz spectrometer and 6.3 μs for the 850 MHz spectrometer, using Hahn echo and aring pulse sequences. The number of scans ranged from 6k to 12k, depending on the signal-to-noise ratio, with a recycle delay of 5 seconds between each pulse. Some of the experiments were conducted at different rotation speeds, specifically at 20 kHz, 25 kHz, and 30 kHz, depending on the ability of the sample to maintain stable rotation or not. The isotropic chemical shifts were calibrated relative to the resonance frequency of fluoroacetophenone ($\text{C}_8\text{H}_7\text{FO}$), which has an isotropic chemical shift of $\delta_{\text{iso}} = -106.6$ ppm.

The ^{23}Na spectra were acquired using a selective excitation pulse of type $\pi/4$, selective for the central transition, with a duration of 1.87 μs at 100 W for the spectrometer operating at a frequency of 500 MHz, 6.25 μs at 4.5 W for the 400 MHz spectrometer, and 2.34 μs at 50 W for the 850 MHz spectrometer. The experimental sequence used was a single pulse excitation sequence. The number of scans performed ranged between 10 000 and 15 000, depending on the desired signal-to-noise ratio, with a relaxation time of 0.5 seconds between each pulse. The isotropic chemical shifts were calibrated relative to the resonance frequency of a NaCl solution, for which the isotropic chemical shift is defined as $\delta_{\text{iso}} = 0$ ppm.

The ^{31}P spectra were acquired by applying a radiofrequency pulse with a $t_{\frac{\pi}{2}}$ duration of 2.67 μs at

100 W on a 500 MHz spectrometer, using a "single pulse" sequence. The number of scans was 1024. An H_3PO_4 (85%) solution at 0 ppm was used as a reference for the ^{31}P chemical shift.

5.3 Electrochemical characterization

Figure 5.2 illustrates the polarization curve over 20 cycles for symmetric sodium cells using electrolytes composed of a mixture of $\text{C}_3\text{mpyrFSI}$, $\text{P}_{111}\text{i}_4\text{FSI}$, and 42 mol% NaFSI . The electrochemical performance was evaluated with polarizing currents of $1 \text{ mA} \cdot \text{cm}^{-2}$. During the first cycle, all systems exhibit an initially high overpotential, likely attributable to the formation of the SEI layer. This overpotential is particularly pronounced for the $\text{C}_3\text{mpyrFSI}$ and $\text{P}_{111}\text{i}_4\text{FSI}-\text{C}_3\text{mpyrFSI}$ (80:20) systems, while other configurations show lower overpotential values. From the second cycle onward, the overall cycles achieve a certain degree of stability. However, occasional overpotentials are observed beyond the initial cycles for all systems, with these phenomena being especially pronounced for the aforementioned systems. This overpotential is likely due to nucleation processes.

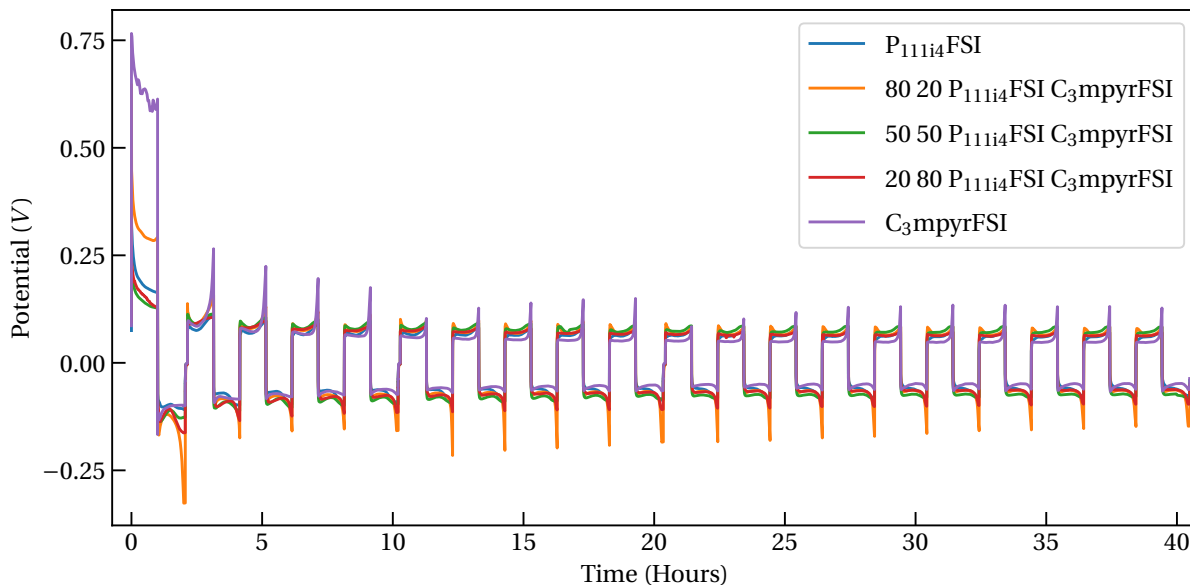


Figure 5.2. Polarization profile of sodium symmetrical cells using electrolytes composed of a mixture of $\text{C}_3\text{mpyrFSI}$, $\text{P}_{111}\text{i}_4\text{FSI}$, and 42 mol% NaFSI , cycled at 50°C with a current density of $1 \text{ mA} \cdot \text{cm}^{-2}$ for 20 cycles, with a polarization period of 1 hour.

5.4 SEI NMR Investigation: Phosphonium and Pyrrolidinium

In this section, we will present the results of MAS NMR spectroscopy on the solid-state SEI formed on sodium metal electrodes. This study initially focuses on electrolytes based on superconcentrated ionic liquids, specifically C₃mpyrFSI and P_{111i4}FSI, both mixed with 42 mol% NaFSI. The aim is to identify the compounds present in the SEI. To ensure the reproducibility and reliability of the measurements, the assembly of coin cells and cycling of batteries were repeated. NMR spectra were acquired at different magnetic fields and in two distinct laboratories, namely the CEMHTI laboratory and the Deakin NMR laboratory, located in Waurin Ponds.

5.4.1 ¹⁹F spectrum of the phosphonium IL system

Table 5.2. Fitting Parameters: δ_{iso} (isotropic chemical shift in ppm), δ_{csa} (chemical shift anisotropy in ppm), γ_{gl} (Gauss-Lorentzian factor of the Voigt function), η (asymmetry parameter), line width, and intensity, determined from the reconstruction of the ¹⁹F NMR spectrum of the SEI product.

¹⁹ F NMR MAS spectrum parameters for the SEI with P _{111i4} FSI mixed with 42 mol% NaFSI								
Line	Peak Model	δ_{iso}	δ_{csa}	width	Intensity	γ_{gl}	η_{csa}	Assignment
1	CSA mas	49.8(2)	−28(4)	3.6	4429.3	0.4	0.2	FSI
2	CSA mas	−81.7(1)	−66(5)	4.7	192.8	0.5	0.4	SO ₂ F
3	CSA mas	−143.6(5)	−74(4)	11.4	19.4	1.0	0.0	CF ₂ H ₂
4	CSA mas	−228.1(1)	−41(3)	6.0	315.8	0.2	0.5	NaF

The MAS ¹⁹F NMR spectrum of the SEI, obtained with the electrolyte consisting of P_{111i4}FSI mixed with 42% mole of NaFSI, is presented in Figure. 5.3. Due to difficulties encountered in stabilising the sample rotation, it was not possible to achieve a speed higher than 22 kHz, therefore, a speed of 20 kHz was chosen for the measurements. This rotation speed poses problems, as it does not allow for the dissociation of the actual peaks from the spinning sidebands, resulting in an overlap between them and the actual signals. Nevertheless, the chemical shift anisotropy (CSA MAS) fitting model available in the Dmfit program can take these sidebands into account and, consequently, identify the actual peaks. This model was applied to fit the ¹⁹F spectrum. The results of the fitting parameters for the ¹⁹F spectrum have been reported in Table 5.2.

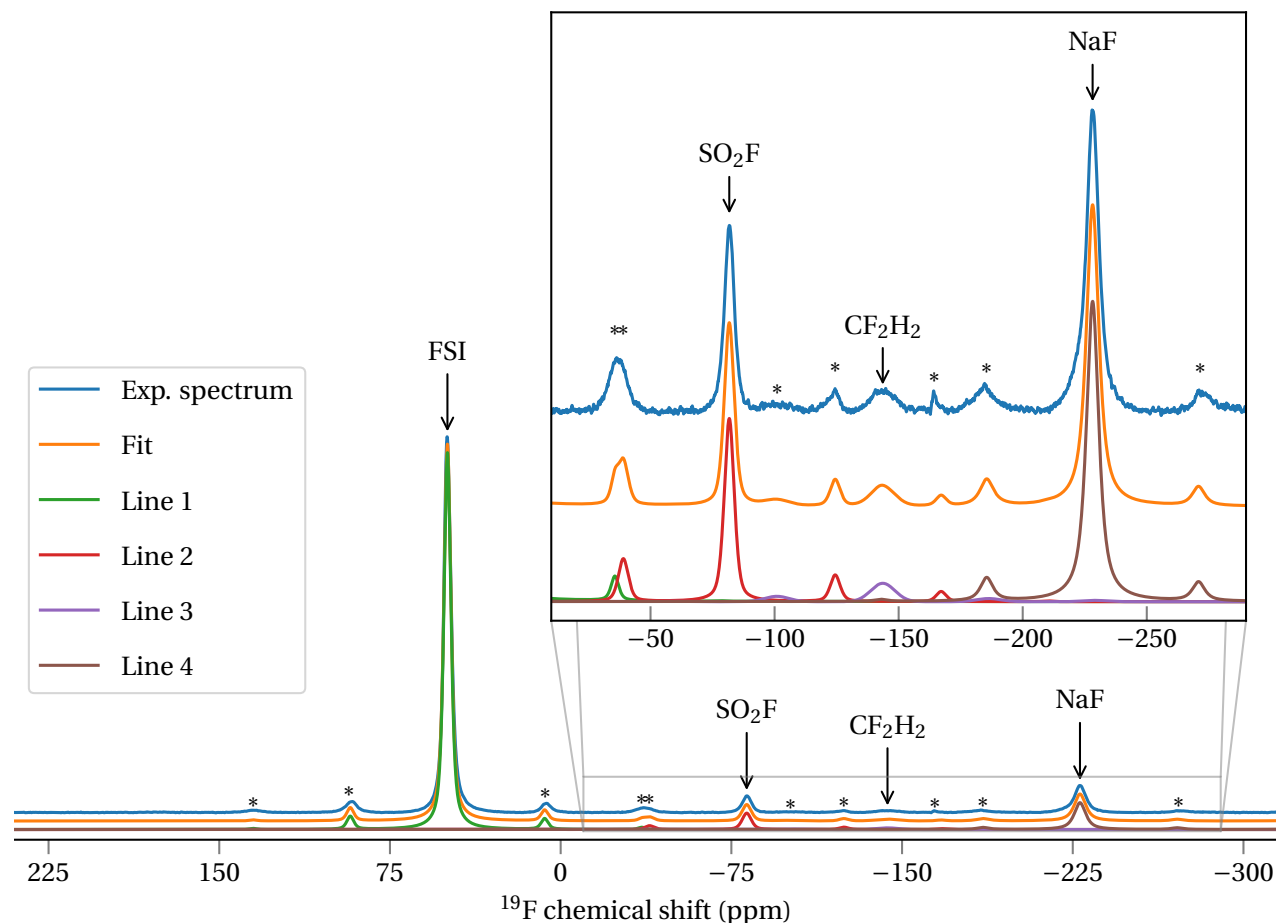


Figure 5.3. NMR ^{19}F MAS spectrum (with a spinning speed of 20 kHz) of SEI products at the surface of metallic sodium, acquired on a spectrometer with a magnetic field strength of 500 MHz (11.7 T). The lines in green, burgundy, violet, and brown represent four individual contributions from the CSA MAS model that allow for the reconstruction of the spectrum. The asterisks (*) indicate spinning sidebands.

Spectral analysis reveals the presence of a strong and narrow signal with a resonance frequency of 50 ppm, which corresponds to that of FSI species, likely originating from residual electrolyte collected during the scraping of the SEI layer. However, this signal exhibits spinning sidebands characteristic of a solid phase, likely crystallised. In the liquid phase, a ^{19}F NMR spectrum should not display such sidebands due to the absence of anisotropic interactions in this medium. Two hypotheses can be put forward to explain the appearance of these spinning sidebands. The first hypothesis suggests that the FSI molecules from the residual electrolyte may be adsorbed by the boron nitride used to mitigate the influence of conductivity on the rotation speed. The adsorbed molecules would have highly restricted (solid-like) dynamics compared to those in the liquid electrolyte and, consequently, would show spinning

5.4. SEI NMR Investigation: Phosphonium and Pyrrolidinium

sidebands in the spectrum. The second hypothesis posits that the FSI molecule could participate directly in the formation of a solid compound within the SEI. Furthermore, an additional signal, whose intensity is twenty-three times lower than that of FSI, appears at a resonance of -81.7 ppm. This signal seems to originate from a relatively ordered compound. Although this chemical shift is not referenced in the current literature, it could correspond to the signature of the $[\text{SO}_2\text{F}]^-$ anion, as suggested by the work of Dungan and Van Wazer.⁴ The formation of this species could be explained by the decomposition of FSI ($[\text{N}(\text{SO}_2\text{F})_2]^+$) molecules, which is expected to decompose via breaking of the N–S bond and deposit in the form of a salt on the surface of the metallic sodium electrode during the SEI formation process. The remaining $[\text{NSO}_2\text{F}]^-$ anion may undergo further breakdown or may show a ^{19}F peak that overlaps with the FSI signal.

Furthermore, an additional signal, slightly broadened, is observed at a chemical shift of -143.6 ppm. This compound appears to exhibit a relatively disordered phase, necessitating the application of a Gaussian peak model for its analysis. According to the work of Dungan and Van Wazer, this chemical shift could be attributed to the compound CF_2H_2 . This hypothesis is supported by research conducted by Sadoc et al.⁵, who evaluated the shielding $\sigma_{\text{iso}}(^{19}\text{F})$ in CF_2H_2 using density functional theory (DFT) with an ultrasoft pseudopotential (USPP) within the framework of GIPAW methods. They determined a value of $\sigma_{\text{iso}} = 298.7$ ppm. By applying their proposed linear regression, expressed by the equation $\delta_{\text{iso}} = -0.80\sigma_{\text{iso}} + 89$, we obtain a theoretical isotropic chemical shift of -149.9 ppm. Therefore, the observed chemical shift of -143.6 ppm could correspond to the CF_2H_2 phase. However, if we consider that the IL anion is the one that decomposes, it seems difficult to explain the generation of this phase, given that carbon is not present in the NaFSI salt. Moreover, the analysis of the ^{31}P spectrum presented in Figure 5.4b reveals the presence of a single peak. This peak indicates the presence of the residual electrolyte taken in addition to the SEI layer, considering that the surface has not been washed. The uniqueness of this peak suggests that phosphorus has only one chemical environment, implying that the ionic liquid cation P_{1114} has not undergone degradation. Thus, a plausible explanation for the detection of this phase would be that it originates from the separator. Indeed, during the scraping performed to recover the SEI layer, a part of the separator was also collected, as fragments of SEI were found to be adhered to it. This separator is likely rich in carbon, which could explain the origin of the fluorine signal associated with carbon.

Finally, a final signal has been detected at a resonance of -228 ppm, which can be associated with

the presence of NaF. This attribution is again validated by the work of Sadoc et al., who calculated the chemical shift of this compound using DFT methods, obtaining a value of -227.6 ppm. The detection of this phase in the SEI layer, formed from an electrolyte containing P_{111i4} FSI and 42% mole of NaFSI, is consistent with previous research and will form through further breakdown of the FSI anion. Indeed, Ferdoussi et al. have demonstrated the formation of NaF using ^{23}Na NMR. The emergence of this phase could prove beneficial due to its stability and electronic insulating properties. As such, it is capable of blocking the passage of electrons, thereby playing a protective role in the SEI layer. However, this compound does not exhibit good ionic conductivity, except when it is highly disordered (this is also the case for LiF). Consequently, this phase might not constitute an ideal compound for the SEI in sodium-based systems.

The ^{19}F MAS NMR spectrum, obtained at a high magnetic field of 20.0 T (see Figure. 5.4a), confirms the presence of the phases FSI, SO_2F , H_2CF_2 , and NaF. The measured chemical shifts are 53.3 ppm, -78.7 ppm, -143.7 ppm, and -226.5 ppm, respectively. These values are considered more accurate due to the increase in magnetic field, which enhances the reliability of the measurements. However, it is worth noting that the spectrum acquired in this high field exhibits a higher noise level than that recorded in an average magnetic field, rendering the sidebands almost invisible, except for the signal associated with the FSI species. This can be explained by the fact that the number of scans performed at 11.7 T was more than twice that conducted at 20.0 T. Furthermore, it is likely that a smaller amount of SEI was present in the rotor. Larger CSA effects at the higher magnetic field may also play a role. Nonetheless, this comparison underscores the reproducibility of the approach, as the independent repetition of the experiment yields identical results.

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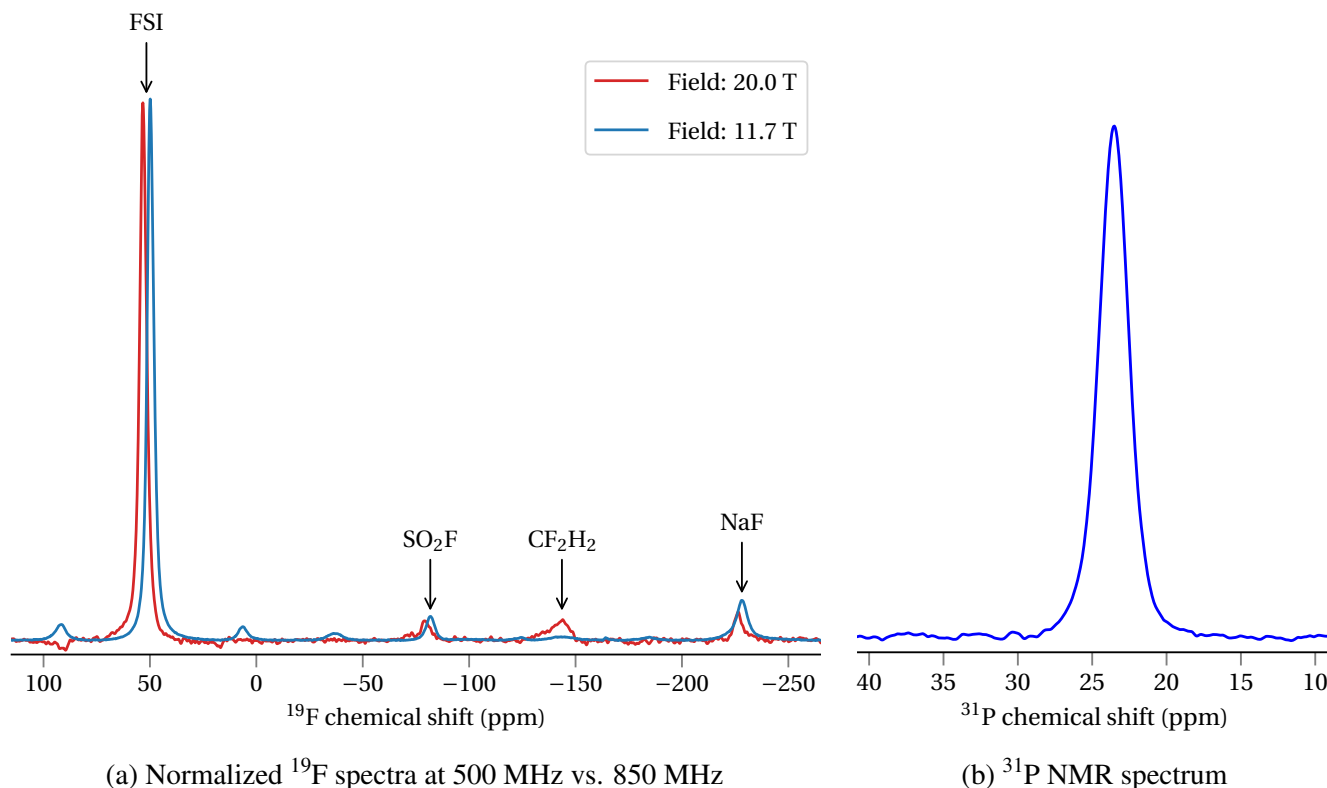


Figure 5.4. Solid-state NMR spectra acquired from the SEI products with $\text{P}_{111\text{i}4}\text{FSI}$: (a) Normalized ^{19}F spectra at 500 MHz and 850 MHz, and (b) ^{31}P NMR spectrum.

5.4.2 ^{19}F spectrum of pyrrolidinium IL vs. phosphonium IL

The MAS ^{19}F NMR spectrum of the SEI product, obtained from the $\text{C}_3\text{mpyrFSI}$ electrolyte containing 42% NaFSI in mole fraction, exhibits spectral characteristics identical to those observed with the $\text{P}_{111\text{i}4}\text{FSI}$ electrolyte. Indeed, the measured chemical shifts correspond to the FSI, SO_2F , CF_2H_2 , and NaF phases, which were detected in the previous spectrum. This suggests that the decomposition of these two electrolytes leads to the formation of the same phases, according to the ^{19}F nucleus analysis. Just like in the previous system, the spectrum does not show conclusive evidence for the ionic liquid cation C_3mpyr undergoing decomposition during the battery cycling. Quantification of the F-containing phases is challenging. Unfortunately, the "aring" pulse sequence is only effective at exciting signals located in the center of the spectral window, while it is less effective for those located at the edges. However, the signals from FSI and NaF are found at the edge of the spectral window, which complicates the quantification of the spectrum. The "single pulse" sequence could have helped quantify the spectrum,

but unfortunately, the signal is distorted. Relative to the signal from the residual FSI (the amount of which is difficult to control), it appears that there are more of the SO_2F , CF_2H_2 , and NaF phases present in the phosphonium system.

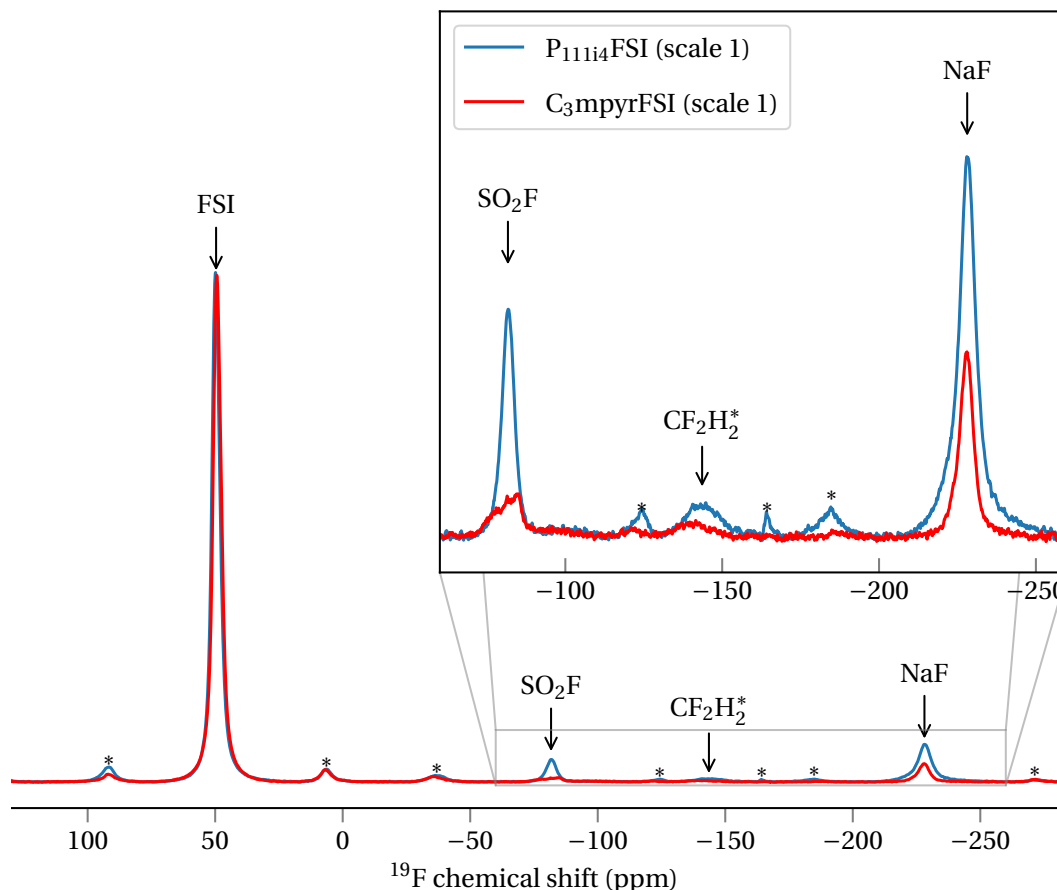


Figure 5.5. ^{19}F MAS NMR spectrum of the SEI products obtained from the $\text{C}_3\text{mpyrFSI}$ electrolyte compared to that obtained from the $\text{P}_{111\text{i}4}\text{FSI}$ electrolyte.

5.4.3 ^{23}Na spectrum of the phosphonium IL system: Two-field fitting

The MQMAS technique, which separates overlapping signals in a second dimension, is recognized as the method providing the best spectral resolution for quadrupolar nuclei. However, its application to our samples did not yield conclusive results with ^{23}Na nuclei. Indeed, the MQMAS experiment conducted on the SEI of the phosphonium IL system showed a signal in the first slice, but it quickly faded in the second slice (suggesting a short T_2 relaxation time). Moreover, the MQMAS experiment performed on the SEI of the pyrrolidinium IL system revealed that the excitation and reconversion pulses associated with the

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single quantum and triple quantum (3Q) transitions were ineffective on certain sites. This inefficiency of MQMAS could be explained by the high conductivity of the samples, probably due to the presence of metallic sodium, which attenuates the signal more rapidly.

An alternative method for analyzing the spectra of quadrupolar nuclei involves multi-field fitting. This approach entails acquiring the spectrum of the quadrupolar nucleus (^{23}Na in our case) from the same sample under different magnetic fields. The line shape of sites characterized by a low (or no) quadrupolar coupling will not show significant variations, whereas the line shape of sites with strong quadrupolar coupling will undergo modifications depending on the applied field intensity. The second-order effects of the quadrupole interaction on the Zeeman energy levels for the central transition become less significant at high fields. Indeed, the frequencies of the second-order quadrupole vary inversely with the magnetic field, as discussed in Chapter 2. Thus, quadrupolar line shapes tend to broaden at low field strength, while they become sharper at high fields. Finding a common set of fitting parameters that accurately reproduce the spectrum at multiple field strengths can therefore result in a fit that is far more reliable than one carried out at just a single field. This method was therefore implemented to fit the ^{23}Na spectrum acquired at fields of 9.4 T and 20.0 T and the results are shown in Figure. 5.6.

For all sodium sites, the Int2QUAD model in DMfit was chosen to fit the spectra, taking into account all transitions (central and satellite). It is necessary to consider all transitions, as they are included in the integral calculations, which allows for a good estimation of the contribution percentage of each measured site. The ^{23}Na nucleus, due to its tendency to form complexes, easily loses an electron. Consequently, its chemical shift anisotropy interaction (δ_{csa}) is very weak. As a result, the observed sidebands are mainly governed by the quadrupolar interaction, whether it is strong or weak in nature. For the spectral fitting, we therefore decided to set the chemical shift anisotropy to zero. Furthermore, by comparing the two ^{23}Na spectra obtained at 9.4 T and 20.0 T in Figure. 5.6, we observe that at least four peaks corresponding to lines 1 to 4 show no apparent shift difference. This observation allows us to already identify four sodium sites. Furthermore, we can go further by stating that these four sites have a weak (or no) quadrupolar coupling and therefore correspond to a highly symmetric sodium environment. This means that their line shape is more akin to that of a Gaussian or a Lorentzian. The remaining peaks were selected in such a way that the calculated parameters best match both spectra. The parameters calculated to fit the two spectra are presented in the Table 5.3. It is noteworthy that the area under the curve of the peaks (lines 2 and 3 in Figure. 5.6) shows a significant difference. This disparity arises from the difficulty in

identifying a unique pair (line broadening, C_Q) that works effectively for both the spectrum at 9.4 T and the one at 20.0 T. Consequently, it was necessary to fix the C_Q parameter and adjust the line broadening. Nevertheless, the calculated parameters are sufficiently accurate to reproduce both spectra, allowing for the extraction of valuable information about the components of the SEI layer.

Table 5.3. Fitting Parameters: δ_{iso} (isotropic chemical shift, ppm), C_Q (quadrupolar coupling constant, MHz), η (asymmetry parameter), intensity (% contribution of the site), line broadening ((+) Lorentzian apodization and (–) Gaussian apodization, ppm), and transitions 3/2 (all transitions accounted for in the calculation)

Line	δ_{iso}	C_Q	η	Intensity (%)	Line broadening	Transitions
1	48.6	0.022	0.0	2.22	2.96	3/2
2	17.1	0.115	0.0	22.82	5.53	3/2
3	5.4	0.078	0.0	38.5	7.77	3/2
4	–12.4	0.002	0.0	6.97	4.00	3/2
5	19.9	3.600	0.15	11.34	–3.33	3/2
6	–8.0	0.048	0.0	8.76	–11.43	3/2
7	6.1	3.530	1.0	9.39	2.45	3/2

The spectrum fitting reveals a narrow peak, referred to as "line 1", with an isotropic chemical shift of 48.6 ppm and a weak quadrupolar coupling of 0.022 MHz. The position of this peak is consistent with the crystalline structure of sodium oxide (Na_2O), which belongs to the space group $\text{Fm}\bar{3}\text{m}$. In this structure, sodium ions occupy a single crystallographic site, characterized by high cubic symmetry. This cubic symmetry accounts for the low observed quadrupolar coupling constant C_Q . The detection of Na_2O as a potential component of the SEI is consistent with previous studies on the surface characterization of metallic electrodes by SEM, EDXS, FTIR, and XPS.^{6–11} Furthermore, the study conducted by Ferdoussi et al.¹² on a similar system revealed a comparable signal, further supporting the attribution of this peak to the formation of Na_2O in the SEI layer. Moreover, the analysis of the spectrum highlights the presence of two peaks, identifiable by line 2 and line 5. The isotropic chemical shifts associated with these peaks were measured at 17.1 ppm and 19.9 ppm, respectively. Line 2 shows a weak quadrupolar coupling constant, estimated at 0.115 MHz, while line 5 displays a high quadrupolar coupling constant, evaluated at 3.6 MHz. The chemical shift observed for line 2 corresponds to a characteristic signature of the sodium hydride compound, NaH , whereas that of line 5 corresponds to the signature of the sodium hydroxide compound, NaOH . Phosphoniums are compounds known for their ability to lose a proton

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under certain conditions. Douglas MacFarlane and his team¹³ studied this phenomenon and demonstrated that some phosphoniums can act as proton shuttles in electrochemical systems. In our case, a proton can be extracted from a phosphonium and then reduced to a hydride ion H^- at the metal surface, thereby enabling the formation of NaH. Similarly, the proton extracted from the phosphonium can combine with an oxygen atom and sodium at the metal surface to form NaOH. Although no notable change is observed in the ^{31}P NMR spectrum, it is possible that a small quantity of protons is indeed extracted and migrates to the surface. Meanwhile, the Ylides remains in the electrolyte, which could explain why it is not detected on the surface.

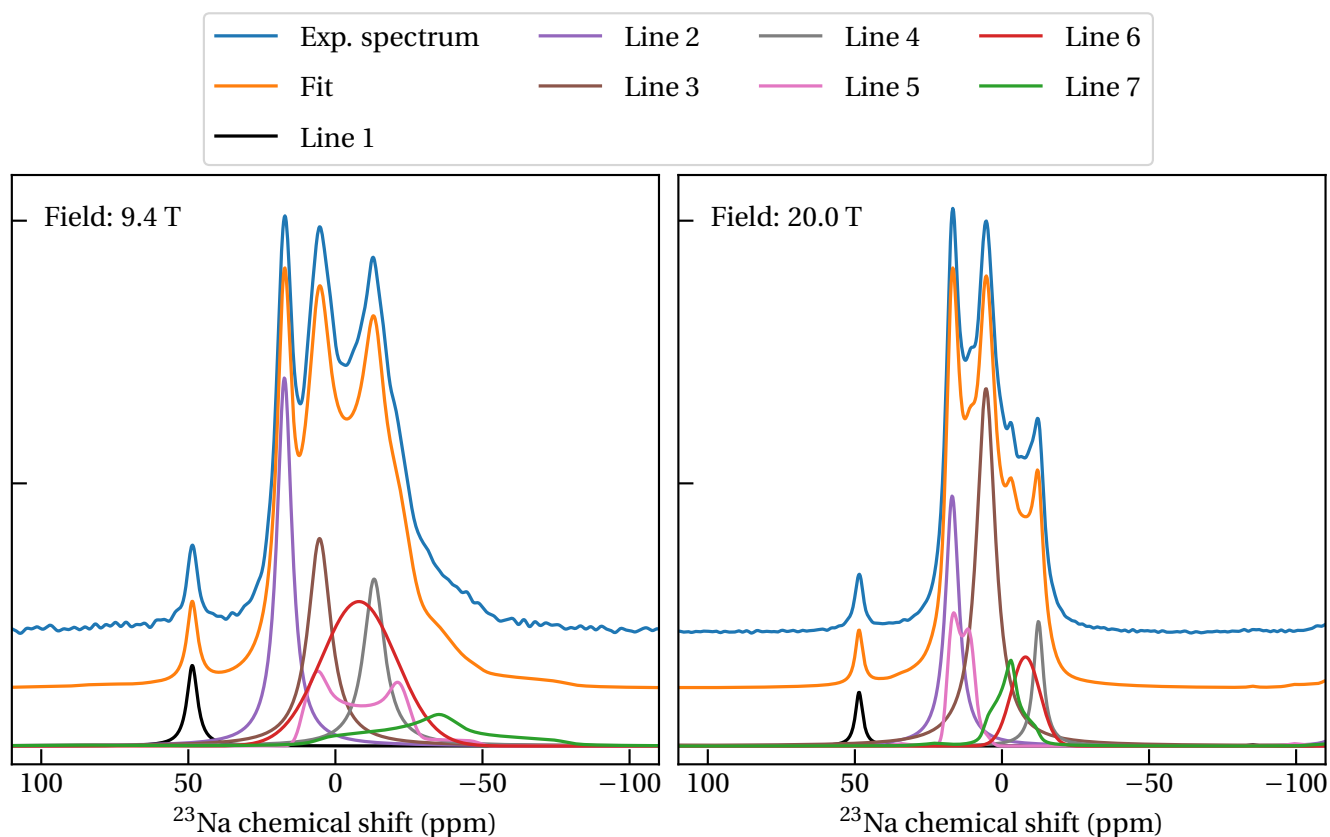


Figure 5.6. MAS spectrum of ^{23}Na from SEI products for the phosphonium system, acquired at 9.4 T and 20.0 T, with a rotation speed of 30 kHz. Lines 1 to 7 represent seven individual contributions from the Int2QUAD model, allowing for the reconstruction of the spectrum.

In addition, the spectrum fitting reveals two narrow peaks, designated as line 3 and line 4, respectively, characterized by a nearly zero C_Q . The chemical shifts associated with these peaks are 5.4 ppm and -12.4 ppm. The chemical shift observed for line 3 likely corresponds to sodium fluoride (NaF). Although

the chemical shift value of ^{23}Na in NaF reported in the literature is generally around 7.4 ppm, some studies have measured a value of 5.6 ppm¹², suggesting relatively minor variation. Moreover, the analysis of the ^{19}F spectrum, discussed in the previous section, confirms the presence of NaF. Therefore, the peak observed at 5.4 ppm, which shows a 2 ppm shift from the 7.4 ppm value and remains within the linewidth range, is attributed to NaF. As for line 4, the chemical shift of -12.4 ppm is attributed to a sodium complex (Na-complex). A Na-complex has been proposed to have the chemical formula $\text{Na}_2[\text{SO}_2\text{-N-SO}_2\text{F}]$, as suggested by Budi et al¹⁴. The presence of this species could be favored by a high concentration of sodium ions, as explained by Ferdoussi and his colleagues¹². It is also possible that this is actually a NaSO_2F salt.

Finally, the spectrum fitting shows two final peaks, designated as line 6 and line 7, respectively. The peak corresponding to line 7 exhibits a quadrupolar shape, characterized by a chemical shift of 6.1 ppm, a quadrupolar coupling C_Q of 3.53 MHz, and an asymmetry parameter η of 1. This spectral signature could be attributed to sodium salts resulting from the degradation of FSI anions such as $[\text{N-SO}_2\text{F}]^-$. Additionally, according to Yue Liu's work based on DFT calculations¹⁵, the decomposition of the FSI anion could lead to the formation of the molecule $[\text{N}(\text{SO}_2)_2\text{F}]^-$, via the breaking of the S-F bond. All these products could then interact with the Na^+ cation to form phases such as $\text{Na}[\text{N}(\text{SO}_2)_2\text{F}]$ or $\text{Na}[\text{N-SO}_2\text{F}]$. The observed ^{23}Na signal peak could potentially correspond to one of these phases. Therefore, from the perspective of the ^{19}F spectrum, the isotropic shift of -143.6 ppm could be attributed to one of these compounds. Regarding line 6, the peak is also broad, with a chemical shift of -8 ppm and presents a low quadrupolar coupling constant, estimated at 0.048 MHz. This value is very close to the isotropic chemical shifts of -7.3 ppm and -8.5 ppm reported by MacKenzie and Smith¹⁶, as well as by Koller et al.¹⁷, which correspond respectively to the compounds NaNO_3 and Na_2SO_4 . However, it seems unlikely that the FSI species decomposes completely to form NaNO_3 , as it is difficult to break the double bond between sulfur and the oxygens. The formation of the Na_2SO_4 compound could be conceivable. Nevertheless, the signal of this compound has a quadrupolar shape with a C_Q of 2.6 MHz. When these parameters are integrated into the fitting of the spectra acquired at 9.4 T and 20.0 T, they do not correlate with the two spectra, particularly with the one at 9.4 T due to the broadening of the central transition line of the second order. An alternative hypothesis is that this signal could originate from the NaSO_2F compound. Indeed, in the ^{19}F spectrum, a signal has been observed corresponding to the anion $[\text{SO}_2\text{F}]^-$. This species could capture a sodium ion to form NaSO_2F . However, it is worth noting

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that no chemical shift for the compound NaSO_2F for sodium or fluorine is referenced in the literature. Kessler and coworkers¹⁸ studied the rotational disorder of $[\text{SO}_2\text{F}]^-$ in alkali metal fluorosulfites through calculations. They reported that the chemical shifts for ^{19}F in KSO_2F are 90 ppm, while for RbSO_2F , the chemical shift is 95 ppm. If we rely on their results, the isotropic chemical shift of ^{19}F in NaSO_2F should not be far from these values. However, we measure an isotropic shift $\delta_{\text{iso}}(^{19}\text{F}) = -78.8$ ppm. It is therefore possible that $[\text{SO}_2\text{F}]^-$ captures another ion, in which case the measured value of $\delta_{\text{iso}}(^{23}\text{Na})$ would correspond to another phase, or that $[\text{SO}_2\text{F}]^-$ captures a Na^+ , which seems to be the most likely option. To clarify this point, it would be relevant to obtain the spectrum of pure NaSO_2F for the nuclei ^{19}F and/or ^{23}Na . The synthesis of this compound presents significant challenges, particularly due to its commercial unavailability and the lack of established protocols in the literature for its production. Furthermore, a calculation of $\delta_{\text{iso}}(^{23}\text{Na})$ using DFT calculations would also be desirable to confirm or refute the presence of this compound as belonging to the SEI.

5.4.4 ^{23}Na spectrum of pyrrolidinium IL vs. phosphonium IL

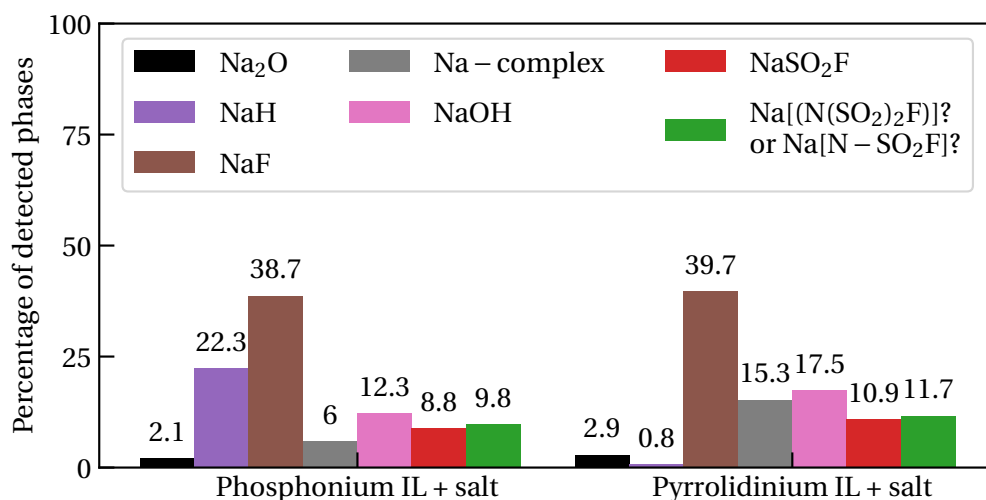


Figure 5.7. Relative quantities of the phases deposited on the surface of metallic sodium and detected by NMR. They are determined from the integrals of each peak in the spectrum.

As part of the study of the ionic liquid $\text{C}_3\text{mpyrFSI}$, the degradation of the electrolyte on the surface of the metal electrode shows notable similarities with that observed in the $\text{P}_{1114}\text{FSI}$ system, as evidenced by the analysis of the ^{19}F NMR spectra. The ^{23}Na spectra (Figure. 5.8) also reveal common resonance frequencies between these two systems. However, significant differences appear in the relative

proportions of the detected compounds. A weak peak was identified at approximately 54 ppm, likely caused by atmospheric contamination (air) during the transfer of the sample from the glove box to the spectrometer. Fortunately, this peak remains isolated and does not impact the overall interpretation of the spectrum.

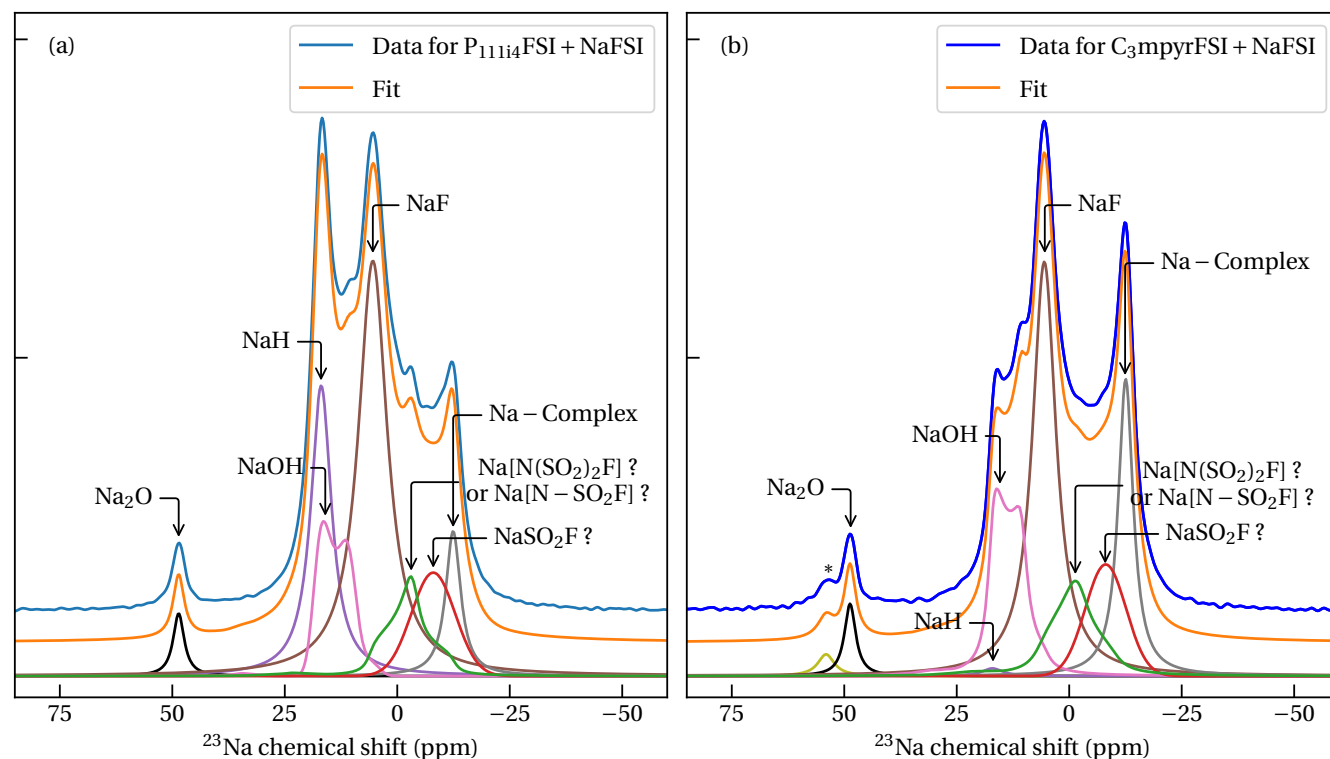


Figure 5.8. High-field solid-state ^{23}Na MAS NMR spectra, acquired at a spinning speed of 30 kHz, obtained from SEI products on the surface of metallic sodium for the ionic liquid electrolytes (a) $\text{P}_{111\text{i}4}\text{FSI}$ and (b) $\text{C}_3\text{mpyrFSI}$ mixed with superconcentrated NaFSI salts (42 mol%). The asterisk indicates that the peak results from air contamination, probably introduced during the transfer of the sample from the glove box to the spectrometer.

A near-total absence of NaH formation is observed in the pyrrolidinium system, in contrast to the phosphonium system. In fact, in the pyrrolidinium system, NaH formation accounts for only 0.75% of the detected species, whereas this proportion reaches 22.3% in the phosphonium system. This difference suggests that NaH formation is conditioned by specific factors present in the $\text{P}_{111\text{i}4}\text{FSI}$ system but absent in the $\text{C}_3\text{mpyrFSI}$ system. This observation is further supported by other studies on analogous systems (the mixture of the two cations and will be discussed in the next section), where the absence of NaH is also noted. Regarding inorganic phases such as NaSO_2F and NaOH , the quantities detected are similar in both

5.5. Influence of Mixed Cations on the SEI Layer

systems. In the scraped SEI, a proportion of 10.9% NaSO_2F was measured for the $\text{C}_3\text{mpyrFSI}$ system compared to 8.8% for the $\text{P}_{111\text{i}4}\text{FSI}$ system. Similarly, NaOH proportions are 17.5% in $\text{C}_3\text{mpyrFSI}$ versus 12.3% in $\text{P}_{111\text{i}4}\text{FSI}$. Furthermore, the $\text{C}_3\text{mpyrFSI}$ system produces a larger amount of sodium complexes, with 15.3% Na -complexes detected in the SEI, compared to 6% for the $\text{P}_{111\text{i}4}\text{FSI}$. Finally, regarding the NaF phase, the proportions are almost identical in both systems, with 39.7% for $\text{C}_3\text{mpyrFSI}$ and 38.7% for $\text{P}_{111\text{i}4}\text{FSI}$.

5.5 Influence of Mixed Cations on the SEI Layer

In the previous section, we have seen that the composition of the SEI layer is similar for the two studied systems, namely the electrolytes containing the cations $\text{C}_3\text{mpyrFSI}$ and $\text{P}_{111\text{i}4}\text{FSI}$. When these two cations are combined with 42 mol% of NaFSI to form an electrolyte, the same phases are detected as those observed when $\text{C}_3\text{mpyrFSI}$ or $\text{P}_{111\text{i}4}\text{FSI}$ are individually mixed with NaFSI . However, it is clear that the ratio between these two cations influences the quantity of the phases detected in the SEI, as illustrated in Figure. 5.9. A peak at 54 ppm is observed in the spectra of samples containing only $\text{C}_3\text{mpyrFSI}$, as well as in those of the mixtures $80\text{P}_{111\text{i}4}\text{FSI} + 20\text{C}_3\text{mpyrFSI}$ and $20\text{P}_{111\text{i}4}\text{FSI} + 80\text{C}_3\text{mpyrFSI}$. This peak is attributed to air contamination that occurred during the transport of the samples from the glove box to the spectrometer, as explained in Section 5.4.4. Although this contamination is more pronounced for the $80\text{P}_{111\text{i}4}\text{FSI} + 20\text{C}_3\text{mpyrFSI}$ sample, it does not hinder the interpretation of the obtained data. It is noted that NaH is detectable only in the sample containing $\text{P}_{111\text{i}4}\text{FSI}$, as well as in the mixture of $\text{C}_3\text{mpyrFSI}$ with $\text{P}_{1444}\text{FSI}$, while it is almost absent in the other systems studied. Furthermore, measurements carried out by our colleagues at IFM indicate that the $\text{P}_{1444}\text{FSI}$ system and the mixture consisting of 80% $\text{C}_3\text{mpyrFSI}$ and 20% $\text{P}_{1444}\text{FSI}$ are the two configurations showing the highest performance. These observations suggest that NaH could play a key role in the composition of the SEI. Conversely, all other phases — Na_2O , NaF , Na -complex, NaOH , NaSO_2F , and $\text{Na}[(\text{N}(\text{SO}_2)_2\text{F})]$ or $\text{Na}[\text{N}-\text{SO}_2\text{F}]$ — are present. The most predominant phase is NaF , with a contribution percentage ranging between 30 and 40% in the ^{23}Na spectra. It is also observed that the mixture of cations in different ratios does not significantly affect the quantity of NaSO_2F and $\text{Na}[(\text{N}(\text{SO}_2)_2\text{F})]$ or $\text{Na}[\text{N}-\text{SO}_2\text{F}]$, as their contribution percentages vary very little, between 18 and 20% for NaSO_2F , and between 10 and 12% for $\text{Na}[(\text{N}(\text{SO}_2)_2\text{F})]$ or $\text{Na}[\text{N}-\text{SO}_2\text{F}]$. Only the Na -complex and NaOH phases are impacted by the mixture of cations at different

ratios. For the 50P_{111i4}FSI + 50C₃mpyrFSI mixture, 30% of NaOH is detected, while for the other mixtures, this phase is present in low quantities, around 12.6%. As for the Na-complex phase, 19.8% of this phase is detected for the 20P_{111i4}FSI + 80C₃mpyrFSI mixture, whereas it is present in low quantities in the 50P_{111i4}FSI + 50C₃mpyrFSI and 80P_{111i4}FSI + 20C₃mpyrFSI mixtures, with only 5.3% and 3%, respectively.

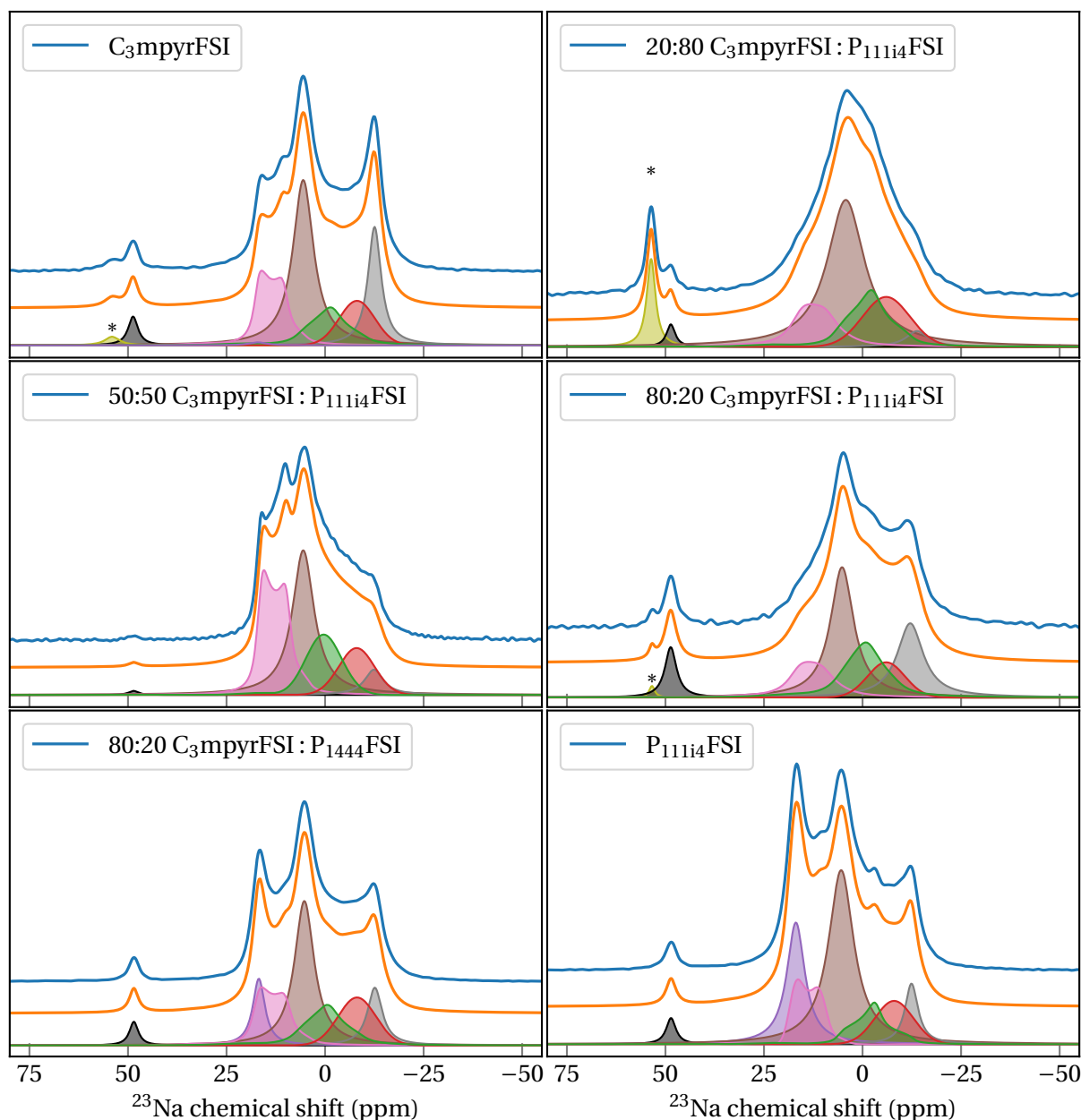


Figure 5.9. Comparison of ^{23}Na spectra as a function of cation mixture ratios.

5.6 Conclusion

In conclusion, in this chapter, we characterized the composition of the SEI layer formed on a metallic sodium anode after 25 cycles in superconcentrated electrolytes based on ionic liquids P_{111i4} FSI and $C_3\text{mpyr}$ FSI, containing 42% NaFSI. Analysis of ^{19}F spectra revealed the presence of the phases FSI, SO_2F , CF_2H_2 , and NaF. The detection of FSI could be related to the adsorption of electrolyte residues or the formation of fluorine-containing complexes. The phases SO_2F and NaF result from the degradation of FSI and from fluorine detaching from FSI to interact with sodium. As for CF_2H_2 , its identification remains uncertain, but at -143.6 ppm, it could be a secondary degradation product of the separator. Through the analysis of ^{23}Na NMR spectra using the two-field fitting method, we identified the presence of the phases Na_2O , NaF, NaH, NaOH, sodium complexes ($\text{Na}_2[\text{SO}_2-\text{N}-\text{SO}_2\text{F}]$), and degradation products of the FSI anion, which could be $[\text{N}(\text{SO}_2)_2\text{F}]^-$ or $\text{Na}[\text{N}-\text{SO}_2\text{F}]$. The Na_2O phase results from the reaction between oxygen released during FSI degradation and sodium. The NaH and NaOH phases result from the reaction between sodium and residual water present in the electrolyte. Complexes such as $\text{Na}[\text{SO}_2\text{F}]$ and $[\text{N}(\text{SO}_2)_2\text{F}]^-$ or $\text{Na}[\text{N}-\text{SO}_2\text{F}]$ are the result of the secondary degradation of the FSI anion, which interacts with sodium ions. When mixing the cations $C_3\text{mpyr}$ FSI and P_{111i4} FSI at different molar ratios, the NaF phase remains predominant in all samples. The phases NaSO_2F , $\text{Na}[(\text{N}(\text{SO}_2)_2\text{F})]$, and $\text{Na}[\text{N}-\text{SO}_2\text{F}]$ exhibit relatively stable proportions regardless of the molar ratio. In contrast, the Na-complex and NaOH phases show significant variability. The exact quantification of these phases remains very challenging, as it depends on the amount of SEI layer scraped off. While we can control the amount of SEI scraped, we do not precisely control the amount of sodium extracted, which impacts the sample rotation. However, the semi-quantification of the sodium spectrum provides an indication of the phases likely to be predominant.

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Conclusions and Perspectives

6.1 General Conclusion

The central issue guiding the research presented in this manuscript focuses on the potential of advanced solid-state NMR spectroscopy techniques to deepen the understanding of the mechanisms underlying the formation of the SEI layer and the solvation environments of ions in sodium-based battery and electrolyte systems. In this research, we studied three major families of distinct and promising materials for sodium batteries.

The first family investigated concerns solid electrolytes based on polymerized ionic block copolymers. Using advanced NMR spectroscopy techniques, based on both one- and two-dimensional methods, we were able to analyze the local-scale behavior of these systems when mixed with NaFSI and the ionic liquid $C_3\text{mpyrFSI}$. Specifically, the $^{13}\text{C}-\{^1\text{H}\}$ cross-polarization technique and direct ^{13}C excitation allowed us to differentiate the rigid, less mobile block from the more dynamic part of the polymer electrolyte. The CP MAS method effectively detects the rigid block through efficient polarization transfer, while direct excitation highlights the mobile ionic components, characterized by sharper peaks and shorter relaxation times. The analysis of the $^{13}\text{C}-\{^{19}\text{F}\}$ and $^1\text{H}-\{^{19}\text{F}\}$ cross-polarization spectra, which study the interactions between the polymer and the anions, reveals very weak or negligible interactions. This is reflected by the absence of significant resonances in the $^{13}\text{C}-\{^{19}\text{F}\}$ spectrum and the low intensity of the signals associated with the TFSI anion, indicating limited coupling between the polymer and the FSI and TFSI molecules. However, the 2D ^{19}F EXSY exchange experiment highlights the coexistence of the cis and trans conformations of TFSI in the

6.1. General Conclusion

electrolyte system composed of the PIL-block and NaFSI. Furthermore, the 2D HETCOR $^{23}\text{Na}-\{^{19}\text{F}\}$ spectrum reveals a marked coordination of the cis-conformation TFSI anions with sodium ions, while the trans-conformation anions exhibit higher mobility. Moreover, the addition of the ionic liquid $\text{C}_3\text{mpyrFSI}$ to the mixture enhances the mobility of the ionic species and alters the balance of TFSI anion conformations, significantly increasing the proportion of anions in the trans conformation. This results in an increase in ionic conductivity and facilitates sodium ion transport in the electrolyte, as trans-conformation TFSI anions interact weakly with Na^+ ions.

The second family studied concerns solid electrolytes based on zwitterionic plastic crystals. The use of advanced NMR spectroscopy techniques, including one-dimensional and two-dimensional methods, allowed for the analysis of the local structure of this system when mixed with two sodium salts, namely NaTFSI and NaFSI, at different concentrations (10, 20, and 50 mol%). The 2D HETCOR $^{23}\text{Na}-\{^{19}\text{F}\}$ spectroscopy experiments revealed that Na^+ cations interact exclusively with the BF_3 groups of the ZPC, while the FSI and TFSI anions compensate their charges by interacting with the $[\text{C}_2\text{mpyr}]^+$ rings of the ZPC. Moreover, the ^{19}F EXSY experiment showed that at low salt concentrations (10 to 20 mol%), phase separation is observed at the NMR lengthscale. One phase corresponds to the residual pure ZPC, while the other results from the interactions between Na^+ cations and the BF_3 groups of the ZPC. These interactions between the salt and the pyrrolidinium matrix seem to induce a complex balance between order and disorder in the material's crystal lattice. Specifically, they promote a rotational disorder, allowing the ZPC to rotate around its own axis. This rotational movement disrupts the interactions between the Na^+ cations and the ZPC, which promotes an improvement in ionic conductivity by facilitating the movement of ions through the network. However, at high concentrations (50 mol%), a single homogeneous phase emerges, presenting chemically complex environments for the sodium cations and anions. Regardless of the type of salt used, at this concentration, two distinct sodium sites are identified. These two sites interact strongly with the BF_3 groups of the ZPC, preventing any rotation of the BF_3 groups around the C–B axis, as well as the rotation of the entire ZPC molecule. This restriction on mobility reduces ionic mobility, leading to a decrease in conductivity. Furthermore, with 50 mol% NaTFSI, the ^{19}F EXSY spectrum highlights rapid exchange between the cis and trans conformations of the TFSI anions. These alternations influence the ion dynamics and could explain why, at this concentration, conductivity is better with NaTFSI than with NaFSI. Thus, in order to optimize the efficiency of this system, it would likely be necessary to limit the salt concentration to a low molar

concentration, so as to avoid strong interactions between the Na^+ and the ZPC.

Finally, we investigated the composition of the SEI layer formed on a metallic sodium anode after 25 cycles in superconcentrated sodium salt electrolytes (42% NaFSI) based on ionic liquids $\text{P}_{11114}\text{FSI}$ and $\text{C}_3\text{mpyrFSI}$. High-field and intermediate-field solid-state MAS NMR confirmed the presence of phases already reported in the literature, as well as the formation of new phases resulting from the degradation of the $[\text{FSI}]^-$ anion. Indeed, the analysis of the ^{19}F spectra identified NaF, a well-established SEI component, and revealed additional phases such as $[\text{FSI}]^-$, $[\text{SO}_2\text{F}]^-$, and CF_2H_2 . The detection of FSI may be due to either the adsorption of electrolyte residues by the boron nitride used to dilute the sample or the formation of fluorinated complexes. The $[\text{SO}_2\text{F}]^-$ compound results from the breakdown of the $[\text{FSI}]^-$ anion, which splits into two. While the identification of CF_2H_2 remains speculative, its chemical shift ($\delta_{\text{iso}} = -143.6$ ppm) might correspond to a secondary degradation product of $[\text{FSI}]^-$, such as $[\text{N}(\text{SO}_2)_2\text{F}]^-$ or $[\text{N}-\text{SO}_2\text{F}]^-$. Further analysis of ^{23}Na NMR spectra using two-field fitting (9.4 and 20.0 T) allowed the identification of Na_2O , NaF, and sodium complexes such as $\text{Na}_2[\text{SO}_2-\text{N}-\text{SO}_2\text{F}]$, as previously reported by Ferdousi. This method also indicated the presence of additional compounds in the SEI layer, particularly NaH and NaOH, which are likely formed from the proton extracted from the phosphonium in the electrolyte and reacting with the sodium at the surface. And new phases such as $\text{Na}[\text{SO}_2\text{F}]$, $\text{Na}[\text{N}(\text{SO}_2)_2\text{F}]$ or $\text{Na}[\text{N}-\text{SO}_2\text{F}]$ may arise from the secondary degradation of the FSI anion interacting with sodium ions. Additionally, when mixing the cations $\text{C}_3\text{mpyrFSI}$ and $\text{P}_{11114}\text{FSI}$ in various molar ratios, the NaF phase remained predominant in all samples, while the $\text{Na}[\text{SO}_2\text{F}]$, $\text{Na}[\text{N}(\text{SO}_2)_2\text{F}]$, and $\text{Na}[\text{N}-\text{SO}_2\text{F}]$ phases maintained relatively constant proportions. In contrast, the Na-complex and NaOH phases exhibited significant variability. The estimation of these phases is complex, as it depends on the amount of SEI layer removed. Although the quantity of SEI scraped off can be controlled, the exact amount of metallic sodium extracted remains difficult to determine due to its influence on sample rotation. Nevertheless, a semi-quantification of the sodium spectrum allows for the identification of the likely predominant phases. The SEI composition alone does not provide a clear correlation with the performance of batteries using these different electrolyte systems. Additional factors, such as the thickness and morphology of the SEI, are likely to be important as well. However, our NMR data do not offer sufficient insight into these aspects. It is important to emphasize that the investigation of these systems is part of a broader and ongoing research initiative, with several team members employing various complementary approaches to study them (Australian Research Council Discovery Project DP210101172). Our data has contributed

new information to this effort and we hope that our findings will be validated and that a more complete picture of the SEI formation in these systems will emerge through the work of our colleagues.

6.2 Perspectives

In electrolytes based on the PIL Block mixed with the NaFSI salt, ionic conductivity improves when a molar ratio of the ionic liquid C₃mpyrFSI equivalent to that of the PIL Block is added. This addition alters the equilibrium of the conformations of the TFSI anion. It would be relevant to examine this equilibrium by progressively increasing the molar ratio of C₃mpyrFSI, while ensuring the mechanical integrity of the mixture is preserved, and correlating these observations with variations in ionic conductivity. Furthermore, another research perspective would be to introduce other ionic liquids, such as P_{111i4}FSI, into the PIL Block mixed with NaFSI system. Such a study could allow for the evaluation of the impact of this addition on mechanical integrity, ionic conductivity, and the local structure of the system.

For electrolytes based on the zwitterionic plastic crystal, in order to complete and enhance our understanding of the structure and phase behaviour of the ZPC-NaFSI or NaTFSI mixtures, it would be relevant to study the crystal structures present using X-ray diffraction for each composition mentioned previously. Subsequently, the structures obtained through XRD could be used to calculate the NMR parameters using DFT methods and compare these results with the experimental data obtained. Although X-ray diffraction does not allow detection of local disorder, this disorder could be studied using molecular dynamics methods. However, XRD can unfortunately be very challenging for plastic crystals due to their inherent disorder and complex phase behaviour. Lower sample temperatures could be applied to mitigate this, and single crystals used where possible.

The strong magnetic field (850 MHz) we used to acquire the ²³Na spectra from the SEI samples enabled us to achieve a resolution higher than that obtained with weaker fields used so far. However, this resolution remains insufficient to fully interpret the sodium spectrum due to remaining peak overlap. The use of even higher magnetic fields (e.g., 1.2 GHz available in Lille or 1.7 GHz in Florida, USA) would significantly improve this resolution. Furthermore, calculations based on DFT and the preparation and characterisation of the various salts proposed to be present such as Na[SO₂F] should be carried out to confirm the NMR parameters of the compounds assumed to be present in the SEI layer. These analyses would contribute to a better understanding of the electrolyte degradation mechanisms.

Appendices

Appendix 1: Python code to read and visualize 1D and 2D NMR data

Useful functions

In this section, we present the two main standard functions developed to read and visualize 1D or 2D NMR data. These functions are contained in the .py file that I named Function.py. The Nmrglue package is used to process multidimensional NMR data. To use this package, it must first be installed.

```
"""
@author: dani kourati
"""

import nmrglue as ng, numpy as np
from matplotlib.pyplot import subplots, rcParams

def Read_Data(file):
    Dict, data = ng.brucker.read_pdata(file, scale_data = True)
    udict = ng.brucker.guess_udic(Dict, data, strip_fake = True)
    uc = ng.fileiobase.uc_from_udic(udict)
    data = data*1e-2 # Not necessary
    if udict["ndim"] == 1:
        x = uc.ppm_scale()
        return x, data
    else:
        x = [ng.fileiobase.uc_from_udic(udict, dim = i).ppm_limits()
              for i in [0, 1]]
        return (list(x[1]+x[0]), (np.linspace(*x[0], data.shape[0]),
                                   np.linspace(*x[1], data.shape[1])), data)

def NMRExperiment2D(file, lev = 10 , m = 10, n = 10, d = 1.1,
                    xlabel = "F2 Frequency (ppm)",
                    ylabel = "F1 Frequency (ppm)",
```

```

        spex = (None, None), spey = (None, None)):
"""
Function to read and display data from a 2D experiment:
- file: Directory of the raw NMR data
- level: Starting level for the contour (default is 10)
- m: Standard deviation relative to the noise mean
    (default is 10)
- n: Number of contour levels (default is 10)
- d: Clipping distance (default is 1.1)
- spex: External spectrum for the F1 dimension
- spey: External spectrum for the F2 dimension
"""

lim, (x_iso, x_mas), data = Read_Data(file)
F1, F2 = [np.array([max(v) for v in data]),
          np.array([max(v) for v in data.T])]

data = abs(data)

noise, base = std(data[-m:, -m:]), average(data[m:, m:])
data = data-base

clev = lev*noise*d**arange(n)

fig, ((ax, bx), (cx, dx)) = subplots(2, 2, figsize = (6.5, 6),
                                     gridspec_kw={"width_ratios": [3, 0.6],
                                     "height_ratios": [0.6, 3]})

for myaxis in (ax, bx, dx):
    myaxis.axis("off")

try:
    x, y = spex
    ax.plot(x, y, "r")
except ValueError:
    ax.plot(x_mas, F2, "r")

try:
    x, y = spey
    dx.plot(y, x, "r")
except ValueError:
    dx.plot(F1, x_iso, "r")

cx.contour(data, extent = lim, levels = clev,
           linewidths = 1, cmap = "Spectral_r")
# cx.plot(x, x, "k", lw = 1)
cx.get_shared_x_axes().join(cx, ax)
cx.get_shared_y_axes().join(cx, dx)

cx.invert_yaxis()
cx.invert_xaxis()
cx.set_xlabel(xlabel)
cx.set_ylabel(ylabel)

```

```
fig.subplots_adjust(top = 1, bottom = 0.106, left = 0.176,
                    right = 1, hspace = 0, wspace = 0)
```

Additionally, other Python scripts have been developed to perform various tasks, including codes for reading and displaying .ascii files generated by DmFit. The following code serves as an example.

```
import sys
sys.path.insert(1, ".../prog. spectrum")
import Function as func
from numpy import loadtxt
from matplotlib.pyplot import subplots

func.parameters(1)

f1, f2 = (".../quad_central_transition.ppm",
          ".../Sodium20NaTFSI.ppm")

x1, spe1, fit1, l1, l2 = loadtxt(f1, skiprows=1).T
x2, spe2, fit2, line = loadtxt(f2, skiprows=1).T

fig, (ax, bx) = subplots(1, 2, sharex=True)

L = [("Experimental", 10), ("Simulated", 10), ("Line 1", 0)]

for y, (l, s) in zip((spe2, fit2, line), L):
    ax.plot(x2, y+s, label = l)

L = [("Experimental", 50), ("Simulated", 50), ("Na2", 0), ("Na1", 0)]

for y, (l, s) in zip((spe1, fit1, l1, l2), L):
    bx.plot(x1, y+s, label = l)

for i, ax in zip(("(a)", "(b)"), (ax, bx)):
    ax.set_xlabel("$^{23}$Na chemical shift (ppm)")
    ax.yaxis.set_ticklabels([])
    ax.text(0.05, 0.925, f"{i}", horizontalalignment="left",
            verticalalignment="center", transform=ax.transAxes)
    ax.legend()
    ax.tick_params(left = None, color = "gray")

ax.invert_xaxis()
```

Example of using the NMRExperiment2D function

```
import sys, os
sys.path.insert(1, ".../prog. spectrum")
import Function as Func
```

```

os.chdir("NMR folder directory")
folder = "folder"

x1 = "$^{23}$Na chemical shift (ppm)"
y1 = "$^{19}$F chemical shift (ppm)"
x1, y1 = read_data(f"{folder}/400/pdata/1") # 1D 23Na spectrum
x0, y0 = read_data(f"{folder}/1/pdata/1") # 1D 19F spectrum

Func.NMRExperiment2D(f"{folder}/503/pdata/1", lev = 18, n = 16,
                     xlabel = x1, ylabel = y1,
                     spex = (x1, y1), spey = (x0, y0))

```

Appendix 2: Supplementary Spectra for ZPC with Sodium Salt Electrolytes

^{13}C MAS NMR spectra

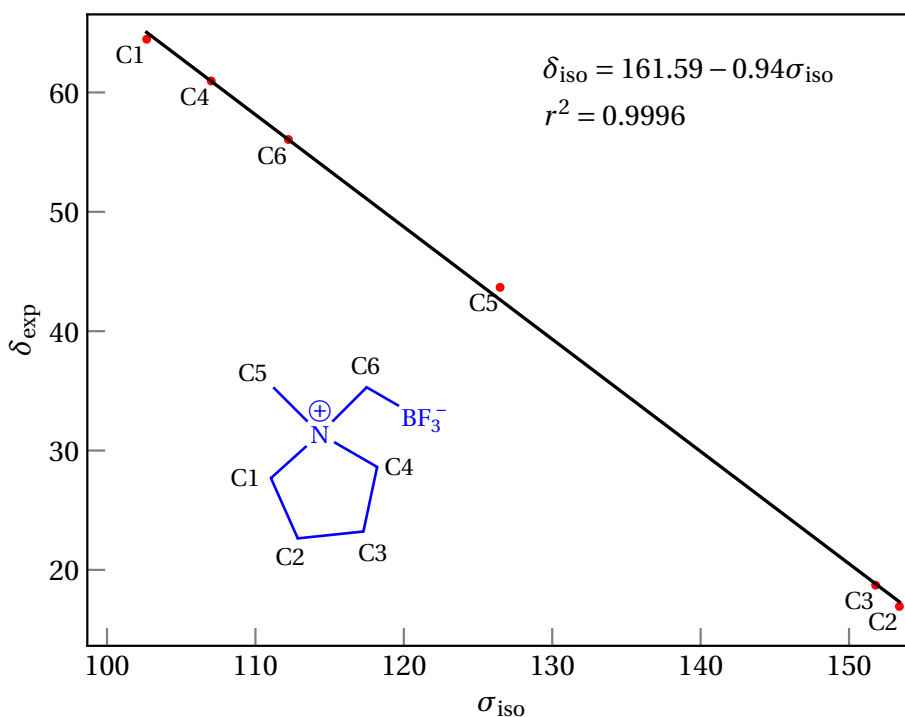


Figure 1. σ_{iso} for ^{13}C is calculated using the DFT method with the CASTEP software, based on the known crystallographic structure of ZPC. δ_{exp} corresponds to the experimentally measured chemical shift. The solid black line represents the calculated linear regression ($\delta_{\text{iso}} = 161.59 - 0.94\sigma_{\text{iso}}$).

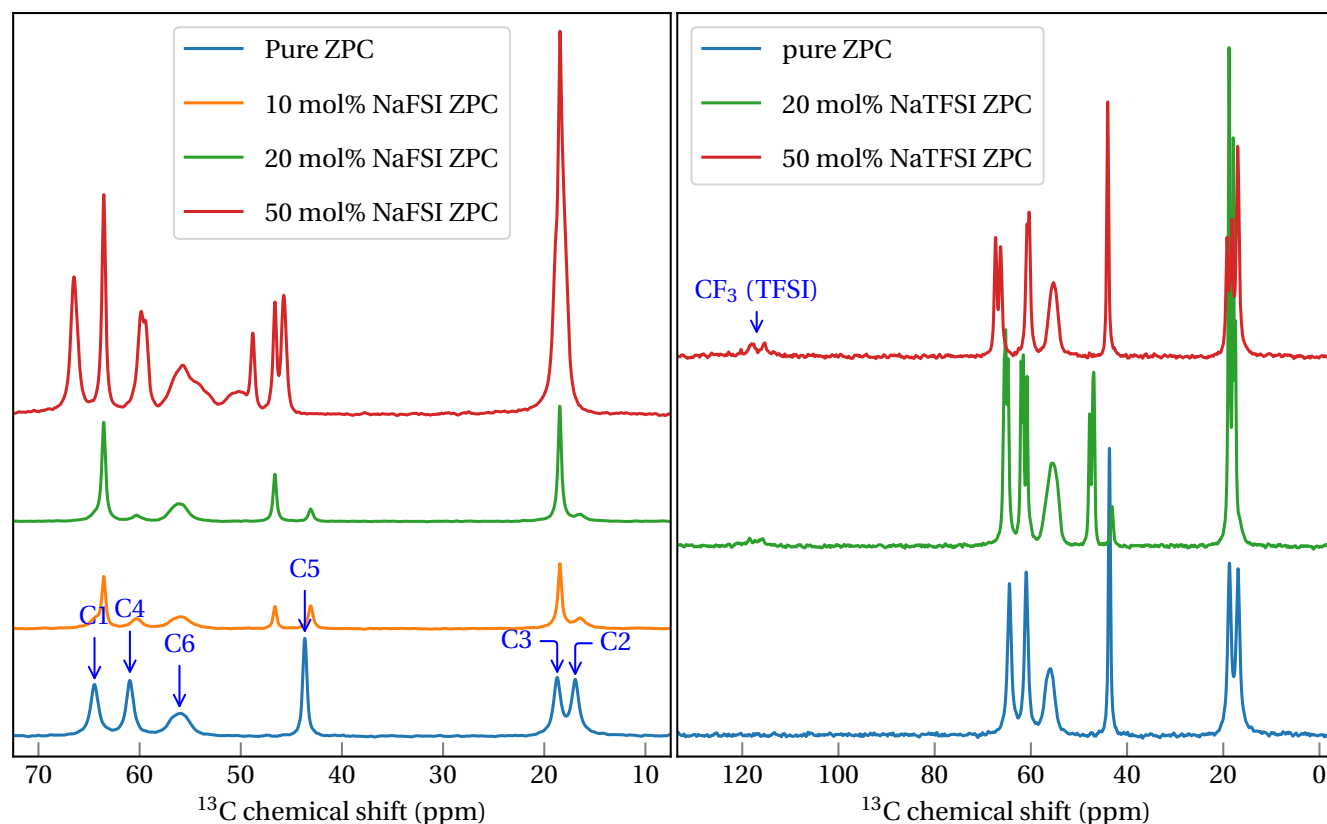


Figure 2. Comparison of the ^{13}C spectra of the pure zwitterion and those obtained from mixtures containing different concentrations of sodium salt.

In the liquid state, the carbon atoms of the zwitterion molecule, specifically C1 and C4, are equivalent. Similarly, the carbons C2 and C3 are also equivalent. However, in our case, we are in the solid state. Calculations performed using density functional theory (DFT) show that these carbons are not equivalent, and these calculations have allowed us to assign the carbons precisely. Carbon C6 produces a broad signal, which corresponds to a quadrupolar coupling of the C–B bond (involving ^{10}B and ^{11}B). By adding 10% and 20% of NaFSI or TFSI, we observe what was described in Chapter 4, namely a phase separation. This is accompanied by the observation of two methyl groups, each favored depending on the percentage of salt concentration. At 50%, multiphase behavior is observed.

^{23}Na Spectroscopy

The sodium spectrum indicates that the two sodium atoms are spatially distant, as mentioned in Chapter 4. This conclusion is supported by the absence of correlation peaks in the spectrum.

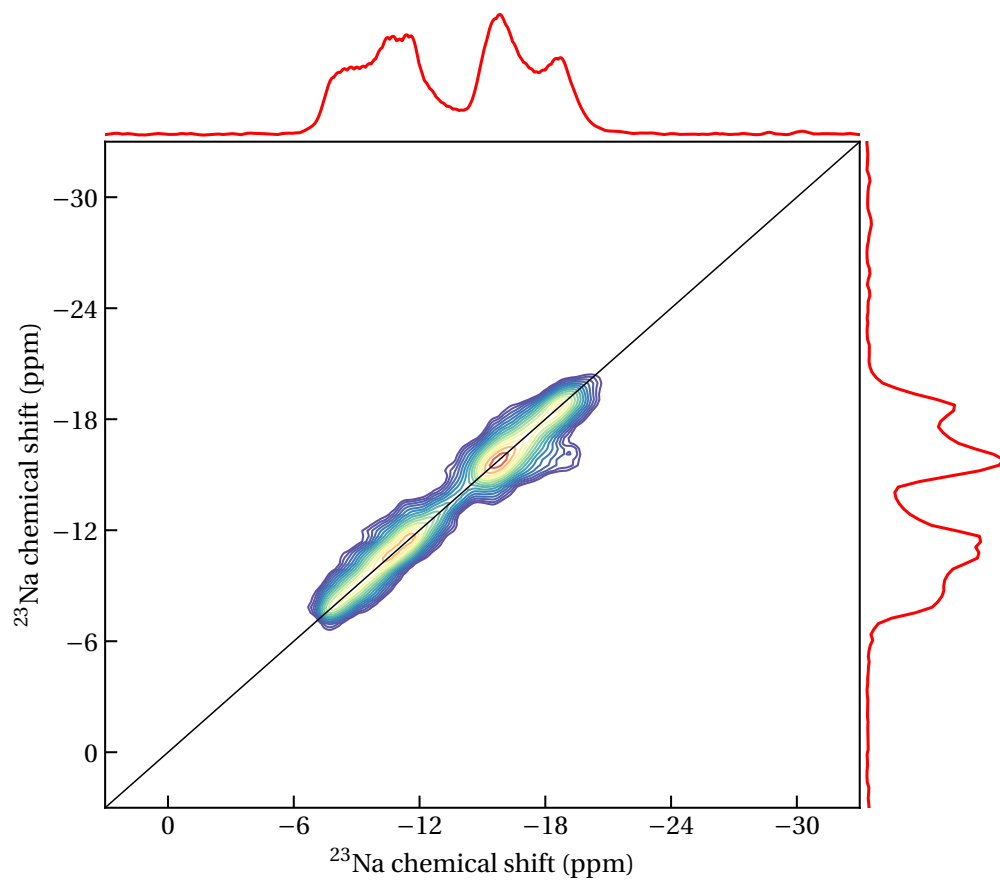


Figure 3. 2D EXSY ^{23}Na NMR spectrum of the 50 mol% NaTFSI ZPC system, with a mixing time of 25.6 ms.

Appendix 3: Full ^{23}Na spectrum on the SEI

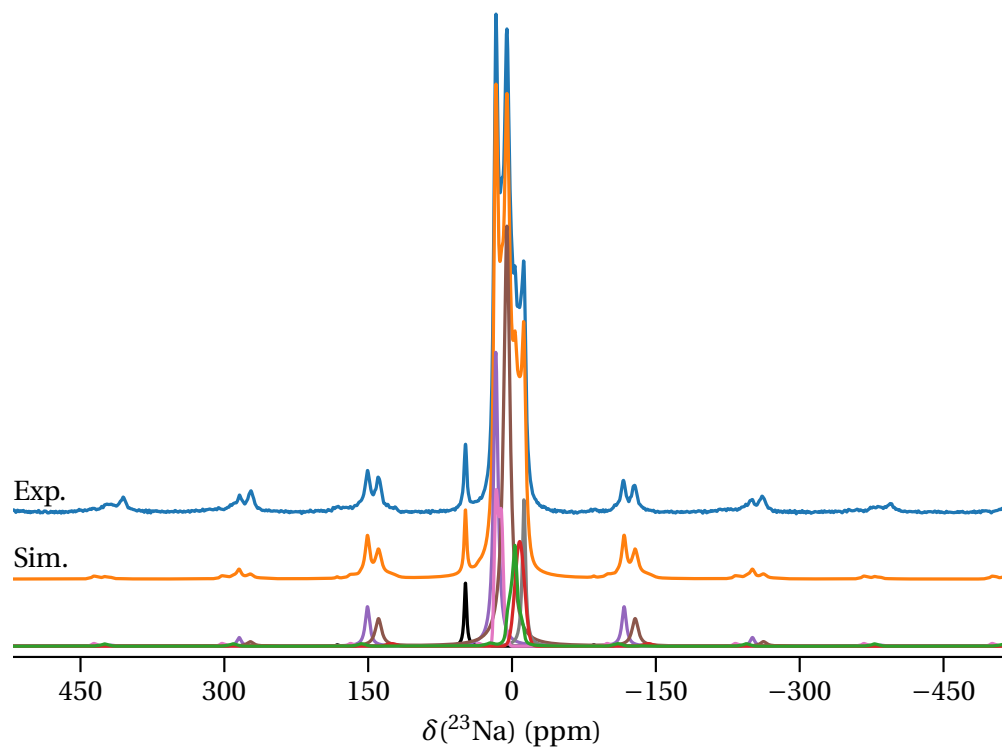


Figure 4. Complete MAS spectrum of ^{23}Na , including rotational sidebands, from SEI products for the phosphonium system, acquired at 20.0 T with a spinning speed of 30 kHz.

Compréhension de la formation de l'interface électrolyte solide (IES) et de la solvation des ions sodium au sein de nouveaux systèmes d'électrolyte via la spectroscopie RMN pour des applications de batteries

Les batteries sodium-ion et sodium-métal offrent une alternative plus durable à celles à base de lithium. Ces technologies présentent le potentiel de fournir une densité énergétique élevée à moindre coût. Toutefois, leur développement requiert la conception d'électrolytes sûrs et stables, capables de faciliter le transport des ions sodium au sein de l'électrolyte. L'un des principaux défis réside dans la forte réactivité du sodium métallique, qui peut engendrer des problèmes de sécurité, réduire la durée de vie des batteries et conduire à la formation de couches interfaciales indésirables entre l'électrolyte et l'électrode, communément appelées couches d'interface électrolyte solide (Solid Electrolyte Interphase, SEI). Dans le cadre de cette thèse, nous avons étudié de nouveaux électrolytes, solides et liquides, à l'aide de la spectroscopie de Résonance Magnétique Nucléaire (RMN) à l'état solide, une technique puissante offrant une compréhension fine, à l'échelle atomique, de la structure et de la dynamique des matériaux. Nous nous sommes concentrés sur deux types d'électrolytes solides : des copolymères blocs contenant des ions polymérisés et des cristaux plastiques zwitterioniques, tous deux dopés avec des sels de sodium afin d'améliorer leur conductivité ionique. Nous avons également analysé les différentes phases présentes dans la couche SEI lorsque le sodium métallique est employé comme électrode en combinaison avec des électrolytes à base de liquides ioniques. Nos résultats montrent que la structure moléculaire, ainsi que les interactions entre les différentes conformations adoptées par le solvant électrolytique et les ions sodium, influencent de manière significative la conductivité de nos électrolytes. Par exemple, une certaine conformation du solvant favorise le transport ionique en raison de sa dynamique plus élevée, tandis qu'une autre, caractérisée par une mobilité très faible, induit des interactions particulièrement fortes entre cette conformation et les ions sodium. Par ailleurs, à des concentrations élevées de sel de sodium mélangé avec le zwitterion, les ions sodium se lient de manière excessive à leur environnement local, ce qui réduit leur mobilité effective. Bien que le zwitterion présente un désordre local, cet effet est atténué par la forte concentration en sel de sodium. Nous avons également identifié des composés clés dans la couche SEI, tels que le fluorure de sodium ainsi que diverses espèces soufrées et oxygénées. Certains de ces composés sont connus pour leur grande stabilité, et sont ainsi bénéfiques pour la SEI, tandis que d'autres, totalement inédits, soulèvent de nouvelles questions concernant le mécanisme de décomposition de l'électrolyte lors du fonctionnement de la batterie. Ce travail a permis d'approfondir la compréhension de la structure locale, de la solvation et des interactions entre les ions sodium grâce à la spectroscopie RMN à l'état solide avancée. Il contribuera à orienter la conception de nouveaux électrolytes fondés sur les liquides ioniques, les zwitterions et les polymères porteurs d'ions, dans la perspective d'atteindre des performances encore meilleures.

Mots clés : RMN à l'état du solide, Batteries, Batteries au sodium, Électrolytes solides, Interface électrolyte solide

Understanding the Formation of Solid Electrolyte Interphase (SEI) and Sodium Ion Solvation within Novel Electrolyte Systems via NMR Spectroscopy for Battery Applications

Sodium-ion and sodium-metal batteries are emerging as more sustainable alternatives to current lithium-based systems. These technologies have the potential to deliver high energy density at lower cost. However, their development requires the design of safe and stable electrolytes capable of facilitating the transport of sodium ions within the electrolyte. One of the main challenges lies in the high reactivity of metallic sodium, which can pose safety concerns, reduce battery lifespan, and lead to the formation of undesirable interfacial layers between the electrolyte and the electrode, commonly referred to as the Solid Electrolyte Interphase (SEI) layer. In this thesis, we investigated novel solid and liquid electrolytes using solid-state Nuclear Magnetic Resonance (NMR) spectroscopy, a powerful technique that provides detailed atomic-level insights into material structure and dynamics. We focused on two types of solid electrolytes: block copolymers containing polymerized ions and zwitterionic plastic crystals, both doped with sodium salts to enhance their ionic conductivity. We also analysed the various phases present in the SEI layer when metallic sodium is employed as the electrode in combination with ionic liquid-based electrolytes. Our results indicate that the molecular structure, as well as the interactions between the different conformations adopted by the electrolyte solvent and sodium ions, significantly influence the conductivity of our electrolytes. For example, one solvent conformation facilitates ion transport due to its higher dynamics, whereas another exhibits very low mobility, promoting particularly strong interactions between this conformation and the sodium ions. Furthermore, at high concentrations of sodium salt mixed with the zwitterion, sodium ions bind excessively to their local environment, thereby reducing their effective mobility. Although the zwitterion exhibits local disorder, this effect is mitigated by the high concentration of sodium salt. Additionally, we identified key compounds in the SEI layer, such as sodium fluoride and various sulfur- and oxygen-based species. Some of these compounds are known to be highly stable and thus beneficial for the SEI, while others are entirely novel, raising new questions regarding the electrolyte decomposition mechanism during battery operation. This work improved understanding of local structure, solvation, and sodium-ion interactions, achieved through advanced solid-state NMR spectroscopy, will guide the design of new electrolytes based on ionic liquids, zwitterions, and ion-containing polymers, with the goal of achieving even higher performance.

Keywords: solid-state NMR, Batteries, Sodium Batteries, Solid Electrolytes, Solid Electrolyte Interface