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Ex situ and in situ NMR spectroscopy and imaging for electrochemical energy storage

Spectroscopie et imagerie RMN ex situ et in situ pour le stockage électrochimique de l'énergie

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2. Résumé étendu

1. Introduction

Le changement climatique et le réchauffement de la planète soulignent la nécessité de remplacer durablement les combustibles fossiles, les sources d'énergie renouvelables jouant un rôle essentiel à cet égard. Cependant, l'utilisation de sources d'énergie renouvelables, telles que l'énergie solaire, éolienne ou houlomotrice, pose des problèmes importants en termes de stockage et de fourniture efficaces de l'énergie. Leur intermittence peut entraîner des instabilités dans l'approvisionnement en énergie, ce qui rend difficile la satisfaction des besoins du réseau électrique. Parallèlement, l'électrification des véhicules nécessite des solutions de stockage d'énergie compactes et légères, capables de fournir la puissance nécessaire à l'accélération et la capacité énergétique requise aux longs trajets. Dans ce contexte, les batteries rechargeables offrent un avantage prometteur en raison de leur capacité à stocker et à fournir de l'énergie « verte », grâce à des réactions chimiques réversibles qui convertissent l'énergie chimique en énergie électrique.

La technologie des batteries lithium-ion, commercialisée par Sony en 1991, a rapidement attiré l'attention du public avec la croissance rapide des produits électroniques portables, et est devenue un centre d'intérêt pour l'industrie des voitures électriques et la transition énergétique. Les batteries sont des systèmes multicomposants sophistiqués dont les performances sont déterminées par des interactions complexes. Obtenir un aperçu du comportement de chaque composant de la batterie et de l'interaction de ces composants sur la performance électrochimique globale est un véritable défi.

Les méthodes de caractérisation par résonance magnétique nucléaire (RMN) *in situ* et *operando* sont prometteuses car, sans détruire la batterie, elles permettent de surveiller les processus et les phases métastables ou réactives à courte durée de vie à différentes étapes de la charge électrochimique. Ceci est essentiel pour comprendre les processus de cyclage et de dégradation et ainsi améliorer les performances électrochimiques des batteries, en particulier dans des conditions abusives telles que les charges rapides. En outre, la connaissance de l'état redox individuel de chaque électrode est essentielle pour identifier les origines de la perte de capacité dans les batteries complètes.

Ici, nos efforts se concentrent sur l'avancement de ces méthodes et le développement d'une nouvelle approche RMN pour la caractérisation des batteries opérationnelles (*operando*) et une étude complète pour le suivi de l'état de charge des électrodes (SOC) dans les batteries lithium-ion (LIB) et les batteries sodium-ion (SIB). Jusqu'à présent, la plupart des études RMN *operando* se sont concentrées sur la spectroscopie RMN du ^7Li ou ^{23}Na pour suivre les processus de lithiation et de dégradation dans les composants des batteries. Nous explorons comment le signal RMN ^1H *operando* du solvant de l'électrolyte liquide peut être

exploité pour suivre l'évolution de l'électrode tout en bénéficiant de la sensibilité élevée de la RMN ^1H à l'état liquide par rapport à la RMN ^7Li ou ^{23}Na .

Nous exploitons la sensibilité du signal RMN ^1H des molécules d'électrolyte à la susceptibilité magnétique des particules voisines du matériau actif de l'électrode positive, dans le contexte d'une batterie $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2 \parallel \text{LiPF}_6$ dans le solvant EC/DMC=1:1 $\parallel$ graphite. Notre objectif ultime est de caractériser la dépendance spatiale et spectrale du signal de l'électrolyte dans l'ensemble de la batterie, pendant la charge et la décharge, et de l'utiliser comme empreinte digitale de l'état de la batterie par le biais des changements induits dans la susceptibilité magnétique.

2. Méthodologie

Nous décrivons ici brièvement les objectifs et la méthodologie appliquée dans chaque chapitre. Après une introduction générale dans le chapitre 1, nous présentons les principes du stockage de l'énergie et des batteries dans le chapitre 2. Plus précisément, il comprend une brève présentation des LIB et des SIB, complétée par un examen de l'état de l'art en matière de détermination de l'état de charge des batteries. Dans le chapitre 3, nous passons brièvement en revue la théorie et les concepts de la RMN et de ses différentes techniques, en particulier celles qui sont nécessaires à la compréhension de ce travail. Il est complété par une vue d'ensemble des travaux liés à la caractérisation RMN *in situ/operando* des batteries. Le chapitre 4 explore le concept de susceptibilité magnétique et les propriétés magnétiques des matériaux actifs d'électrode positive, en explorant le lien avec leur état d'oxydation. Il est suivi d'un aperçu de la littérature sur l'impact du paramagnétisme sur la RMN et sur la manière dont il peut modifier le signal RMN.

Le chapitre 5 présente la stratégie employée pour déterminer l'effet des composants de la batterie, y compris les séparateurs, les collecteurs de courant, les matériaux actifs et les électrodes commerciales : Nous avons identifié les descripteurs du spectre RMN ^1H , sur un des solvants de l'électrolyte (carbonate de diméthyle, DMC), qui sont pertinents pour cette approche. Ces résultats expérimentaux nous ont permis de vérifier la sensibilité de notre approche à la structure électronique et à la susceptibilité magnétique des matériaux d'électrode. Enfin, un tube spécialement conçu a été utilisé pour de l'imagerie de déplacement chimique (CSI), une technique permettant d'obtenir des spectres RMN localisés. Nous avons analysé l'origine spatiale des composantes du spectre RMN ^1H du liquide perturbé par le matériau d'électrode.

Enfin, au chapitre 6, nous étendons cette approche expérimentale à la RMN *ex situ*, en utilisant des électrodes extraites à différents états de charge d'une batterie complète. Nous décrivons le protocole et la préparation de l'échantillon pour la caractérisation RMN *ex situ* et validons la sensibilité du spectre RMN

^1H du DMC liquide à l'état de charge de l'électrode positive. Cette approche est ensuite étendue à un autre système de batterie avec LiFePO_4 comme électrode positive. Ce chapitre détaille enfin les premières mesures RMN *operando* réalisées à l'aide de cette approche et les informations qui peuvent être obtenues sur l'état redox des électrodes à l'intérieur d'une batterie en fonctionnement. En conclusion, nous présentons les perspectives offertes par ce travail et proposons une série d'applications potentielles qui pourraient bénéficier de notre approche.

3. Principes de base des batteries de stockage électrochimique (chapitre 2)

Une batterie est un dispositif capable de stocker de l'énergie et de la restituer en cas de besoin. Une cellule primaire ou une batterie (cellule galvanique) est une cellule qui stocke l'énergie sous forme chimique et la restitue sous forme électrique. Ces piles sont destinées à un usage unique et ne peuvent être rechargées en raison des réactions électrochimiques non réversibles qui se produisent à l'intérieur.

En revanche, les batteries secondaires peuvent stocker de l'énergie chimique à partir d'énergie électrique (pendant la charge). Cette réaction est réversible, ce qui leur permet de subir plusieurs cycles de charge et de décharge. Ces processus sont permis par des réactions électrochimiques connues sous le nom de réactions d'oxydoréduction, qui impliquent le transfert d'électrons entre les matériaux des électrodes à travers l'électrolyte, éventuellement accompagné d'un échange d'ions.

Une cellule électrochimique fonctionne en employant un oxydant et un réducteur qui subissent une réaction d'oxydation-réduction thermodynamiquement favorable pendant la décharge. Lorsque ces matériaux sont en contact l'une avec l'autre, un échange d'électrons se produit, entraînant des réactions de réduction et d'oxydation. En séparant électriquement deux électrodes par un électrolyte isolant électronique pour empêcher l'échange direct d'électrons, on force l'échange d'électrons via un circuit externe et on obtient une cellule électrochimique. L'équilibre des charges est assuré par la migration des ions dans l'électrolyte, qui est un bon conducteur ionique mais un isolant électronique placé entre les électrodes.

Lors de la décharge de la cellule (figure 1), deux réactions électrochimiques se produisent simultanément : l'oxydation à l'anode et la réduction à la cathode. L'anode subit une oxydation qui libère des électrons (et parfois des cations), tandis que la cathode accepte ces électrons et ces cations pour subir une réduction. Les ions se déplacent dans l'électrolyte, tandis que les électrons sont collectés par des collecteurs de courant métalliques et conduits dans le circuit externe. Une fois que les électrodes sont reliées électriquement, cette réaction d'oxydoréduction, favorisée par la thermodynamique, commence et facilite le transfert d'électrons et d'ions.

Les matériaux d'électrode positive utilisés dans ce travail de thèse sont l'oxyde de lithium et de cobalt LiCoO_2 , le phosphate de fer et de lithium LiFePO_4 , l'oxyde de manganèse et de lithium spinelle LiMn_2O_4 , différents oxydes de lithium, nickel, manganèse et cobalt ($\text{N}_x\text{M}_y\text{C}_z$, $\text{LiNi}_x\text{Mn}_y\text{Co}_z$), et un fluorophosphate de vanadium et de sodium, $\text{Na}_3\text{V}_2(\text{PO}_4)\text{F}_3$. Du côté des électrodes négatives, nous avons utilisé du graphite ou du carbone dur. Les électrolytes étaient des sels de lithium ou sodium (LiPF_6 ou NaPF_6) dilués dans des solvants carbonatés.

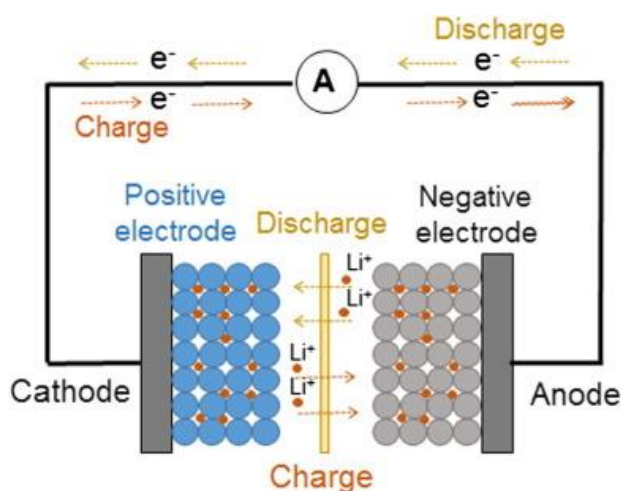


Figure 1 Schéma du fonctionnement électrochimique de la LIB pendant la charge et la décharge. Lors de la décharge de la cellule, des ions lithium sortent de l'électrode négative, se déplacent dans l'électrolyte et s'intercalent dans l'électrode positive. Lors de la charge, des ions sortent de l'électrode positive, retournent dans l'électrolyte et s'intercalent dans l'électrode négative.¹

Le vieillissement non-uniforme des batteries complique la gestion du processus de charge/décharge. La caractérisation de la performance électrochimique d'une batterie passe par plusieurs indicateurs dont voici les trois plus importants: (i) sa capacité, la quantité de charge qu'elle peut stocker, (ii) son efficacité coulombique, le rapport entre la capacité obtenue en décharge et celle donnée en charge, (iii) sa rétention de capacité, le rapport entre la capacité obtenue en décharge à un cycle N par rapport à celle obtenue au départ. Les batteries fonctionnent dans des conditions d'exploitation ou des facteurs environnementaux variables, tels que des régimes de charge variables, des temps de stockages plus ou moins longs, des variations de température... De nombreux systèmes sont sensibles à la décharge profonde ou à la surcharge, car un état de charge extrêmement élevé ou trop faible peut causer des dommages irréversibles à la batterie. Le système de gestion de la batterie doit être donc ajusté pour tenir compte des altérations de la capacité de charge.

Cependant, malgré le développement continu des techniques d'estimation dans le système de gestion de la batterie, la détermination de l'état de charge des batteries reste un des plus gros challenges. La spectroscopie d'impédance est coûteuse, le comptage coulombique nécessite des recalibrations régulières et dépend des réactions parasites, les mesures de potentiel demandent un long temps de repos, les tests de décharge ne sont pas possible pendant l'utilisation.

C'est pourquoi il est essentiel de continuer la recherche et le développement dans le domaine de la technologie des batteries, des techniques de mesure et des algorithmes d'estimation de l'état de charge. Par conséquent, nous avons travaillé à une autre mesure directe de l'état de charge de chacune des électrodes, en lien avec un comptage de Coulomb, pour permettre une détermination plus précise et plus directe de l'état de charge et des réactions secondaires.

4. Les principes de la résonance magnétique nucléaire (chapitre 3)

La résonance magnétique nucléaire est un outil polyvalent et essentiel de la recherche scientifique, qui permet aux scientifiques de révéler des processus dynamiques, des compositions chimiques, des structures, des cinétiques de réaction ou de réaliser une imagerie non invasive. Les progrès incessants de la technologie RMN contribuent à de nombreuses découvertes scientifiques et continuent d'étendre ses applications, notamment dans le domaine des dispositifs de stockage électrochimique. Les batteries lithium-ion et sodium-ion sont des systèmes complexes dans lesquels les processus électrochimiques et chimiques se produisent simultanément et s'influencent mutuellement. Il est nécessaire de comprendre ces processus interdépendants pour expliquer les mécanismes à l'origine des défaillances des batteries et améliorer leurs performances globales. En général, deux grandes familles de mesures, *ex situ* et *in situ*, peuvent être utilisées pour étudier les batteries.

En RMN *ex situ*, la procédure habituelle consiste à extraire la partie intéressante de la batterie dans une boîte à gants remplie d'argon (car les matériaux sont sensibles à l'air), puis à la placer dans un rotor RMN. La mise en rotation à l'angle magique (MAS) est une technique essentielle pour l'acquisition de spectres RMN résolus de matériaux solides, et constitue le principal atout de la RMN *ex situ* lorsqu'il s'agit d'analyser les composants solides d'une batterie. La RMN *ex situ* est traditionnellement utilisée pour analyser les changements dans les composants solides à différents états de charge de la batterie. Plus récemment, elle a aussi été utilisée pour étudier l'interface entre les électrodes et l'électrolyte solide ou liquide et pour étudier la réactivité et la dynamique d'électrolytes solides.

Dans le contexte de la RMN *in situ* et *operando*, la batterie entière est placée dans l'aimant RMN et la bobine de détection. La RMN *in situ* offre de précieux avantages, principalement en raison de l'élimination de l'ouverture destructive de la batterie. En outre, cette technique permet d'acquérir des spectres pour différents états de charge à partir d'une seule batterie. En mode *operando*, la batterie complète n'est pas seulement placée dans l'aimant RMN, mais elle est également chargée et la déchargée. Cela permet de détecter les phases transitoires en temps réel et présente un intérêt particulier en raison de la forte réactivité chimique des matériaux de batterie.

Les études traditionnelles de RMN ^7Li *in situ* des batteries, malgré leurs avantages, se heurtent à des limites de résolution pour les électrodes paramagnétiques ou conductrices. La première limitation-clé est la résolution temporelle, qui permet de saisir les changements au sein d'un système suffisamment vite pour les suivre. Dans notre cas, la résolution temporelle est limitée par la faible sensibilité de la technique de RMN qui nécessite une accumulation de signal sur plusieurs minutes.

Une autre limitation concerne la résolution spectrale, c'est-à-dire la capacité à distinguer et à résoudre diverses caractéristiques spectrales ou composantes dans le spectre RMN, particulièrement limités pour les études *in situ*. Dans le cas de la RMN du ^7Li , il peut être difficile de distinguer les différents environnements chimiques ou structuraux des ions Li^+ dans la batterie, en raison du chevauchement des pics ou d'un élargissement important pour les matériaux paramagnétiques. Cette capacité réduite à identifier des espèces ou des composés d'ions Li^+ spécifiques peut être problématique pour la compréhension de la chimie et de la dynamique qui se produisent au sein d'une batterie.

Pour ces raisons, les analyses *in situ* des batteries lithium ou sodium-ion se limitent généralement à observer les décalages importants de pics pendant la charge-décharge, en combinaison avec des analyses *ex situ*. Les batteries Na-ion sont confrontées à des défis encore plus grands en raison de la faible sensibilité de la RMN du ^{23}Na , due au faible rapport gyromagnétique, à la nature quadropolaire et à la relaxation rapide du ^{23}Na . Par ailleurs, ces limites réduisent les applications de type imagerie (IRM).

Pour tenter de résoudre ces problèmes, nous explorons une approche dans laquelle nous nous concentrons sur les changements locaux de susceptibilité magnétique à l'intérieur de la cellule en fonctionnement. La susceptibilité magnétique est principalement influencée par la configuration électronique du matériau. Par conséquent, des changements significatifs de la susceptibilité magnétique se produisent lors des réactions d'oxydoréduction utilisées dans les charge et décharge des batteries. En particulier, les susceptibilités magnétiques des matériaux d'électrode positive dépendent fortement de leur état de lithiation.

Dans notre approche, au lieu de regarder directement les atomes de lithium ou sodium dans les électrodes, nous nous concentrons sur le signal ^1H du solvant de l'électrolyte liquide (un carbonate) qui peut être utilisé

pour observer l'évolution des électrodes. Cette mesure indirecte des changements de susceptibilité magnétique des électrodes à travers le signal de l'électrolyte peut alors être corrélée à l'état d'oxydation des électrodes et fournir des informations détaillées sur les processus électrochimiques, ce qui est essentiel pour identifier les origines de la perte de capacité dans les batteries complètes.

Un avantage important de cette approche est l'amélioration significative de la sensibilité par l'utilisation du ^1H au lieu du $^7\text{Li}/^{23}\text{Na}$ conventionnel et son applicabilité à divers systèmes de batteries. L'amélioration de la vitesse d'acquisition par la méthode ^1H devrait apporter un avantage notable par rapport aux autres méthodes existantes en ce qui concerne la résolution temporelle. Cet avantage sera crucial dans un mode *operando* pour l'étude des comportements de cyclage qui se produisent dans des échelles de temps très courtes.

5. Susceptibilité magnétique des matériaux et RMN (chapitre 4)

Les mesures magnétiques sont essentielles pour l'étude de la structure magnétique et des propriétés électroniques des matériaux d'oxydoréduction dans les batteries lithium ou sodium-ion. Différentes techniques peuvent être employées pour étudier les propriétés magnétiques des matériaux, telles que la diffractométrie ou diffusion des neutrons, la magnétométrie, la RMN et la résonance de spin électronique.

Le magnétisme des matériaux provient des propriétés magnétiques de leurs particules constitutives au niveau atomique. Dans la majorité des cas, ce magnétisme est principalement déterminé par les moments magnétiques des électrons. La susceptibilité magnétique d'un matériau est influencée par la disposition et le comportement de ses électrons, y compris leur spin, leur mouvement orbital et leurs interactions les uns avec les autres. La structure électronique des matériaux d'électrode contribue donc de manière significative à leur susceptibilité magnétique.

Dans le contexte de la charge et décharge des batteries, les processus électrochimiques impliquent le transfert d'électrons, ce qui a un impact sur la structure électronique et, par conséquent, sur les propriétés magnétiques des électrodes. Dans cette thèse, nous essayons de sonder la susceptibilité magnétique des électrodes à travers leur effet sur le spectre RMN ^1H du solvant de l'électrolyte. Le tableau 1 présente des données bibliographiques sur la susceptibilité magnétique à température ambiante des matériaux actifs purs qui sont utilisés dans nos études.

Tableau 1 Susceptibilité magnétique des matériaux utilisés dans cette thèse.

Substances	Susceptibilité magnétique à 300K (emu.mol ⁻¹)	Température de Curie-Weiss (K)	Constante de Curie (emu K. mol ⁻¹)	Réf
Carbone noir	$\approx -2.92 \times 10^{-8}$	-	-	2,3
LP30	$\approx -5.34 \times 10^{-8}$	-	-	4
Graphite (monocristal)	$-(6 \text{ to } 264) \times 10^{-6}$	-	-	5
LiCoO ₂ (stoechiométrique)	$+9 \times 10^{-5}$	-	-	6
NMC 111	$+2.5 \times 10^{-3}$	-62.1	0.916	7
NMC442	$+2.9 \times 10^{-3}$	-65.8	1.068	7
LiMn ₂ O ₄ (LMO)	$+8.7 \times 10^{-3}$	-260	4.85	8
LiFePO ₄ (LFP)	$+9.4 \times 10^{-3}$	-145	4.18	8

La spectroscopie RMN est sensible au comportement magnétique des matériaux au niveau atomique ou moléculaire. Le paramagnétisme des matériaux de batteries peut affecter le spectre RMN par différents mécanismes.

Lorsqu'un échantillon est soumis à un champ magnétique H_0 , il subit une magnétisation qui génère son propre champ magnétique H_D , connu sous le nom de champ induit ou démagnétisant. Ce champ induit modifie le champ local et par conséquent le spectre RMN. Les discontinuités de susceptibilité magnétique entre deux matériaux conduisent à la présence de gradients de champ magnétique à l'interface, qui se manifestent par un élargissement du signal RMN pour les spins localisés à l'interface. Dans cette perspective, le shift dans le spectre RMN peut être considéré comme une mesure du champ magnétique local à ces interfaces.

La majorité des ions métalliques présents dans les électrodes positives sont paramagnétiques et certains, comme le manganèse, sont connus pour se dissoudre dans le solvant de l'électrolyte. La RMN à l'état liquide a été utilisée pour analyser les électrolytes et obtenir des informations sur les espèces dissoutes. Les espèces paramagnétiques dissoutes dans le solvant entraînent une accélération de la relaxation (affectant à la fois les temps de relaxation T_1 et T_2), car les électrons non appariés des espèces paramagnétiques créent des champs magnétiques fluctuants qui relaxent efficacement les spins nucléaires à proximité. De même, lorsque du lithium métallique (contenant des électrons de conduction) est en contact avec un électrolyte liquide, le

spectre du liquide est affecté de manière significative avec une distorsion, des modifications du shift et des effets de relaxation du spectre.

Pour la RMN à l'état liquide, l'échantillon est homogène aux échelles de temps considérées par l'effet du mouvement brownien. Au contraire, dans les poudres polycristallines plusieurs échelles doivent être prises en compte. La susceptibilité magnétique *bulk* est un effet macroscopique qui trouve son origine dans les couplages dipolaires entre les spins nucléaires et les moments magnétiques des électrons. La susceptibilité magnétique peut présenter une dépendance orientationnelle dans une particule et dans l'ensemble de la poudre lorsque la forme de la particule n'est pas sphérique ou lorsque la distribution des spins paramagnétiques au sein de l'échantillon n'est pas uniforme.

6. Vérification de la sensibilité de la RMN à la susceptibilité magnétique (chapitre 5)

Nous présentons ici nos efforts pour utiliser le signal RMN ^1H liquide du solvant de l'électrolyte (carbonates) pour "espionner" les électrodes tout en bénéficiant de la plus grande sensibilité de la RMN ^1H par rapport à la RMN ^7Li . Contrairement aux atomes de lithium, les atomes d'hydrogène dans le solvant de l'électrolyte ne sont pas une sonde directe de l'état de charge de l'électrode, mais ils sont sensibles aux changements de susceptibilité magnétique des électrodes voisines. L'objectif est d'appliquer cette technique à la caractérisation RMN *operando* rapide de batteries en fonctionnement, qui sera présentée au chapitre 6. Nous avons commencé par étudier l'effet de chacune d'entre elles sur le spectre RMN ^1H du diméthylcarbonate (DMC), pour nous assurer que la variation du spectre RMN à l'état liquide de l'électrolyte reflète bien le changement de l'état d'oxydoréduction.

Dans ce chapitre, le protocole expérimental pour la mesure RMN *ex situ* est présenté. Le DMC pur a été choisi car tous ses protons sont équivalents, avec un pic unique dans le spectre ^1H . Le mélange EC/DMC est plus complexe, avec deux singulets à 3,9 ppm (DMC) et à 4,7 ppm (EC), comme présenté en Figure 2. Le signal ^1H du DMC dans l'électrolyte LP30 est déplacé d'environ 0,2 ppm par rapport au signal du DMC pur. Ce déplacement peut être attribué à un effet de susceptibilité magnétique.

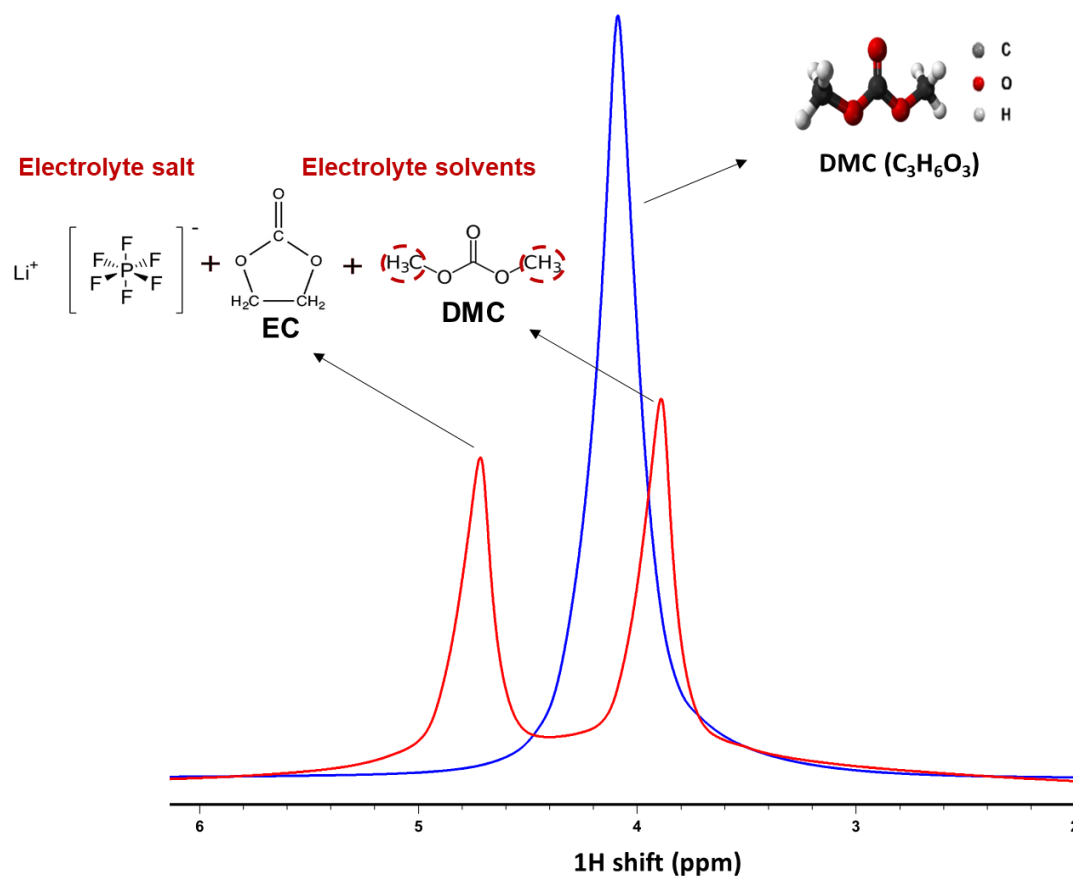


Figure 2 Signal ^1H du solvant DMC (bleu) et de l'électrolyte LP30 (rouge). Le tube RMN est complètement plein.

Pour vérifier la sensibilité de notre mesure *ex situ*, nous avons utilisé quatre matériaux actifs d'électrode positive (avec une susceptibilité magnétique différente) connus pour leur activité électrochimique : LiFePO_4 (LFP), LiMn_2O_4 (LMO), $\text{LiNi}_{0,33}\text{Mn}_{0,33}\text{Co}_{0,33}\text{O}_2$ (NMC 111) et LiCoO_2 (LCO). Nous avons fabriqué des pastilles de 5 mm de diamètre à partir de 20 mg de poudre avec une pastilleuse et une presse hydraulique. Les 200 μL de DMC puis les pastilles ont été placés dans le tube RMN, qui a été fermé par un bouchon en plastique. Une fine bande de parafilm a été enroulée autour du joint entre le tube et le bouchon pour réduire l'évaporation du DMC pendant la mesure.

La figure 3 montre que les spectres RMN ^1H du DMC sont élargis et décalés par l'introduction des pastilles. En outre, des distorsions apparaissent et empêchent la modélisation par des modèles standard de raies lorentziennes ou gaussiennes. La position du maximum du pic et la largeur à mi-hauteur ne sont plus pertinents pour décrire le signal. Trois descripteurs (l'aire, le *shift* moyen pondéré et la largeur à différentes

hauteurs de pic) sont introduits et mesurés à l'aide de MATLAB pour permettre de quantifier les changements dans le spectre RMN. Dans ce qui suit, le *shift* moyen pondéré sera simplifié en *shift*.

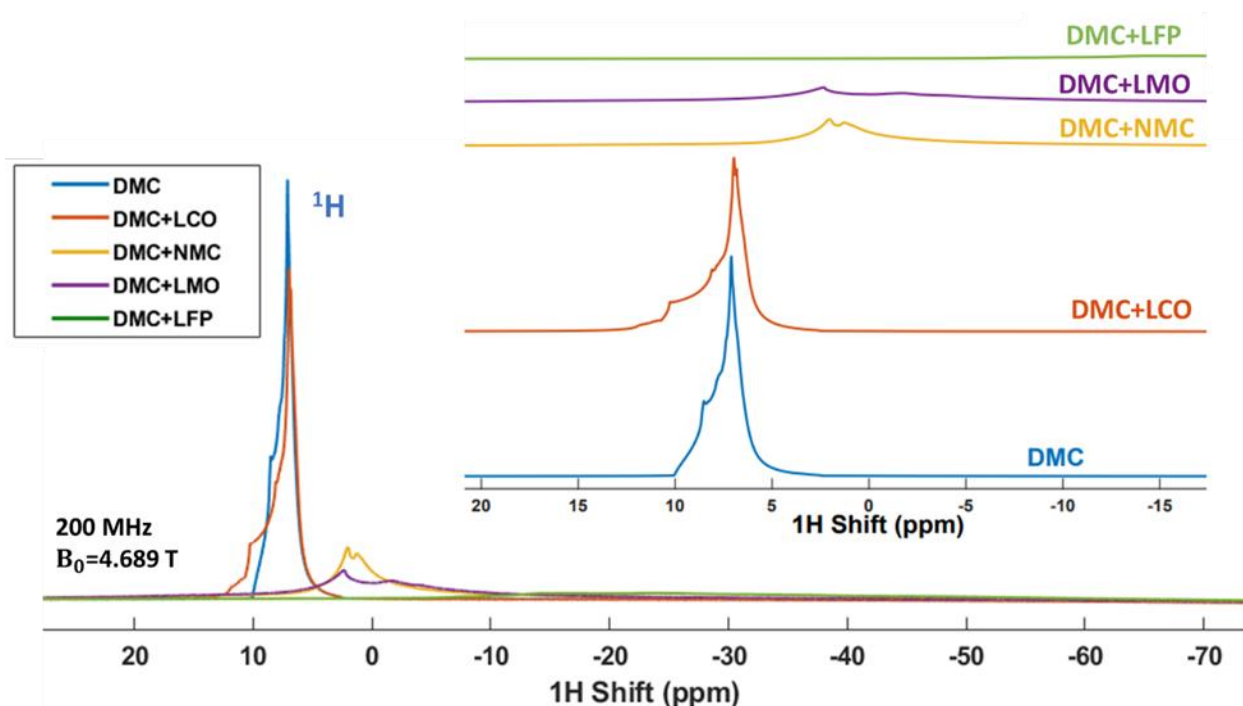


Figure 3 Spectres RMN ^1H du DMC en présence de pastilles de matériaux actifs d'électrodes positives.

Les descripteurs introduits sont sensibles à la variation de la susceptibilité magnétique des matériaux actifs. Avec l'augmentation de la susceptibilité magnétique (croissante de LCO à LFP), le spectre ^1H du DMC est plus distordu, ce qui se traduit par un *shift* et un élargissement du signal ^1H plus importants (figure 4). Ces résultats sont prometteurs le suivi des changements de susceptibilité magnétique des électrodes dans la batterie.

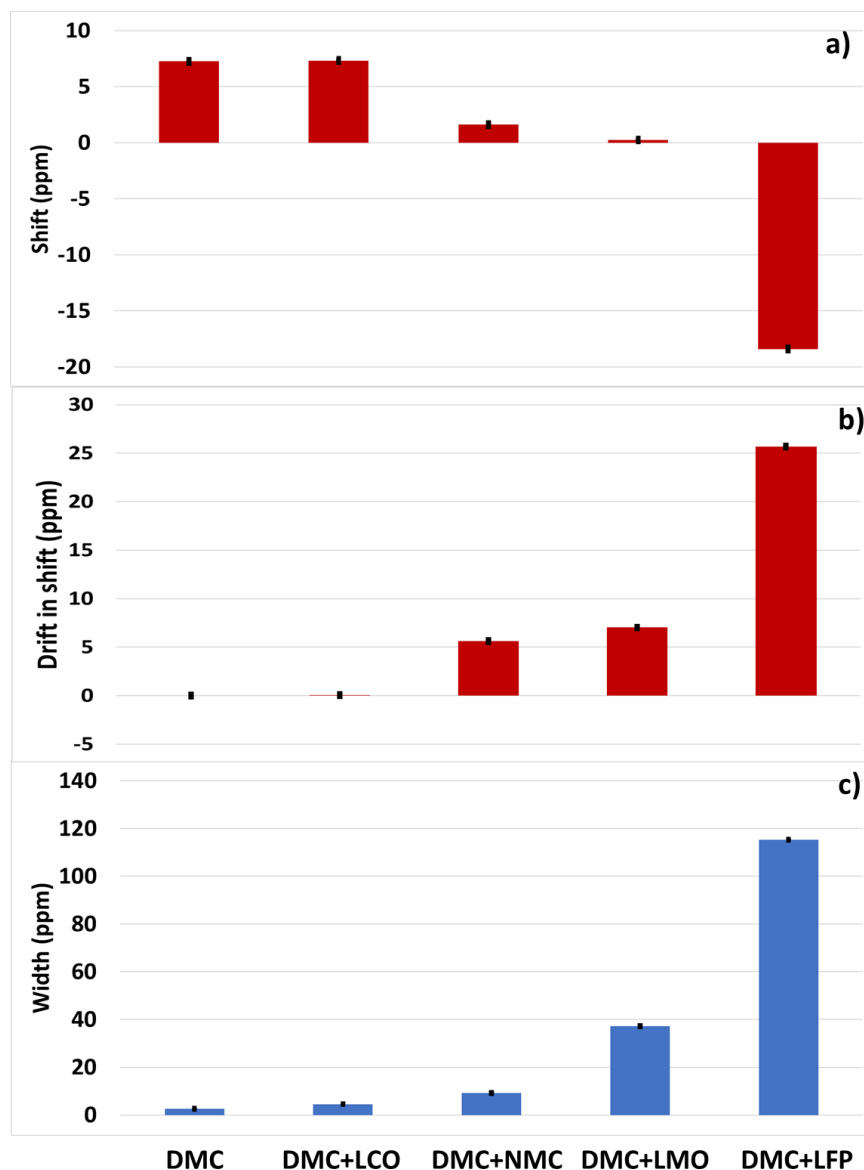


Figure 4 Effet des matériaux actifs sur (a) le shift moyen absolu, (b) la dérive du shift moyen par rapport au DMC pur, et (c) la largeur des spectres ^1H .

Nous avons également évalué l'effet de chaque composant de la batterie sur le spectre ^1H du solvant DMC : l'électrode positive NMC (matériau actif NMC 622, noir de carbone et liant, enduit sur une face d'une feuille d'aluminium), l'électrode négative en graphite (matériau actif en graphite, noir de carbone et liant, enduit sur une face d'une feuille de cuivre), les collecteurs de courant en cuivre et en aluminium, et le séparateur en fibre de verre.

La figure 5 présente le signal ^1H du DMC en contact avec les composants de la batterie et révèle que la distorsion la plus importante du signal ^1H du DMC provient de l'électrode NMC 622 alors que les autres composants de la batterie ont un effet négligeable.

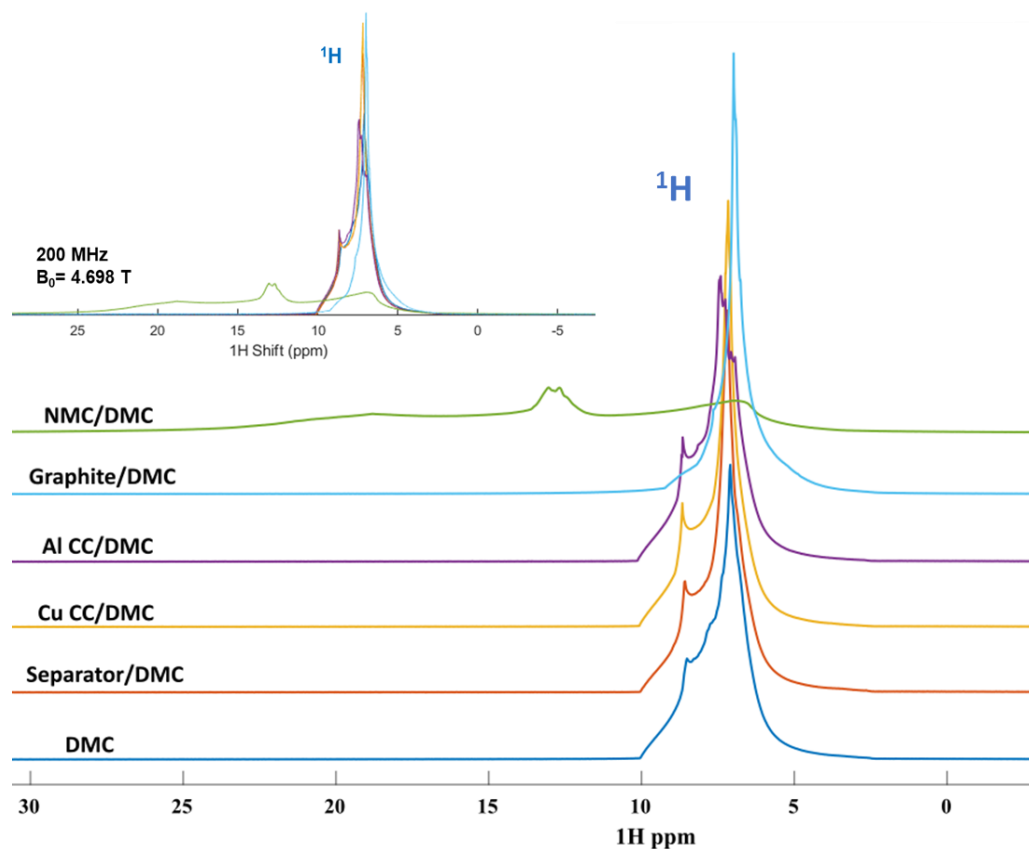


Figure 5 Signal ^1H du DMC en présence des composants de la batterie.

Les figures 6 et 7 quantifient l'impact individuel des composants de la batterie sur le *shift* et la largeur des spectres ^1H du DMC. L'électrode NMC exerce l'influence la plus prononcée sur le signal ^1H du DMC.

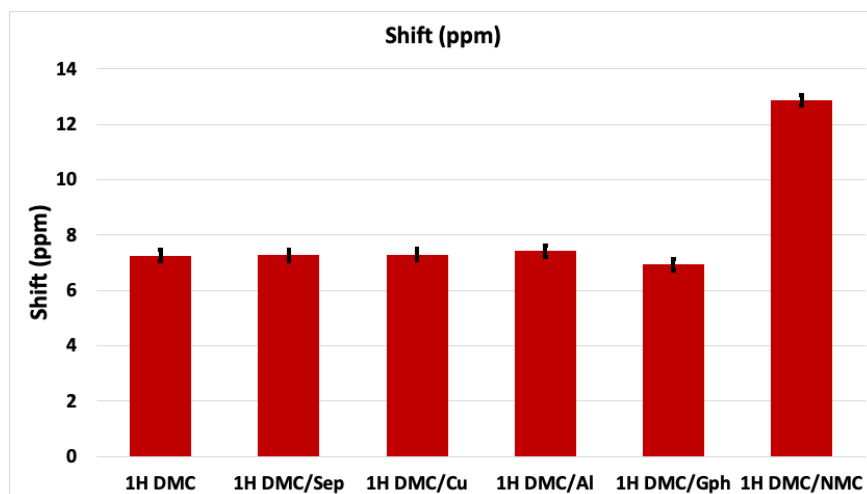


Figure 6 Effet des composants de la batterie sur le shift du spectre ^1H du DMC.

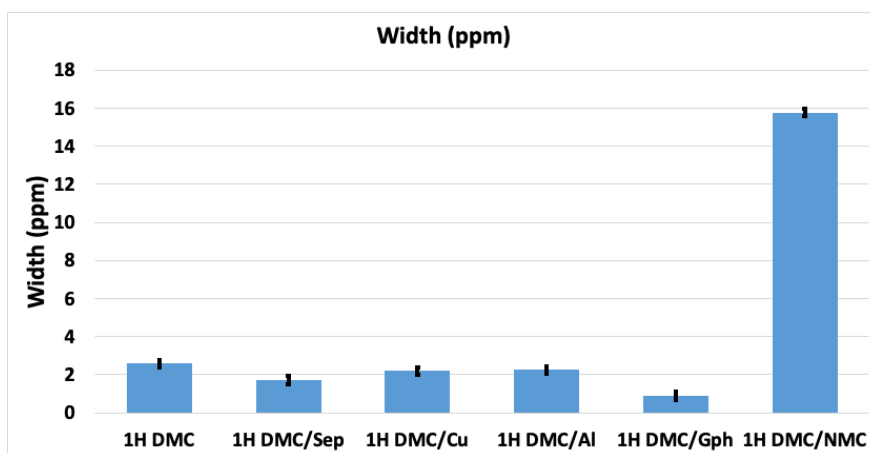


Figure 7 Effet des composants de la batterie sur la largeur des spectres DMC ^1H .

La figure 8 présente l'aire du signal ^1H du DMC à proximité des composants, avec différentes plages d'intégration. La distorsion de la ligne de base est responsable des variations d'aire avec la plage d'intégration. Pour une même quantité de DMC, l'aire mesurée est inférieure pour l'échantillon de graphite/DMC et, dans une moindre mesure, pour celui de NMC/DMC. Ceci indique qu'une partie du signal des ^1H à proximité des électrodes n'est pas détectable à cause d'une relaxation trop rapide, induite par la conductivité du graphite et le paramagnétisme de la NMC.

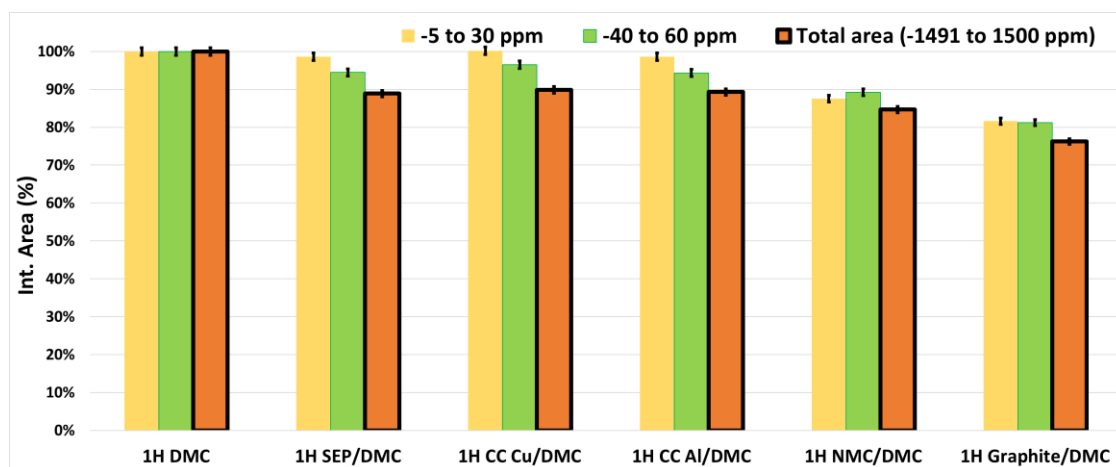


Figure 8 Effet des composants de la batterie sur la zone d'intégration sous les spectres DMC ^1H .

La figure 9 présente les constantes caractéristiques de relaxation du ^1H dans le DMC en contact avec différents composants de la batterie. L'effet le plus significatif est observé pour l'électrode NMC paramagnétique en contact avec le solvant DMC, avec une relaxation accélérée en moyenne pour les ^1H qui sont détectables.

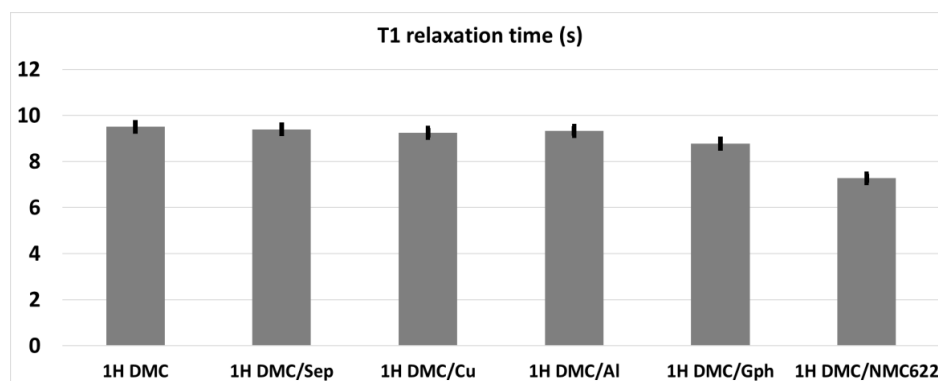


Figure 9 Effet des composants de la batterie sur la constante T_1 du DMC ^1H .

Dans ce chapitre, nous avons également utilisé la technique d'imagerie du déplacement chimique pour résoudre spatialement la distribution des spectres RMN ^1H de 200 μL de DMC à l'intérieur d'un tube PEEK RMN spécifiquement conçu pour contrôler la position de l'électrode en contact avec le solvant DMC. Une électrode LiFePO_4 (LFP) paramagnétique a été mise en contact avec le solvant DMC à l'intérieur du tube en PEEK.

Une distorsion significative du spectre RMN ^1H du DMC a été observée près de l'électrode LFP, au fond du tube PEEK, avec un *shift* et un élargissement significatif (figure 10). En s'éloignant de l'électrode, la distorsion observée diminue comme attendu.

La distribution spatiale de la relaxation longitudinale a été étudiée en collectant des données avec deux temps de recyclage différents. La diminution du délai de recyclage de 45 s à 1 s entraîne une réduction du signal ^1H dans l'ensemble du tube. En réduisant encore le temps de recyclage, le signal du DMC peu affecté par l'électrode est saturé, et nous pouvons nous concentrer sur le DMC proche de l'électrode LFP.

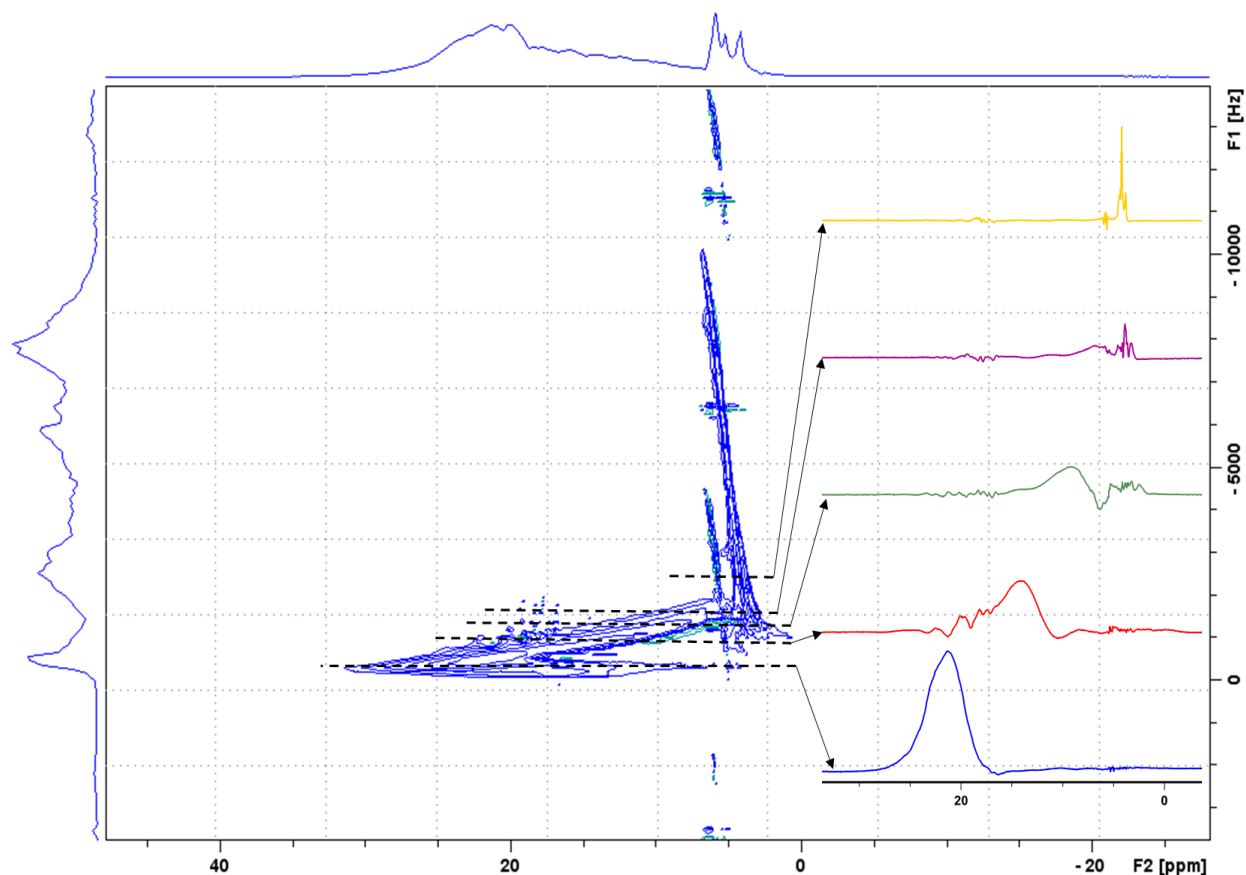


Figure 10 ^1H CSI de 200 μl de DMC en contact avec l'électrode LFP dans le tube PEEK avec un délai de recyclage de 45 s (partie inférieure du tube).

En conclusion, ce chapitre a comparé l'effet de chaque composant de batterie pristine sur le signal ^1H de l'électrolyte liquide. L'effet le plus notable sur le signal ^1H du DMC est attribué à l'électrode paramagnétique NMC parmi tous les composants de la batterie, visible en termes de *shift* moyen du spectre ^1H , de largeur de raie et de temps de relaxation T_1 . Par conséquent ces descripteurs seront utilisés dans la suite de cette thèse. La prochaine étape consiste à déterminer la sensibilité de cette approche à l'état de charge d'une électrode, pour finalement l'appliquer à une cellule complète dans une mesure RMN *operando*.

7. Effet de l'état de charge et de décharge sur les différents systèmes de batteries (chapitre 6)

La compréhension des changements dans la structure électronique des électrodes pendant le cyclage et leur relation avec l'état de charge (le SOC) est cruciale pour optimiser la conception et la performance des LIB. Dans ce chapitre, nous étudions comment l'état d'oxydoréduction des électrodes positives de la batterie en charge peut être suivi indirectement, par la distorsion du spectre RMN ^1H de l'électrolyte près de l'électrode positive. La susceptibilité magnétique des électrodes change lorsque la batterie est chargée et déchargée, de sorte que le changement d'état d'oxydation de l'électrode positive devrait pouvoir être détecté par RMN. L'objectif ultime est de permettre la mesure, *operando*, de l'état d'oxydoréduction des électrodes positives dans les batteries, même lorsque leurs signaux RMN ne peuvent pas être détectés. La connaissance exacte de l'état redox de chaque électrode contribuera à une meilleure caractérisation des pertes de capacité observées électrochimiquement dans les batteries complètes.

La structure électronique des matériaux actifs positifs tels que le NMC 622 est modifiée par l'activité redox au cours du cycle dans une cellule (NMC 622//LP30//Graphite). Au cours du processus de charge, les ions lithium et les électrons sont extraits de l'électrode NMC 622, ce qui entraîne une augmentation de l'état redox des métaux de transition Ni, Mn ou Co et une diminution du degré de lithiation du matériau. Le SOC, défini comme le pourcentage d'avancement de la charge de la batterie, est un paramètre clé pour décrire la charge de la batterie.

En suivant la stratégie expérimentale développée dans ce chapitre, nous étudions la sensibilité du spectres RMN ^1H du DMC à l'état redox des matériaux d'électrode à différents états de charge dans une batterie. Des cellules (NMC 622//LP30//Graphite et LiFePO_4 //LP30//Graphite) ont été assemblées puis cyclées selon un protocole de charge-décharge spécifique. Les cellules ont été arrêtées à un SOC spécifique, et les électrodes positives et négatives ont été extraites des cellules puis préparées pour une analyse RMN ^1H *ex situ* (figure 11). Enfin, les mesures RMN ^1H *operando* de l'électrolyte à l'intérieur d'une batterie en fonctionnement composée d'une cellule complète NMC/LP30/Gph ont été effectuées et les résultats *operando* du 5ème cycle (après les 4 cycles de formation initiaux) sont discutés.

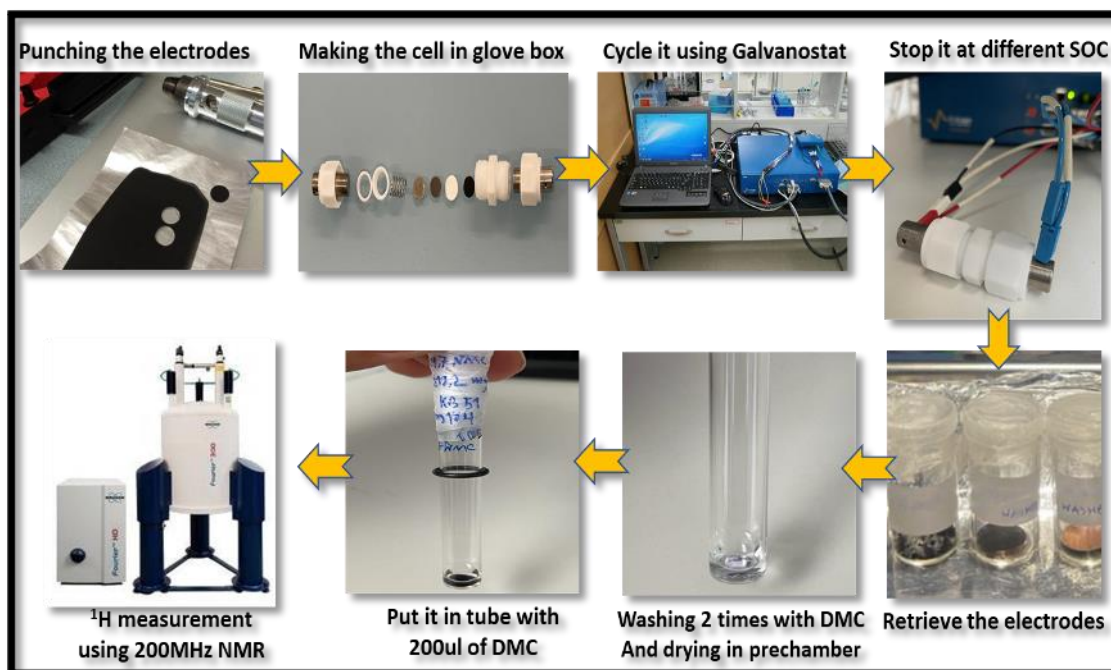


Figure 11 RMN *ex situ* du ^1H en solution : protocole de préparation d'échantillons DMC/électrode.

La figure 12 présente l'effet des cathodes paramagnétiques NMC 622 arrêtées à différents SOC sur le signal RMN ^1H du DMC de référence. Un *shift* et un élargissement importants sont observés, qui semblent liés à l'état de charge.

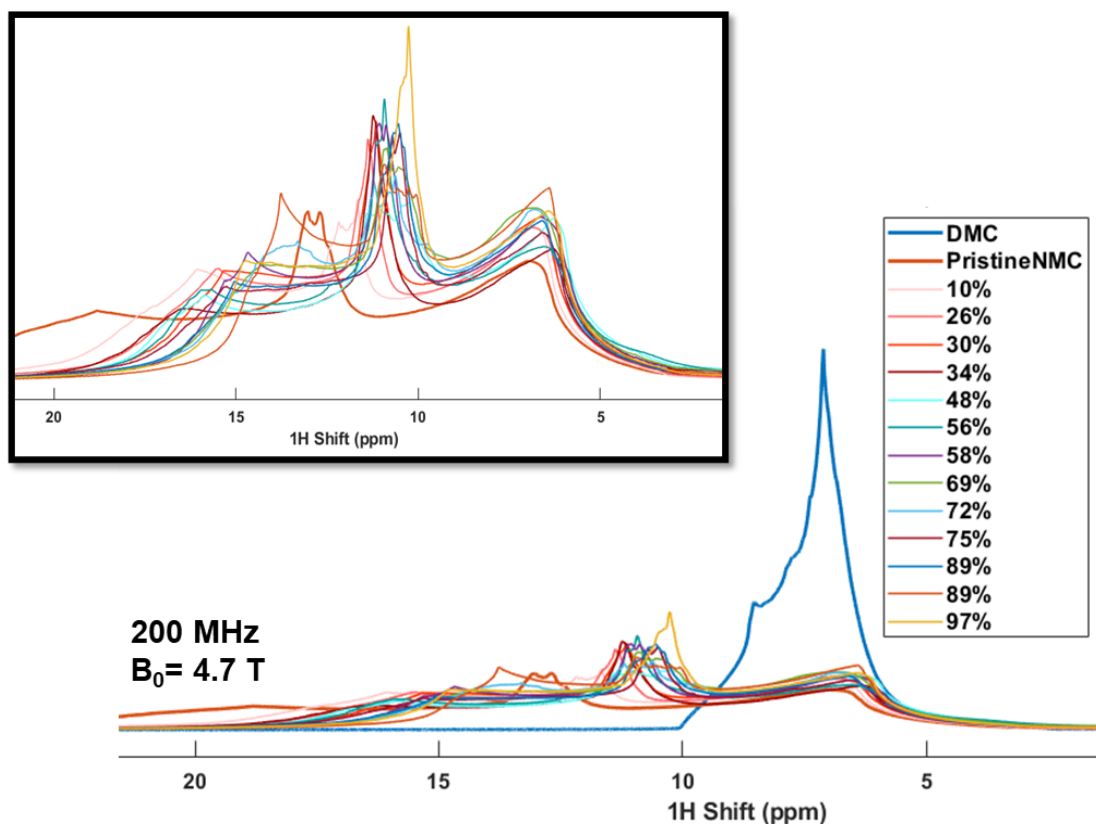


Figure 12 Signal ^1H du DMC en présence de cathodes NMC 622 à différents SOC.

Dans la figure 13, le *shift* moyen présente une tendance descendante avec l'augmentation du SOC, ce qui correspond à l'oxydation de l'électrode NMC 622 et au processus de délithiation. Cependant, la deuxième moitié de charge montre une sensibilité moindre à l'état. Le *shift* est donc plus sensible au changement de la susceptibilité magnétique au début de la délithiation.

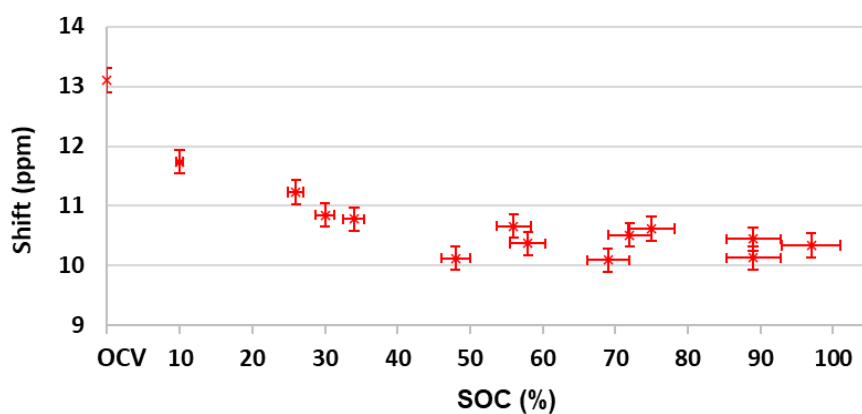


Figure 13 Effet de la variation du SOC des électrodes NMC sur le shift des spectres DMC ^1H .

Une tendance descendante est également observée pour la largeur de raie lors de l'oxydation de l'électrode NMC622 (processus de délithiation) dans la deuxième partie de la charge. Dans la première moitié de la charge, la tendance n'est pas monotone.

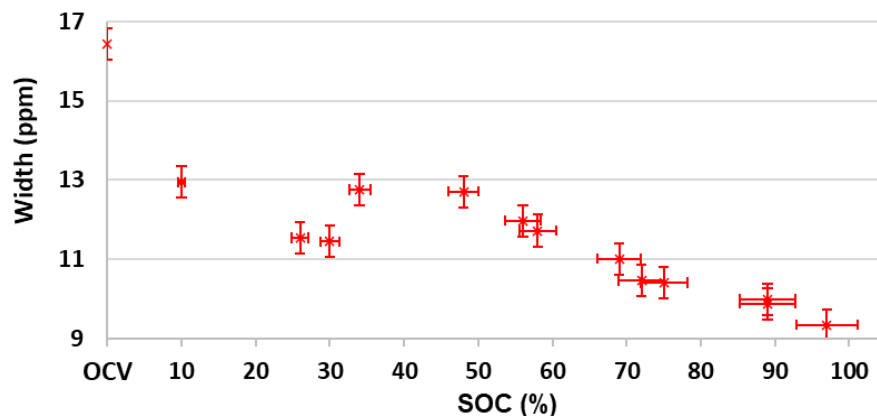


Figure 14 Effet de la variation du SOC des électrodes NMC sur la largeur des spectres DMC ¹H.

Le même protocole est utilisé pour décharger les cellules, extraire les électrodes et mesurer le spectre RMN ¹H. La comparaison entre les différents états de charge (SOC) et de décharge (SOD) des électrodes NMC est présentée dans les figures 15 et 16. Le comportement en charge et en décharge est similaire pour le *shift* et la largeur de raie, en accord avec la réversibilité des processus de charge-décharge dans ces cellules. La corrélation entre la variation du *shift* et la variation du SOC et SOD est plus forte que la largeur. Le *shift* moyen du DMC en RMN ¹H est donc le meilleur descripteur de l'état d'oxydoréduction de l'électrode.

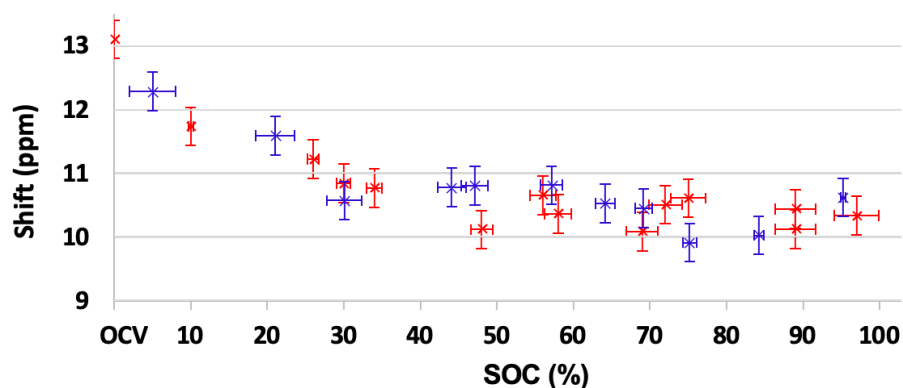


Figure 15 Comparaison de l'effet des électrodes NMC sur le shift du signal ¹H du DMC à différents SOC (rouge) et SOD (bleu).

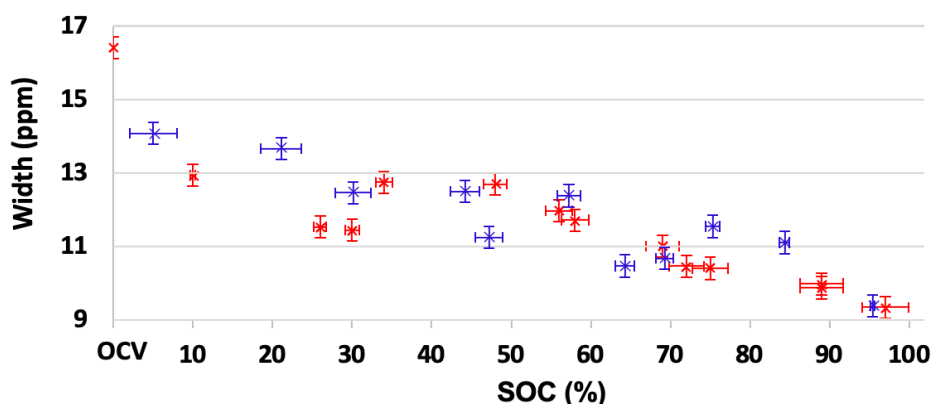


Figure 16 Comparaison de l'effet des électrodes NMC sur la largeur du signal ^1H du DMC à différents SOC (rouge) et SOD (bleu).

La même tendance de *shift* et de largeur des signaux ^1H du DMC est observée pour les cathodes LFP à différents SOC et SOD, confirmant la généralité des observations précédentes. Par contre, le spectre RMN ^1H du DMC en contact avec des électrodes de graphite présente une très faible sensibilité aux changements de leur SOC ou SOD. Par conséquent, nous pouvons considérer que la mesure RMN ^1H de l'électrolyte dans la batterie complète nous informera principalement sur l'état redox de l'électrode positive. Cette section élargit aussi les applications aux batteries Na-ion. La détection par RMN ^1H de l'électrolyte est encore plus avantageuse dans ce cas, car le ^{23}Na est moins sensible que le ^7Li et présente un élargissement à l'état solide et une relaxation accélérée en raison de son caractère quadripolaire.

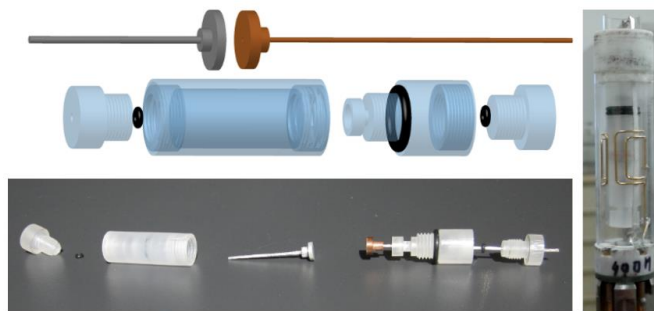


Figure 17 La cellule électrochimique Kel-F in situ , Copyright 2014 American Chemical Society.¹⁰

Enfin, les mesures *operando* ont été effectuées à l'aide de cellules *in situ* fabriquées à partir de matériau Kel-F (figure 17), spécialement conçues dans le laboratoire du CEMHTI pour les mesures RMN. L'assemblage de ces cellules a été réalisé dans une boîte à gants remplie d'Ar, avec des niveaux d'eau et d'oxygène

maintenus en dessous de 1 ppm. La cellule est assemblée avec une électrode positive NMC 622 (5 mm de diamètre), une électrode négative de graphite, un séparateur en fibre de verre de 6 mm de diamètre et 200 μl de LP30. Les cellules *in situ* ont été soumises à des cycles de charge-décharge identiques aux études *ex situ* en cellule Swagelok, à une vitesse de charge de C/10, à température ambiante et sous atmosphère N_2 , sur une plage de tension allant de 2,7 V et 4,2 V. La tension a été maintenue pendant les périodes de CV jusqu'à ce que le courant soit inférieur à C/50.

La figure 18 montre, pendant le 5e cycle, l'évolution des spectres ^1H successifs provenant de l'électrolyte à l'intérieur de la cellule, après soustraction du spectre ^1H initial (obtenu en OCV, avant le début de charge). Le statut électrochimique de chaque spectre est indiqué par des points (signes en croix) dans le profil de courant en fonction du temps sur la figure 18 à droite (en orange).

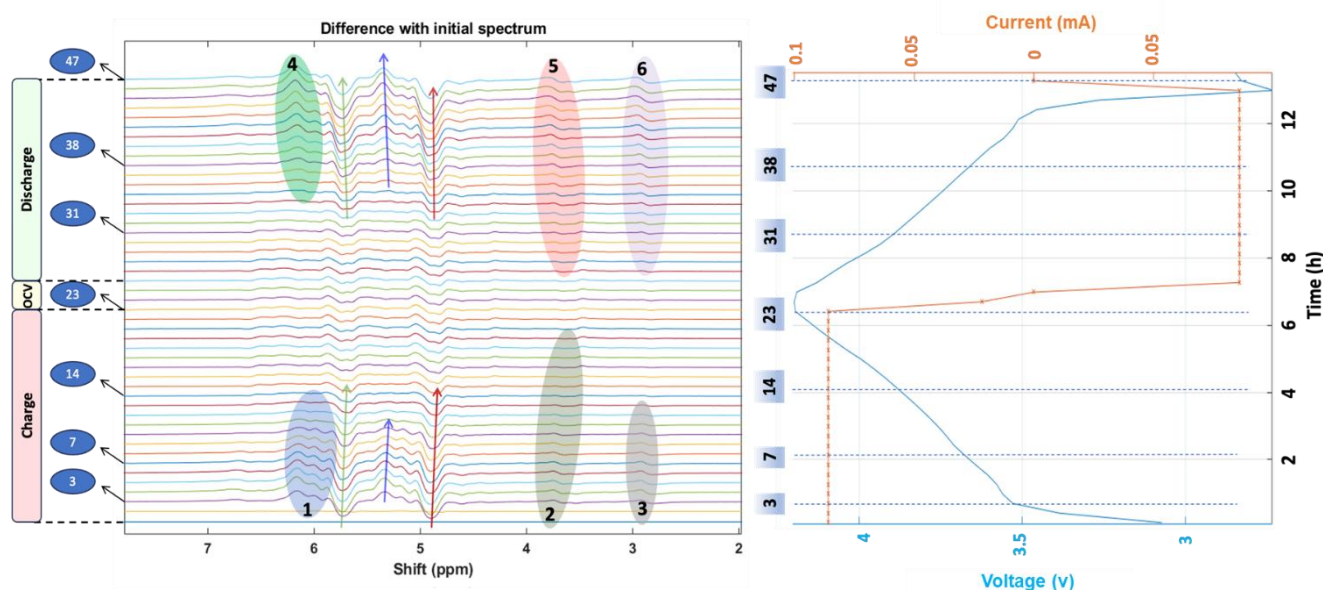


Figure 18 Empilement de spectres ^1H de l'électrolyte (au 5ème cycle) après soustraction du 1er spectre (gauche) et profil de tension-courant (droite) au 5ème cycle.

Sur la figure 18 gauche, une altération notable (décalage) du signal ^1H est observée à partir du spectre 3 ($\sim 3,54$ V), principalement pour les deux pics principaux à 5,1 et 5,9 ppm. Nous supposons que cette altération du signal est due à un changement significatif de la susceptibilité magnétique locale dans la batterie, principalement attribuée à l'altération de l'état redox de l'électrode NMC. Ce décalage du pic

subsiste dans les spectres suivants pendant le processus de charge jusqu'à environ 3,8 V (spectre 14), bien qu'il diminue progressivement et se décale légèrement vers la droite (indiqué par les flèches).

En charge entre 3,8 V et 4,2 V, durant l'étape de CV à 4.2 V, et entre 4,2 V et 3,9 V lors de la décharge, les altérations des spectres sont minimales. Cependant le décalage inverse apparaît lorsque la tension diminue jusqu'à 2,8 V pendant la lithiation de la cathode NMC (décharge). Les spectres affichent un léger décalage vers la gauche, comme le souligne la flèche colorée en haut de la figure. Ce phénomène est conforme à un effet de susceptibilité magnétique découlant de l'état d'oxydoréduction de la NMC, puisqu'il est inversé en charge et en décharge.

De plus, nous observons de légères altérations dans les spectres ^1H sur les côtés gauches et droits des pics principaux, mises en évidence par des ellipses colorées numérotées 1, 2 et 3 (4, 5 et 6 en décharge). Ces changements, à l'exception des zones 1 et 4, sont minimes et tendent à s'atténuer à mesure que la tension augmente pendant la charge. Dans la zone 1, cependant, cette altération est plus importante, avec un léger déplacement vers la droite pendant la charge. Pendant la phase de décharge, ces altérations des spectres ^1H réapparaissent, plus prononcées et plus visibles dans la zone 4. La zone 4 présente une distorsion croissante et un déplacement vers la gauche à mesure que la tension diminue pendant la décharge.

Là encore, les variations sont globalement symétriques par rapport au sommet de charge et valident notre hypothèse selon laquelle les ^1H du signal de l'électrolyte sont sensibles aux changements des états redox de l'électrode positive. L'état en fin de décharge n'est cependant pas strictement identique à l'état avant charge, ce qui est attendu étant donné que l'efficacité coulombique n'est pas de 100%.

En conclusion, ce chapitre montre que les changements de l'état redox et de la susceptibilité magnétique de différentes électrodes positives se reflètent effectivement dans le signal RMN ^1H très sensible du solvant DMC en contact avec ces électrodes, comme l'indiquent les décalages et les changements de largeur observés. Notamment, la corrélation entre les décalages RMN et les changements dans le SOC et le SOD est plus forte qu'avec la largeur du signal, ce qui fait du décalage RMN moyen un indicateur plus fiable de l'état d'oxydoréduction de l'électrode. Par contre, lorsque le signal RMN ^1H de la DMC interagit avec des électrodes de graphite négatives, la sensibilité aux variations de SOC ou de SOD est significativement réduite.

Enfin, les mesures RMN ^1H *operando* sur un électrolyte LP30 dans une cellule complète NMC//LP30//graphite en fonctionnement pendant le 5ème cycle révèlent une sensibilité aux changements d'état redox et à la susceptibilité magnétique locale. Cette sensibilité, bien que réduite, montre des tendances en termes de décalage et de largeur du signal en accord avec les mesures *ex situ*.

8. Conclusion

La détermination de l'état de charge (SOC) des batteries est essentielle pour évaluer l'énergie disponible et prévoir la durée de vie des appareils. Cependant, les méthodes existantes de détermination de l'état de charge se heurtent à des difficultés considérables. Notre étude examine l'application de la RMN *operando* pour surveiller les changements dans les propriétés magnétiques des batteries en tant qu'indicateurs de l'état de charge.

Notre étude s'est concentrée sur les changements de susceptibilité magnétique locale influencés par les réactions redox à l'intérieur de la batterie. Au lieu d'examiner directement les atomes de lithium, nous avons analysé le signal ^1H du solvant de l'électrolyte liquide. Ce signal est influencé par l'état d'oxydation des électrodes, ce qui permet d'obtenir des informations détaillées sur les processus électrochimiques et d'identifier les sources de perte de capacité.

Notre étude détaillée a révélé que les pastilles de LFP induisent une distorsion significative du signal ^1H de la DMC par comparaison avec le LMO, le NMC et le LCO, en raison d'une susceptibilité magnétique plus élevée. La distorsion résultante, quantifiée par le déplacement, la largeur spectrale, le temps de relaxation T_1 et la surface, démontre la faisabilité de la détection des variations de susceptibilité magnétique via le signal RMN ^1H du DMC.

Nous avons également évalué l'influence de divers composants de la batterie sur le signal ^1H , et avons observé un impact négligeable par rapport à celui de l'électrode positive paramagnétique NMC 622. En utilisant un tube PEEK RMN développé spécialement pour ce travail, nous avons évalué les effets de la forme et de la planéité de l'électrode sur le signal ^1H . La comparaison a montré une distorsion notable des signaux de protons près de l'électrode LFP, attribuée à la susceptibilité magnétique et aux effets d'interface.

Les résultats de la RMN *ex situ* indiquent que le signal ^1H de la DMC est sensible aux variations de l'état redox des électrodes. Les changements de SOC et de SOD des électrodes NMC affectent considérablement le spectre RMN ^1H , le *shift* étant le plus efficace descripteur pour déduire l'état redox. Les résultats de la RMN *Operando* ont confirmé la sensibilité aux changements du signal ^1H de l'électrolyte pendant le cycle, ce qui est consistant avec les observations *ex situ*. L'utilisation de la RMN ^1H améliore considérablement la sensibilité et la résolution temporelle, ce qui sera crucial pour étudier les comportements de cyclage rapide.

Les résultats de cette thèse démontrent également que cette approche peut être étendue aux batteries Na-ion. L'utilisation de la RMN ^1H pour détecter les changements dans l'électrolyte est particulièrement avantageuse

dans ce cas puisque le ^{23}Na est moins sensible que le ^7Li et qu'il présente un élargissement à l'état solide lié à son caractère quadripolaire. Notre approche offre la possibilité d'identifier les origines de la perte de capacité et de corréler le SOC avec des marqueurs électrochimiques tels que la tension, la rétention de capacité et l'efficacité coulombienne. Ces résultats pourraient être intégrés dans des systèmes de gestion de batterie afin de mieux prédire la capacité à venir et de prévenir les défaillances.

9. Perspectives

Mesure *ex situ*:

Nous avons optimisé la conception d'une cellule Swagelok pour des électrodes de 8 mm de diamètre, améliorant ainsi la reproductibilité et la compatibilité avec les mesures de tubes RMN à l'état liquide. Cette amélioration réduit l'incertitude des futures mesures SOC. La nouvelle conception du tube en PEEK offre un meilleur contrôle de la géométrie de l'interface électrode/DMC, ce qui augmente la précision de la comparaison des électrodes à différents états redox.

Nous avons observé une tendance dans les déplacements de la RMN ^1H avec le SOC et nous proposons d'étendre cette étude à d'autres chimies de batteries (par exemple, LFP//LiPF₆//Graphite, NVPF//NaPF₆//HC) pour obtenir de meilleures statistiques. Nous suggérons également d'utiliser la magnéto-métrie VSM ou SQUID pour corréler la susceptibilité magnétique des électrodes avec les mesures RMN ^1H *ex situ*, en assurant une préparation attentive des échantillons. De plus, l'extension de l'étude T_1 de la DMC ^1H en contact avec divers matériaux peut révéler des distributions locales de champ magnétique à différentes distances des électrodes.

Analyse des données:

Le développement d'un modèle analytique pour quantifier la distorsion du signal RMN causée par les effets de la susceptibilité magnétique peut améliorer notre compréhension de l'élargissement et des changements de forme du signal. L'analyse actuelle mesure des moyennes pondérées des *shifts* et des largeurs à différentes hauteurs de signal. En nous concentrant sur le pic unique et net du DMC, nous visons à corréler la forme du signal ^1H avec les états redox de la batterie, ce qui pourrait aider au développement d'un modèle pour les signaux à différents états de charge.

Mesure *Operando*:

Nous proposons également d'étendre notre approche de mesure *operando* à d'autres systèmes de batteries, notamment les batteries Na-ion, pour lesquelles enregistrer la RMN du ^{23}Na *in situ* est un challenge. L'ajustement des délais de recyclage pendant les mesures *operando* permettrait de sélectionner des environnements DMC spécifiques près des électrodes. L'imagerie de déplacement chimique peut localiser les zones proches des électrodes dans l'espace en jouant sur les différences de relaxation.

Notre approche est assez sensible pour suivre les changements de SOC au cours d'un seul cycle de charge-décharge. Les étapes futures pourraient être des mesures *operando* sur plusieurs cycles pour suivre l'évolution de l'état redox des électrodes positives, qui peut différer de la SOC déterminée par des mesures galvanostatiques ou de l'efficacité coulombienne. Cette méthode est prometteuse pour étudier l'imprégnation des électrodes par l'électrolyte et les réactions parasites entre les électrodes et les électrolytes. Nous visons également à analyser les effets de différents additifs d'électrolyte.

Chapter 1 General Introduction

Global warming and climate change highlight the critical necessity for the sustainable replacement of fossil fuels, in which renewable energy sources play a key role. However, the use of renewable energy sources, such as solar, wind, wave energy, presents significant challenges in terms of efficient storing and supply of energy. Their intermittency can result in instabilities in the energy supply, making it challenging to meet the demands of the electricity grid. Simultaneously, the drive towards vehicle electrification requires compact and lightweight energy storage solutions capable of supplying the required power for acceleration and the energy capacity for long travel distances. In this context, rechargeable batteries offer a promising advantage due to their ability to store and provide green energy, through reversible chemical reactions which convert chemical energy into electrical energy. This advantage introduces batteries as a turning point and crucial technology for reducing environmental impacts and greenhouse gas emissions.

The lithium-ion battery (LIB) technology, commercialized by Sony in 1991, quickly captured the public attention with rapid growth of the industry for electric cars and portable electronic products, and became a focal point of interest for the energy transition. Batteries are sophisticated multicomponent systems with complex interactions defining their performance. Getting insight into the behavior of every battery component and the interplay of these components on the global electrochemical performance is a challenging investigation.

Among the different methods used for these investigations, *in situ* and *operando* Nuclear Magnetic Resonance (NMR) characterization methods are promising since, without destroying the battery, they enable monitoring of the processes, local structural changes, and short-lived metastable or reactive phases at various steps of the electrochemical charge. This is critical to understanding the cycling and degradation processes and increasing their electrochemical performance, especially in abusive conditions like during fast charges. Besides, knowledge of the redox state of each electrode separately is essential to identify the origins of capacity loss in full batteries.

Herein, our efforts are focusing on advancing these methods and developing a new NMR approach for the characterization of operational batteries (*operando*) and comprehensive study for tracking the electrode state of charge (SOC) in LIBs and sodium-Ion Batteries (SIBs). Up to now, most

operando NMR studies have focused on ^7Li NMR spectroscopy to follow the lithiation and degradation processes in the solid electrodes of LIBs. We explore how the ^1H *operando* NMR signal of the liquid electrolyte solvent can be exploited to follow the electrode evolution while benefiting from the high sensitivity of ^1H liquid-state NMR compared to ^7Li NMR.

We exploit the sensitivity of the ^1H NMR signal of the electrolyte molecules to the magnetic susceptibility of the neighboring particles of positive electrode active material, in the context of a $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622)/ LiPF_6 //graphite battery. Our ultimate goal is to characterize the spatial and spectral dependence of the electrolyte signal in the whole battery, during the charge and the discharge and use it as a fingerprint of the battery state through the induced changes in magnetic susceptibility. A brief overview of this work is presented below.

Chapter 2 deals with the principles of energy storage and batteries. More particularly, it includes a brief presentation of LIBs and SIBs, supplemented by a review of the state-of-the-art in determining the state of charge of batteries.

In Chapter 3, we provide a brief review of the theory and concepts of NMR and its various techniques, particularly those necessary to understand this work. This is complemented by an overview of the related work in the state-of-the-art *in situ/operando* NMR characterization of batteries.

Chapter 4 delves into the concept of magnetic susceptibility and the magnetic properties of positive active materials, exploring the connection to their oxidation state. This is followed by a literature overview of the impact of paramagnetism on the NMR and how it can alter the NMR signal.

Chapter 5 explains the strategy employed to determine the effect of battery components, including separators, current collectors, active materials, and commercial electrodes: We identified the descriptors of the ^1H NMR spectrum of the electrolyte solvent (dimethyl carbonate, DMC) that are relevant for this approach. These experimental results enabled us to check the sensitivity of our approach to electronic structure and the magnetic susceptibility of the materials. Finally, a specifically designed tube was used with chemical shift imaging (CSI), a technique to obtain localized NMR spectra. We analyzed the spatial origin of the components in the ^1H NMR spectrum of the liquid perturbed by the material.

In Chapter 6, we expand this experimental approach to *ex situ* NMR, using electrodes extracted at various states of charge. We outline the protocol and the sample preparation for the *ex situ* NMR characterization and validate the sensitivity of the ^1H NMR spectrum of liquid DMC to the state of charge of the positive electrode. This approach is then extended to another battery system with LiFePO_4 as a positive electrode. This chapter finally details the first *operando* NMR measurements using this approach and the insights that can be gained into the redox state of the electrodes inside the functioning battery.

In conclusion, we present the perspectives provided by this work and propose a range of potential applications that could benefit from our approach.

Chapter 2 Electrochemical storage in batteries

2.1 Introduction

Electrochemical energy storage devices like batteries and supercapacitors have played a crucial role in the energy revolution, changing how we power our portable electronic gadgets. In this chapter, we will briefly describe the theory behind electrochemical batteries, how the battery experiences reversible electrochemical reactions and all the basic principles for understanding it. Next, we will explore the significance of determining the state-of-charge within a battery and addressing the challenges that come with it.

2.2 Basic principle of electrochemical energy storage and reversible electrochemical reactions in batteries

A battery is a device that can store energy and release it when it is needed. A primary cell or battery (galvanic cell) is one that stores energy in chemical form and releases it in electrical form. These cells are intended for a single-use and cannot be recharged due to non-reversible electrochemical reactions occurring inside them.

However, secondary batteries can store chemical energy by transforming electrical energy (during charge). They are also capable of reversing this reaction, which enables them to undergo multiple charge and discharge cycles. These processes are facilitated through electrochemical reactions known as redox reactions, which involve the transfer of electrons between electrode materials across the electrolyte, potentially accompanied by ion exchange.

In order to compare the operational performance of various energy storage and conversion devices, it is common to examine the graph of specific power density (W/kg) plotted against specific energy density (Wh/kg), known as a Ragone plot (figure 2-1). This plot illustrates the specific energy and power at a cell level for different types of batteries, from consumer electronics to electric vehicles (EV). Energy and power are two requests from battery users, the first one gives the autonomy of the powered device while the second one gives the rate of charge and discharge. It is usually difficult to enhance one side without losing on the other side.

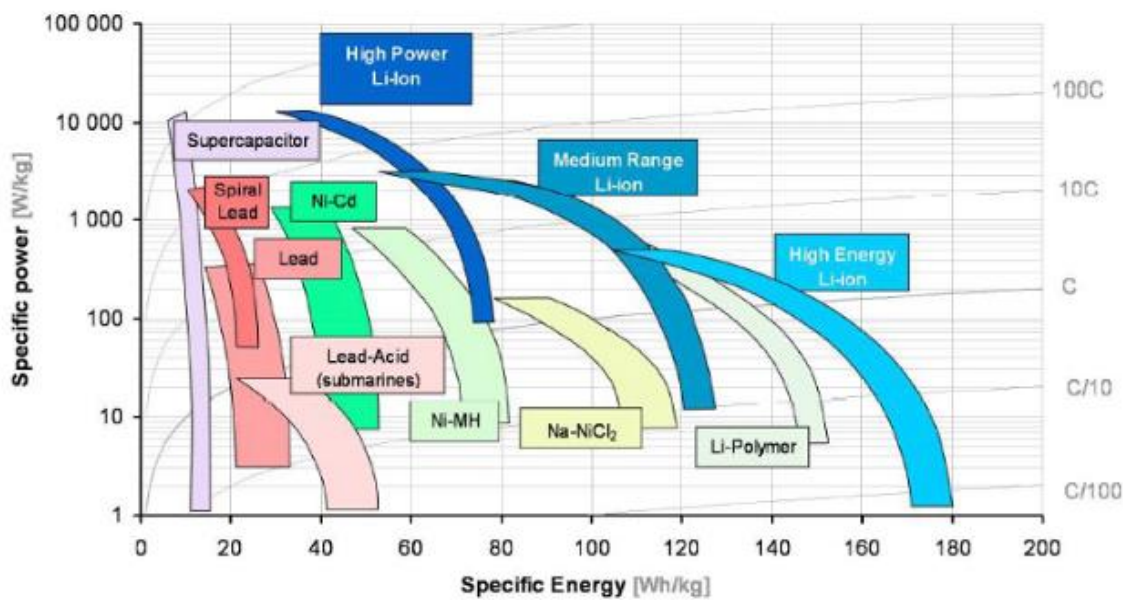


Figure 2-1 Ragone plots used to compare various cell chemistries and alternative energy storage devices.¹¹

Oxido-reduction half-reactions, known as redox half-reactions, represent fundamental electrochemical mechanisms involving the electron exchange between reactants. During an oxidation half-reaction, a substance (reducer) undergoes electron loss, leading to an increase in its oxidation state. In contrast, within a reduction half-reaction, a substance acquires electrons (oxidizer), leading to a reduction in its oxidation state. These half-reactions are an essential part of redox reactions, where one substance undergoes oxidation while another undergoes reduction, mediated through electron transfer and enabling the conversion of chemical energy into electrical energy and vice versa.



In Equation 1, species A experiences oxidation through the loss of two electrons, leading to the creation of A^{2+} ions. Simultaneously, in Equation 2, species B^{2+} undergoes reduction by gaining two electrons, resulting in the formation of B. These species form an oxidizing-reducing pair which is known as a redox couple.

The Nernst equation can be used to calculate the equilibrium potential of a redox couple which is as follows:

$$E = E^{\circ} - \frac{RT}{nF} \ln(Q) \quad \text{Equation 3}$$

The Nernst equation represents the relationship among the standard electrode potential (E°), the actual electrode potential (E), Faraday's constant (F), the gas constant (R), absolute temperature (T), the number of electrons exchanged in an electrochemical reaction (n), and the reaction quotient (Q), which signifies the ratio of products activities to reactants activities.

The potential of an electrode is determined by the active redox couples it contains and to provide a preliminary estimation of its redox activity, the standard potential E° is commonly used. This potential is acquired under standard conditions (pressure at 1 atm and temperature at 25°C, pure solid phases, or concentrations equal to 1M...), with $Q=1$. Changing the Nernst equation into the following equation, as the activities of species are standardized to 1;

$$E = E^{\circ} \quad \text{Equation 4}$$

Under these standard conditions, the electrode potential becomes equal to the standard electrode potential. Potentials are defined in the International System against the standard hydrogen electrode (NHE).

In the field of Lithium-ion batteries (LIBs), the potential is commonly referenced relative to the Li^+/Li couple, which has the lowest available potential and results in potentials that are always positive and easier to handle, with Li^+ activity approximately equal to 1 when $[\text{Li}^+] = 1 \text{ mol/L}$ and the activity of the solid metallic lithium also equal to 1. Figure 2-2 shows the standard electrode potentials (E°) for some of the materials used in LIBs.

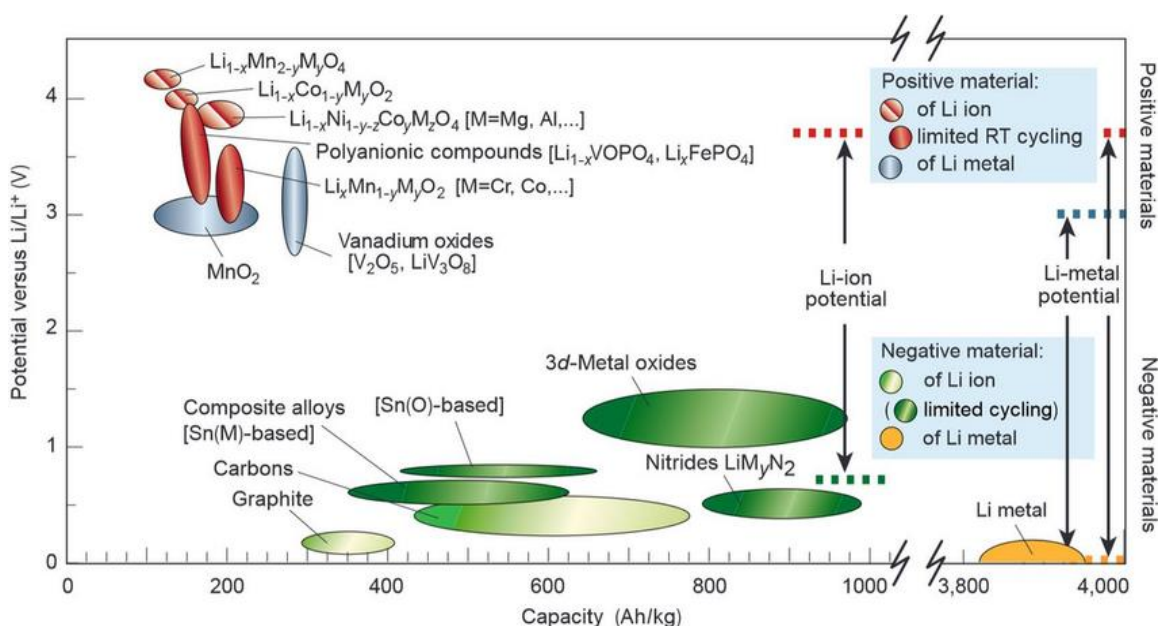


Figure 2-2 Example of standard potentials for LIB electrode materials.¹²

2.2.1 Secondary electrochemical cell: redox reactions

As mentioned earlier, an electrochemical cell operates by employing an oxidizer and a reducer that undergo a thermodynamically favored oxidation-reduction reaction during discharge. When these substances are in contact with each other, electron exchange occurs, leading to reduction and oxidation reactions. Through forcing electron exchange via an external circuit, an electrochemical cell is obtained where two electrodes are separated to prevent direct electron exchange. Instead, the balance of charges is achieved through ion migration facilitated by the electrolyte between the electrodes.

Upon discharging the cell, two electrochemical reactions occur simultaneously: oxidation at the anode and reduction at the cathode. The anode undergoes oxidation, resulting in the release of electrons (and sometimes cations), while the cathode accepts these electrons (to retain charge neutrality) and cations to undergo reduction. Ion movement takes place within the electrolyte while electrons are gathered by metallic current collectors and conducted through the external circuit. Once the electrodes are electrically linked, this thermodynamically favored redox reaction starts and facilitates the transfer of electrons and ions.

However, upon battery charging process, which involves the reversal of the electrochemical reactions, energy in the form of current is supplied to counter the natural thermodynamic tendencies. Therefore, reduction now occurs at the anode, where electrons are accepted, while oxidation occurs at the cathode, where electrons are released.

This transformation of electrical energy into chemical energy necessitates an external source of electrical energy which will be provided by an external generator connected to the cell, known as the load. This additional energy input ensures that the electrons migrate against their thermodynamically favored direction which facilitates the storage of electrical energy in the battery in the form of potential energy.

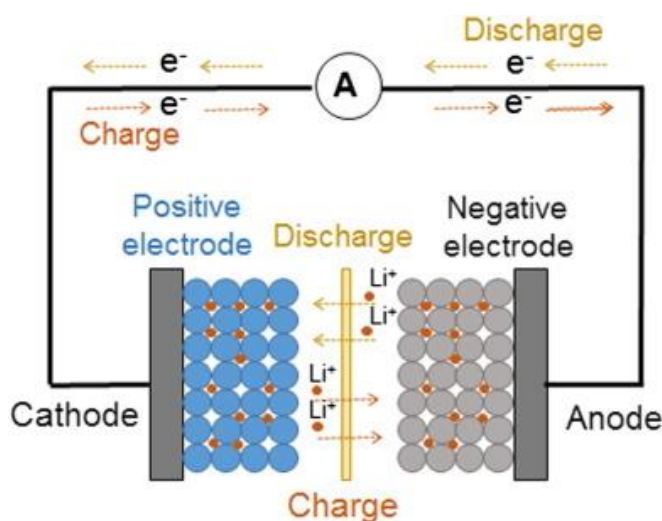


Figure 2-3 Schematic of electrochemical LIB operation during charge and discharge. Upon discharging of the cell, the lithium ions move through the electrolyte and intercalate into the cathode. While upon charging, the ions move back into the electrolyte.¹

Batteries are usually defined by their voltage, expressed in volts (V), which represents the electric potential difference between their positive and negative terminals (equation 5).

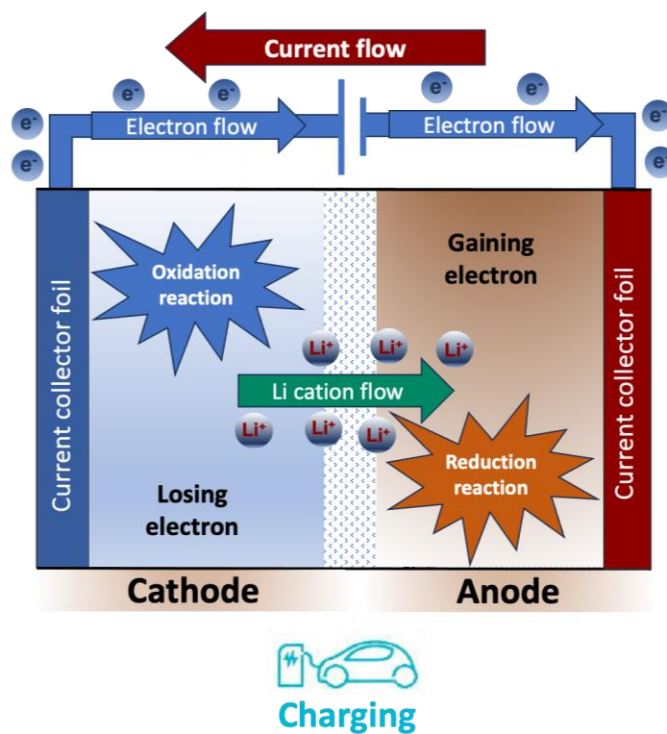
$$E_{cell} = E_{positive} - E_{negative} \quad \text{Equation 5}$$

The cell voltage (E_{cell}), also known as the electromotive force (emf), is a measure of the energy available per unit of charge, indicating the force that drives the flow of electrons through an external circuit.

2.2.2 Operating principle

The amount of charge stored within a cell is dependent on both the potential difference generated by electrochemical reactions at the two electrodes, as well as the quantity of electrons engaged in each of these reactions. It is possible to enhance the stored charge or system capacity by either increasing the potential difference between the electrodes or by employing ions involving multiple electrons. Both elements are controlled by the mechanism through which the transfer of charge occurs.

Intercalation of ions into layered materials, like graphite or transition metal oxides, is widely employed in ion batteries as a charge transfer method which involves inserting or extracting ions within the interlayer spaces of these layered structures¹³. This process does not typically alter the host structure, except for a disturbance in the interlayer spacing¹⁴. This insertion or removal of ions is termed intercalation or deintercalation. The energy change during this process is facilitated by charge transfer between the host ion and the guest structure, commonly through a redox reaction. In the following we present the redox reaction in Li-ion cell composed of NMC//1M LiPF₆//graphite.

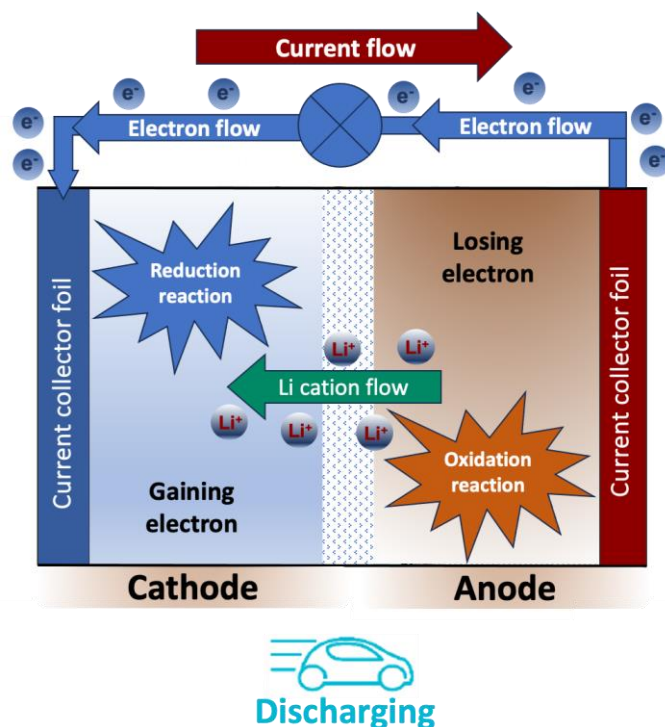


Positive electrode : $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2 \rightarrow \text{Li}_{1-k}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2 + k\text{Li}^+ + k\text{e}^-$

Negative electrode: $\text{C}_6 + k\text{Li}^+ + k\text{e}^- \rightarrow \text{Li}_k\text{C}_6$

Complete reaction: $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2 + \text{C}_6 \rightarrow \text{Li}_{1-k}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2 + \text{Li}_k\text{C}_6$

Figure 2-4 Principle of operation of an NMC/Graphite full battery during charging.



Positive electrode: $\text{Li}_{1-k}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2 + k\text{Li}^+ + k\text{e}^- \rightarrow \text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$

Negative electrode: $\text{Li}_k\text{C}_6 \rightarrow \text{C}_6 + k\text{Li}^+ + k\text{e}^-$

Complete reaction: $\text{Li}_{1-k}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2 + \text{Li}_k\text{C}_6 \rightarrow \text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2 + \text{C}_6$

Figure 2-5 Principle of operation of an NMC/Graphite full battery during discharge.

2.3 Contents of commercial Li-ion and Na-ion batteries

Nowadays, battery technologies offer a wide range of applications, from powering devices like smartphones and electric vehicles to medical equipment and renewable energy storage. Common rechargeable batteries, such as lead-acid batteries, nickel-metal hydride (Ni-MH) batteries, and LIBs, have each played crucial roles in powering various devices and applications. In this thesis, we focus mostly on lithium and sodium-ion batteries (SIBs).

2.3.1 Battery components

The primary research in the field of battery focused on the chemistry of electrode active materials, as they play a crucial role in enhancing energy density. However, these active materials, alone, are

insufficient for the proper operation of a Li-ion or Na-ion cell. Effective operation of a battery requires the presence of various components including two separate electrodes (cathode and anode), an electrolyte, a separator, and current collectors. The separator and current collectors are inert but ensure that the electric current goes through the external circuit for charge and discharge. The other components are collaborating in an interactive electrochemical process that is constantly undergoing structural and chemical changes upon cycling. Therefore, the selection and optimization of its components are crucial in determination of battery efficiency and performance.

In the following section, we aim to provide a brief overview of batteries (mainly LIBs) and the different cell configurations.

2.3.1.1 Electrodes

Electrode materials in battery technology contain active material, a binder, a solvent, and additional additives aiming to enhance performance.

The active materials, such as transition metal oxides, graphite, or hard carbon, are responsible for the redox reactions and are fundamental to battery operation. In Li-ion and Na-ion technology, there is now a wide variety of materials available serving as positive and negative active materials.

2.3.1.1.1 Positive active materials

Positive electrodes for LIBs can be classified into several common types based on their chemical composition and crystal structure. The most common categories include layered oxides, spinels, lithium phosphates or composite materials.

Regarding SIBs, we can mention layered oxides (NaMO_2 , $M = \text{Mn, Ni, Fe and Co}$), polyanionic compounds (NaFePO_4 , $\text{Na}_2\text{FeP}_2\text{O}_7$, $\text{Na}_2\text{CoPO}_4\text{F}$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$), Prussian blue analogues compounds and organic compounds¹⁵ as potential cathode materials.

In the following we provide an overview on some positive electrodes, mainly those that have been used in our study.

2.3.1.1.1.1 Lithium Cobalt Oxide (LiCoO_2)

The family of layered oxides with the chemical formula LiMO_2 (where $M = \text{Co, Mn, Ni}$) has emerged as the most extensively utilized and commercialized cathode materials for LIBs. LiCoO_2 (LCO), the progenitor of this LiMO_2 family, was initially proposed as an intercalation compound for rechargeable LIBs by Goodenough and Mizushima et al. in 1976¹⁶. In the early 1990s, Sony

Corporation successfully commercialized these materials¹⁷. LCO is the most used active cathode material for commercial LIBs. LCO has a nominal operating voltage of approximately 3.7 to 4.2 volts against 0 volts, depending on the specific battery design. This voltage range is suitable for various applications, as such electronic devices.

The crystal structure of LCO can exhibit two distinct types depending on the synthesis temperature. At lower temperatures (around 350 °C), a cubic spinel structure is formed, which undergoes a conversion to a layered trigonal (also referred to as hexagonal) structure at approximately 750 °C.¹⁸ The material with the layered lattice exhibits superior electrochemical performance compared to the cubic spinel lattice.

The crystal structure of layered LCO belongs to the rhombohedral space group ($R\bar{3}m$) (at ambient temperature) where lithium and cobalt ions are in octahedral 3a and 3b sites, respectively. These sites are separated by layers of oxygen ions arranged in a cubic close-packed arrangement. The unit cell of the layered LCO consists of three slabs of CoO_6 octahedra that share edges, with interstitial layers of lithium ions between them (Figure 2-6). This phase is also known as the O_3 phase, and it features an ABC...ABC stacking arrangement of the layers, with the alkali metal ion (Li) residing in the octahedral interstitial sites.

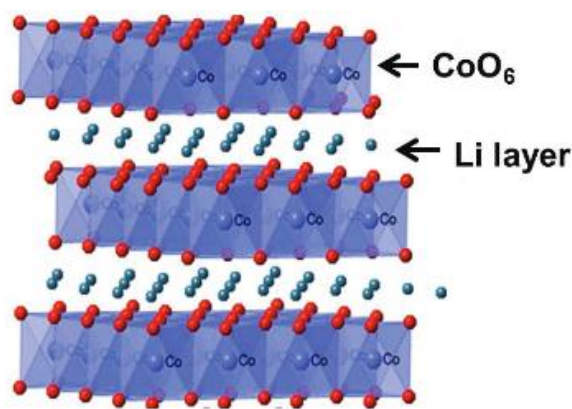


Figure 2-6 Crystal structure of LiCoO_2 .¹⁹

The crystallographic structures of the lithium oxide compounds often vary depending on the amount of lithium content. In its fully lithiated state, LCO maintains its layered structure with

hexagonal unit cells. During charging and upon removal of Li from the layered crystal lattice, nonstoichiometric $\text{Li}_{1-x}\text{CoO}_2$ compounds are formed upon the oxidation of Co^{3+} into Co^{4+} .

Notably, when approximately 50% of the lithium has been extracted from the parent structure, a structural transformation from the hexagonal phase to a monoclinic phase is observed¹⁹. During repeated cycling of lithium in the compositional range of $0.5 \leq x \leq 1$ in Li_xCoO_2 , the process of deintercalation and reinsertion of lithium ions occurs while maintaining the integrity of the layered structure^{20,21}.

The arrangement of electrons in LCO electronic structure affects its chemical reactivity, electrical conductivity, and magnetic behavior. The partially filled d orbitals of Co^{3+} contribute to the compound ability to undergo redox reactions and intercalate lithium ions during battery charging and discharging. The combination of Li^+ and Co^{3+} ions, along with the oxygen (O^{2-}) ions, forms a crystal structure in which lithium ions act as charge reservoirs, while cobalt ions facilitate the reversible insertion and extraction of lithium ions during the battery operation.

2.3.1.1.1.2 Lithium Iron Phosphate (LiFePO_4)

LiFePO_4 is a promising cathode material due to several advantageous properties, such as cost-effectiveness, abundant availability, low toxicity, low volume expansion, relatively high specific capacity, low-capacity fade, and high safety, as first reported by Padhi et al.²²

LiFePO_4 exhibits a flat discharge plateau at 3.4 V versus Li/Li^+ and approaches its theoretical capacity of 170 mAh/g.²³ As illustrated in figure 2-7, the structure of LiFePO_4 belongs to the space group $Pnma$, where Li, Fe, and P atoms occupy octahedral 4a, octahedral 4c, and tetrahedral 4c sites, respectively. Oxygen atoms adopt a slightly distorted, hexagonal close-packed arrangement. The FeO_6 octahedra are interconnected at their corners within the bc plane, while LiO_6 octahedra form a linear edge-shared chain parallel to the b direction. A FeO_6 octahedron shares edges with two LiO_6 octahedra and one PO_4 tetrahedron. The presence of PO_4 polyanions between the FeO_6 octahedra results in a significant reduction of electronic conductivity ($\sim 10^{-9}$ S/cm at room temperature).^{19,24}

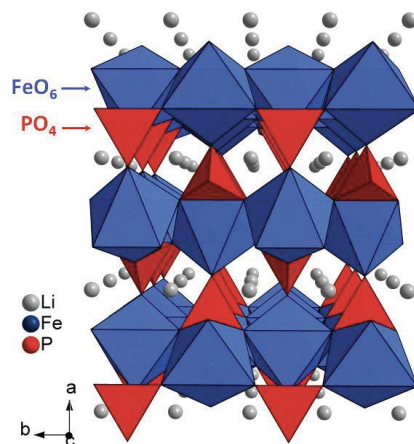


Figure 2-7 Olivine structure of LiFePO_4 ¹⁹.

The nature of Li ion transport and reaction mechanism in LiFePO_4 during lithiation and delithiation has been a subject of ongoing debate since the material initial discovery. It is widely accepted that Li ion transport in LiFePO_4 occurs in a 1D manner along the b-axis, as the Li ion diffusion energy is lower along this direction compared to others.^{25–27} However, the possibility of a 2D diffusion mechanism has also been proposed and remains a topic of discussion.^{28,29}

The Fe 3d states in Li_xFePO_4 adopt a high-spin configuration due to the relatively smaller crystal field splitting compared to the exchange splitting.^{30–33} As Li intercalates into the material, the iron 3d shell configuration undergoes a transition from a spin-saturated $3d^5$ to a $3d^6$ system. In the case of a half-filled high spin $3d^5$ setup, the d electrons align their spins following Hund's first rule, driven by a reduction in Coulomb energy when electrons of the same spin are kept apart by the exchange hole, a result of Pauli's exclusion principle. Consequently, in FePO_4 , five unpaired electrons per Fe^{3+} ion occupy the t_{2g} and e_g orbitals, all sharing the same (majority) spin state.

2.3.1.1.3 Lithium Manganese Oxide (LiMn_2O_4)

Spinel oxides with the chemical formula LiMn_2O_4 was first proposed as potential cathode materials for LIBs in the early 1980s, by Michael Thackeray.³⁴ These oxides offer several advantages over other cathode materials (such as LCO), including lower cost, environmental friendliness, and enhanced safety. The unique MnO_2 framework in the LiMn_2O_4 structure creates a 3D diffusion pathway for Lithium ions within the material, facilitating their movement during charging and discharging processes. In the LiMn_2O_4 oxide, the M cation (in this case, Mn) always occupies 1/4 of the octahedral sites in the lithium layer, resulting in 1/4 of the octahedral sites remaining vacant.

Lithium ions consistently occupy the tetrahedral sites and share faces with the empty octahedral sites in the transition metal (TM) layer. This specific arrangement of ions contributes to the overall stability and performance of LiMn_2O_4 as a cathode material for Lithium-ion batteries.

Figure 2-8 shows the structure of the typical LiMn_2O_4 . This material benefits from a 3D diffusion path that contributes to excellent rate capability, allowing for efficient Li-ion movement during charge and discharge processes. However, when cycled at elevated temperatures, LiMn_2O_4 experiences severe capacity fading.^{35,36}

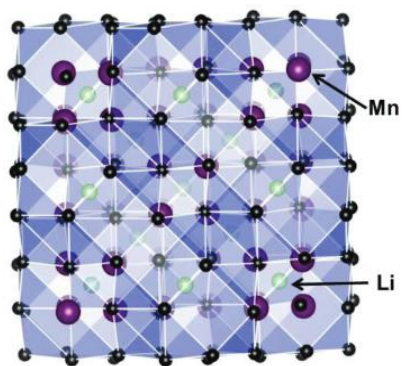


Figure 2-8 Crystal structure of LiMn_2O_4 .¹⁹

Despite the safety and low cost of these spinel oxides, they fall short in their practical capacity and energy density when compared to other cathode materials. Different strategies have been developed to suppress Mn dissolution and lower the capacity fading. Among these, doping (with dopants such as Ni, Mg, Al, Cr, Zn, Ti, Fe, Co, Ni, Cu, Nd, and La) has been very useful in enhancing the electrochemical performance of LiMn_2O_4 .³⁷

2.3.1.1.1.4 Lithium Nickel Manganese Cobalt Oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$)

The limited theoretical capacity of LCO, as one of the most common cathode materials, and the use of expensive and toxic Co have generated significant interest in developing alternative cathodes that offer higher capacities and improved safety features. In this regard, layered LiNiO_2 presents several appealing features compared to LCO, such as better chemical stability, cost-effectiveness, and lower toxicity due to the replacement of Co with Ni^{38,39}. However, LiNiO_2 has exhibited certain drawbacks, such as irreversible phase transitions and the exothermic release of oxygen in the

charged state at high temperatures.^{40,41} To address these challenges, extensive research has been conducted over the past decade to partially substitute the Ni with other metal ions.^{42,43}

$\text{LiNi}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ (NMC) compounds hold significant interest as they mix the advantages of Ni, Co, and Mn, as illustrated in Figure 2-9. Manganese contributes cost-effectiveness and thermal stability, nickel enhances capacity, and cobalt enhances the operational voltage, thereby yielding enhanced power characteristics.

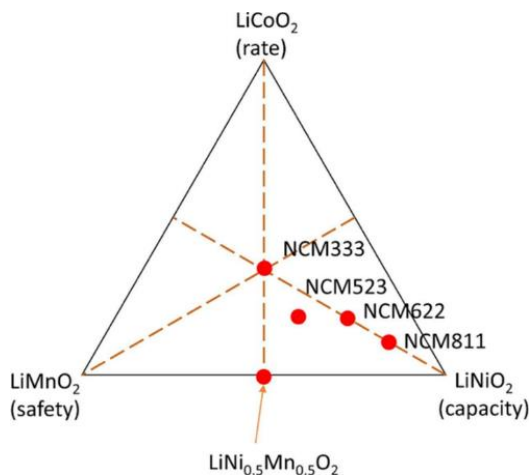


Figure 2-9 The ternary system phase diagram between LCO, LMO, and LNO with some representative compositions shown⁴⁴.

$\text{LiNi}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ compounds share the layered O3 structure with space group $R\bar{3}m$ (Figure 2-10) where the oxidation states of Ni and Mn are $2+$ and $4+$, respectively. Herein, Ni^{2+} serves as the electrochemically active ion, while the octahedrally coordinated Mn^{4+} ion, with its d^3 electronic configuration, contributes to the structure stability. However, due to the close similarity in the ionic radii of Ni^{2+} and Li^+ , there is considerable mixing of these ions, potentially impeding lithium diffusion and reducing electrochemical performance.^{45,7}

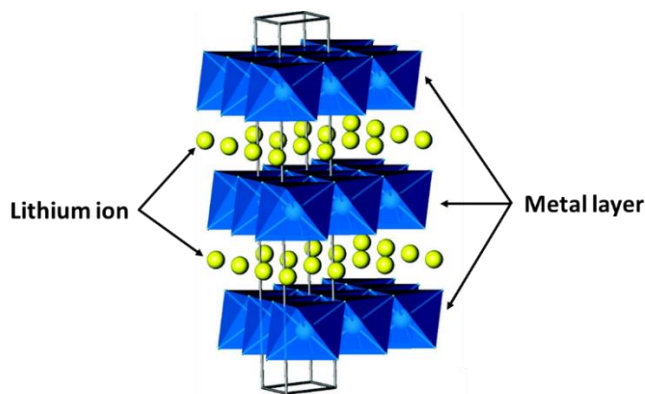


Figure 2-10 Structure of $\text{LiNi}_x\text{Mn}_x\text{Co}_{1-2x}\text{O}_2$, Copyright (2007) American Chemical Society.⁷

The layered $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC 111) has drawn significant attention due to its substantially higher capacity, approaching 200 mAh/g, and improved safety features.^{46–49} Electronic structure studies have shown the presence of Ni^{2+} , Mn^{4+} , and Co^{3+} in this compound. The reversible capacity involves the oxidation of Ni^{2+} to Ni^{4+} with a two-electron transfer during the initial stage and the oxidation of Co^{3+} to Co^{4+} in the later stage.^{50–52} As a result, the enhanced capacity of the layered NMC 111 may be attributed to the improved chemical stability associated with the $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$ redox couples when compared to the $\text{Co}^{3+/4+}$ redox couple.⁵³

$\text{LiNi}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$, specifically the Nickel-rich variant e.g., $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622), holds significant promise, particularly for electric vehicle applications. This is due to its ability to achieve high deliverable capacity (> 200 mAh/g), high energy density (~ 800 Wh/kg), good structural stability, good cyclability, and low cost. The higher capacity, primarily attributed to Nickel content in NMC622 materials, is a significant advantage. Additionally, cobalt presence helps in enhancing rate capability by mitigating Ni/Li ion mixing, while manganese contributes to structural and thermal stability.

2.3.1.1.1.5 Sodium vanadium fluorophosphate ($\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$)

Recently, SIBs have drawn significant attention as a promising energy storage solution for various applications. However, there are still unexplored domains in this field. Enhancing the performance and reliability of SIBs depends partly on the development of efficient cathode materials. One particularly promising candidate for a cathode material in SIBs is $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) due to its high theoretical specific capacity, superior long cycling performance, superior rate capability, and high energy density. This material was initially reported by Le Meins et al in 1999⁵⁴.

NVPF is composed of oxygen-shared $[\text{V}_2\text{O}_8\text{F}_3]$ bi-octahedron and $[\text{PO}_4]$ tetrahedron and possesses 3D ion diffusion channels. Two Na^+ ions can be reversibly intercalated/extracted from the host structure during the battery operation which shows a theoretical specific capacity of 128 mAh.g^{-1} . This involves a two-step reaction located at two higher plateaus of 3.7 V and 4.2 V, which appear in the charge and discharge process and can lead to a high energy density^{55–57}.

Additionally, NVPF shows good cycling stability and remarkable reversibility, contributing to its potential as a long-lasting cathode material for SIBs. These properties make it particularly suitable for applications where extended cycle life and energy density are needed.

2.3.1.1.2 Negative active materials

Nowadays, various negative electrode materials are available, including carbon-based materials like graphite and hard carbons, titanium-based oxides (LTO), and innovative hybrids based on graphite and silicon (Si/C blends) in which each of them offers unique electrochemical properties and advantages.

Commercial carbon anodes can be categorized into two main types. Graphitic carbons, characterized by large graphite grains, can achieve their theoretical charge capacity and are a popular choice due to their optimal performance characteristics and safety advantages over lithium metal.⁵⁸

2.3.1.1.2.1 Graphite

The graphite anode revolutionized the commercial viability of LIBs over two decades ago and remains the preferred choice today. Its electrochemical activity arises from Li intercalation between graphene planes, providing excellent 2D mechanical stability, electrical conductivity, and Li transport (Fig. 11). It can store up to 1 Li atom per 6C in this manner. Graphite possesses a combination of advantageous properties, including low cost, low delithiation potential and abundant availability compared to Li, high electrical conductivity and Li diffusivity and relatively low volume change during lithiation/delithiation. As a result, graphite offers an attractive balance between cost, abundance, moderate energy density, power density, and cycle life compared to other intercalation-type anode materials. While graphite gravimetric capacity is higher than most cathode materials, the volumetric capacity of commercial graphite electrodes remains relatively small ($330\text{--}430 \text{ mAh.cm}^{-3}$).⁵⁹

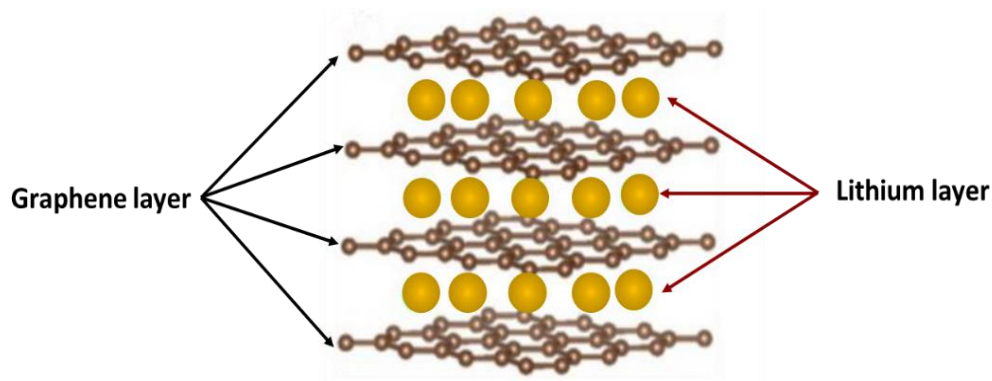


Figure 2-11 Schematic illustration of lithium intercalation into the graphite structure.⁶⁰

Lithiated graphite refers to graphite that has undergone the process of Li intercalation, which occurs upon the charging of the cell. This process results in changes in the properties and the electronic structure of the graphite material. One can easily notice the change in color (figure 2-12), indicative of the changes in the electronic structure, as lithiation progresses.

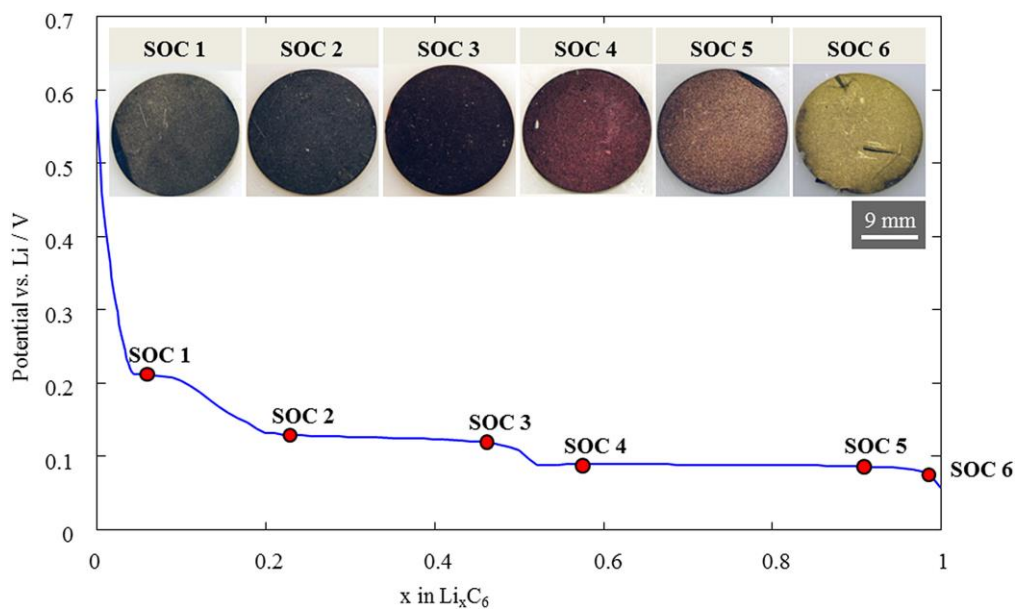


Figure 2-12 The open-circuit potential profile of lithiated graphite.⁶¹

Graphite face challenges when used with propylene carbonate (PC)-based electrolyte, which would be preferred for its low melting point and rapid Li transport. PC intercalates with Li^+ between the graphitic planes, causing graphite to exfoliate and lose capacity⁶². Plating is another challenging issue associated with the utilization of graphite anodes in LIBs. Specifically, during charging, Li^+ ions are expected to intercalate into the graphite structure to store energy. However, under certain

conditions such as overcharge and high charging rates, excess lithium ions can be deposited on the surface of the graphite anode instead of intercalating within the layers. This phenomenon is known as lithium plating, which can lead to serious safety issues, capacity loss within the cell, and a subsequent impact on the overall battery performance.

2.3.1.1.2.2 Hard carbons

Hard carbons are characterized by small graphitic grains with a disordered orientation, making them highly resistant to exfoliation and favorable for good electrochemical performance.^{63,64} These grains feature nanovoids between them, leading to reduced and uniform volume expansion. Additionally, the presence of nanovoids and defects allows for excess gravimetric capacity, enabling a capacity higher than the theoretical 372 mAh.g^{-1} ^{65–67} and even exceeding 500 mAh.g^{-1} more recently.⁶⁸

These unique properties could make hard carbons excellent materials for achieving both high capacity and a long cycle life. However, hard carbon is typically the preferred choice for anodes in SIBs since Na does not effectively intercalate between the graphene layers of graphite.

2.3.1.1.3 Binder and additives

As a commonly used additive, we can mention carbon black, which substantially improves the electronic conductivity of the electrode active material. This conductivity enhancement is essential for facilitating the electron conduction within the electrode. The binder (e.g., polyvinylidene fluoride, PVDF) is another essential component of the electrode, which facilitates cohesion between the active material particles and with carbon black, thereby creating a cohesive structure within the electrode able to resist the volume change upon repetitive charge and discharge.

2.3.1.2 Current collectors

Current collectors are responsible for electrical connections of the battery to the other parts of the electrical circuit. They are electronically conductive substrates that connect the electrodes and the external circuit. Common current collectors include thin foils of copper or aluminum onto which electrode slurries are deposited, dried and calendered.

2.3.1.3 Electrolyte

The electrolyte inside the battery is a critical component that facilitates the main electrochemical processes necessary during cycling. Battery electrolyte is composed of a salt that is dissolved

within an organic solvent, usually in the form of liquid or gel. Electrolyte allows the movement of ions between cathode and anode while maintaining electrical neutrality within the cell. In the field of LIBs, the classical salt of choice is LiPF_6 (Lithium Hexafluorophosphate) which contains Li^+ ions and participates in redox reactions.

The common electrolyte solvent in LIBs is a combination of organic solvents, usually containing a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC). These solvents are usually mixed and then combined with the LiPF_6 salt, to reach a balanced combination of properties such as thermal and chemical stability, viscosity, and conductivity.

2.3.1.4 Separator

A separator is a thin, porous material (commonly glass fiber or Celgard) placed between the cathode and anode, serving as an electrical insulator to prevent direct contact and spontaneous reactions between them. During cell assembly, using the anode and cathode in their initial states, spontaneous chemical reactions occur at the interfaces between the electrodes and the liquid electrolyte (Figure 2-13).

These reactions are associated with the formation of oxides, hydroxides, or salts that passivate the electrode surface. This passivating layer is called the Cathode Electrolyte Interface (CEI)⁶⁹ for the cathode and the Solid Electrolyte Interface (SEI)⁷⁰ for the anode. The quality of the SEI is critical in the irreversible capacity loss, safety, and cyclability of LIBs due to its role in the prevention of further electrolyte decomposition.

The SEI can also impede the ionic movement inside the cell resulting in degradation of the cell. However, electrolyte can be engineered using additives to form stable, ionically conductive SEIs.⁷¹

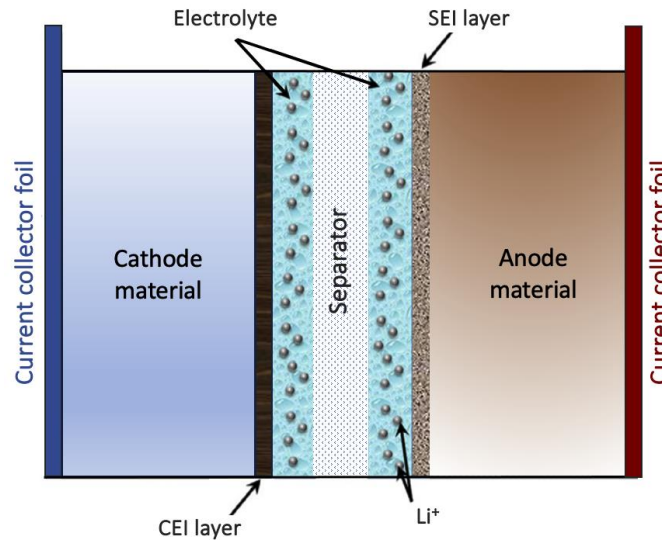


Figure 2-13 Cross section of lithium-ion cell including SEI and CEI position.

2.3.2 Cell assembly and packaging

A battery pack comprises the assembly of multiple cells. The way these cells are interconnected, whether in a series or parallel arrangement, introduces various options for diverse battery system configurations, dependent on the intended application. When cells are linked in series, the total voltage of the battery pack becomes the sum of each individual cell voltage. However, connecting cells in parallel facilitates achieving greater capacity while maintaining the same voltage.

Electrochemical batteries come in various designs, whether they are commercial or experimental. Experimental cells are typically designed for testing on a small scale, for instance, for evaluating new materials. However, commercial cells are generally optimized by manufacturers to align with optimal use according to the intended application and to be as simple and cost-effective as possible.

Various cell packaging designs exist, including cylindrical and prismatic cells that feature solid metallic casing primarily using aluminum or stainless steel (figure 2-14). In contrast, pouch cells adopt a flexible packaging composed of multiple layers of polymer films and aluminum.⁷² The assembly of electrodes and separators will be accomplished through winding for cylindrical and prismatic cells, while pouch cells stack these components on top of each other.

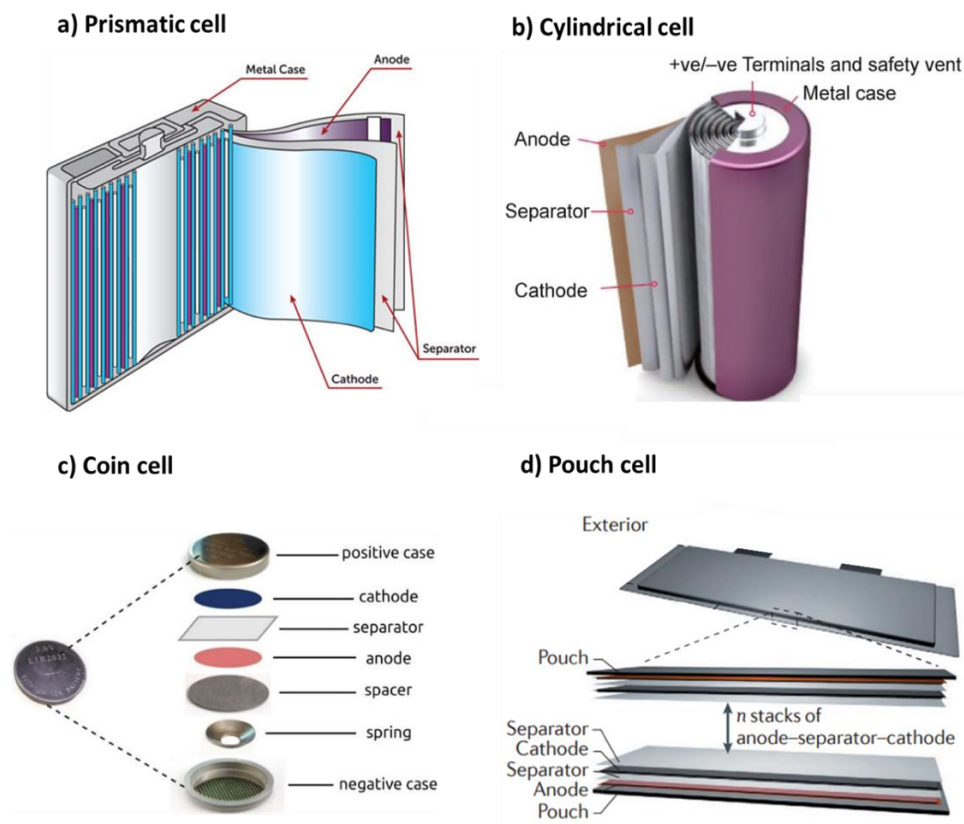


Figure 2-14 Schematic of standard cell designs (adapted from references ^{73,74})

Coin cells (Figure 2-14c) are made with their small electrode disks which are commonly used on a laboratory scale for conducting electrochemical tests.

Cells prepared with lithium metal are referred to as "half-cells" (they are made against the reference redox couple), distinguishing them from "full cells" where another type of anode is utilized.

The Swagelok cell is another type of cell that is widely used in laboratory scale research to perform electrochemical tests. The design is similar to a coin cell where electrodes are stacked, and pressure is applied by a spring.

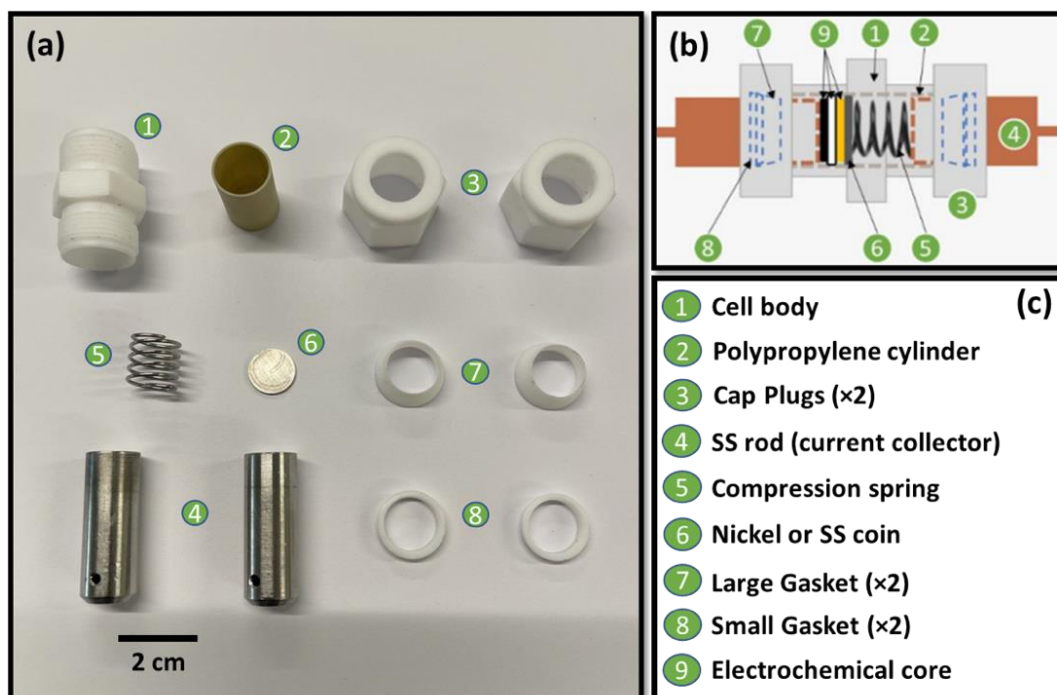


Figure 2-15 Illustration of a Swagelok cell: (a) Components, (b) Assembly schematic, (c) legend.

Figure 2-15 shows the Swagelok cell components and assembly in which most parts are made of Teflon, a material relatively inert to the electrolyte, except for those ensuring electronic conductivity such as plungers, spring, and nickel or stainless-steel coin.

The standard Swagelok cell configuration is suitable for cycling the cell with 10 mm electrodes. Nevertheless, for electrodes of different sizes (either larger or smaller) modifications are necessary, requiring adjustments to the components.

2.3.3 The degradation and ageing mechanisms of LIBs and their failure modes

Cell failure is usually attributed to three primary types of failure: internal short circuit, gas generation, or impedance growth. However, this categorization is a simplification, as these failures arise from various underlying events, and nearly every potential failure mode ultimately falls into one of these three categories. In Figure 2-16, the left side shows some potential causes of cell failures, while the right side represents the results that ultimately lead to cell failure and often thermal runaway.

Notably, both internal and external short circuits, active material dissolution, lithium plating, and SEI growth can all contribute to these three types of failures, and in many cases, these issues can stack upon one another.

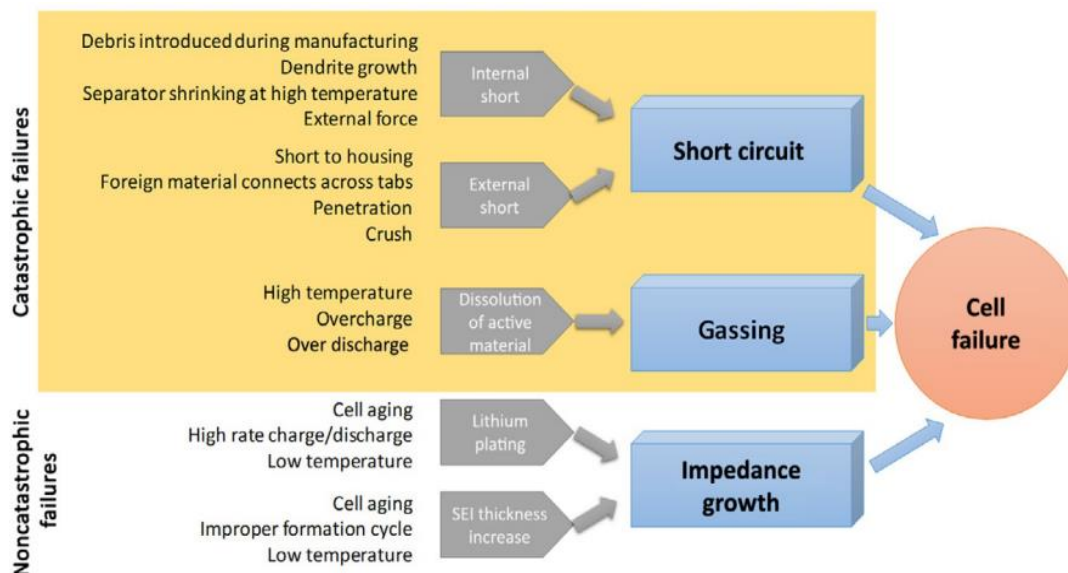


Figure 2-16 Different types of cell failure and causes⁷⁵.

Numerous degradation mechanisms can occur with LIBs that may affect their performance and cause aging and decrease in their lifespan. Some of the key degradation mechanisms are presented in Figure 2-17.

The origin of these mechanisms may be related to individual components, chemical or physical reactions, or external parameters unrelated to the cell, such as ambient temperature or user usage.

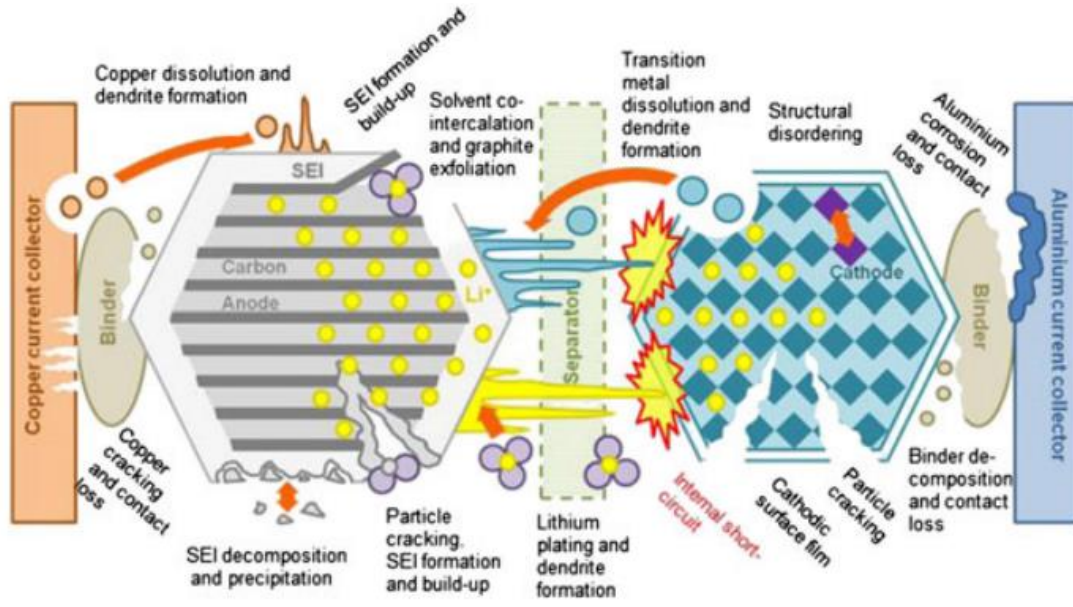


Figure 2-17 Different degradation mechanisms in LIBs.⁷⁶

Battery aging⁷⁷ can result in capacity or power fading, or a combination of both, often worsened by factors like high cycling rates, extreme temperatures, both low and high state of charge (SOC, which is the ratio of the current available capacity to the maximum potential charge a battery can hold; section 4.2.4), overcharging, over-discharging, high depth of discharge (DOD), and moisture.⁷⁶ Moreover, given batteries interdependent components, the aging of one component influences others, accelerating overall system aging.

2.3.4 Battery Management Systems (BMS) and necessity of SOC estimation

Monitoring and maintaining SOC in batteries are crucial parameters for various applications, including electric vehicles, portable electronics, and renewable energy systems. Proper SOC control is essential for ensuring reliable power responses in response to changes in operating conditions and ensuring overall system stability and performance. It also plays a critical role in preventing overcharging, which can cause battery damage, as well as over-discharging, leading to reduced battery lifespan and potential damage.

Moreover, SOC assessment is crucial for assessing the battery lifetime and hence Battery Management Systems (BMS) that is commonly used for monitoring and controlling SOC (figure 2-18) to ensure the safe and efficient operation of batteries.

Although the BMS is engineered to protect the battery system, it is not flawless and without imperfections. In fact, batteries can potentially overcharge, even when equipped with a BMS, primarily due to malfunctioning or faulty BMS. When BMS is not operating correctly, it may misread the cell charge level or fail to cut off charging process at the appropriate moment. Another factor contributing to overcharging is poor calibration. The BMS requires precise tuning to the specific battery it is looking after and without this calibration, it may struggle to accurately determine when the battery reaches full charge.

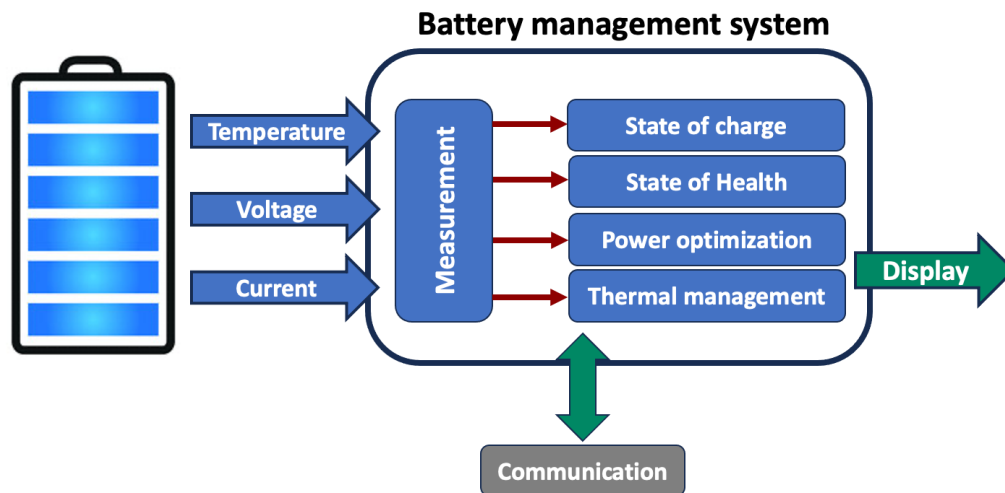


Figure 2-18 Battery management system.

Accurately determining the SOC of a battery remains a significant challenge in battery management^{78,79} and there is currently no simple technique available to achieve precise SOC estimation. For instance, in LIBs for electrical vehicle applications, accurately measuring the lithium content within an electrode presents considerable difficulties. LIBs show gradual decreases in their actual available capacities and thus their performance during charge/discharge cycling and in storage, often known as calendar ageing.⁸⁰ This decrease in capacity can result from issues such as loss of charge acceptance of the active materials on both electrodes, alterations in the physical properties of the electrolyte, or corrosion of the current collectors.

Non-uniform ageing in the LIBs complicates battery management, more particularly upon the charge/discharge process, as the batteries work under different operating conditions such as various c-rate. If the BMS is unaware of or has not been adjusted to account for aging alterations, it may wrongly think the battery is young and consequently overcharge it which results in overcharging since the battery cannot retain as much charge as it did when it was young. Therefore, many systems are sensitive to deep discharge or overcharge, since extremely high or too low SOC can cause irreversible damage to the battery.⁷⁹

Additionally, environmental factors such as varying temperatures can influence the situation. For example, very cold or hot temperatures can pose challenges for the BMS in accurately assessing the battery charge level, potentially resulting in overcharging.

Currently, there are several methods and strategies available for determining SOC, with some of them summarized in Table 2-1 as well as their relative advantages and drawbacks.

Table 2-1 Different methods for determination of SOC.⁷⁹

Technique	Application field	Advantages	Drawbacks
Discharge test	Used for capacity determination at the beginning of life	Easy and accurate; independent of SoH	Offline, time intensive, modifies the battery state, loss of energy
Coulomb counting	All battery systems, most applications	Accurate if enough re-calibration points are available and with good current measurements	Sensitive to parasite reactions; needs regular re-calibration points
OCV	Lead, lithium, Zn/Br	Online, cheap, OCV prediction	Needs long rest time (current = 0)
EMF	Lead, lithium	Online, cheap, EMF prediction	Needs long rest time (current = 0)
Linear model	Lead photovoltaic	Online, easy	Needs reference data for fitting parameters
Impedance spectroscopy	All systems	Gives information about SoH and quality	Temperature sensitive, cost intensive
DC internal resistance	Lead, Ni/Cd	Gives information about SoH; possibility of online measurements	Good accuracy, but only for a short time interval
Artificial neural networks	All battery systems	Online	Needs training data of a similar battery, expensive to implement
Fuzzy logic	All battery systems	Online	Ask memory in real-word application
Kalman filters	All battery systems, PV, dynamic application	Online; dynamic	Difficult to implement the filtering algorithm that considers all features as, e.g., nonnormalities and nonlinearities

However, despite the ongoing development and refinement of SOC estimation techniques, including advanced algorithms and BMS, the determination of SOC within batteries still faces certain challenges and limitations.

Therefore, it is crucial to continue research and development in battery technology, measurement techniques, and SOC estimation algorithms to address these issues and further enhance the accuracy of SOC estimation in batteries.

2.4 Electrochemical characterization of battery performance

Electrochemical characterization of battery performance involves a detailed examination of the battery capacity and behavior using different electrochemical techniques such as Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD), Impedance Spectroscopy (EIS), etc. These techniques can provide insights into the functioning and efficiency of the battery and how they operate in different conditions.

The methods for implementing battery cycling protocols and subsequently analyzing the acquired cycle data are based on common codes. This facilitates the electrochemical community in interpreting their data in a similar way, thereby enabling meaningful comparisons across batteries featuring diverse technologies.

2.4.1 Cycling programming

When programming battery cycles, it is particularly important to define the specific operational regimes and modes. In this context, we introduce only the concepts that will be employed in the thesis.

2.4.1.1 Galvanostatic Charge-Discharge cycling

An electrochemical cycle consists of an entire charge and discharge of the cell. As the cell is generally (dis)charged galvanostatically (i.e., at constant current), the electrochemical cycle is generally characterized by the evolution of the cell voltage over time. We distinguish four modes of battery cycling as shown in figure 2-19:

- 1) Open Circuit Voltage (OCV): No current or voltage is applied, and the battery is in an open circuit state.
- 2) Constant current (CC): A current intensity is applied, and the voltage is measured.
- 3) Constant voltage (CV): A voltage is applied, and the current intensity is measured.
- 4) Constant current discharging: A current is imposed, and the voltage is measured.

Cycling conditions for NMC/Graphite batteries (chapter 6) are optimized to avoid electrolyte and material degradation. The operational voltage window is set to 2.7-4.2 V with a C/50 cut-off current.

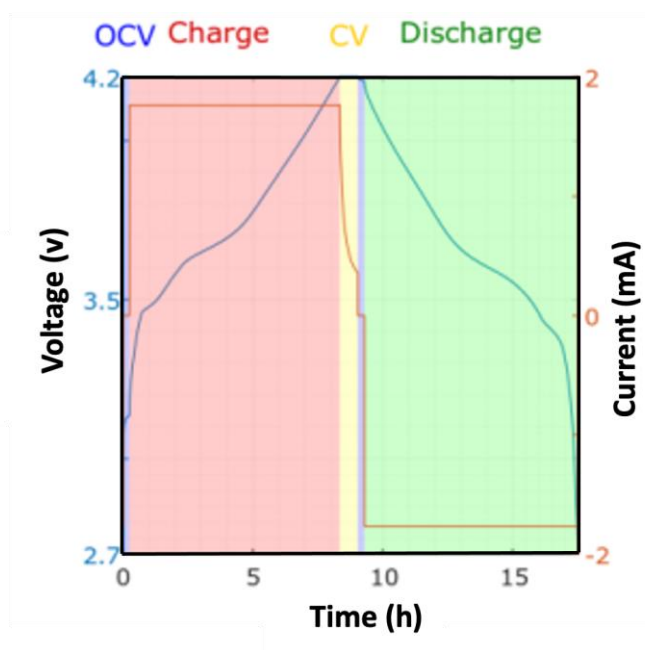


Figure 2-19 Example of a cycle representing the different modes including OCV, charging, CV, discharging.

2.4.1.2 Capacity

Within commercial battery technologies, the fundamental metric for characterization of the cell is the capacity, usually denoted in ampere-hours (Ah). Capacity (Q) of battery, quantifies its ability to either discharge or store electric charge, expressed in Coulomb (C) and equating to 1 ampere-second (A·s).

The overall capacity of a battery is established by the electrode possessing the lowest capacity, acting as the limiting factor that determines the maximum quantity of charges exchangeable within the system. In commercial contexts, this constraining capacity is often attributed to the positive electrode. Therefore, the capacity of the cathode typically governs the total capacity of the cell, thereby dictating its charge-carrying and discharging capabilities.

In weight-sensitive applications, the assessment of electrode performance in relation to its mass or surface area is necessary to enable comparisons of various designs or materials. The theoretical capacity of an electrode can be calculated through:

$$C_{th} = n \cdot N_A \cdot e = n \cdot F \quad \text{Equation 6}$$

Where:

C_{th} : the theoretical capacity in coulomb (C), expressed in ampere-hour (Ah) for convenience, i.e., $1C = 1As = 1/3600 Ah$.

n : the number of moles of electrons exchanged during the reaction (mol).

N_A : Avogadro constant ($N_A = 6.022 \cdot 10^{23} mol^{-1}$).

e : the elementary charge ($e = 1.602 \cdot 10^{-19}C$).

F : Faraday constant ($F = 96,485 C \cdot mol^{-1} = 26.8 Ah \cdot mol^{-1}$).

The theoretical specific capacity ($C_{th,m}$) in $Ah \cdot g^{-1}$ of a battery governed by:

$$C_{th,m} = \frac{n_e \cdot F}{m_{AM}} \quad \text{Equation 7}$$

Where $n_e = n \cdot N_A$ and represent the number of electrons exchanged during the redox reaction. Considering values from the electrode supplier such as surface capacity $C_{Cons,S}$ ($mAh \cdot cm^{-2}$), the percentage of active material AM_{cons} (%), surface density $\rho_{Cons,S}$ ($mg \cdot cm^{-2}$) and relative density d_{cons} ($g \cdot cm^{-3}$) we can easily calculate the manufacturer gravimetric capacity $C_{Cons,m}$ (in $mAh \cdot g^{-1}$) as following equation.

$$C_{Cons,m} = \frac{C_{Cons,S}}{\rho_{Cons,S}} \quad \text{Equation 8}$$

2.4.1.3 The formation of a cell: the determination of experimental capacity

Battery formation is the process of performing initial charge-discharge cycles within the battery to obtain a stable behavior. During the first cycles, the cell undergoes an irreversible loss of capacity which is due to the growth of passivation layers at the interface between the negative (usually graphite) and positive electrodes during intercalation and de-intercalation of Li^+ ions. However,

once the SEI/CEI has been built up, the capacity loss due to this phenomenon will be relatively reduced.

2.4.1.4 N/P ratio

The N/P ratio or balancing represents the ratio of the capacities of the negative (N) and positive (P) electrodes. In an ideal battery with no parasitic reactions, we would use a ratio equal to 1. However, commercial graphite-based cells have a ratio greater than 1, indicating the capacity of the negative electrode is greater than that of the positive. Moreover, for commercial batteries, as a precautionary measure, the N/P ratio is generally between 1.08 and 1.12 to avoid overlithiation of graphite, which can be problematic as it generates non-reversible and degrading parallel reactions.⁸¹

Overlithiation occurs when the capacity supplied to the negative electrode is greater than its capacity to reduce which in the case of graphite, this leads to the onset of degradation phenomena, potentially dangerous for system stability.⁸¹

2.4.1.5 Charging rate

The charging rate (C/n) or C-rate is used to describe the charging speed which is a different presentation of the intensity of the applied current. It has the advantage of showing the theoretical charging time more directly: by applying a given current I , the cell (of capacity C) will be fully charged in n hours. For a charging rate of $n \cdot C$, full charge will therefore be achieved in $1/n$ hours.

2.4.2 Data analysis

The electrochemical data analysis not only allows the comprehensive assessment of battery performance but also facilitates the comparison of its performance within different cycles or with other batteries with the same conditions.

2.4.2.1 Coulombic efficiency

Coulombic efficiency (CE) involves the calculation of the ratio between discharge and charge capacities in a single charge-discharge cycle, giving insight into how efficiently a battery can store and deliver energy without notable losses due to internal or parasitic reactions. CE can be calculated as follows:

$$CE (\%) = \frac{Q_{Discharge}}{Q_{Charge}} \times 100 \quad \text{Equation 9}$$

In this equation, the discharge and charge capacity are the amount of charge that the battery delivers during its discharge and charge phase, respectively. By comparing these two capacities, CE provides an understanding of the overall energy losses within the battery during a single cycle.

2.4.2.2 Capacity retention

Capacity retention (CR) is a measure of battery ability to maintain the initial storage capacity over time and after multiple cycles. CR is a crucial measure of a battery's long-term durability and performance. CR can be calculated mathematically as follows:

$$CR (\%) = \frac{Q_{Discharge,final}}{Q_{Discharge,initial}} \times 100 \quad \text{equation 10}$$

Where, the final capacity refers to the remaining capacity of the cell after a certain number of cycles or a specific period upon discharge, while initial capacity represents the discharge capacity of the cell upon first formation cycle.

2.4.2.3 Self-discharge

Battery self-discharge is a phenomenon in which the charged battery loses its stored energy over time due to internal chemical reactions, even without using the device. This energy loss can be due to an unwanted chemical process occurring within the battery itself. As an example of self-discharge, we can mention the drop in voltage of a cell after charging when there is no load or connection, which is known as an open-circuit condition. The effect of this self-discharge can vary depending on the type of battery chemistry.

2.4.2.4 State of charge

The state of charge (SOC) is defined as the ratio of the available capacity, Q_t , within the battery to its fully charged capacity, Q_{max} . SOC reveals how much charge is stored in the battery compared to its maximum expected charge, typically expressed as a percentage.

$$SOC (\%) = \frac{Q_t}{Q_{max}} \quad \text{Equation 11}$$

A fully charged battery has an SOC of 100%, signifying that it has its maximum energy capacity ready for use while a fully discharged battery has an SOC of 0%.

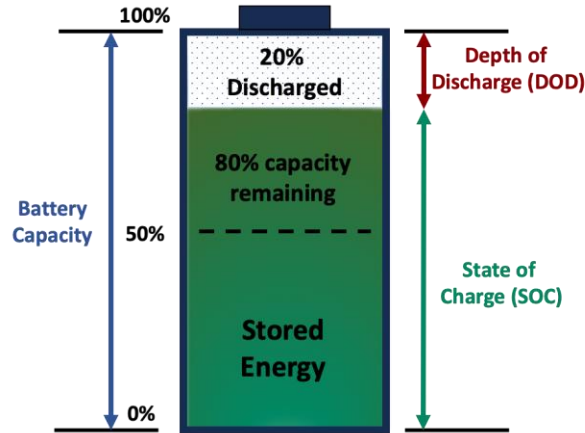


Figure 2-20 Schematic illustration of SOC and DOD.

Sometimes, the DOD is employed to assess the extent of battery discharge, i.e., how deeply it has been discharged (figure 2-20). In most cases, it is associated with SOC and can be calculated using the following formula:

$$\text{DOD (\%)} = 100 - \text{SOC (\%)} \quad \text{Equation 12}$$

2.5 Conclusion

The fast-growing market for rechargeable batteries necessitates the rapid development of battery technologies at an unprecedented rate. The battery SOC estimation assists in defining the actual available energy in the battery and provides information on the remaining working time and lifetime of the device. The design of batteries requires some battery management features in which the determination of the SOC remains as one of the most challenging ones.

Current strategies and techniques for determining SOC often encounter drawbacks. For instance, impedance spectroscopy is cost intensive and temperature sensitive, Coulomb counting requires continuous recalibration and is sensitive to side reactions, measurements of OCV or EMF demand long rest times before application, discharge tests are not applicable online, Kalman filters require large computing capacities, a suitable battery model, and the determination of initial parameters and artificial neural networks necessitate intensive training with a similar battery.

Consequently, an alternative, direct measure of SOC of electrodes and comparison with Coulomb counting would be desirable and could ultimately enable more accurate and straightforward determination of SOC and side-reactions.

The objective of our study is to evaluate whether NMR is sensitive enough to detect changes in the magnetic properties of a LIB during charge and discharge cycles, to serve as an indicator for the SOC. This approach can be utilized to develop a model for implementation in the BMS for direct and instant measuring of SOC of the electrodes in battery.

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Chapter 3 Basics on Nuclear Magnetic Resonance

3.1 Introduction and history

The history of Nuclear Magnetic Resonance (NMR) dates back to the early 20th century when scientists were beginning to explore the mysteries of atomic and molecular properties. In 1938, Isidor Rabi, a physicist, and his colleagues at Columbia University discovered the phenomenon of magnetic resonance while studying atomic beams in a magnetic field.⁸² Rabi was awarded the Nobel Prize in Physics in 1944 for his contribution to the discovery of magnetic resonance.

In 1946, Felix Bloch and Edward Purcell, working independently, demonstrated nuclear magnetic resonance in liquids⁸³ and solids,⁸⁴ respectively, providing the foundation for the development of NMR as a spectroscopic technique. For their groundbreaking work, both Bloch and Purcell were awarded the Nobel Prize in Physics in 1952.^{85,86}

Over the following decades, NMR spectroscopy and imaging techniques advanced significantly, finding applications in chemistry, biology, and medicine. The development of powerful magnets, sophisticated pulse sequences, and computer technology further revolutionized NMR, allowing researchers to gain unprecedented insights into the structures and behavior of complex molecules.

Today, NMR remains a versatile and essential tool in scientific research, enabling scientists to reveal dynamic processes, chemical compositions, structures, reaction kinetics and perform non-invasive imaging. The unceasing advancements in NMR technology continue to expand its applications and contribute to numerous discoveries in various fields of science.

NMR spectroscopy is the main technique used in this research work. This chapter will provide a brief overview of the fundamental theory and subsequently delve deeper into the aspects most relevant to my research study. I will focus specifically on key points and techniques that have been employed for the analysis and experimental development of *ex situ* and *operando* NMR measurements of batteries (Chapters 5 and 6).

3.2 Principle of NMR

This section begins by reviewing the basic theory required to comprehend the essence of our study, without going through the entire basics of quantum physics. We aim to present a concise overview that enables readers to understand the core principles that underlie our research. For a more comprehensive understanding of the topics discussed, we highly recommend referring to

"Understanding NMR Spectroscopy" written by J. Keeler, and "Spin Dynamics" written by M. Levitt.^{87,88}

3.2.1 Nuclear spin and magnetic moment

In nuclear physics, spin is defined as an intrinsic quantum property, the "intrinsic angular momentum of a particle." Each component of an atom, including protons, neutrons, and electrons, has its own spin. Each possess a spin with a value of $+\frac{1}{2}$. The most stable combination of the spins of protons and neutrons, located in the atomic nucleus, is referred to as the ground state nuclear spin. Electrons, which form a cloud around the nucleus, possess their own spin, known as electronic spin.

For each spin angular momentum (nuclear or electronic), there is an associated magnetic moment.^{89,90}

$$\vec{\mu}_s = \gamma \cdot \vec{S} \quad \text{Equation 1}$$

With μ_s representing as the spin magnetic moment, S denotes the spin angular momentum, and γ represents the gyromagnetic ratio.

3.2.2 The Zeeman interaction

Numerous nuclei (not all) possess a nuclear spin, which is quantified by the quantum number I. This nuclear spin results in $2I + 1$ distinct states specified by the quantum number m_I , taking values $-I; -I+1/2; \dots; I-1/2; I$. In the presence of an applied external magnetic field, the energy levels of these states split and become non-degenerate due to the nuclear Zeeman interaction.

Figure 3-1 illustrates the nuclear Zeeman levels of ^1H nucleus as a function of applied magnetic field. The ^1H possesses a spin of $1/2$, leading to the division of its nuclear ground state into two sublevels when subjected to the magnetic field⁸⁷.

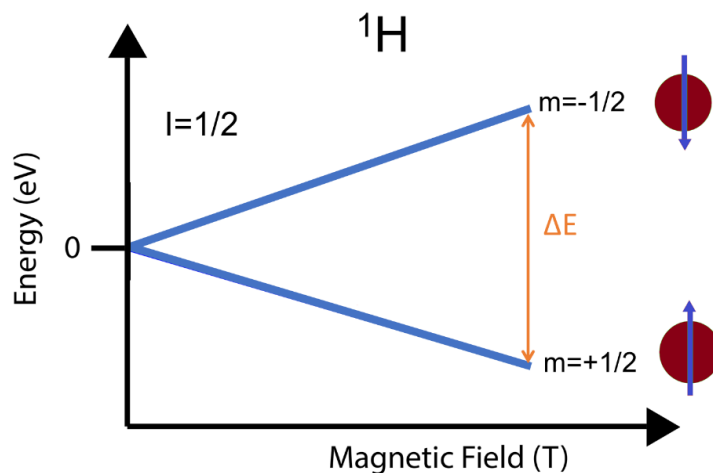


Figure 3-1 Nuclear Zeeman sublevels of the ^1H .

3.2.3 Vector model

Herein, we are giving a brief introduction to the vector model, a representation used to describe the nuclear spin behavior in a magnetic field which is a helpful construct for comprehending how pulsed NMR experiments function.⁸⁸

When a sample is positioned within a magnetic field B_0 , it induces the splitting of previously equivalent nuclear energy levels due to the Zeeman effect. This process causes an excess of nuclear spins to align more parallel to B_0 , resulting in the appearance of a macroscopic nuclear magnetization M aligned with B_0 (figure 3-2) and it is what is most convenient to understand pulsed NMR experiments.

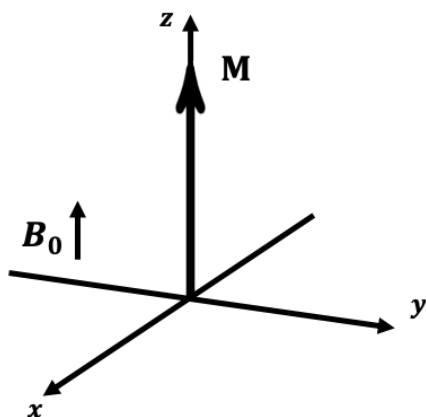


Figure 3-2 Illustration of nuclear macroscopic magnetization M at equilibrium.

To enable transitions between the Zeeman energy levels, a time-varying magnetic field B_1 is introduced, oscillating at Larmor frequency ω_0 ($\text{rad} \cdot \text{s}^{-1}$) within a plane perpendicular to B_0 which can be calculated as follows:

$$\omega_0 = -\gamma \cdot B_0 \quad \text{Equation 2}$$

For a nuclear spin characterized by the gyromagnetic ratio γ (measured in units of $\text{rad} \cdot \text{s}^{-1} \cdot \text{T}^{-1}$) within an applied magnetic field B_0 (T). If we want the frequency in Hz, it is given by:

$$\nu_0 = \frac{-\gamma \cdot B_0}{2\pi} \quad \text{Equation 3}$$

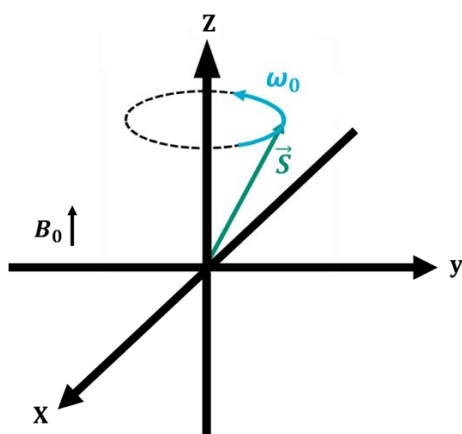


Figure 3-3 Illustration of Larmor frequency.

The sign of the Larmor frequency indicates the direction of spin precession around the field. Most nuclei have a positive gyromagnetic ratio, so the Larmor frequency is negative. This means that the precession is clockwise.⁸⁷ Table 3-1 shows the properties of some isotopes with a non-zero nuclear spin that were mostly used in our study.⁸⁸

Table 3-1 Properties of certain isotopes with a non-zero nuclear spin.⁸⁸

Nuclei	Spin	Natural abundancy (%)	γ ($10^8 \text{ rad}\cdot\text{s}^{-1}\cdot\text{T}^{-1}$)	ω_0 (MHz) at 4,7 T
^1H	$\frac{1}{2}$	99,99	2,675	-200
^7Li	$\frac{3}{2}$	92,57	1,040	-77,728
^{11}Na	$\frac{3}{2}$	0.0034	108	-505.2
^{13}C	$\frac{1}{2}$	1,108	0,673	-50,290
^{17}O	$\frac{3}{2}$	0,37	-0,363	+27,113
^{19}F	$\frac{1}{2}$	100	2,517	-188,188
^{31}P	$\frac{1}{2}$	100	1,083	-80,961
^{119}Sn	$\frac{1}{2}$	8,58	-10,031	+39.289

3.3 Pulsed NMR (Techniques in NMR spectroscopy)

The possibility of generating pulse sequences has resulted in the advancement of various NMR techniques that offer comprehensive insights into a range of structural characteristics of the sample. In the following, we will briefly outline these techniques, mainly those that have been used in our study.

3.3.1 One pulse

In the vector model, the application to a spin system of a radiofrequency magnetic field ($\vec{B}_1$, oscillating at the Larmor frequency) for a duration τ , perturbs the initial alignment of the macroscopic nuclear magnetization ($\vec{M}$), which is originally oriented with respect to $\vec{B}_0$ (along the z axis). In the frame rotating at the Larmor frequency, the magnetization is deviated from its equilibrium position, by an angle $\theta = \gamma B_1 \tau$ from $\vec{B}_0$ (Figure 3-4a).

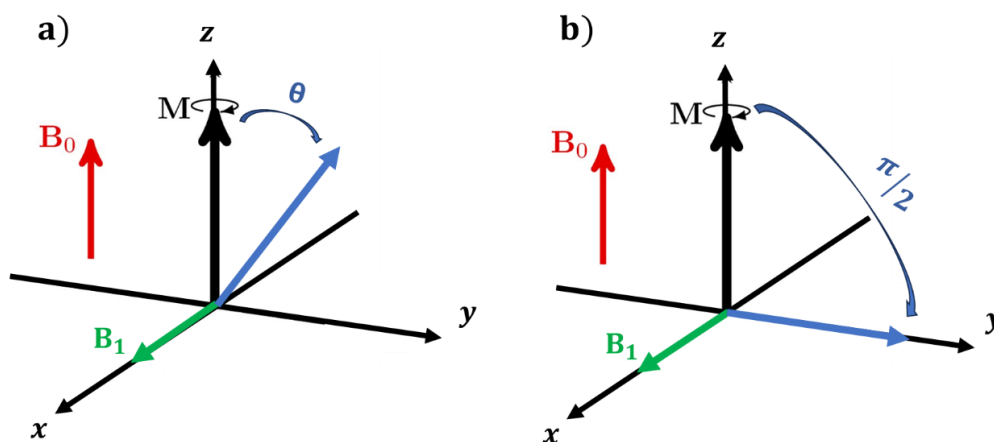


Figure 3-4 (a) The rotation of the nuclear macroscopic magnetization M by an angle θ through applying a B_1 field pulse around B_0 , (b) The magnetization M undergoing a rotation of $\pi/2$ towards the (xy) plane through application of a 90° (or $\pi/2$) B_1 for a duration τ .

The flipping of the magnetization by an angle $\theta = \pi/2$ (Figure 3-4b) with respect to $\vec{B}_0$ is the simplest pulse sequence used in NMR spectroscopy. In the so-called “one pulse” experiment, the magnetization is tilted in the transverse plan (x and y axis): this is the excitation step. Once $\vec{B}_1$ is cut off, the spin system evolves toward its equilibrium position (Figure 3-5).

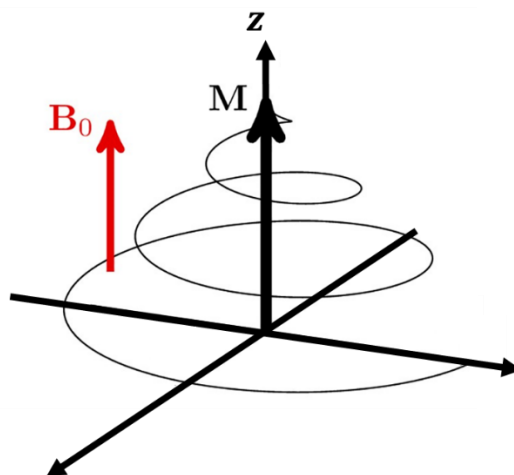


Figure 3-5 Return to equilibrium of magnetization M in the laboratory frame.

The return of magnetization to equilibrium can be tracked through the evolution of its longitudinal (M_z) and transverse (M_x and M_y) components over time. M_z usually recovers completely following an exponential law with a longitudinal relaxation time constant T_1 while M_x and M_y are assumed

to completely disappear in the xy plane, often following an exponential decay law with a characteristic time constant the transverse relaxation time T_2 .

Experimentally, the transverse components generate an electrical signal in the NMR detection coil, referred to as the Free Induction Decay (FID), which is the NMR raw data. Figure 3-6 shows the relevant parameters used for recording the data after an excitation pulse. In a typical NMR acquisition, this pulse sequence is repeated multiple times aiming to improve the signal-to-noise ratio (S/N).

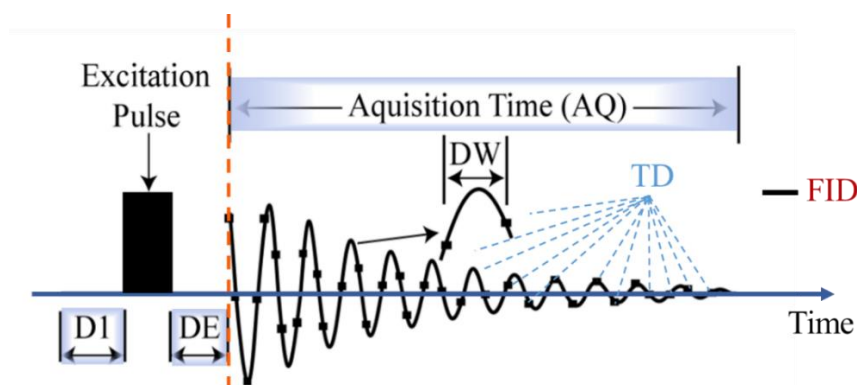


Figure 3-6 Representation of FID signal with acquisition time (AQ), Pre-scan delay (DE), Dwell Time (DW); time between points during data acquisition, Recycle delay (D1).

The Fourier transform converts the data from the time domain to the frequency domain (Figure 3-7), and subsequently results in a spectrum.

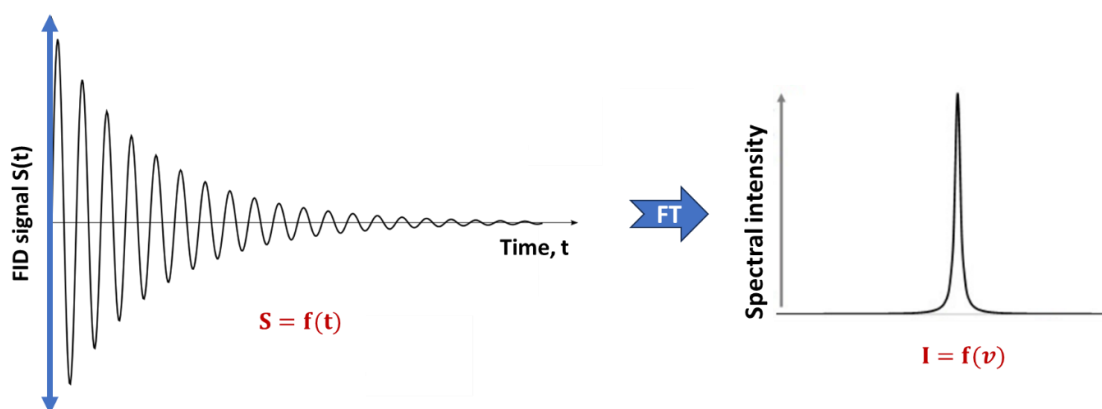


Figure 3-7 Diagram of a time signal S transformed into the frequency domain by Fourier transform.

The horizontal axis of the NMR spectrum is chemical shift (δ), expressed in parts per million (ppm) which represents the difference between the resonance frequency of a nuclear spin and a reference frequency.

Except for very simple samples, an NMR spectrum contains several peaks or resonances. This happens because nuclear spins are sensitive and can interact with their surroundings. Each peak or resonance in the spectrum is associated with a distinct chemical shift value, which is related to the magnetic environment of the nucleus. This crucial spectral characteristic, indicative of the structural environment, allows for effective structure analysis as it provides valuable insights into the nucleus interactions and sensitivities.

Chemical shift δ is usually expressed in:

$$\delta = \frac{\nu_{sample} - \nu_{ref}}{\nu_{ref}} \quad \text{Equation 4}$$

ν_{sample} represents the absolute resonance frequency of the sample, while ν_{ref} is the absolute resonance frequency of a standard reference compound, measured within the same applied magnetic field B_0 .

The vertical axis of the NMR spectrum represents the intensity or amplitude of the NMR signals at various chemical shift positions. The area under a peak (or spectral line) is proportional to the number of spins involved, provided that the sample was at equilibrium before the measurement and transverse relaxation processes are not excessively rapid.

The key limitation of the single pulse NMR technique, particularly at the beginning of data acquisition, relates to the generation of the FID, since herein the NMR coil serves a dual role: it acts as a transmitter when imposing the radiofrequency pulse (B_1), and it functions as a receiver when measuring the FID signal. This dual-role scenario leads to a short time interval (DE in Figure 3-6), typically lasting a few microseconds, during which it becomes challenging to record the initial points of the FID accurately. As a result, the FID signal is truncated, and this can have importance, especially when we are dealing with broad signals, leading to the inaccurate observation of shorter FID components. The truncation results in a first-order phase-roll of the spectrum with chemical shift and necessitates a process known as spectrum phasing in the first order.

3.3.2 Spin echo

One of the most commonly employed pulse sequence in NMR is the spin (Hahn) echo experiment. In this method, a 90° pulse is initially applied to generate transverse magnetization. During a time delay τ , the magnetization vectors of three families of spins undergo precession at their offset frequencies Ω_i , leading to phase differences represented by $\Omega_i\tau$ (stage 2 in figure 3-8). A subsequent 180° pulse alters the magnetization phases to $(2\pi - \Omega_i\tau)$ (stage 3 in figure 3-8). Subsequently, a further period of free precession for a duration τ causes all magnetization phases to reach 2π , equivalent to 0. The spin echo pulse sequence is then referred to as “refocusing” the magnetizations of all families of spins.

By employing the spin echo experiment, the challenge encountered in the one-pulse experiment is avoided since the dead time is indirectly integrated into the second τ delay.⁹¹ An additional benefit of spin echo experiments is the suppression of background signals originating from the NMR probe. This suppression occurs since these components are external to the NMR coil and thus encounter much weaker radio frequency pulses which mean both the durations of the 90° and 180° pulses are notably extended.⁹² On the other hand, transverse relaxation occurs during the two τ periods, which results in a weighing of the areas and loss of quantitativity if the families of spins have very different relaxation rates.

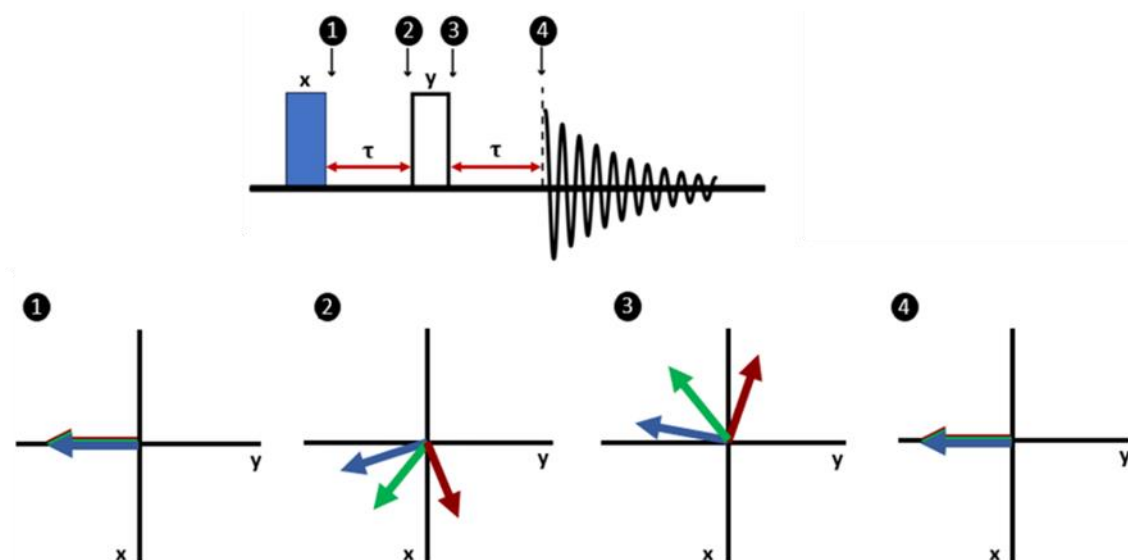


Figure 3-8 Pulse sequence of the spin echo. Solid pulses represent 90° pulses, while unfilled ones represent 180° pulses. Phases of the pulses indicated as (x, y, etc.). Diagrams illustrate magnetization vector positions in the rotating frame for three sites with distinct offset frequencies, at different stages of the pulse sequence.⁹²

3.3.3 Relaxation time measurement

As explained in section 3.1 the realignment of magnetization M with the main magnetic field B_0 occurs due to two relaxation phenomena: longitudinal relaxation and transverse relaxation.⁸³

Longitudinal relaxation or spin-lattice relaxation is described by a characteristic time, T_1 , the time constant governing the return of the magnetization along the B_0 axis.

The relaxation phenomenon follows an exponential trend and can be accurately modeled by the following formula for magnetization arising from spins $\frac{1}{2}$ and starting from the transverse plane:

$$M_z(\tau) = M_0 \cdot (1 - e^{-\frac{\tau}{T_1}}) \quad \text{Equation 5}$$

Where M is the magnetization, M_0 the equilibrium magnetization and τ the waiting time. To ensure the complete return of magnetization to its equilibrium state, the recycling time between two consecutive experiments should be sufficiently long. If aiming for quantitative measurement, the waiting time is usually chosen to be equal to $5T_1$, which, based on Equation 5, results in the recovery of 99.33% of the initial magnetization M_0 .

Transverse relaxation or spin-spin relaxation is responsible for the decay of transverse magnetization within the transverse plane. The constant time T_2 quantifies this decay.

In the following two pulse sequences used for measuring longitudinal relaxation times are presented.

3.3.3.1 Inversion recovery

This experiment involves initiating a 180° pulse that inverts magnetization, followed by a variable delay (D_2) before an excitation pulse, as shown in Figure 3-9. To determine T_1 , the D_2 delay is systematically increased. During D_2 period, magnetization relaxation occurs along the z-axis, and the subsequent excitation pulse enables measurement of the magnetization vector magnitude after this process. When D_2 is short, an inverted signal emerges, and as the recovery time increases, the signal crosses zero, becomes positive and goes back to equilibrium.

The intensity of the signal can be described by the following equation:

$$I(\tau) = I_0 \left[1 - 2 \exp\left(-\frac{\tau}{T_1}\right) \right] \quad \text{Equation 6}$$

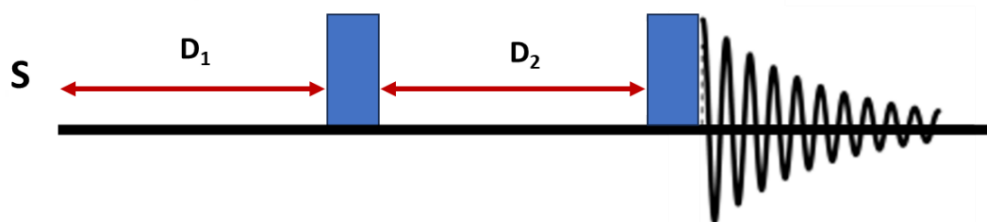


Figure 3-9 The inversion recovery pulse sequence, $D1$ represents the recycle delay between consecutive experiments (this delay allows the magnetization to return to its equilibrium state before the initiation of a new scan).

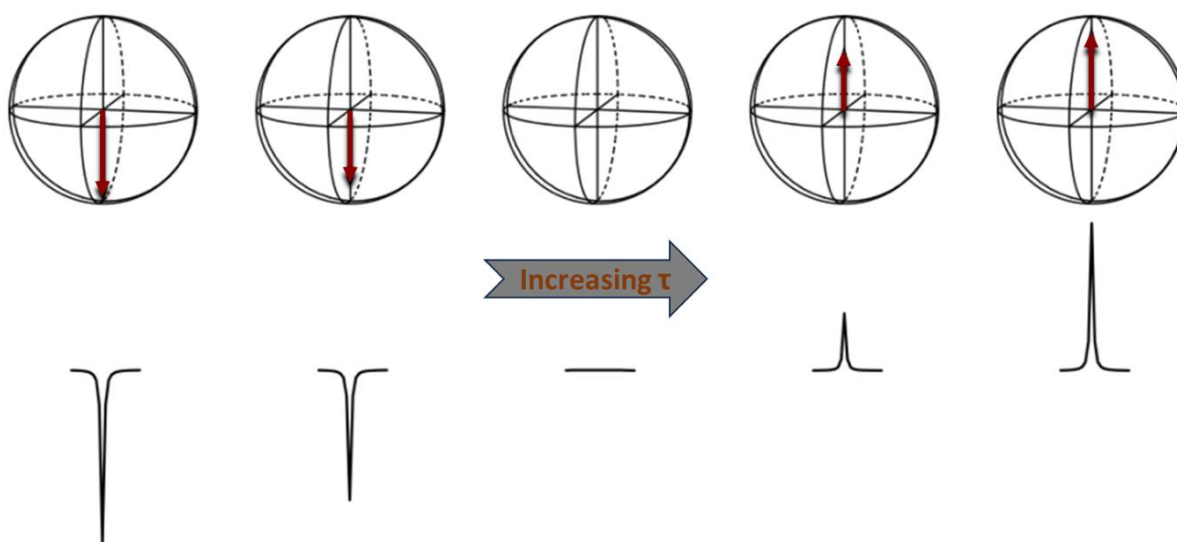


Figure 3-10 Variation of signal intensity due to longitudinal relaxation as a function of $D2$ variable delay, with the zero crossing.⁸⁷

3.3.3.2 Saturation recovery

In this approach, a series of 90° pulses known as a "saturation train" is applied with delays, d , between them, typically on the order of milliseconds, to suppress (saturate) magnetization (as seen at time-point 2 in Figure 3-11). Subsequently, magnetization begins to recover towards its equilibrium state during a delay time (τ), before being converted into transverse magnetization through a 90° pulse for measurement.⁹² By performing multiple experiments with varying τ times, the resulting signal, $I(\tau)$, is analyzed through fitting to determine the T_1 value using the formula :

$$I(\tau) = I_0 \left[1 - \exp\left(\frac{-\tau}{T_1}\right) \right] \quad \text{Equation 7}$$

Here, I_0 represents the signal acquired under the limit of complete longitudinal relaxation.

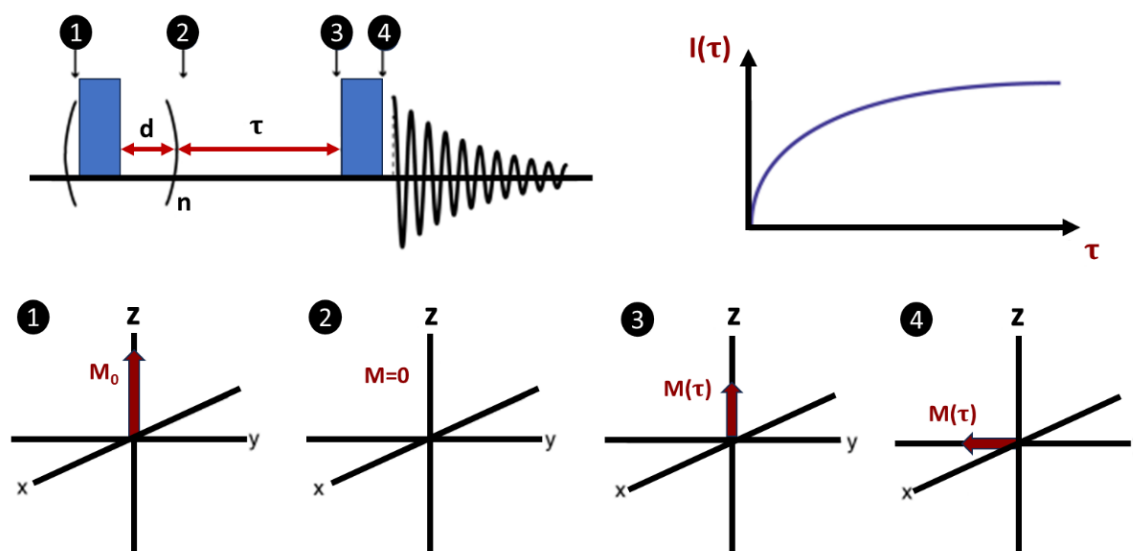


Figure 3-11 Diagrams illustrate the configuration of the magnetization vector for a single chemical environment, along with a representation of signal intensity buildup while the time τ is varied.

3.4 NMR in practice (experiment classification)

NMR experiments are traditionally categorized into solution-state or solid-state NMR experiments based on the rate of reorientational motion of the species under investigation. If the reorientational motion is slow enough that the observed characteristics are not fully motionally averaged, the spectral features are spread over a wider frequency range. In solution-state NMR experiments, the behavior of the spectrometer in generating the pulse sequence can generally be approximated as ideal. The behavior of most MRI spectrometers is more similar to that of a solution-state spectrometer than a solid-state spectrometer.

3.4.1 Solution NMR

Solution-state NMR is dealing with samples dissolved in a solvent, usually employed for small organic molecules and biomolecules in solution. It involves samples containing the molecules dissolved in a liquid solvent (e.g. suitable deuterated solvent), giving insight into solution phase chemistry and molecular dynamics.⁹³

NMR analysis also extends to dissolved solids, such as precipitates arising in electrolyte solutions and films on electrodes (SEI, see chapter 2). Solvents like D_2O ,^{94,95} $DMSO-d_6$,^{15,16} C_6D_6 ,⁹⁸ acetone- d_6 ,⁹⁹ DCl in D_2O ,¹⁰⁰ and EMC ¹⁰¹ are used for this purpose, though CD_3CN is not effective for dissolving SEI components.¹⁰² In some cases, researchers rinse cell components with solvents to extract residual electrolyte solution, while others do the same to dissolve surface films. Consequently, the difference between solution NMR of solutions and the NMR of dissolved solids is not always clear.¹⁰³ Moreover, solution NMR can also be employed to study the ion mobility and the diffusion coefficient of all the different species in the electrolyte.

3.4.2 Solid state NMR

Solid-state NMR (ssNMR) is a powerful technique for analyzing the dynamics, chemical structure, and interactions of materials in solids or semi-solids. ssNMR can provide insights into a broad range of materials such as crystals, ceramics, polymers, and biomolecules within membranes. Contrary to liquid-state NMR where the molecules easily move, ssNMR deals with samples where molecular motion is limited. There are various important interactions that are not active in liquids due to molecular motion as their average value becomes null, however in solids less averaging occurs, and the interactions are all active and broaden the spectra.

Luckily, techniques such as MAS can be used to average out most anisotropic interactions, leading to improved resolution and sensitivity.¹⁰⁴

3.4.3 Magic angle spinning

In solid-state NMR, both dipolar couplings and chemical shifts exhibit orientation dependence, anisotropic interactions dominate lineshapes and give rise to broad spectra in solid-state powders.

A common approach involves rapid rotation of the sample around an axis tilted at approximately 54.7° with respect to the B_0 direction (figure 3-12a), recognized as the magic angle.¹⁰⁵ This technique, known as Magic Angle Spinning (MAS), serves to cancel the effects of some strong internuclear interactions that result in broadening of the signals in NMR spectra of solid samples and hence significantly improves resolution. Line narrowing is achieved only when the sample is rotated at this angle.⁸⁹

The mathematical significance of the magic angle lies in its ability to interchange x, y, and z axes in the laboratory frame.⁴ To do so, specialized probes are employed, incorporating additional

elements such as a stator with an adjustable spinning angle, containing a rotor that contains the solid sample (as shown in Figure 3-12b). The rotor geometry prompts rapid spinning through the influence of a gas stream, while the RF coil is also positioned with a tilt inside the stator around the rotor.

MAS is particularly effective when the spinning speed in Hz surpasses the strength (in Hz) of the broadening interaction, resulting in an isotropic spectrum. Lower spinning rates, on the other hand, lead to the observation of spinning sidebands, separated by multiples of the rotation rate. In heterogeneous systems, such as soaked powders, where the liquid settles within porous media, molecular environments can become anisotropic, resembling solid like behavior.⁴

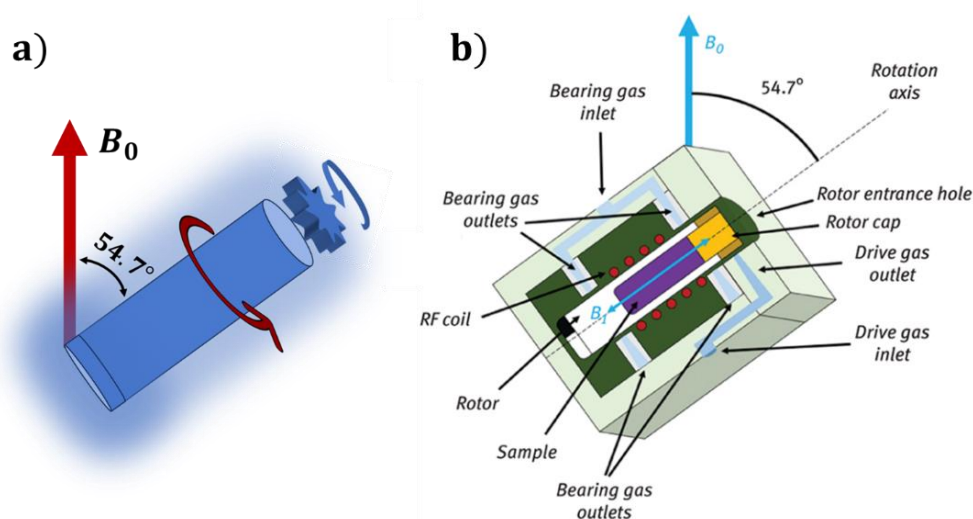


Figure 3-12 Illustration of, (a) a sample undergoing MAS in the laboratory frame, (b) the inside of a MAS probe stator⁸⁹.

3.5 Interactions in NMR

Interactions influence and modify the resonance frequency of atoms. In the following we will briefly outline them.

3.5.1 Shielding effect

The shielding effect is a phenomenon in which the electron cloud surrounding a nucleus partially shields it from the external magnetic field. When an external magnetic field is applied (as in NMR experiments), the electron cloud of the neighboring atoms creates an opposing magnetic field, slightly reducing the net magnetic field experienced by the nucleus. This reduction in the effective magnetic field results in a resonance frequency shift, leading to a change in the chemical shift. The

shielding effect is related to the distribution of electron density in the molecule and contributes to the variation in resonance frequencies for different types of nuclei in different chemical environments.¹⁰⁶

3.5.2 Dipolar interaction

Dipolar coupling is a through-space interaction between neighboring spins. This interaction depends on the angle between the nuclear vector and the magnetic field and creates broadening in the spectrum. MAS and decoupling sequences are excellent at removing heteronuclear dipolar interaction; it is trickier for homonuclear dipolar coupling.

3.5.3 Hyperfine coupling

The majority of positive electrode materials used in batteries, generally LIBs and sodium ion batteries (SIBs) contain transition metal ions, which can possess unpaired electrons that give rise to paramagnetic properties. NMR is highly sensitive to the presence of these unpaired electrons within the vicinity of the probed nucleus. The hyperfine coupling between a nucleus and an unpaired electron leads to both a shift and broadening of the NMR signals.

3.5.3.1 Fermi contact interaction

The Fermi contact interaction arises due to the existence of a specific density of unpaired electrons localized at the probed nucleus site. This interaction between these electronic spins typically induces significant shifts in NMR signals, which are commonly referred to as Fermi contact shifts.¹⁰⁷

In cases where the environment of the probed nucleus comprises numerous electron spins or multiple paramagnetic ions, the Fermi contact is considered additive. In such a case, the shifts induced by these ions are the sum of all shifts caused by each individual ion on this nucleus. The interaction can be so strong sometimes and the resulting shifts become so large (and broaden significantly due to the dipolar interaction, as described below) that they are no longer observable.¹⁰⁸

Fermi contact shifts are proportional to the magnetic susceptibility of the material. Consequently, within the paramagnetic domain, we do expect to observe a less shifted spectrum with rising temperatures.^{109,110} This expectation arises from the characteristic behavior of the magnetic susceptibility of paramagnetic materials, which often follows the Curie-Weiss law (will be

described in Chapter 4) and will generally decrease as temperature increases, contributing to less shifted signals.

3.5.3.2 Dipolar interaction

The other contribution to the hyperfine coupling is due to the dipolar nuclear spin-electronic spin interaction, which occurs through space between the electron spin and the probed nuclear spin and varies inversely with the cube of the distance ($1/r^3$). The strength of this interaction depends on the proximity of the individual electron relative to the probed nucleus. This interaction, like other dipolar interactions, can be partially suppressed by employing MAS due to its inherent anisotropic nature. In the case of an anisotropic magnetic susceptibility, the electronic dipolar interaction further contributes to the shift observed in the MAS-acquired signal which is commonly referred to as the "pseudo-contact shift".

The observed shift is primarily a result of the combined contributions of the Fermi contact and pseudo-contact shifts. Since the second contribution is typically significantly smaller than the first, the Fermi contact term is regarded as the dominant factor for the majority of inorganic paramagnetic materials.

3.5.4 Knight shift

The Knight shift quantifies the extent to which conduction electrons influence the NMR signal of the nucleus being studied in metals and semiconductors. Knight shift is observed in metallic lithium and in electronically conductive materials.

3.5.5 Quadrupolar interaction

Quadrupolar interaction is a significant phenomenon within NMR spectroscopy, uniquely present in nuclei with spin greater than $I=1/2$. It arises from the interaction between the electric field gradients within the vicinity of a nucleus and its nuclear quadrupole moment. The electric field gradients around a nucleus with non-spherical charge distribution can be uneven due to nearby chemical bonds or molecular geometry. This unevenness causes the nucleus to experience different magnetic environments depending on its orientation relative to the electric field gradients. Consequently, the resonance frequency of the nucleus varies for different orientations, resulting in the phenomenon known as quadrupolar splitting.

In practical terms, the quadrupolar interaction leads to the appearance of multiple satellite peaks around the main NMR peak. The number and arrangement of these satellite peaks depend on the specific nuclear spin and the asymmetry of the electric field gradients. The NMR signals of quadrupolar nuclei are typically broader than those of spin $I=1/2$ nuclei because of rapid quadrupolar relaxation.

Despite the analytical challenges posed by quadrupolar interactions, they are essential in studying complex molecular structures, particularly in ssNMR studies and in systems containing quadrupolar nuclei such as ^2H , ^{14}N , ^{35}Cl , etc. While quadrupolar interactions can complicate NMR spectra, they are valuable for probing the complex details of molecular environments which would not be accessible through other means of spectroscopy.

3.5.6 Bulk magnetic susceptibility effects

The magnetic susceptibility (χ) of the sample is another inner property, the effect of which is influenced by the overall shape of the sample. The degree of magnetization of sample in exposure to the magnetic field relies on its χ , mostly driven by the electron magnetic properties, and the intensity of the applied magnetic field.¹¹¹ This generated magnetization also generates its own magnetic field that influences the sample overall magnetic field, which results in a demagnetizing field.⁸⁷

When we examine a uniformly spherical sample, we observe that the magnitude of demagnetizing field it generates remains similar, no matter of how we position the external magnetic field within the sample shape. This means that the strength of the magnetic field induced within the sample is unchanged irrespective of its orientation. However, when we introduce an ellipsoid-shaped sample, an intriguing phenomenon emerges. The demagnetizing field remains uniform within the sample but becomes dependent on the orientation of the magnetic field relative to the sample geometry. This dynamic behavior leads to what we know as bulk magnetic susceptibility (BMS) shift. Remarkably, this shift does not result in any broadening of the NMR spectrum.¹¹²

In the case of a homogeneous sample of arbitrary shape, both BMS shift, and broadening are usually present. They are dependent on the sample shape and how it is oriented within the applied magnetic field (will be explained in detail in chapter 4).^{112,113} This occurs due to variations in the demagnetizing field across different parts of the sample.

In solution state NMR experiments, the impact of magnetic susceptibility is generally quite small, although it might be the element restricting resolution. Notable BMS shifts and broadenings can be detected in cases involving static liquid samples within irregularly shaped solids, such as in investigations of liquid crystal films and biomembranes confined between glass plates.^{113–115} In solid-state NMR, susceptibility broadening is typically less significant compared to other factors influencing linewidth, like chemical shift anisotropy and dipolar coupling. Nevertheless, with strongly paramagnetic materials like in static NMR studies of LIBs containing paramagnetic cathode material^{116,117} or paramagnetic solutes¹¹⁸ they become dominant.

3.6 Imaging

Magnetic Resonance Imaging (MRI) is another great aspect and extension of NMR experiment that adds a crucial dimension: spatial information, where localization is achieved by dividing the sample into numerous single volumes of interest (voxels), with each voxel producing an independently accessible NMR signal. In the simplest case, the signal from each voxel is just an intensity representing an average over all species present (without chemical shift information).

By employing magnetic field gradients in different spatial directions, MRI can encode the position of nuclei within the sample which is necessary for diffusion measurements and imaging. When RF pulses are applied, nuclei in distinct spatial locations emit signals at different frequencies, which will be used to build a spatial map of the sample. By collecting and processing these signals, MRI generates highly detailed images that allow visualizing the internal structures of objects, making it a valuable tool in the field of materials science, medicine, and more recently energy materials.^{119,120} In conventional MRI, spin density (typically water in ^1H MRI) is measured in 3D by using pulsed magnetic field gradients oriented in three orthogonal spatial directions.

Moreover, MRI is able to generate different types of images (often contrast images) by exploiting variations in the relaxation times (T_1 and T_2 relaxation times) of the sample spins. T_1 -weighted images represent the differences in spin density and T_2 -weighted images deal with differences in relaxation times.

Another approach is to combine MRI with traditional NMR spectroscopy to preserve the chemical shift information. Each voxel then contributes to a spectrum¹²¹ and localized spectroscopic

information is obtained. The following of this chapter is strongly inspired from a former thesis in the laboratory.¹²²

3.6.1 Frequency encoding of spatial position along one dimension

The additional magnetic field B_z varies linearly with position in z , according to a gradient G : $B_z = G \cdot z$. Considering equation 2 and with the magnetic field gradient B_z , the effective frequency becomes:

$$\omega_{\text{eff}} = \omega_0 + \gamma B_z = \omega_0 + \gamma G z \quad \text{Equation 8}$$

The following figure shows the effective Larmor frequency for spins at different positions in the sample. This will create a spatial dependence of the resonance frequency of the spins in the sample, enabling discrimination of identical species by their position along the gradient axis (vertical).

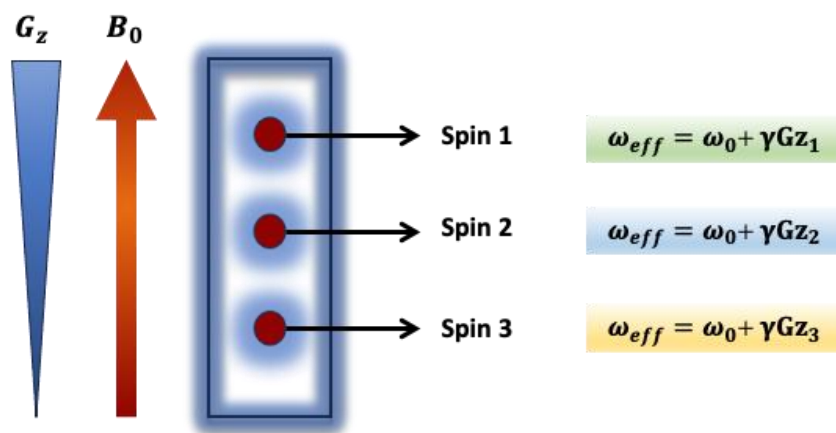


Figure 3-13 Spin precession frequency in the presence of a magnetic field gradient varying linearly in one direction in the sample.

3.6.2 Chemical Shift Imaging

Chemical shift imaging (CSI) combines imaging and spectroscopy. The principle is to correlate position and chemical shift in a 2D map. To achieve this, a series of experiments is acquired by adding a magnetic field gradient during the first time τ of the standard spin echo sequence (Figure 3-14). With each experiment, the amplitude of the magnetic field gradient is increased, and an FID signal is acquired.

The data are reconstructed by Fourier transformation along two dimensions (spatial and spectral), resulting in a spectroscopic image with one dimension containing chemical shift information (direct

dimension) and one dimension containing localization information (indirect dimension) (as illustrated in figure 3-15).¹²²

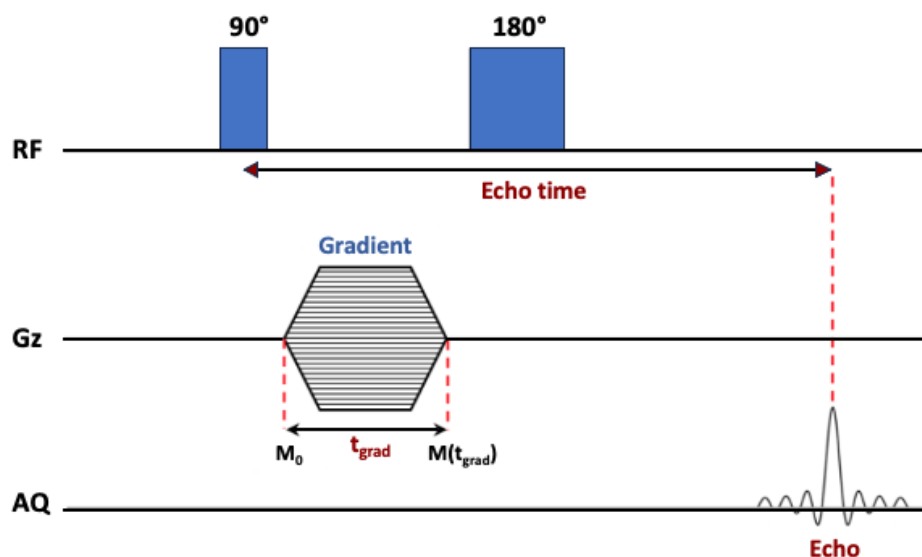


Figure 3-14 Pulse sequence for a CSI experiment with a magnetic field gradient.¹²²

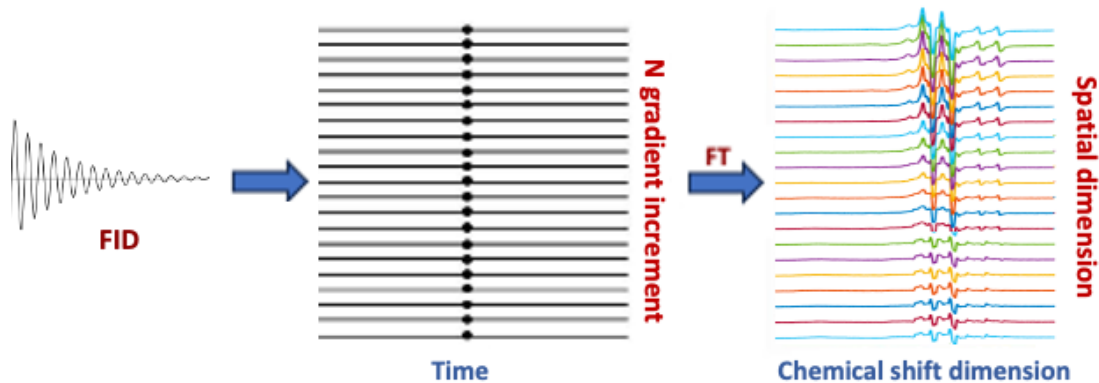


Figure 3-15 Left: *K*-space representation with *N* FIDs obtained for each gradient increment along the *z*-axis, right: spectral-spatial correlation obtained after the Fourier transform in both dimensions.¹²²

In this sequence, spatial encoding is performed in phase, meaning that the sequence establishes a phase dependence of magnetization based on its location. When the gradient is turned off at $t = t_{\text{grad}}$, the accumulated phase is:

$$\varphi = \gamma B_0 t_{\text{grad}} + \gamma G t_{\text{grad}} z \quad \text{Equation 9}$$

Here, t_{grad} is constant and we can therefore consider the wave vector $k = \gamma G t_{\text{grad}} / 2\pi$. The Fourier transform in the indirect direction gives an image with a field of view (FOV) given by:

$$\frac{1}{\Delta k} = \frac{2\pi}{\gamma \Delta G t_{\text{grad}}} \quad \text{Equation 10}$$

As G is increased from $-G_{\text{max}}$ to $+G_{\text{max}}$ in N steps,

$$\Delta G = 2 \frac{G_{\text{max}}}{N} \quad \text{Equation 11}$$

Combining with Equation 10, the FOV can be expressed as:

$$\text{FOV} = \frac{\pi N}{\gamma t_{\text{grad}} G_{\text{max}}} \quad \text{Equation 12}$$

In the following, the slice thickness will be referred as T :

$$T = \frac{\text{FOV}}{N} \quad \text{Equation 13}$$

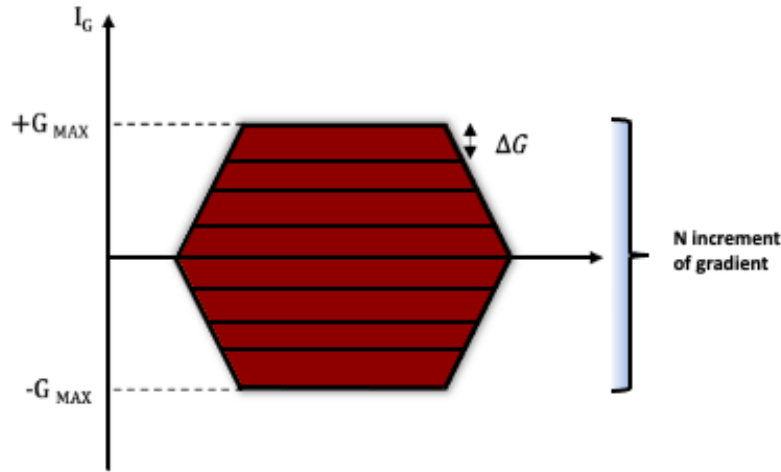


Figure 3-16 Representation of the gradient pulse applied during the CSI sequence.¹²²

3.7 NMR for studying rechargeable batteries

LIBs and SIBs are intricate systems where various electrochemical and chemical processes occur simultaneously, which affect each other. Therefore, comprehending these interlinked processes is necessary for explaining the mechanisms behind battery failures and enhancing their overall performance.

Generally, two main families of measurements, *ex situ* and *in situ*, can be employed to study batteries. In the following, we will provide an overview of the current NMR and MRI research on batteries using *ex situ*, *in situ* and *operando* techniques. The following sections contain excerpts from our recent published review paper in which for more detailed information, we refer the reader to this review.¹²³

3.7.1 *Ex situ* NMR

In *ex situ* NMR, the usual procedure involves extracting the part of the interest from the battery within an argon-filled glovebox and then placing it into an NMR rotor. MAS is an invaluable technique for acquiring resolved NMR spectra of solid materials, serving as the primary asset of *ex situ* NMR when it comes to analyzing the solid components of a battery.

Ex situ NMR is traditionally performed to analyze the bulk changes in the solid components at different states of charge (SOC) of the battery.¹²⁴ More recently, it was employed to study the SEI for the anodes,^{125–130} the solid electrolyte reactivity and dynamics¹³¹ and the CEI for the cathodes.¹³²

3.7.2 *In situ* / *operando* NMR and MRI

In the context of *in situ* NMR, the entire battery is placed within the NMR magnet and the radiofrequency coil. *In situ* NMR offers valuable advantages, primarily due to the elimination of a destructive battery opening. Additionally, this technique enables the acquisition of spectra across various SOC from a single battery. However, in *operando* mode, not only the full battery is placed inside the NMR magnet, but also current flow for the further charge and discharge of the battery. This enables the detection of transient phases in real-time, a capability that holds particular interest within the field of batteries due to the highly chemically reactive environment.¹²³

In situ studies of batteries, despite these advantages, are facing challenges due to resolution and sensitivity limitations of common conventional atoms such as ^7Li or ^{23}Na . Another limitation, challenging to resolve under typical operating conditions, arises from the metallic nature of electrodes (not always) and cell casing, composed of conductive materials that shield RF irradiation and reduce considerably the signal-to-noise ratio. Nevertheless, *in situ* NMR in the “modern” way was first applied in 2003 to characterize half cells¹³³ and was subsequently advanced by different research groups^{134–136,124,123} for various specific purposes.

More recently, research has been focused on questions that remain answerable despite the relatively lower resolution when dealing with static samples, mainly Li or Na plating, which can be easily distinguished from other Li-containing compounds due to their large Knight shifts.

In 2015, Arai and Gotoh studied the deposition of metallic lithium during overcharging of graphite and hard carbon electrodes as well as the behavior of the deposited Li through *in situ* ssNMR.¹³⁷ In another work by Gotoh et al., the sodiation and oversodiation mechanisms of hard carbon Na metal half-cell, were studied using *operando* NMR.¹³⁸ Kayser et al. further revealed the formation and evolution of mossy and dendritic Li microstructures on graphite through *operando* NMR, using an optimized cylindrical *in situ* cell and probe.¹³⁹ Sanders et al. studied the effect of fast charge on graphite and the formation of dead lithium.¹⁴⁰ Afonso et al. investigated the onset of metastable lithium deposits in an NMC622/graphite cell at low temperatures and during rapid charging using *operando* NMR.¹⁴¹ Silicon electrodes were covered by Grey and Eckert.^{142–144} *Operando* NMR was employed by Lopez et al. to follow the mechanisms of capacity fading, lithiation, and delithiation in Sn electrodes.¹⁴⁵

Regarding positive electrodes, the electrochemical behavior of $\text{Li}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$ electrodes were explored by Salager et al.¹¹⁹ through *operando* NMR. Märker et al.¹⁴⁶ analyzed, *operando*, the evolution of the signal of NMC 811 with temperature and charging, together with lithium plating on graphite.

The investigation of temperature-dependent electrolyte polarization under an applied current was conducted by Bazak et al. through the application of *in situ* MRI technique¹⁴⁷. Using MRI technique, they also quantified the electrolyte transport parameters with spatial resolution within an *in situ* lithium-ion cell.¹⁴⁸

For *in situ* investigations of electrolyte decomposition products using liquid-state NMR, we direct the reader to another comprehensive review.¹⁴⁹

3.7.3 MRI

As previously discussed, spatial selectivity can be achieved through MRI methods, allowing signals from similar components to be separated based on their respective positions within the battery.^{150,148,151–156} This proves particularly valuable for comparing the similar electrodes of the symmetrical Li//Li or Na//Na cell. An important advantage of MRI lies in its chemical selectivity,

where the image is generated using only a single type of atom, along with its capability to acquire localized spectroscopic parameters. The challenge lies in achieving high spatial resolution with sufficient sensitivity, which requires strong magnetic field gradients and long signal lifetimes. This methodology offers a means to locate the spins with a precision of approximately 1 μm in optimal scenarios for ^1H MRI, and down to a few hundred μm in most cases. In the following, we will mention examples of recent investigations.

An initial attempt to image paramagnetic LiFePO_4 using stray-field NMR failed due to its strong paramagnetism. The resulting image was strongly distorted, making it very challenging to gain information.¹⁵⁷ Although, alternative methods have been developed to image paramagnetic battery materials with ultra-short T_2 ,^{158–161} none of these approaches allow the simultaneous acquisition of both the NMR spectrum and the image.

In conventional spectroscopic imaging methods such as CSI and volume-selective localized spectroscopy (utilizing spin/stimulated echoes),^{162–164} the application of strong pulsed magnetic field gradients (PFG) is common to spatially labeled transverse magnetization. To capture high-resolution NMR spectra, it is essential to deactivate the gradient, a step which cannot be completed in a time faster than 0.5–1 ms for significant PFG strengths.

The NMR signal within the electrodes experiences a rapid decay (typically less than 100 μs) due to presence of the paramagnetic transition metal atoms which results in a short T_2 even for neighboring Li atoms. Therefore, traditional spectroscopic imaging methodologies are not that practical for electrode materials detection through imaging.¹¹⁹ However they are good enough for the liquid electrolyte¹²⁰ or solid electrolyte.^{154,165}

Tang et al. developed the S-ISIS approach to obtain the ^7Li image of a 5 mm-diameter operating battery ($\text{LCO}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)) with a remarkable resolution of 100 μm for paramagnetic electrodes.¹⁶⁶ Their work enabled real-time visualization of the lithiation front displacement within the thick paramagnetic electrodes during battery cycling.

Another methodology for the noninvasive evaluation of commercial Li-ion battery cells has been employed by A. J. Ilott et al. In this approach, the growth of microstructure and dendrites is indirectly monitored through ^1H MRI of the electrolyte in three dimensions at various charging states.¹⁶⁷

An interesting derivation of this ^1H NMR approach to image indirectly the battery state was developed by Ilott et al.¹⁶⁸ The battery is placed within a holder that contains a detection medium (water and later highly protonated polymer¹⁶⁹). The ^1H NMR signature of this polymer is modified by the magnetic susceptibility of the neighboring battery (change in local magnetic field). As the battery is cycled, its magnetic susceptibility is altered so that the NMR signal of the polymer next to it is sensitive to its SOC. Following these developments, Romanenko et al. utilized io-SPRITE to analyze the magnetic field distribution within commercial batteries, achieving a highly sensitive mapping of weak magnetic field perturbations.^{169–172} This approach provides information on magnetic field distortion as measured from the outside of the pouch cell.

3.8 Conclusions

The *operando* characterization of batteries is essential for comprehending degradation mechanisms and enhancing their electrochemical efficacy. This arises from real-time monitoring of electrochemical processes and formation of short-lived transient or reactive phases, without necessitating cell dismantlement.

In-situ investigations involving conventional ^7Li NMR within batteries encounter resolution limitations for paramagnetic or conductive electrodes. As the first key limitation we can mention temporal resolution which refers to the ability to monitor and capture changes within a system as they occur over time. In the case of *in situ* ^7Li NMR analyses of the battery, temporal resolution is limited as the technique cannot always provide data at a sufficiently high frequency to capture fast changes or dynamic processes within the battery. Electrochemical reactions within a battery can occur on short time scales so if the NMR data acquisition rate is too slow, valuable information may be missed.

Another limitation is regarding the spectral resolution, the ability to distinguish and resolve various spectral features or components within the NMR spectrum. In the case of ^7Li NMR, it may be difficult to distinguish between different chemical or structural environments of Li-ions within the battery, due to peak overlap or large broadening for paramagnetic materials. This reduced ability to identify specific Li-ion species or compounds can be problematic particularly when we try to

gain insight into the complex chemistry and dynamics occurring within a battery in an *operando* mode (during its operation).

As a result of those above-mentioned resolution limitations, *in situ* analysis of the LIBs typically analyze strong shift changes in NMR during charge-discharge or are used in combination with *ex situ* examinations. Similar challenges extend to Na-ion batteries due to the low sensitivity of ^{23}Na NMR, arising from the lower gyromagnetic ratio, quadrupolar nature and fast relaxation of ^{23}Na . Thus, acquiring accurate signals from the existing ^7Li and ^{23}Na nuclei within the LIBs and SIBs remains challenging. Additionally, imaging time is constrained by the inherent low sensitivity of ^7Li and ^{23}Na .

Although MAS NMR holds significant potential, is not widely applicable to functional batteries due to the strong eddy currents induced by the spinning of metallic components in a strong magnetic field.

To overcome these challenges, we explore an approach in which we focus on the local magnetic susceptibility changes within the operating cell. Magnetic susceptibility is principally influenced by the material's electronic configuration. Consequently, significant changes in magnetic susceptibility can occur during redox reactions like battery charge and discharge processes. Notably, the magnetic susceptibilities of commonly employed cathode materials like lithium nickel manganese cobalt oxides, lithium iron phosphates, lithium manganese oxides, and lithium cobalt oxides are dependent on their lithiation state.

In our approach, instead of looking directly at lithium atoms within the electrodes, we focus on the ^1H signal of the liquid electrolyte solvent which can be used to spy on the electrode evolution. This indirect measurement of the magnetic susceptibility changes of the electrodes through the electrolyte signal can then be correlated to the oxidation state of the electrodes and yield detailed information about electrochemical processes which is essential to identify the origins of capacity loss in full batteries.

A significant advantage of this approach is the considerable enhancement in sensitivity due to the use of ^1H (with a high gyromagnetic ratio and narrow lines) instead of conventional ^7Li and its applicability to various battery systems. Additionally, the fast measurement provided by the ^1H

method should bring a notable advantage over other existing methods regarding time resolution. This advantage will be crucial for investigating various cycling behaviors in an operando mode, especially those occurring within very short time scales. Moreover, it opens up diverse applications across various battery chemistries, including Na-ion batteries, and allows for the utilization of electrodes containing NMR nuclei that are less responsive or inactive, like zinc.¹⁶⁸

3.9 References

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Chapter 4 Magnetic susceptibility of materials and NMR

4.1 Introduction

Magnetic measurements play a crucial role in studying the magnetic structure and electronic properties of redox-active materials in LIBs. Magnetic properties also hold significant interest as they can detect impurities and nanoparticles, particularly when traditional analysis methods like X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and others fail to do so.

The magnetizability of materials originates from the magnetic properties of their constituent particles at the atomic level. In most cases, this magnetism is primarily determined by the magnetic moments of the electrons. The electronic structure of electrodes plays a significant role in determining their magnetic susceptibility. The magnetic susceptibility of a material is influenced by the arrangement and behavior of its electrons, including their spin, orbital motion, and interactions with each other and the surrounding environment.

In the context of battery electrodes, understanding the electronic structure is particularly crucial for comprehending their behavior during electrochemical processes, such as battery charging and discharging, also known as redox reactions in electrochemical cells. These processes involve the transfer of electrons, which impacts the electronic configuration and, consequently, the magnetic properties of the electrodes. NMR spectroscopy can be sensitive to the magnetic behavior of materials at the atomic or molecular level.

This chapter presents the relationship between magnetic susceptibility and the electronic structure of battery electrodes. We then present the latest research on *ex situ* measurements of magnetic susceptibility in battery electrodes using NMR. Finally, we discuss the impact of magnetic susceptibility on NMR measurements.

4.2 Theory of Magnetism

This part introduces a few concepts of magnetism necessary to understand magnetic susceptibility.

4.2.1 Magnetization

The magnitude of magnetization, denoted as M , is defined as the total magnetic moment per unit volume.

$$\vec{M} = \vec{\mu} \frac{N}{V} \quad \text{Equation 1}$$

where N is the total number of magnetic moments, V is the volume of the material and μ represents the total magnetic moment.

Typically, magnetization is expressed on a length scale that is sufficiently large to involve the averaging of multiple atomic magnetic moments. Under such circumstances, magnetization can be treated as a smoothly varying vector field.

Vacuum has no magnetization (M is equal to zero).¹⁷³ While all materials contain electrons, in the absence of an external magnetic field, the magnetic moments of electrons typically either pair up or exhibit random orientations, resulting in zero overall magnetism (except for ferromagnetism).

4.2.2 Magnetic Induction

The response of a material to an externally applied magnetic field H , resulting in the generation of a magnetic force within the material, is known as magnetic induction or magnetic flux density B . The relationship between H and B is a characteristic property of the material itself. In vacuum, there exists a linear correlation between B and H :

$$\vec{B} = \mu_0 \vec{H} \quad \text{Equation 2}$$

Where μ_0 is a constant known as the magnetic permeability of free space and characterizes how magnetic fields propagate through vacuum. B and H are vector quantities since they possess both magnitude and direction; their directions are typically aligned in vacuum.

However, inside a magnetic material, the magnetic induction B and the applied magnetic field H may differ in magnitude and direction. This discrepancy arises due to the presence of magnetization M within the material.

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}) \quad \text{Equation 3}$$

In the subsequent discussion, we will use the term "magnetic field" to refer to both the magnetic induction (B) and the applied magnetic field (H), as it is commonly done in literature.^{173,174}

4.2.3 Magnetic Susceptibility

Often, a linear relationship between the magnetic induction B and the applied magnetic field H continues to hold. It is characterized by the magnetic susceptibility χ of the material:

$$\vec{M} = \chi \vec{H} \quad \text{Equation 4}$$

χ is a measure of how much a material will become magnetized in an applied magnetic field. In general, magnetic susceptibility in solids is tensorial in nature, with an orientational dependence.

As a result, Equation 3 becomes:

$$\vec{B} = \mu_0(1 + \chi)\vec{H} \quad \text{Equation 5}$$

$$= \mu_0 \mu_r \vec{H} \quad \text{Equation 6}$$

with $\mu_r = 1 + \chi$ being the relative permeability. χ is often expressed in terms of mass units, i.e. per gram, or as molar susceptibility, χ_m , due to convenience of measurement.^{175,176}

4.2.4 Classification of Magnetic Material

A preliminary categorization into three groups is accomplished based on the magnetic susceptibility χ and materials response to magnetic fields. Magnetic susceptibility serves as an indicator of whether a material exhibits attraction or repulsion when subjected to a magnetic field. In addition to the applied field, the materials own magnetization contributes to the overall magnetic field, causing the field lines to concentrate in paramagnetism, or be excluded in diamagnetism.^{173,177,178}

4.2.4.1 Diamagnetism

Diamagnetism is purely an induction effect. When subjected to an external magnetic field H , magnetic moments are induced such that they align antiparallel to the applied field in accordance with Lenz rule. As a result, the susceptibility associated with diamagnetism is very small and negative:

$$\chi^{dia} < 0 \quad \text{Equation 7}$$

Diamagnetism is an inherent characteristic observed in all materials. It becomes significant only when paramagnetism and ferromagnetism are absent. Diamagnetic properties can be observed in almost all organic substances, as well as in certain metals such as mercury (Hg), and superconductors below their critical temperature.

4.2.4.2 Paramagnetism

The susceptibility of paramagnetic materials is characterized by:

$$\chi^{para} > 0 \quad \text{Equation 8}$$

The emergence of paramagnetism relies on the presence of permanent magnetic moments, mainly from unpaired electrons within the material, which align with the external magnetic field H .¹⁷³ Paramagnetism happens principally for materials whose electronic structure is not closed-shell.

4.2.4.3 Collective magnetism

In collective magnetism, the susceptibility demonstrates a significantly more complicated functional dependence on various parameters in comparison to diamagnetism and paramagnetism. Collective magnetism arises from the exchange interaction among permanent magnetic moments which can only be explained by quantum mechanics. In materials exhibiting collective magnetism, a critical temperature T^* is observed. Below T^* , a spontaneous magnetization emerges, indicating that the magnetic dipoles align themselves without the need for an external magnetic field to enforce the alignment.¹⁷⁹

Collective magnetism, within its subclasses, can be further categorized into three main types: Ferromagnetism, Ferrimagnetism, and Antiferromagnetism. While each of these subclasses has distinct characteristics and behaviors and we will not delve into the specific details of each type here.^{173,179–181}

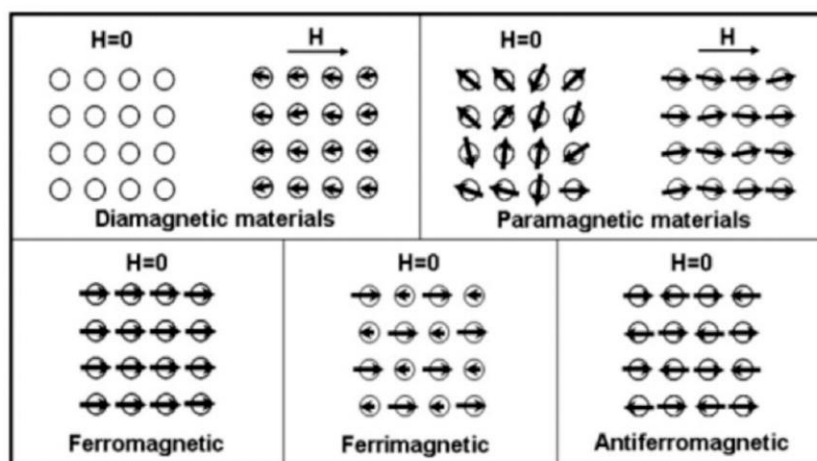


Figure 4-1 Illustration of the behavior of the magnetic dipole moments in five types of magnetic materials with and without an external magnetic field (H).¹⁸¹

4.3 Paramagnetic active materials

The electronic structure of positive electrodes in batteries is intimately connected to their magnetic susceptibility. The magnetic susceptibility of a material is influenced by its electronic band structure, which describes the distribution of energy levels and allowed electron states. Transition metal ions, commonly found in positive electrode materials, can have varying oxidation states that impact the electronic configuration. The oxidation state of transition metal ions affects the number of unpaired electrons and their spin orientations, which in turn influence the material magnetic moment.^{175,182} Due to the utilization of paramagnetic active materials in our experiment, our primary focus going forward will be on their paramagnetic properties and the connection between their electronic structure and magnetic susceptibility.

As mentioned earlier, paramagnetic substances exhibit a positive magnetic susceptibility, causing them to be attracted to an applied magnetic field. This behavior arises from the interaction between unpaired electrons and the applied magnetic field, which is described by the quantum-mechanical distribution of electrons across energy levels within an atom exposed to a magnetic field. Van Vleck¹⁸³ derived a general equation that gives rise to two forms of paramagnetism: temperature-independent (referred to as Van Vleck paramagnetism) and Curie-Weiss paramagnetism.¹⁸²

In the context of Li-ion battery materials, most of the magnetic centers are d-metal ions, so we will mostly focus on them in this chapter.

4.3.1 Ligand crystalline field theory

The ligand crystalline field theory is usually used in d-transition-metal oxide materials to predict the electronic structure. The oxide ligands lift the degeneracy of the five d-orbitals. For instance, in an octahedral field, the d-orbitals split into three lower-energy t_{2g} and two higher-energy e_g orbitals as illustrated in Figure 4-2.

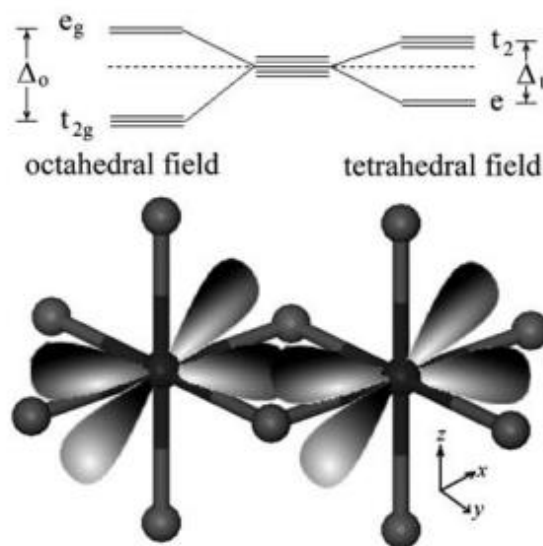


Figure 4-2 Illustration of the splitting of *d*-orbitals in an octahedral and tetrahedral crystal field.¹⁸²

The energy difference between t_{2g} and e_g orbitals, known as Δ , is influenced by the strength of the ligands. When strong field ligands are present, the energy level splitting Δ , becomes larger than the Coulombic repulsion U , leading to the formation of low-spin complexes. In these complexes, electrons preferentially occupy the t_{2g} orbitals with paired spins. On the other hand, in high-spin complexes with weak field ligands and $\Delta < U$, electrons occupy all five *d* orbitals with unpaired spins (d^1 – d^5) before pairing (d^6 – d^{10}).

4.3.2 Curie-Weiss paramagnetism

The magnetic susceptibility of localized electrons follows an inverse temperature dependence due to the thermal agitation of spin moments. In the absence of strong ferromagnetic, ferrimagnetic, or antiferromagnetic couplings, the magnetic molar susceptibility of localized moments displays a Curie-Weiss behavior.⁸

Compounds containing localized unpaired electrons, such as those of *d*- or *f*-metals, exhibit Curie-Weiss paramagnetic behavior. This behavior is described by the Curie-Weiss law.

$$\chi = C/(T - \theta) \quad \text{Equation 9}$$

Where C represents the Curie-Weiss constant and θ is the Weiss temperature.

4.3.3 Van Vleck paramagnetism

The temperature-independent paramagnetism occurs when the energy difference between the ground state singlet and the next excited state greatly exceeds the thermal energy. Conversely, Curie-Weiss paramagnetism arises when the ground state is degenerate, and thermally accessible excited states exist.¹⁸² The contribution of Van Vleck paramagnetism is frequently observed in compounds that contain d-metal ions in their highest oxidation state, characterized by a d^0 electronic configuration. This contribution leads to a susceptibility on the order of 10^{-4} emu.mol⁻¹.

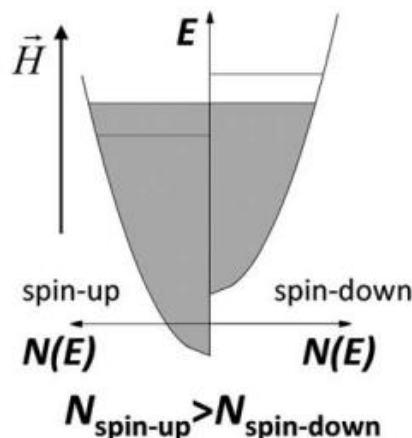


Figure 4-3 Splitting of the conduction band in the presence of a magnetic field, resulting in Pauli spin paramagnetism.¹⁸²

4.3.4 Pauli paramagnetism

Bulk metal electrodes possess itinerant electrons and exhibit Pauli paramagnetism.¹⁸⁴ It is important to acknowledge that in bulk metals, conduction electrons are not spatially localized as electrons in partially filled ionic shells. As a result, the magnetic susceptibility of metals shows temperature-independent Pauli paramagnetism due to the splitting of energy bands into "spin-up" and "spin-down" states in the presence of a magnetic field.^{182,185}

4.4 Ex situ measurement of magnetic susceptibility

Superconducting quantum interference devices (SQUID) have currently become a standard and widely used technique for ultrasensitive magnetic measurements. To achieve exceptional sensitivity in measuring the magnetic moment, a SQUID device utilizes a liquid-helium-cooled amplifier that can accurately measure magnetic within a range of 10^{-7} to 300 emu. Moreover, the

SQUID field range spans from -5.5 to $+5.5$ T, making it a versatile tool for various applications in magnetic research and technology.

Experimental data on the temperature dependence of susceptibility is collected using two modes to determine the magnetic behavior: zero-field cooling (ZFC) and field-cooling (FC). These modes involve consecutive magnetization measurements. In ZFC, the sample is initially cooled without an applied magnetic field and then measured with increasing temperature in the presence of a magnetic field. Similarly, in FC, the sample is cooled in a magnetic field, and measurements are taken as the temperature decreases.

Various techniques can also be employed to study the magnetic properties in materials such as neutron diffractometry, magnetometry, NMR, and electron spin resonance. Additionally, two resonance spectroscopies are also valuable tools for examining the local structure of materials. To investigate the microscopic magnetic structure of materials, it is common to employ neutron scattering techniques. These experiments enable the measurement of the structure and excitations of various types of magnetic materials.

More recently, synchrotron sources have also been employed for magnetic scattering studies. The wide range of wavelength and energy associated with thermal moderated neutrons enables researchers to explore not only the nuclear long-range, static properties of solids but also their dynamics, including phonons. This comprehensive approach provides valuable insights into the magnetic behavior and characteristics of materials.^{8,186}

In this thesis, we aim at probing the magnetic susceptibility of electrodes through their effect on the ^1H NMR spectrum of the electrolyte. In this context, we report literature data on the magnetic susceptibility at ambient temperature of pure active materials that will be used in the following.

4.4.1 LiCoO_2 (LCO)

Perfectly stoichiometric LiCoO_2 contains low-spin configuration ($t_{2g}^6 e_g^0$; $S=0$) Co^{3+} ions with paired d-electrons when fully lithiated and displays diamagnetic plus Van Vleck paramagnetism.⁶ This configuration suggests the absence of a local spin moment in perfectly stoichiometric LCO.^{6,187} The magnetic susceptibility of stoichiometric LCO at room temperature was measured to be $+9 \times 10^{-5}$ emu/mol by Menetrier et al.⁶ It is important to note that these values vary deeply for imperfections in the stoichiometry of LCO (up to $+20 \times 10^{-5}$ emu/mol).

When the material is delithiated, Co^{3+} undergoes a partial oxidation to the +4 state ($\text{Co}^{4+} : d^5$), and the material undergoes a transition in electronic structure to metallic, through semi-conductor. This change results in variations of the magnetic properties.^{6,187}

4.4.2 LiMn_2O_4 (LMO)

LiMn_2O_4 is a mixed-valence compound containing both Mn^{3+} (d^4) and Mn^{4+} (d^3) ions. Due to the presence of unpaired electrons in the Manganese ions, the magnetic susceptibility of spinel LMO at was measured as $+8.7 \times 10^{-3}$ emu/mol,⁸ with a Curie-Weiss temperature of -260 K and a Curie constant of 4.85 emu.K/mol.

The Mn^{3+} ions can be oxidized to Mn^{4+} upon charging of LiMn_2O_4 and reduced back to Mn^{3+} during discharge, leading to changes in the magnetic moments of manganese ions.

4.4.3 $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMCXYZ)

The magnetic properties of NMC arise from the presence of nickel, manganese, and cobalt transition metal ions. As shown in figure 4-4 the temperature dependencies of the dc magnetic susceptibility of NMC follow the Curie-Weiss law at high temperatures. However, as the temperature decreases, there is an observable increase in magnetic susceptibility, which is most significant in the 550 compounds.

As the concentration of nonmagnetic Co^{3+} ions (with a low-spin d^6 configuration) increases, the number and size of magnetic clusters decreases. Consequently, the total magnetic moment per formula unit decreases as well.

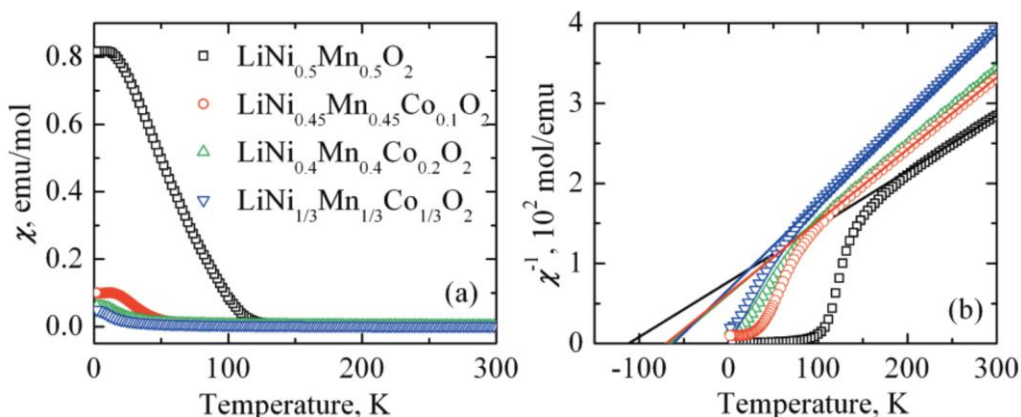


Figure 4-4 (a) Temperature dependences of magnetic susceptibilities of $\text{LiNi}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$ and (b) the reciprocal susceptibilities and their fit to the Curie-Weiss law, Copyright 2007 American Chemical Society.⁷

In Chernova et al., the magnetic susceptibility of $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC 111) at 300 K was measured at $+2.5 \times 10^{-3} \text{ emu/mol}$, with a Curie-Weiss temperature of -62.1 K and a Curie constant of 0.916 emu.K/mol.⁷ NMC442 had a magnetic susceptibility of $+2.9 \times 10^{-3} \text{ emu/mol}$ (Curie-Weiss temperature: -65.8 K, Curie constant 1.068 emu.K/mol. We did not find reports of the magnetic susceptibility for $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) in the literature. We assume that it would likely exhibit a similar trend to other materials at room temperature.

4.4.4 LiFePO₄ (LFP)

The magnetic properties of LFP primarily arise from the presence of iron ions in the divalent Fe^{2+} state (occupy only the M2 site, i.e., the center of the FeO_6 octahedron unit). According to available literature, the magnetic susceptibility of LFP electrodes at 300 K was measured by Julien et al. to be $9.4 \times 10^{-3} \text{ emu/mol}$ with a Curie Weiss temperature of -145 K and a Curie constant of 4.18 emu.K/mol.⁸ LFP displays an antiferromagnetic transition at 52 K or a ferromagnetic behavior below 216K, depending on the synthesis parameters. The presence of ferromagnetic particles in some cases seems to be the source of these variations.⁸

During cycling, Fe undergoes a reversible redox reaction, alternating between the +2 and +3 oxidation states (as lithium ions are inserted into the structure during charging, iron undergoes redox reactions and changes to the +3 oxidation state). This redox reaction results in variations in the number of unpaired electrons in the Fe 3d-orbitals, impacting its magnetic moment.^{8,188,189}

4.4.5 Graphite

Graphite is strongly diamagnetic and has a highly anisotropic susceptibility. For a single crystal at room temperature, $\chi_{\parallel} = -264 \times 10^{-6}$ emu/mol, et $\chi_{\perp} = -6 \times 10^{-6}$ emu/mol.⁵

Graphite can be considered a quasi-semi-metal, exhibiting exceptionally low carrier density and density of states at the Fermi level. The diamagnetic susceptibility is temperature-dependent, and therefore similarly are the local fields it will induce.¹⁹⁰ Upon lithium intercalation, the materials become conductive and displays Pauli paramagnetism.

4.4.6 Conclusion

The magnetic properties of relevant materials are summarized in table 4-1.

Table 4-1 Magnetic susceptibilities of some materials used in this thesis.

Substances	Magnetic susceptibility at 300K (emu.mol ⁻¹)	Curie-Weiss temperature (K)	Curie constant (emu K. mol ⁻¹)	Refs
Carbon black	$\approx -2.92 \times 10^{-8}$	-	-	2,3
LP30	$\approx -5.34 \times 10^{-8}$	-	-	4
Graphite (single crystal)	$-(6 \text{ to } 264) \times 10^{-6}$	-	-	5
LiCoO ₂ (stoichiometric)	$+9 \times 10^{-5}$	-	-	6
NMC 111	$+2.5 \times 10^{-3}$	-62.1	0.916	7
NMC442	$+2.9 \times 10^{-3}$	-65.8	1.068	7
LiMn ₂ O ₄ (LMO)	$+8.7 \times 10^{-3}$	-260	4.85	8
LiFePO ₄ (LFP)	$+9.4 \times 10^{-3}$	-145	4.18	8

4.5 Paramagnetism and the NMR signal

4.5.1 Bulk Magnetic Susceptibility (BMS) effect

When a sample is subject to a magnetic field H_0 , it undergoes magnetization and in response generates its own magnetic field H_D which is known as the induced or demagnetizing field. This induced field will modify the local shift and induce broadening in the NMR spectra at the interface.¹⁹¹

Discontinuities in magnetic susceptibility between two materials lead to the presence of magnetic field gradients at the interface. In that perspective, the NMR shift can be seen a measurement of the local magnetic field at these interfaces. The impact of these field gradients on linewidth was explored by Hahn in 1950,¹⁹² and later by Carr & Purcell.¹⁹³

This effect is well-known in liquid-state NMR, for which homogeneous liquids usually give rise to extremely narrow peaks provided that the NMR magnet is well-shimmed. In such a case, the magnetic field gradients created at the interface with the NMR tube become limiting for resolution.

4.5.2 Dissolved transition metal ions

Most metal ions that dissolve from cathodes inside the electrolyte solvent are paramagnetic. Liquid-state NMR has been used to analyze electrolytes and obtain information of the dissolved species. Dissolved paramagnetic species in the solvent lead to relaxation enhancement (affecting both T_1 and T_2 relaxation times), where the unpaired electrons of the paramagnetic species create fluctuating magnetic fields that efficiently relax nearby nuclei.^{194–197} This paramagnetic relaxation enhancement (PRE) is used to study the folding of metalloproteins in solution. J.P. Allen et al. demonstrated that they could measure the concentration of dissolved paramagnetic transition metal ions in electrolyte from the ^1H and ^{19}F PRE, up to 5 mM for Mn^{2+} . The calibration curves were however inaccurate for degraded electrolyte.¹⁹⁸

Dissolved paramagnetic transition metal ions also create a BMS shift at the “interface” between the ion and the solvent molecules that can be exploited. To the best of our knowledge, this had not been exploited in NMR of classical batteries when this thesis started. A couple of articles were published since. J.P. Allen et al investigated the use of bulk magnetic susceptibility shifts to detect the oxidation state of dissolved transition metal ions. In the simple case of a single dissolved species concentration of could also be determined.¹⁹⁹ In another report, they studied how dissolved Ni^{2+} and Mn^{2+} in LiPF_6 electrolyte solutions affected ^1H , ^{19}F , and ^{31}P NMR spectra, including the potential loss of peaks from degradation species and the mitigation of spectral broadening.¹⁰³

In the context of redox-flow batteries, Zhao et al used the linear relationship between the shift of water resonances in ^1H NMR spectra and the electrolyte solution bulk magnetization to monitor, *in situ*, the redox activity of a ferro/ferri cyanide catholyte solution. The effective magnetic moments of dissolved ferricyanide anions were also calculated and to determine the battery SOC during

cycling.²⁰⁰ In 2020, they also reported how the ^1H water shift could follow the redox activity the anthraquinone-derived anolyte solution of a redox flow batteries.²⁰¹

4.5.3 Metallic lithium dendrites in liquid electrolyte

The presence of paramagnetic metallic lithium²⁰² in contact with liquid electrolyte significantly affects the liquid spectrum through signal distortion, shift and relaxation effects.

Ilott et al. introduced an approach to indirectly measure dendrite growth by observing the ^1H image of the electrolyte and modelling three different effects. The first effect is the displaced volume in the electrolyte. The second effect is the BMS effect on the electrolyte and the latter is the radiofrequency (RF) field distortion by the metal. They result in frequency and phase changes near the interface, enabling a complete 3D measurement for tracking dendrite growth over time (figure 4-5).¹⁶⁷

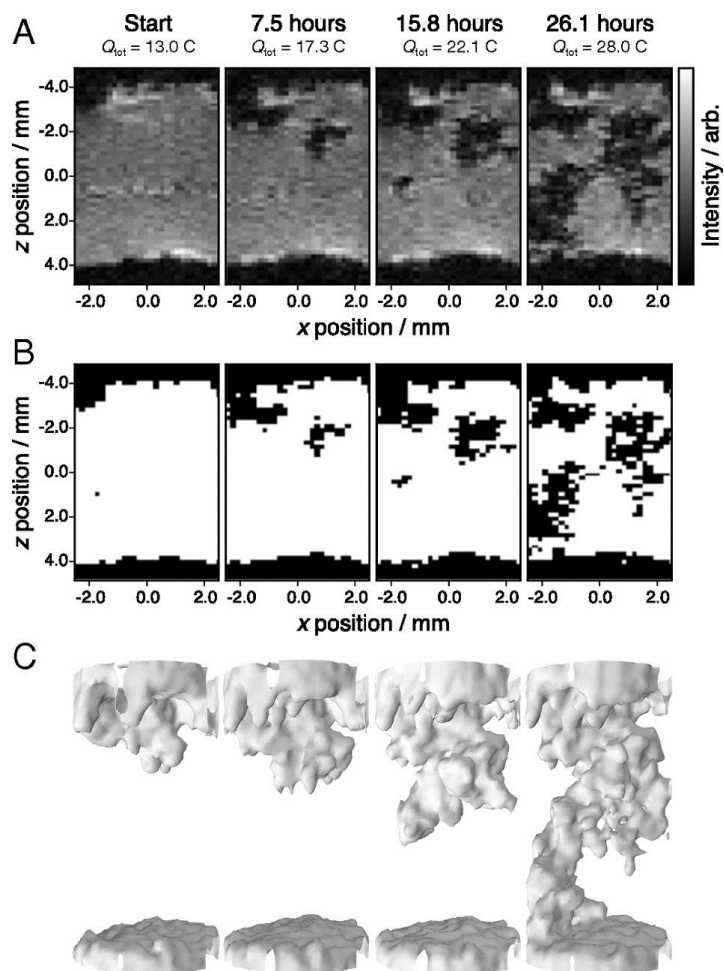


Figure 4-5 In situ ^1H 3D FLASH imaging of electrochemical cell (A) 2D slices from four time points. (B) Segmented images of the results from A (C) 3D segmented images for enhanced visualization.¹⁶⁷

4.5.4 Specific case of solids

While for liquid-state NMR the sample is homogeneous, in polycrystalline powders several scales need to be considered. The BMS mechanism is a macroscopic effect that can exhibit spatial variation throughout a particle and the entire sample. It is rooted in the dipolar couplings between nuclear spins and electron magnetic moments, and it arises when the sample shape is non-spherical or if the distribution of paramagnetic spins within the sample is non-uniform. Pell et al. covered the microscopic description of this effect in their recent review and linked the bulk magnetic susceptibility to the paramagnetic shift and the hyperfine coupling.¹⁹¹

4.5.4.1 Calculation of BMS for solids

To address BMS effects, a common approach involves treating a specific region within the sample as a sphere, where BMS effects are absent, and separately considering the remaining part of the sample (excluding the spherical region) that contributes to BMS effects.

By calculating and summing long-range contributions from all other volume elements in the rest part of the sample (acting like point dipoles), the BMS shift, and broadening can be determined.^{112,113}

The impact of the demagnetizing field on a nuclear spin within a crystallite can be divided into three contributions (figure 4-6), following the model proposed by Terao and coworkers :^{116,203} the intra-dipolar field, S_E , which originates from all the paramagnetic ions (p_k) within the Lorentz sphere; (2) the demagnetization field, S_O , generated by a given crystallite, which is dependent on its shape, orientation, and BMS of the crystallite; (3) the inter-dipolar field, obtained by summing up the contributions from all crystallites (i) within the entire sample, which is influenced by the overall sample shape (e.g., the sample container).

The first contribution is responsible for the nuclear-electron through-space dipolar interaction, leading to broadening in all cases and causing a pseudocontact shift if there exists an anisotropic component to the magnetic susceptibility of the paramagnetic ions. The second and third contributions collectively give rise to what is known as the BMS shift, involving the local (crystallite/particle shape, S_0) and macroscopic shape components, respectively.

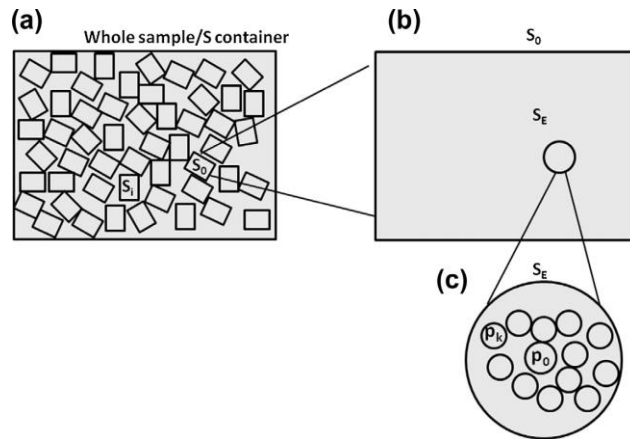


Figure 4-6 Model of a polycrystalline sample in a container S , based on that described in previous work.²⁰³ (a) Crystallites (S_i) are assumed to be randomly packed into a cuboid shaped sample. (b) The crystallite containing the observed nucleus, $S_0(i = 0)$, has a volume magnetic susceptibility, $\chi_{V_f} =$

χ_{mf}/V_i where χ_{mf} and V_i are the molar magnetic susceptibility and volume of the i th crystallite, respectively. (c) S_E is a Lorentz sphere with a radius much smaller than the size of the crystallite, but large enough so that the dipolar average over the lattice points converges. p_0 and p_k indicate the observed nuclear and paramagnetic ions within the Lorentz sphere, respectively.¹¹⁶

In cases where exact solutions of classical magnetostatic equations are not available for sample geometries, the technique introduced by Salomir et al. enables a rapid estimation of the magnetic field inhomogeneity arising from a sample with varying shape and magnetic susceptibility.²⁰⁴

4.5.4.2 NMR measurements for batteries

Pigliapochi et al. investigated the NMR shift of a paramagnetic material and its dependence on the local environment of the observed nucleus and the shape of the particles. The study analyzed the dependence of the NMR shift on the crystal shapes and the anisotropy of the particles' aspect ratio for LiFePO_4 powders.²⁰⁵

Regarding *in situ* NMR studies, Trease et al. revealed on plastic bag batteries using $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$ electrode that the BMS effects resulted in shifts and broadening,¹¹⁷ and that it depended on the orientation of the battery in the magnetic field.

Zhou et al. studied the orientation-dependence of the BMS effect in electrode films made of 70% $\text{Li}_{1.08}\text{Mn}_{1.92}\text{O}_4$. A macroscopic shape effect was observed and simulated successfully.¹¹⁶

4.6 Conclusion

LIBs, being the most common type of rechargeable batteries, have lithium ions as the charge carriers that move between cathode and anode during charge and discharge cycles. ^7Li NMR spectroscopy is a powerful technique to directly probe the behavior of lithium ions in the battery's electrodes.

When lithium ions enter or leave the electrode material during charging or discharging, the local environment surrounding these ions changes, resulting in shifts in the ^7Li NMR signal. These shifts provide valuable information about the lithiation and delithiation processes, as well as the structural changes and degradation occurring in the electrodes over time. However, despite the informative nature of ^7Li NMR spectroscopy, there are certain limitations associated with this technique. The signal from lithium ions in the solid electrodes can be broad and highly shifted, making it challenging to determine fine details in the NMR spectrum. Additionally, the sensitivity of ^7Li NMR is relatively lower compared to other NMR nuclei, such as ^1H , which can impact the detection of signals from low-concentration species or rapid changes in the battery components upon redox reaction.

In this chapter, we introduced the concepts of magnetism and more particularly bulk magnetic susceptibility and its effect on the NMR spectrum. This effect is stronger for paramagnetic material, like those encountered in Li-ion batteries. The signal of the solvent was exploited for the *in situ* NMR characterization of SOC in redox-flow batteries, but never tested for Li-ion batteries to the best of our knowledge. The phenomenon was studied and modelled to better understand the complex ^7Li NMR spectra of batteries, an archetype of a heterogeneous, multi-component and paramagnetic device.

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Chapter 5 Testing the sensitivity of NMR to magnetic susceptibility

5.1 Introduction

The characterization of batteries is critical to improve our understanding of the cycling and degradation processes and to increase their electrochemical performance, especially in abusive conditions like during fast charges. Among all parameters, knowledge of the exact redox state of each electrode is essential to identify the origins of capacity loss in full batteries. The design of battery packs necessitates battery management system (BMS) technologies, in which the determination of the SOC remains as one of the most challenging parts.⁷⁸ Better determination of the SOC, without the need for a specific three-electrode setup, would help constrain the models used by BMS to estimate the actual available energy in the battery and provide information on the remaining working time of the device and hence battery lifetime.

Among the methods used for these investigations, NMR methods are promising since they enable monitoring of the electrochemical processes, the formation of short-lived metastable or reactive phases, and how the local structures change on extended cycling. Liquid-state NMR was also extensively used to characterize the degradation products in the liquid electrolyte.²⁰⁶

Operando NMR spectroscopy of Li-ion batteries is challenging due to the strong heterogeneity of the battery, which results in broadening and distortions of the NMR spectrum. Several atoms can be probed by NMR in the electrolyte to try and follow the state of charge of the battery. The first that comes to mind is Li^+ , as it is involved in the reactions at both electrodes. However, the ^7Li pure chemical shift is not highly sensitive to its environment (excluding paramagnetic and Knight shift). The range of chemical shift values for diamagnetic species in ^7Li NMR is extremely narrow and sometimes it is not possible to distinguish between resonances arising from various local environments in the NMR spectra of diamagnetic materials.^{103,107,191,199}

Therefore, up to now, most *operando* NMR studies used ^7Li NMR spectroscopy to follow lithiation and degradation processes of electrodes displaying highly shifted peaks and relatively narrow peaks (lithiation of graphite and silicon, lithium plating). *Operando* studies of paramagnetic electrodes is possible with ^7Li NMR, but the extremely broad static NMR spectra restrict the sensitivity (hence time resolution) and precision of the interpretation.^{107,116,10,146}

Although the liquid electrolyte located inside the battery provides a more sensitive (narrower and stronger) *in situ* NMR signal, it has not been fully exploited until now, except to characterize degradation products. NMR of the atoms contained in the electrodes directly probes the change in oxidation state of the material. In contrast, NMR of the liquid electrolyte is not directly sensitive to the oxidation state of the electrodes, but rather indirectly through perturbation of its magnetic and electronic environment.

Paramagnetic materials contain unpaired electrons, which generate strong local demagnetizing fields when placed in a strong magnetic field. These can interact with the surrounding environment, including the liquid, and induce distortions in the NMR signal. These distortions appear as line broadenings, decreasing signal intensities, or even complete signal loss in severe cases (strong induced magnetic field gradients or relaxation).^{103,107,116,117,167,191,199,207,208}

In this thesis, we explored the potential of this indirect sensitivity to changes in the magnetic properties of the neighboring electrodes. This chapter presents our efforts to use the liquid ^1H NMR signal of the electrolyte solvent (carbonates) to “spy” on the electrodes while benefiting from the higher sensitivity of ^1H NMR compared to ^7Li NMR. Contrary to lithium atoms, hydrogen atoms in the electrolyte solvent are not a direct probe of the state of charge of the electrode, but they are sensitive to changes in the magnetic susceptibility of the neighboring electrodes. It was important to distinguish the effect of each of them on the ^1H NMR spectrum of dimethylcarbonate (DMC) to ensure that the change in the redox state was indeed the main effect on the liquid-state NMR spectrum of the electrolyte. The goal is to apply this technique for fast *operando* NMR characterization of operating batteries which will be presented in chapter 6.

5.2 Experimental approach

The studies in this chapter are performed preliminary to *operando* characterization. The battery container developed in our laboratory for *operando* NMR has a 6 mm inner diameter.¹⁰ It is usually assembled with 5 mm-diameter electrodes punched out of coated aluminum or copper foils and activated with 200 μl of electrolyte, supplied by Solvionic® (99.9% purity). A volume of 200 μl of DMC was chosen as this is the volume used for the electrolyte in the *in situ* NMR battery.

The electrolyte is composed of a salt of lithium hexafluorophosphate (LiPF_6) of concentration 1 mol.L^{-1} dissolved in an organic solvent consisting of ethylene carbonate (EC) and dimethyl carbonate (DMC) at the ratio volume ratio 1:1.

5.2.1 Choice of sequence

In a one-pulse sequence, a dead time occurs during which the system is unresponsive or unable to acquire data immediately after the pulse sequence, resulting in significant signal distortion. The Hahn echo experiment is affected by its echo time ($>100\ \mu\text{s}$), leading to signal loss for short T_1 and T_2 relaxation times. Nevertheless, the echo sequence provides a lower baseline distortion (effect of dead time removed from long-enough echoes) compared to a one-pulse sequence. Therefore, in the case of slow relaxation, it is preferable to perform a Hahn echo.

In our experiment, due to the short relaxation time (T_1 and T_2) of paramagnetic materials, we chose a one-pulse sequence with reduced dead time ($<10\ \mu\text{s}$) to better focus on signals that relax quickly, especially those with short T_2 . This approach enhances the sensitivity of our experiment to all signals coming from the liquid. Therefore, for the rest of the NMR measurements, we will use the one-pulse sequence.

5.2.2 NMR experiments

The ^1H NMR spectra for all the samples were recorded at room temperature under N_2 using a Bruker 200 MHz spectrometer equipped with a narrow bore Bruker Sample Transfer Line and a commercial Bruker diff probe. This probe was equipped with a RF coil tuned to the ^1H Larmor frequency (200 MHz at 4.7 T) and a Bruker micro5 (5 G/A/cm) pulsed field gradient (Figure 5-1).

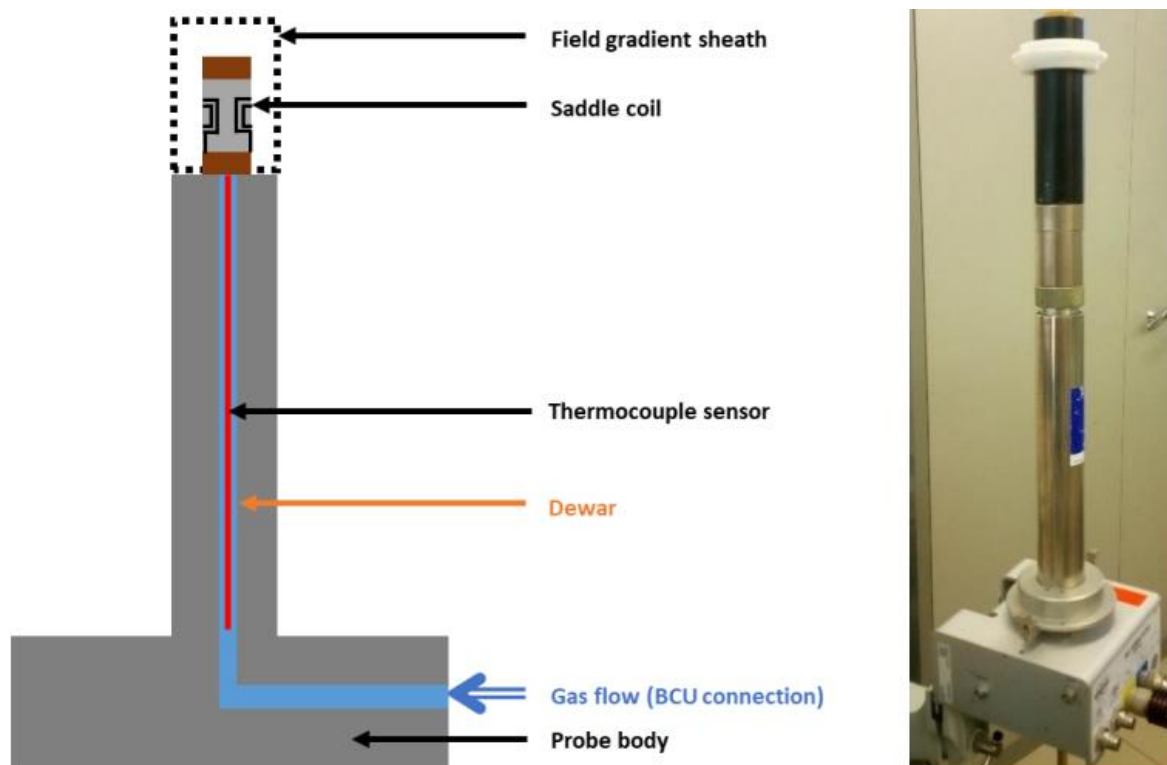


Figure 5-1 Diagram and photo of the diffusion probe and its saddle coil.

A standard one-pulse ^1H NMR sequence was used to ensure quantitativity, with a 90° pulse length of $12\ \mu\text{s}$ ($\pm 1\ \mu\text{s}$, optimized for each sample) using an output power of 25 W. The free induction decay signal (FID) was sampled with a dwell time of $0.833\ \mu\text{s}$ (spectral width 600 kHz), an acquisition time of 40 ms. 4 transients were co-added with a repetition time of 42 s. The NMR spectra were recorded and processed using Topspin 3.6.2 (Bruker). The FID was Fourier-transformed without line broadening parameter ($\text{LB} = 0\ \text{Hz}$). Each spectrum took approximately 4 minutes ($\pm 30\ \text{s}$) to record. The ^1H NMR spectrum was externally referenced to a 2 M Gadolinium doped aqueous solution at 4.8 ppm.

^1H T_1 measurements of DMC in contact with pellets were recorded for each sample to ensure quantitative measurements, using a saturation-recovery sequence.

5.2.3 NMR data analysis

Data analysis and plotting were carried out with home-written MATLAB scripts, based on MatNMR scripts for reading data and metadata.

5.2.4 Choice of pure DMC

We chose to use pure DMC (supplied by Alfa Aesar® - 99% purity) for our *ex situ* measurement, as its ^1H spectrum consists of a unique peak for all equivalent protons, compared to the EC/DMC mixture that contains two singlet peaks at 3.9 ppm corresponding to DMC and one at 4.7 ppm corresponding to EC (Figure 5-2). We observed that the ^1H signal of DMC in the LiPF_6 electrolyte is shifted by approximately 0.2 ppm compared to the signal of pure DMC. This shift can be assigned to a magnetic susceptibility effect.

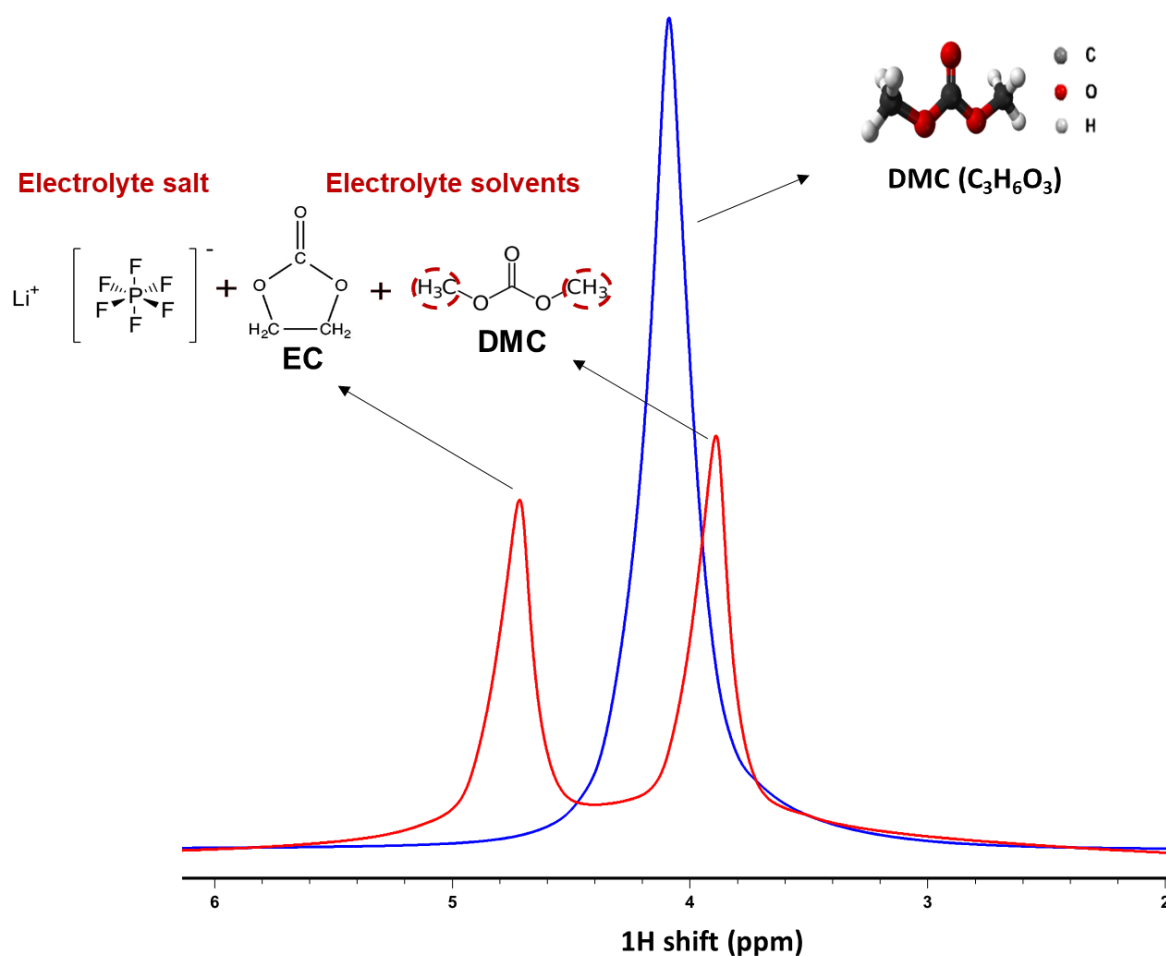


Figure 5-2 ^1H signal of DMC solvent and LiPF_6 in EC/DMC=1:1 electrolyte (fully filled in NMR tube).

5.2.5 Distortion of DMC spectrum by interfaces

For each measurement, a 10 mm standard NMR glass tube was filled with 200 μ l of electrolyte solvent to keep the amount similar to that in an *operando* NMR battery.

The tube was centered in the NMR coil through an O-ring. This O-ring was placed at a constant distance (47 mm) from the bottom of glass tube to ensure the positioning of the 200 μ l of electrolyte solvent in the center of NMR coil (Figure 5-3a, b). This distance was maintained for all *ex situ* measurements to ensure that we remained within the homogeneous zone of the RF coil, ensuring reproducibility and facilitating result comparison.

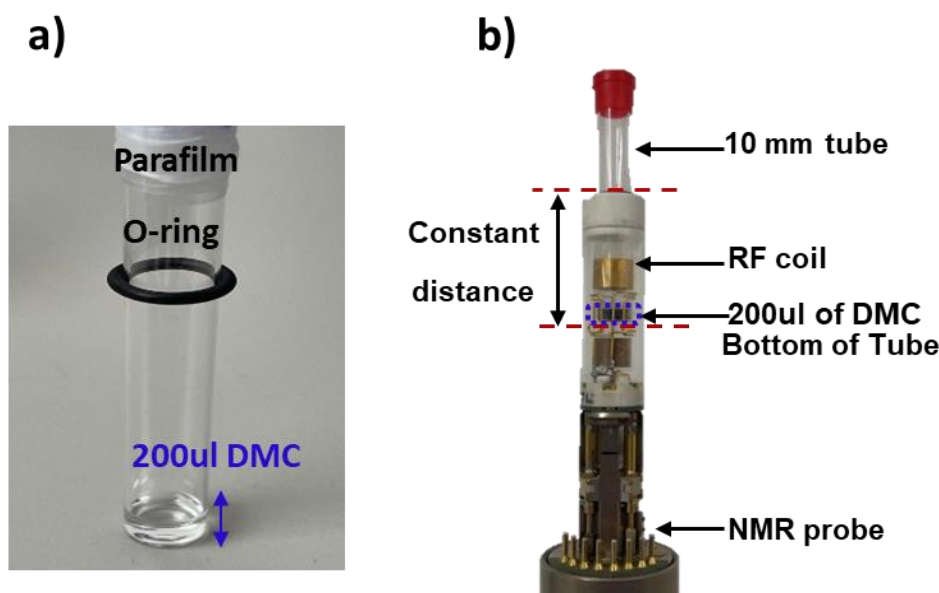


Figure 5-3(a) 200 μ l of DMC in 10 mm NMR glass tube, (b) 10 mm NMR glass tube inside ^1H NMR coil placed on the top of NMR diffusion probe.

As shown in Figure 5-4, for 200 μ l of DMC, the ^1H NMR signal shifts by roughly 3 ppm (from 4 to 7 ppm), and the shape of the spectrum broadens due to magnetic susceptibility jumps at the interface between liquid and air at the meniscus on top of the liquid and between liquid and glass at the bottom of the tube. The broadening and shift of the spectrum is a signature of the local magnetic field perturbation at these interfaces. We chose not to shim the sample to be in conditions close to a real battery for which lots of interfaces disturb the local fields.

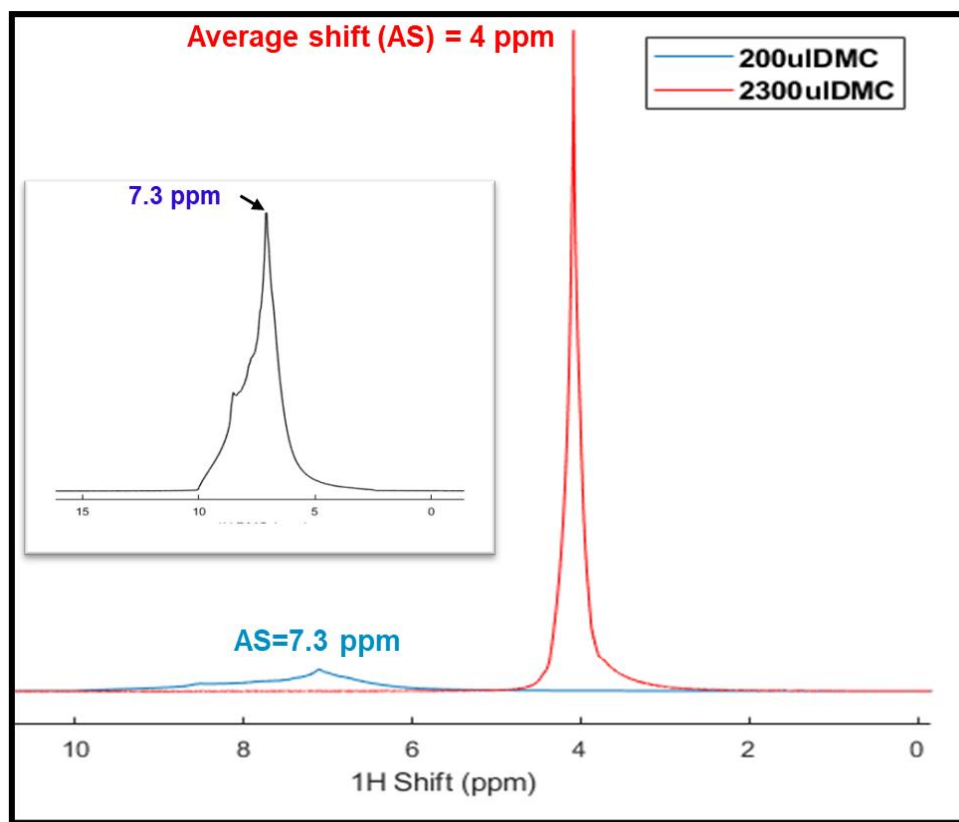


Figure 5-4 ^1H signal of 200 μl and 2300 μl (full tube) of DMC.

5.3 Effect of electrochemically-active pristine materials on the DMC spectrum

5.3.1 Choice of positive redox-active materials

Battery active materials as one of the battery components are responsible for storing and releasing energy during the charging and discharging process of the batteries. Transition metal oxides with layered (e.g. LiMO_2 , where $\text{M} = \text{Co}, \text{Mn}, \text{Ni}$ such as lithium nickel manganese cobalt oxide), spinel (e.g. lithium manganese oxide LiMn_2O_4), and olivine (e.g. lithium iron phosphate LiFePO_4) structures are the most attractive and commonly used positive active materials for LIBs due to their high theoretical capacities, reasonable cost, and natural abundance.^{209,182,13,19}

As explained earlier in Chapter 4, the NMR spectra are strongly influenced by local magnetic fields, related to the electronic structure of the materials. It is often possible to distinguish between insulators and conductors. For insulating materials, diamagnetic and paramagnetic materials have very different spectra. Many battery materials are paramagnetic in the discharged or charged state.

In this chapter, we used four positive active materials known for their electrochemical activity: LiFePO_4 (LFP), LiMn_2O_4 (LMO), $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC 111) and LiCoO_2 (LCO). LFP, LMO, NMC, and LCO positive active materials were obtained from Sigma Aldrich. The full overview of these active materials was reported in Chapter Two; magnetic susceptibility values are summarized in Figure 5-5.

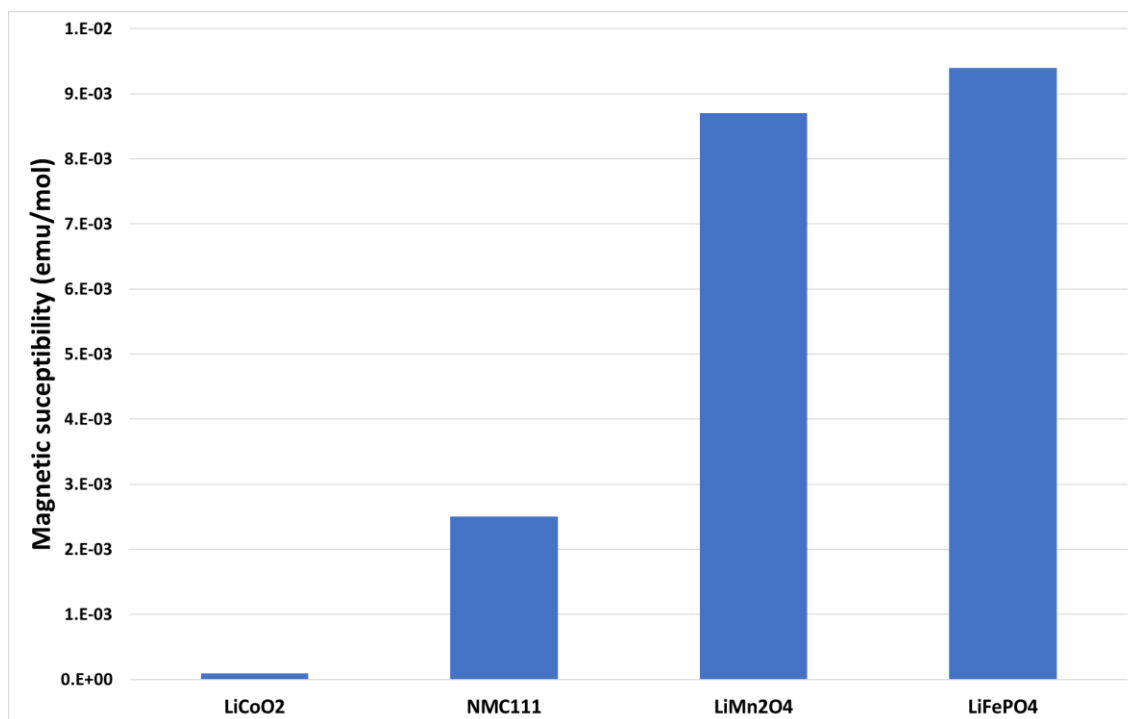


Figure 5-5 Magnetic susceptibilities of active materials (as outlined in Table 4-1 in Chapter 4).

5.3.2 Sample preparation

We made 5 mm-diameter pellets out of 20 mg of powder (from each of the above-mentioned positive active materials) using a standard pellet die and hydraulic press (Figures 5-6 and 5-7). This size was chosen to match that of the 5 mm of electrodes inside the *in situ* NMR cell. A smoothly increasing pressure (up to $2000\text{kg/cm}^2 = 1.96\text{bars}$) was applied for 5 seconds and then released. The pellet was carefully taken off to avoid breaking it.

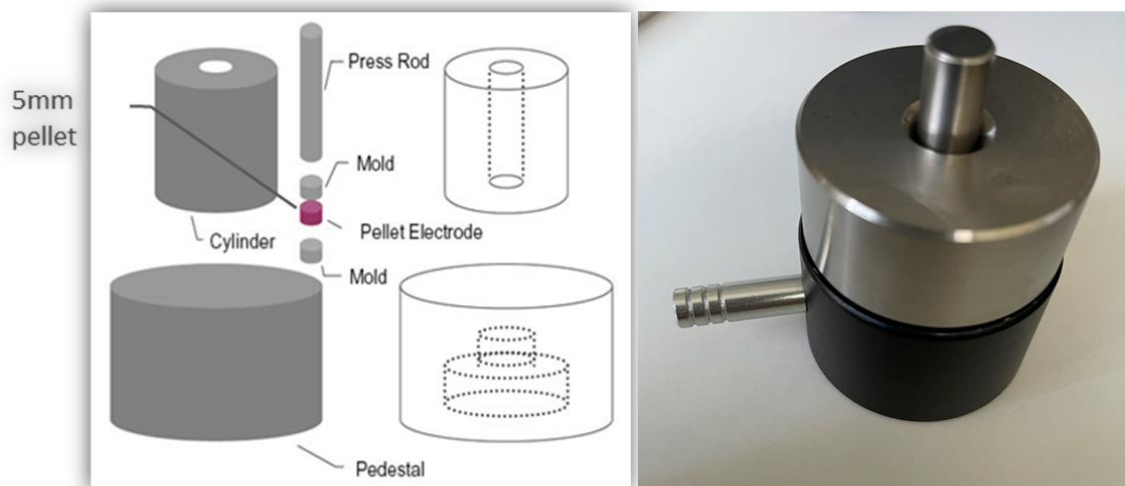


Figure 5-6 Schematics, and photo of the pellet press for making pellets of paramagnetic material.

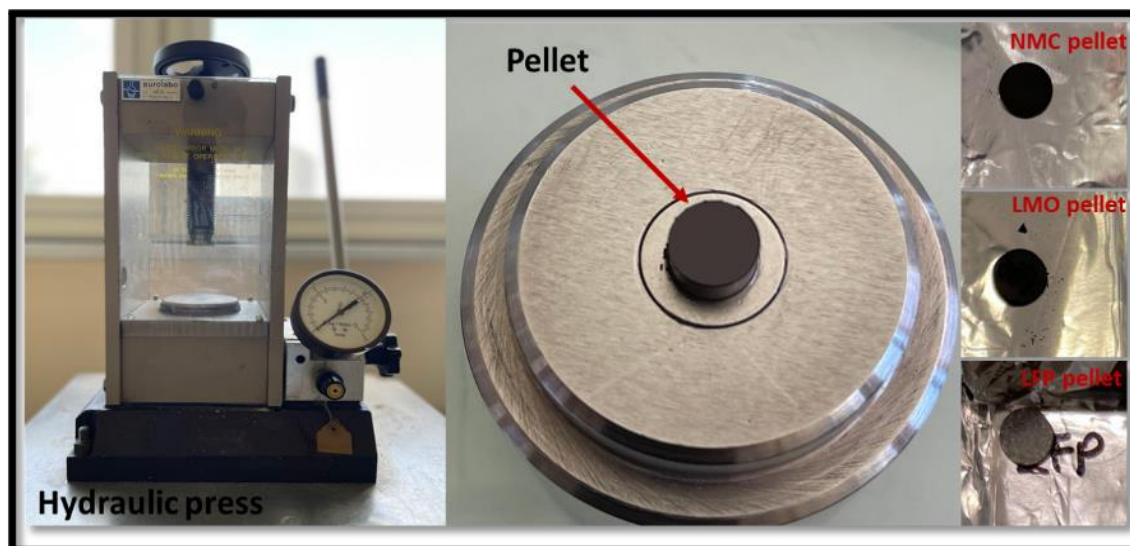


Figure 5-7 Pellet made from powder active materials.

Each pellet electrode (Figure 5-7) was then transferred inside a glovebox with an Argon atmosphere (H_2O and O_2 levels below 1 ppm).

The NMR tubes were washed with acetone at the last stage of cleaning, then kept upside down in a fume hood overnight, and finally moved to the glovebox. The 200 μl of DMC were placed in the NMR tube using a sartorius micropipette (Proline 20-200 μl). DMC is volatile, so the NMR tube was weighed to precisely determine the amount of DMC.

Then the pellets were transferred into the NMR tube, and it was closed by a plastic cap. As shown in Figure 5-8, a thin strip of parafilm was wrapped around the joint between the tube and cap to lower the risk of DMC evaporation throughout the measurement.



Figure 5-8 200 μ l of liquid DMC solvent with 5mm pellet in 10 mm NMR glass tube wrapped with parafilm.

5.4 Descriptors of changes in the NMR spectrum

As shown in Figure 5-9, the effect of the pellets on the shape of ^1H NMR spectra is large and complex. The spectra are broadened and shifted; in addition, distortions appear and prevent fitting with standard Lorentzian or Gaussian shapes. Peak maximum and width at half-height are not relevant anymore. Three adapted descriptors are introduced in the following to allow quantification of the changes in the NMR spectrum.

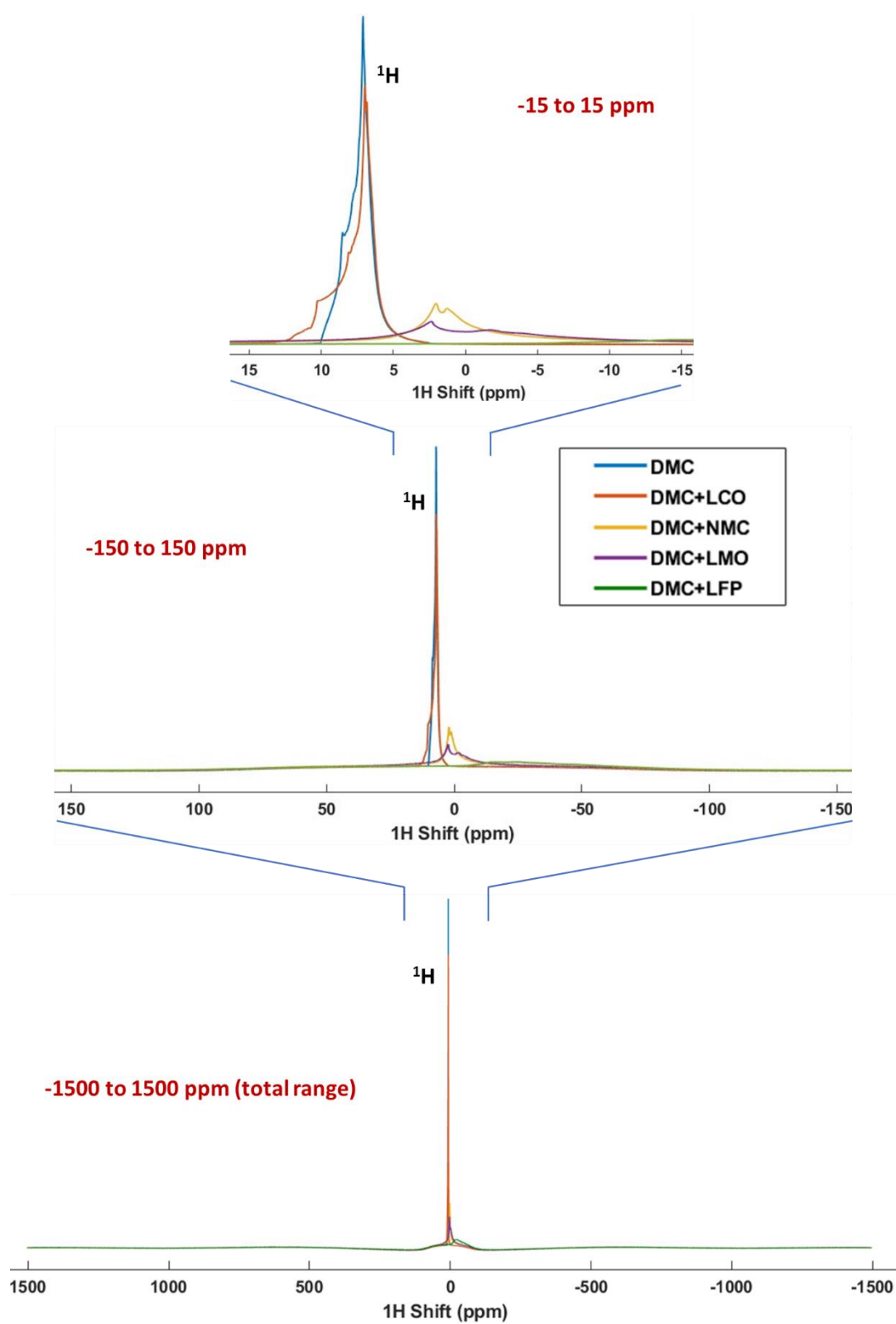


Figure 5-9 Effect of the different active materials pellets on the shape of ^1H NMR spectra of DMC

5.4.1 Area

The area of the spectrum is the integral of the signal intensity. The area under a specific peak or resonance in the NMR signal is directly proportional to the number of nuclei or spins giving rise to that signal and can provide valuable information about the relative abundance or concentration of the corresponding environment in the sample. Difficulties arise when the baseline is strongly distorted, as it is the case for one pulse measurements due to dead time. However, we chose to keep one-pulse acquisition as Hahn echo may miss part of the signal due to fast T_2 relaxation next to the paramagnetic pellet.

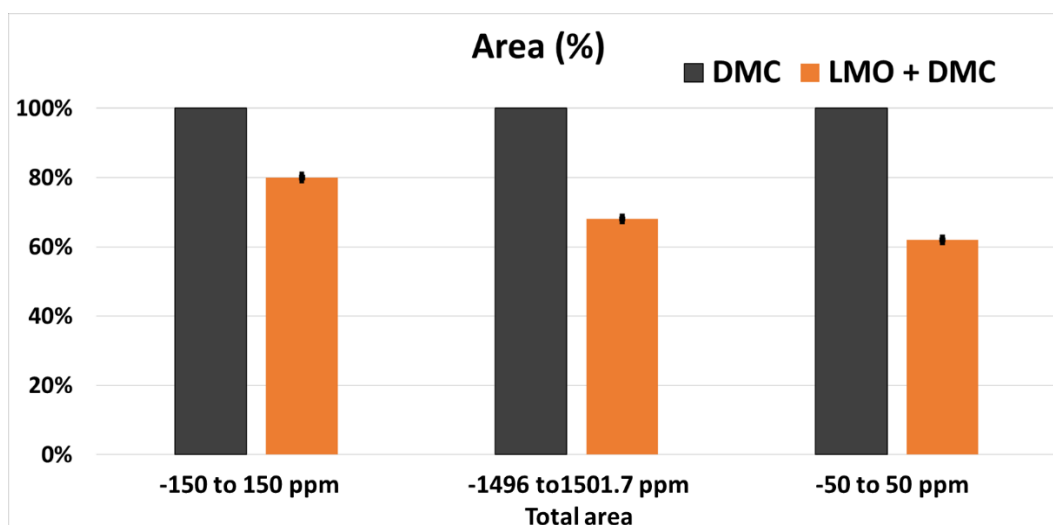


Figure 5-10 Effect of varying the integration range on the area under the ^1H signal of DMC in contact with an LMO pellet.

As shown in Figure 5-10, changing the integration range of ^1H NMR spectra leads to different integration values, as a result of the distorted baseline.

Consequently, the ^1H NMR signal of DMC experiences distortion and strong broadening, rendering the capture of the entire signal impossible within a narrow integration range (e.g., range 3). Therefore, it is crucial to carefully select appropriate integration ranges when comparing samples to avoid overlooking the portion of the signal that is greatly affected by these distortions. Therefore, depending on the materials under study, we choose a different range for the integration, which will be discussed afterward.

5.4.2 Weighted average shift (WAS)

The weighted average shift (WAS) of a “peak” determines an average shift based on the variations of intensities across the peak. For a perfectly symmetric peak, the shift of the maximum and the WAS are identical (Figure 5-11, a). This is not the case for a highly non-symmetric peak, as observed in our measurement of DMC containing an LFP pellet (Figure 5-11, b). In practice, the spectrum is bucketed, and each shift is assigned a weight from the area of the bucket.

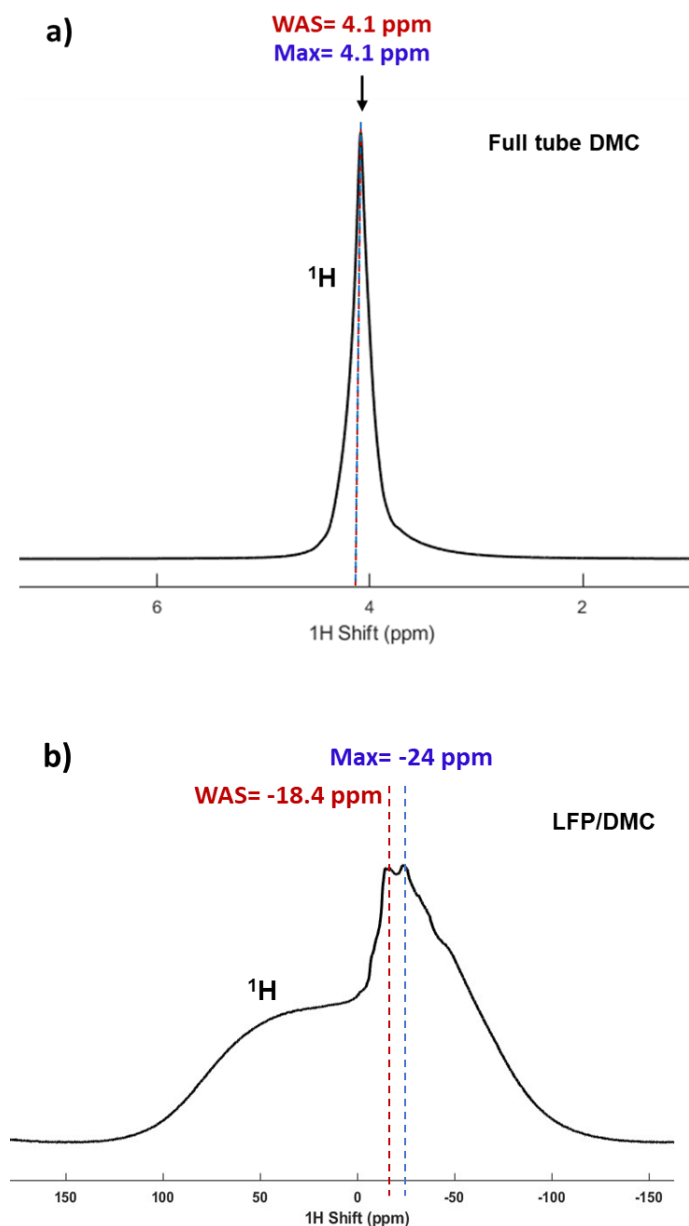


Figure 5-11 Difference between shift of the maximum and WAS for (a) symmetric and (b) non-symmetric spectra.

By factoring in the relative importance of each part of the peak, this type of average offers a more precise representation, placing greater emphasis on the area compared to particularities in the shape of the peak. Mathematically, the weighted average shift can be expressed as follows:

$$\text{Weighted Average Shift} = (\Sigma(\text{Shift} \times \text{Weight})) / (\Sigma \text{Weight})$$

Where:

Shift: Shift of a specific bucket.

Weight: Weight (here, area of the curve in the bucket).

Sum of Weights: The total area of the spectrum.

In our case, we bucketed the spectrum from -150 to 150 ppm (300 ppm spectral width), in 1 ppm-wide buckets. From this point forward in the manuscript, we will refer to the previously mentioned 'weighted average shift' as simply 'shift' for the sake of brevity and clarity.

5.4.3 Full width at different heights

The standard description of the width for a symmetric peak is the full width at half height (FWHH). It corresponds to the distance between the two points for which the intensity is equal to 50% of the height of the peak. For non-symmetric peaks, we adapt the definition to use 50% of the height at the weighted average shift (FW50%HWAS), rather than at the shift of maximum height. In addition, we had to use the full width of the NMR signal at fractions of intensity lower than 50% to take into account specifically broad bases.

Figure 5-12 shows examples of the weighted average shift position and full width at different heights of shift on the ^1H NMR spectrum for a full tube of DMC. For symmetric peaks, FWHH and FW50%WAS are equivalent. Other fractions, such as full width at tenth maximum of shift (FW10%HWAS) or full width at three-tenths maximum of shift (FW30%HWAS), were also employed to assess the signal width at different heights (Figure 5-12).

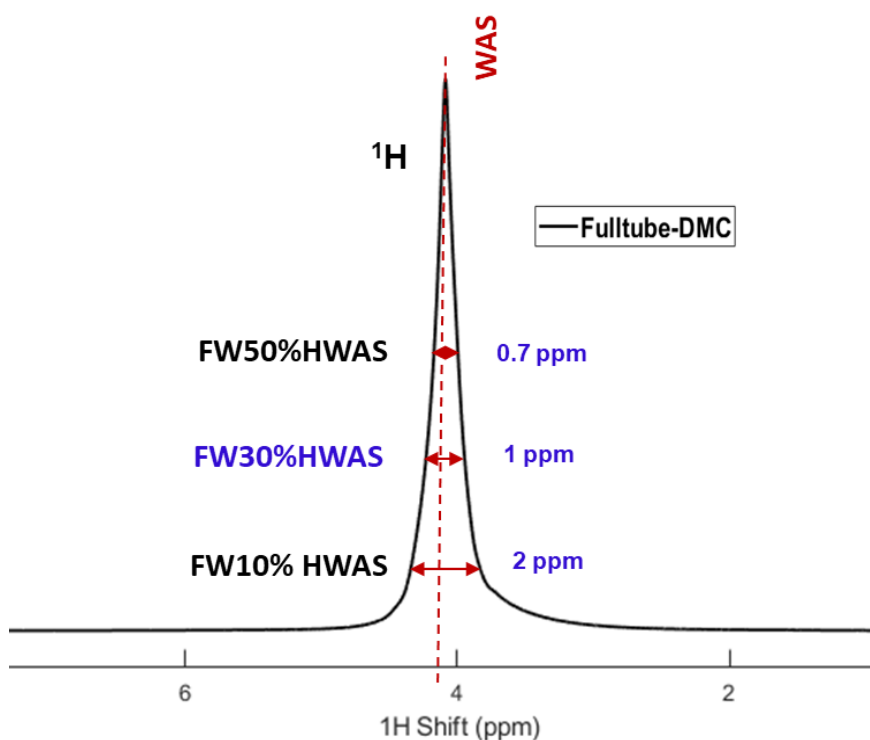


Figure 5-12 The weighted average shift, and full width at different heights of average shift for ^1H NMR signal of full tube DMC.

Figure 5-13 displays in blue the proton signal of the 200 μl of DMC solvent, with different linewidth values specified at various shift heights. The distortions are relatively symmetric so that the average weighted shift and the shift at maximum intensity are quite similar. In that case, the linewidths obtained using the shift at maximum intensity or the average shift do not differ strongly.

In the case of the paramagnetic pristine LMO pellet (in contact with 200 μl of DMC solvent, red), however, the intensity of the maximum and that of the WAS are significantly different. Hence the linewidths differences and the use of $\text{FW}x\%\text{HWAS}$. In addition, the linewidths change considerably from 50% height to 30% height of the shift. Therefore, for the subsequent analyses in our study, the linewidth at 30% height of the shift has been considered for comparison between samples. We chose this height, as this was the most discriminating between the samples and to avoid considering the very broad width at the 10% height and the narrow width at the 50% height of the shift. However, we will demonstrate the width at different heights of the shift in the following experiments to gain an idea of how they are changing.

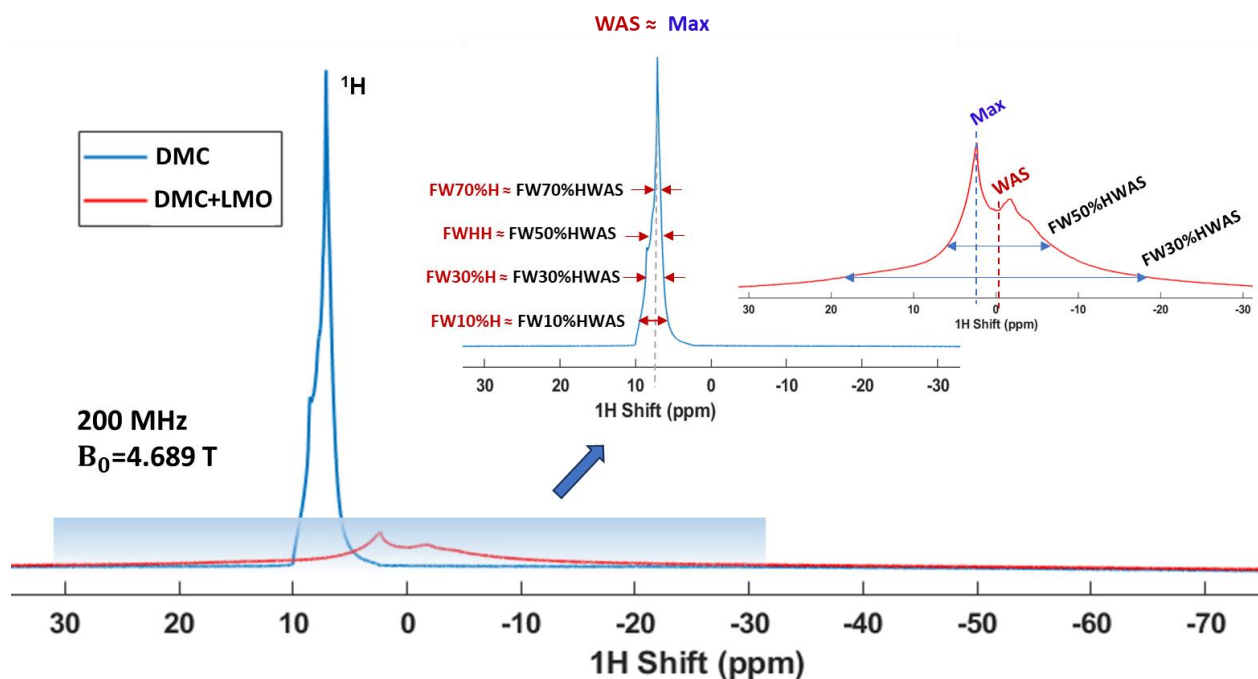


Figure 5-13 ^1H NMR of DMC solvent in contact with a LMO pellet, showing the various definitions of width.

5.4.4 Longitudinal relaxation time

Longitudinal relaxation time (T_1) will also be tested as a descriptor of the effect of electrodes in our measurements. The introduction of new interfaces and paramagnetic materials into the liquid solvent may indeed accelerate the relaxation process.^{103,196}

5.5 Effect of paramagnetic materials

In this section, we analyze how the ^1H NMR signal of liquid DMC (Dimethyl Carbonate) is affected by the presence of the paramagnetic pure materials, in the form of pellets. Figure 5-14 demonstrates the ^1H signal of DMC in presence of positive active materials including paramagnetic LiFePO_4 (LFP), LiMn_2O_4 (LMO), $\text{Li}_{0.33}\text{Ni}_{0.33}\text{Mn}_{0.33}\text{CoO}_2$ (NMC 111), and diamagnetic LiCoO_2 (LCO).

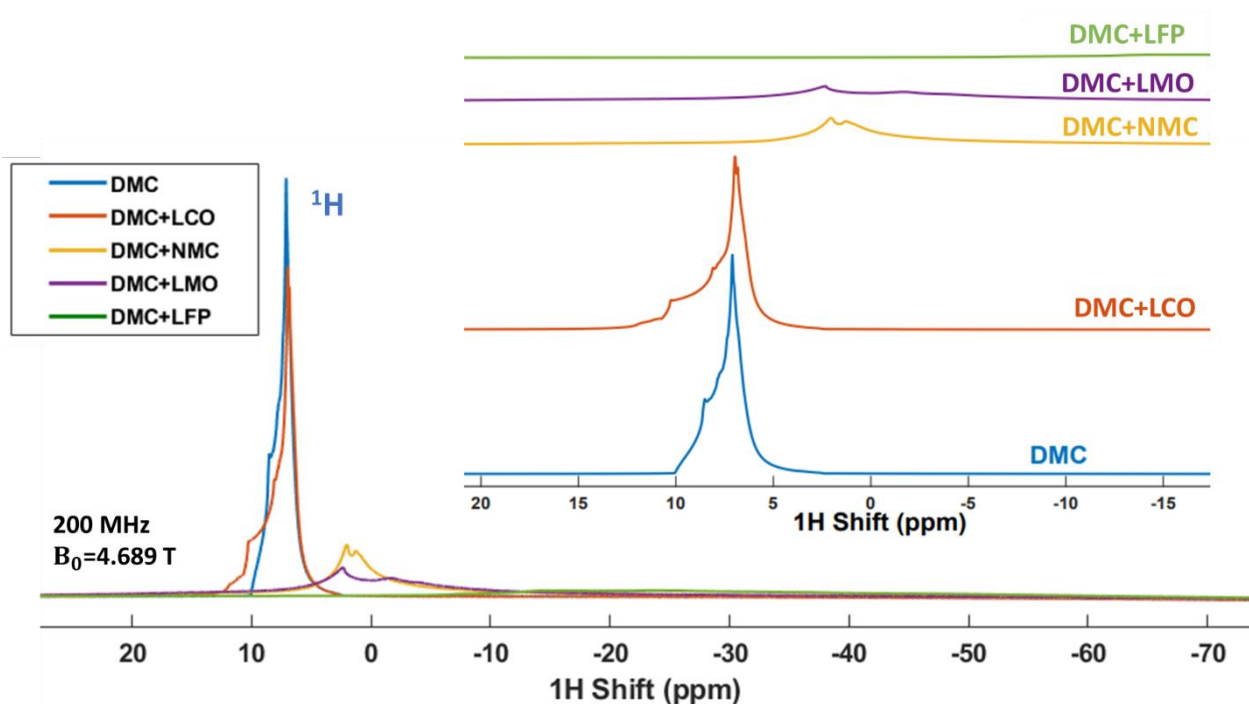


Figure 5-14 ^1H NMR spectra of DMC in the presence of positive electrode active materials.

5.5.1 Effect on shift and width

For diamagnetic materials like LiCoO_2 , the effects on the ^1H NMR signal of DMC are small,^{107,207,210} due to its small magnetic susceptibility. As shown in Figure 5-14, the shape of the peak is mainly maintained but broadened with a FW30%HWAS going from 2.6 ppm for pure 200 μL of DMC to 4.6 ppm when the 200 μL of DMC are in contact with the LCO pellet (figure 5-15c). The WAS shift stays the same as for pure 200 μL of DMC at 7.3 ppm.

However, this broadening is observed to increase for DMC in contact with NMC, LMO, and LFP powders, respectively. Moreover, the ^1H spectrum of DMC becomes entirely distorted, exhibiting a significant change in shape, and broadening with FW30% HWAS varying from 2.6 ppm to 9.1 ppm, 37.3 ppm, and 115.3 ppm due to the presence of NMC, LMO, and LFP, respectively.

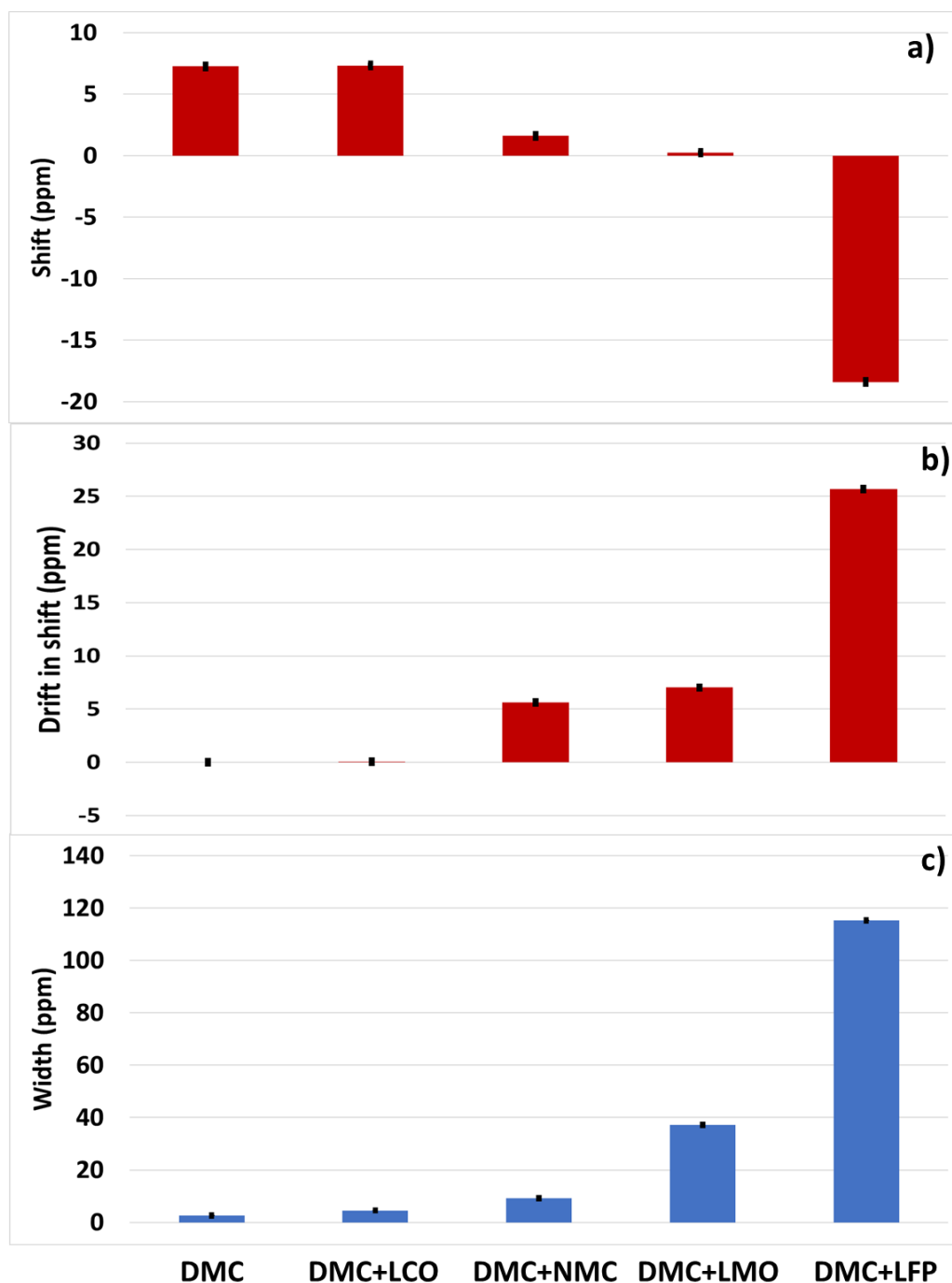


Figure 5-15 Effect of active materials on the (a) absolute WAS shift, (b) drift in WAS shift compared to pure DMC, and (c) width (FW30%HWAS) of the ^1H spectra.

Additionally, the WAS values (Figure 5-15a) are increased for pure 200 μL of DMC from 7.3 ppm to 1.6 ppm (5.7 ppm shift), 0.2 ppm (7.1 ppm shift), and -18.4 ppm (25.7 ppm shift) when in contact with NMC, LMO, and LFP, respectively. It should be noted that the values indicated in Figure 5-

15b are the result of subtracting the values of WAS in active materials compared to pure DMC (drift in shift compared to the pure DMC spectrum).

The local susceptibility effect felt by surrounded liquid DMC, does not only depend on the type of redox-active paramagnetic ions ($\text{Ni}^{2/3+}$, Co^{4+} , $\text{Mn}^{3/4+}$), but also on the electronic structure of the crystalline pellets.

The trend in shift and width of the DMC spectrum, due to the pellets, aligns with the trend in magnetic susceptibility (as shown in Figure 5-5), with materials with higher magnetic susceptibility generating more significant changes in shift and width.

5.5.2 Sensitivity to the definition of width

In this part, we analyzed the effect of the definition of the width for analyzing the broadening of the ^1H NMR spectrum of DMC. In Figure 5-16, the full width at different shift heights was measured.

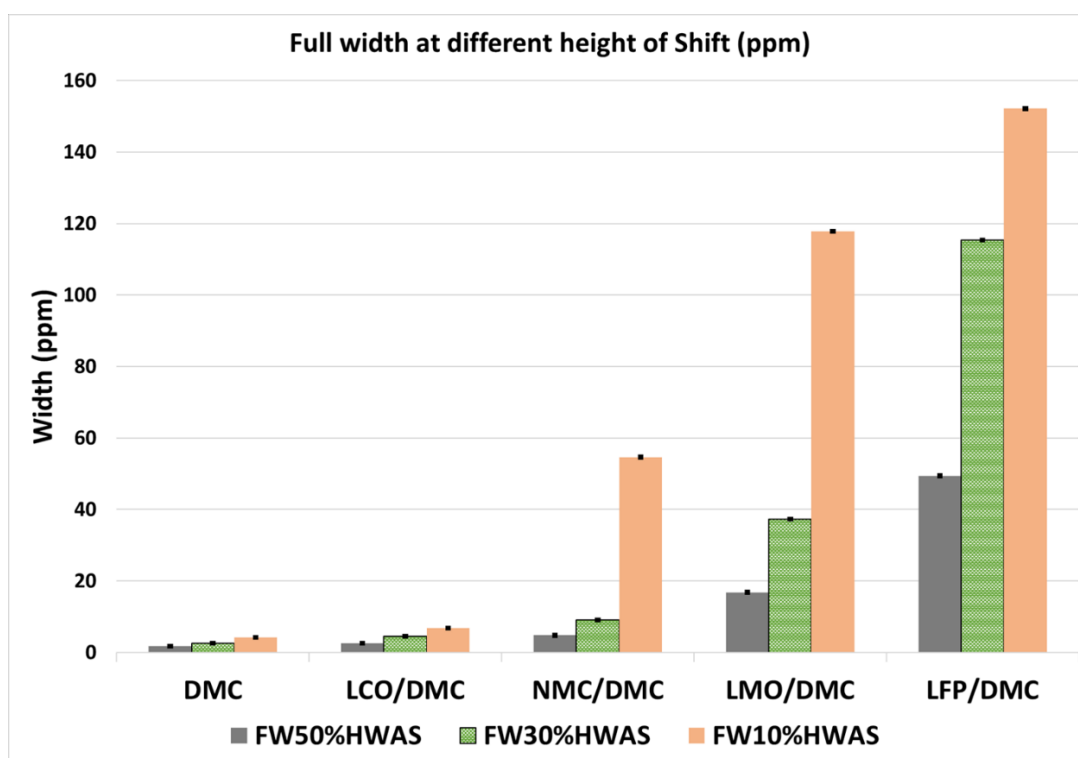


Figure 5-16 Effect of active materials on the full width at different heights of shift of the DMC ^1H spectrum.

For example, in the case of LFP in contact with DMC, the ^1H spectra show a significant shift in broadening of about 47.7 ppm, 112.8 ppm and 148.0 ppm at 50%, 30% and 10% height of shift respectively, compared to the pure DMC solvent.

All definitions display the same trend, with a large width for a lower height of shift. The relative differences are large for 30% height, so this is what we used in the following.

5.5.3 Effect on area

Figure 5-17 also shows that by increasing the magnetic susceptibility of the active materials, the area of ^1H NMR signal of DMC is decreasing. In fact, the signal from the liquid next to the paramagnetic solid disappears due to fast relaxation.

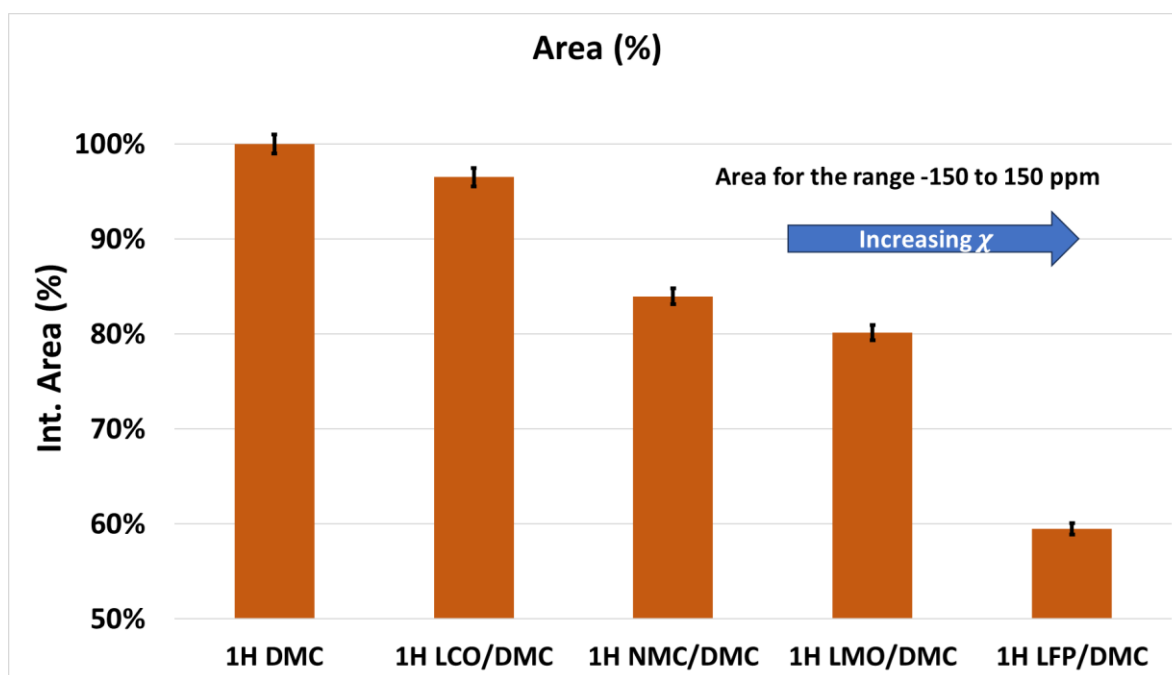


Figure 5-17 Effect of active materials on the area of DMC ^1H spectra (range -150 to 150 ppm).

The proton NMR spectra of liquid DMC were disturbed by paramagnetic NMC, LMO, and LFP and experienced a shift and broadening which is due to bulk magnetic susceptibility effects.^{107,191,207,211} This effect is increasing from NMC ($\chi_m \approx 2.5 \times 10^{-3}$ emu/mol), LMO ($\chi_m \approx 8.7 \times 10^{-3}$ emu/mol) to LFP ($\chi_m \approx 9.4 \times 10^{-3}$ emu/mol). As indicated in Figure 5-17, the area under ^1H spectrum of DMC in contact with LCO, NMC, and LMO shows a decrease, around 3%, 16%, and 20% respectively, compared to ^1H signal of pure DMC. However, in the case of LFP the area

under ^1H spectrum of DMC decreases by about 40% which shows a considerable change compared to the effect of other active materials. Here, we can observe that the trend of lowering the area under the ^1H NMR signal correlates with increasing magnetic susceptibility, with materials with higher magnetic susceptibility demonstrating a more pronounced decrease in the signal intensity.

5.5.4 Sensitivity to the integration range

In this part, we analyzed the effect of changing the integration range on measured area. Three ranges were used: ± 50 ppm (range 3); ± 150 ppm (range 2) and ± 1500 ppm (range 1). In Figure 5-18, increasing the integration range from ± 50 ppm (range 3) to ± 150 ppm (range 2) provides a higher area as expected for broadened signals. This is not true anymore when going to ± 1500 ppm (range 1). We assign this effect to the strong negative baseline distortion around ± 200 ppm. This baseline distortion was not corrected to avoid spectrum-dependent variations. The spectrum of DMC with LCO stands out, with one stronger decrease in range 1, which we assign to the relatively narrow spectrum.

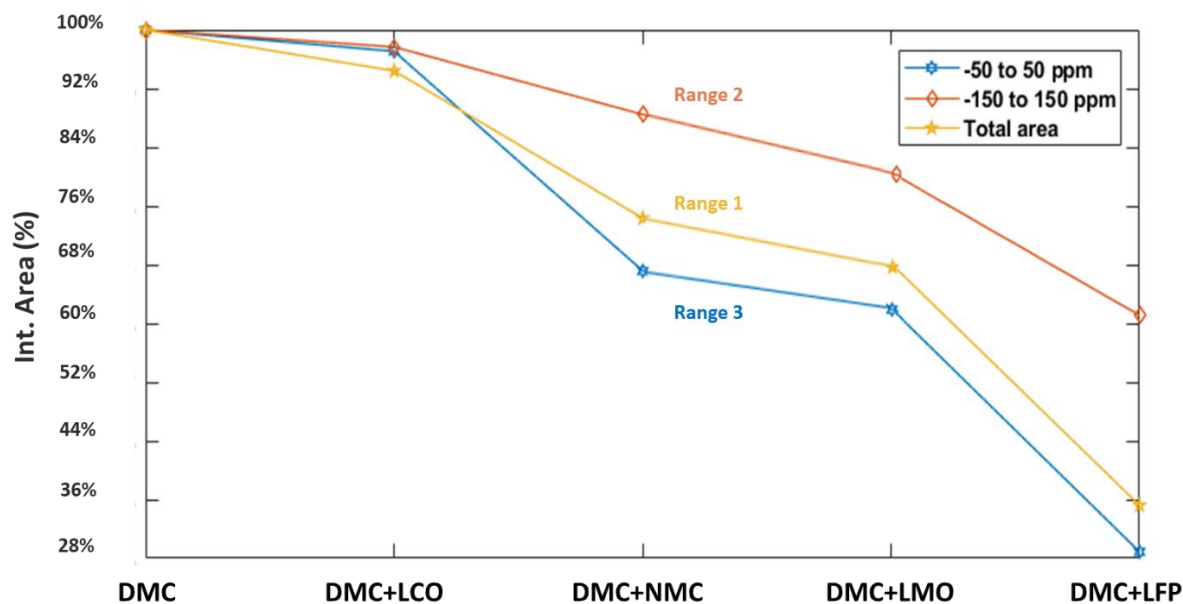


Figure 5-18 Effect of changing the integration range of the ^1H NMR spectra of DMC.

In the case of DMC+LFP, for smaller integration range as we are dealing with highly distorted spectrum, the integration value is much less compared to the total range area. This means that LFP has the more dominant effect and leads to very broadened spectra in which small integration range will not consider the whole signal under the ^1H DMC spectra.

5.5.5 Effect on longitudinal relaxation

The T_1 relaxation measurements were conducted using the saturation recovery experiment with the same acquisition parameters. The resulting T_1 values are outlined in Figure 5-19 for DMC, DMC+LMO and DMC+NMC. We had to define 2 components in the relaxation model to obtain a reasonable fit. We assign these two components to bulk DMC (longer T_1) and to DMC in the vicinity of the paramagnetic pellet (shorter T_1). As expected for pure DMC, a single component is needed since there is no pellet and we obtain one value for T_1 (~9.5 s).

Herein we can see that T_1 for DMC in close contact with paramagnetic pellets is strongly influenced, with a very fast relaxation of 0.5 s for NMC and 0.5 s for LMO. Bulk DMC is also slightly influenced (8.5 s for NMC and 6.9 s for LMO), most probably due to the fast diffusion of DMC in the electrolyte.

To conclude, we observe that the longitudinal relaxation time of bulk DMC around the NMC and LMO follows the expected trend of increase with increasing magnetic susceptibility. For DMC in the vicinity of the pellets, the fits are not as constrained, and the results were not as discriminant. Longitudinal relaxation seems therefore less reliable than the shift, width, and area. The other active materials, including LFP and LCO were therefore not measured.

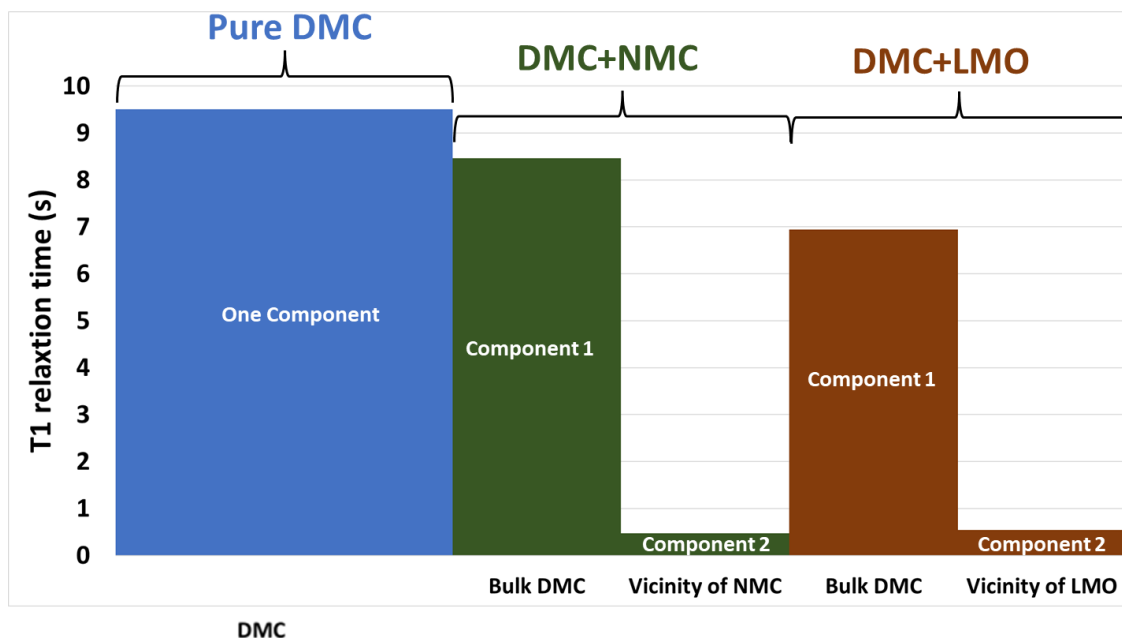


Figure 5-19 Effect of NMC and LMO active materials on the T_1 relaxation constant of 200 μl DMC.

5.5.6 Conclusion

All introduced descriptors are sensitive to the change in magnetic susceptibility of active materials, with longitudinal relaxation being slightly less discriminating. These results are promising regarding the sensitivity of our measurements to the changes in the magnetic susceptibility of the battery electrodes.

The next step involves correlating the change in magnetic susceptibility with the SOC of the electrodes inside the battery, which will be explored in Chapter 6. Prior to this, we will evaluate the effect on the ^1H spectrum of the DMC solvent of each battery component, such as the NMC cathode electrode (NMC 622 active material, carbon black and binder, coated on one side of an aluminum foil), the graphite negative electrode (graphite active material, carbon black and binder, coated on one side of a copper foil), the copper and aluminum current collectors, and the glass fiber separator.

5.6 Effect of battery components

5.6.1 Effect of non-electrochemically active battery components

The effect of non-electrochemically active battery components including aluminum, and copper current collectors, and glass fiber separators on the ^1H spectra of DMC was studied to determine their effect.

5.6.1.1 Sample preparation

Herein we used 5mm diameter disks of Cu and Al current collectors, punched out of the side of the commercially graphite and NMC (622) electrode foils respectively.

Also, a Whatman grade GF/D glass microfiber filter (with a thickness of 670 μm) was used as a separator. The preparation of the sample for ^1H NMR measurement followed the same procedure as previously explained (in the experimental approach section): each component was placed in 200 μl of DMC in a 10 mm glass NMR tube (Figure 5-20) and the ^1H NMR of DMC was measured.



Figure 5-20 Non-electrochemically active battery components near 200 μl of DMC solvent inside 10mm NMR glass tube.

5.6.1.2 Effect of current collectors and separator on DMC ^1H spectra

Results (Figure 5-21) show that current collectors and separators have a small impact and there is no significant change in the shape of ^1H spectra of DMC in contact with Cu and Al currents collectors or with the separators.

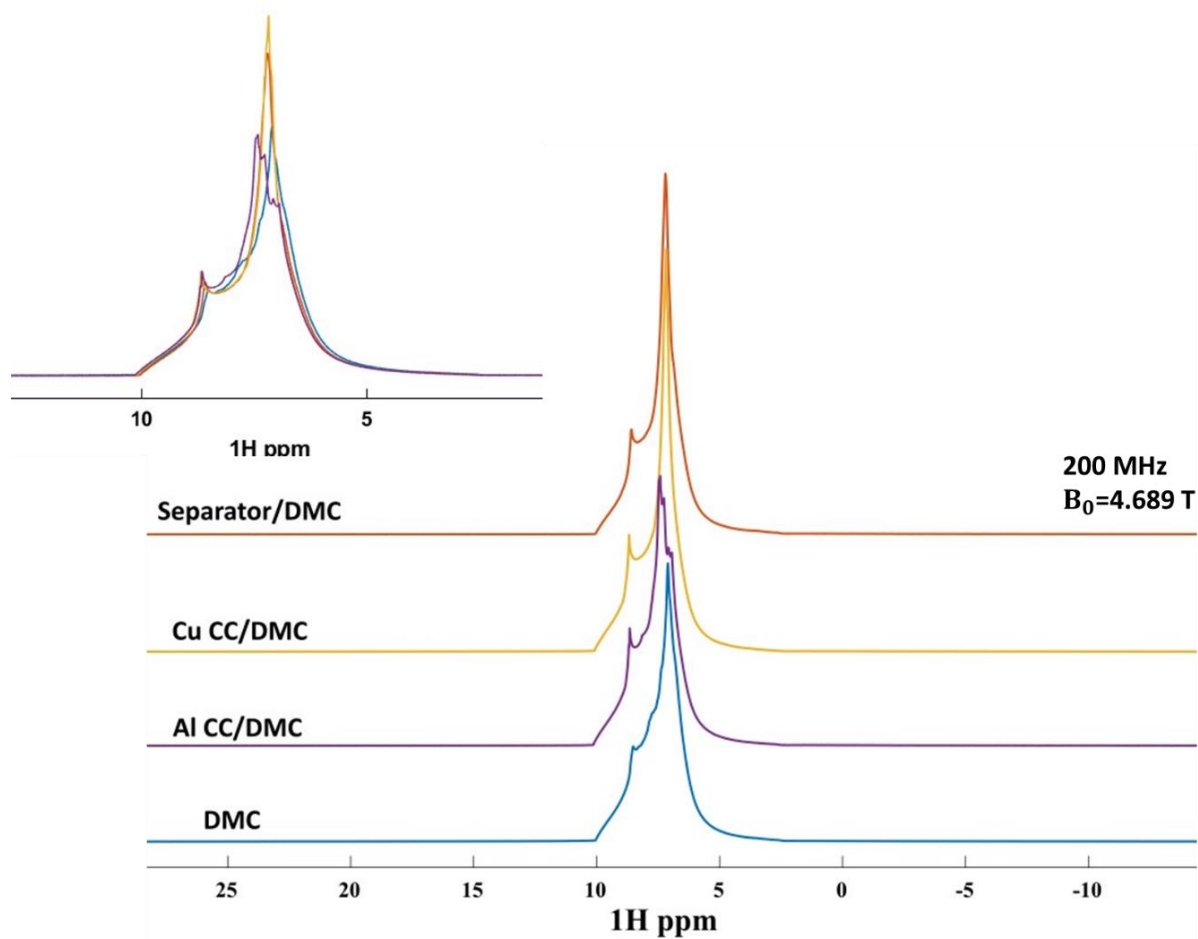


Figure 5-21 ^1H signal of DMC in the presence of Aluminum and copper current collector and separator.

Alternating magnetic fields during NMR experiments can induce eddy currents in conductive materials such as aluminum and copper if not properly aligned with the applied exciting RF field. These eddy currents generate their own magnetic fields, which can interfere with the applied magnetic field and cause signal distortions or line broadening in the ^1H NMR spectrum of DMC.^{212,213} Here we used a geometry that minimizes these effects (parallel to RF field direction).

5.6.1.3 Effect on shift of the DMC ^1H spectrum

Figure 5-22 shows that the presence of copper current collector and separator has a negligible effect on the WAS of pure DMC and the variation in shift is less than 0.02 ppm.

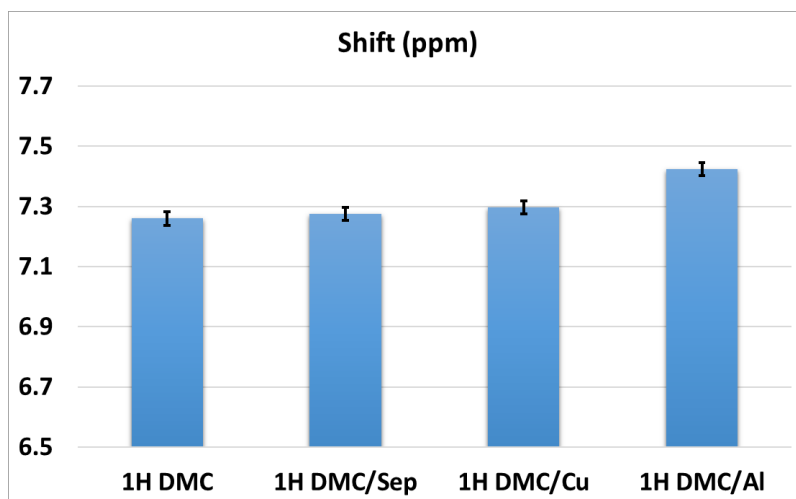


Figure 5-22 Effect of non-electrochemically active battery components on the shift of the DMC ^1H spectra.

This effect in the case of Aluminum current collector is a bit stronger compared to the two other components as its presence near 200 μl of DMC resulted in 0.1 ppm shift compared to that of 200 μl pure DMC.

5.6.1.4 Effect on width of the DMC ^1H spectrum

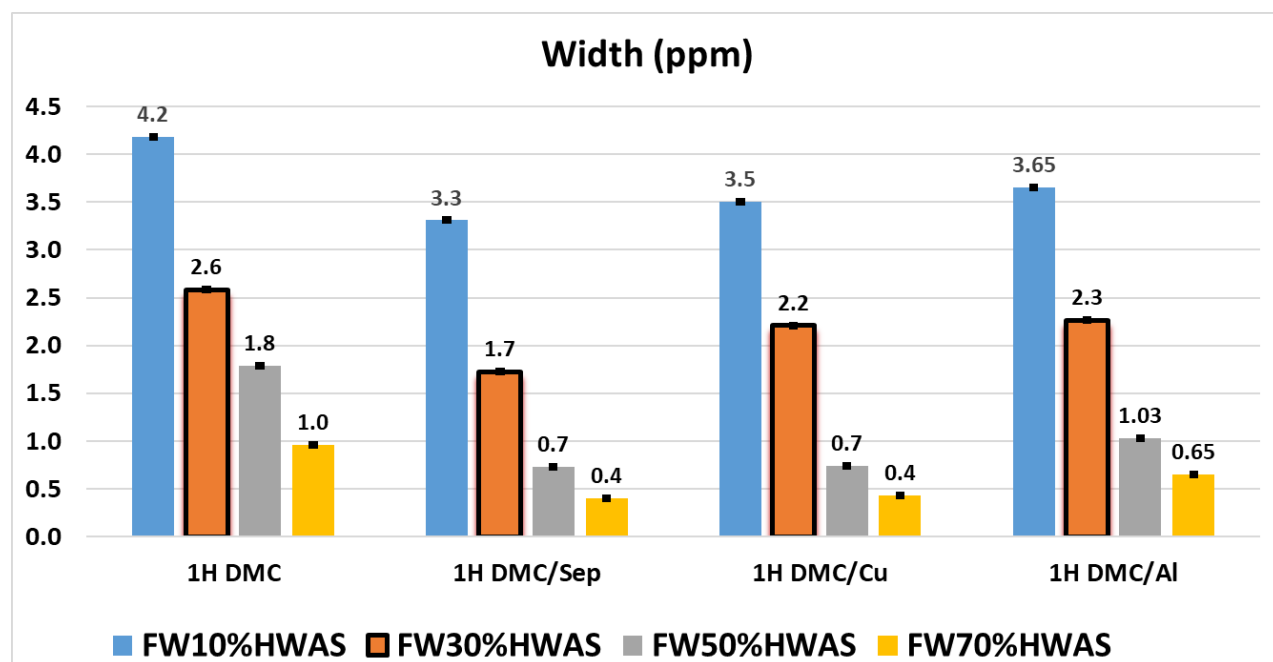


Figure 5-23 Effect of non-electrochemically active battery components on width of the ^1H DMC spectra at different heights of Shift.

As shown in Figure 5-23, the full width at various heights of the shifts was determined to quantitatively assess the broadening observed in the ^1H NMR spectrum of DMC resulting from the presence of non-electrochemically active battery components.

Results show that the contact of these components with 200 μl of DMC results in a change in the width of the ^1H DMC spectrum which is less than 1 ppm (for FW30%HWAS) for all the components. These variations are considered to be within our uncertainty (change in thickness, magnetic susceptibility, orientation in the tube) and are at least one order of magnitude smaller than those created by paramagnetic compounds.

5.6.1.5 Effect on area of the DMC ^1H spectrum

Figure 5-24 shows the integrated area for all non-electroactive components. The full area integration under the ^1H signal of DMC in the vicinity of both current collectors and separators is quite similar (with a difference of less than 2 percent compared to each other). This suggests that we are losing a similar order of ^1H signal from pure DMC due to the presence of these components, and that this loss is negligible compared to that generated by paramagnetic materials.

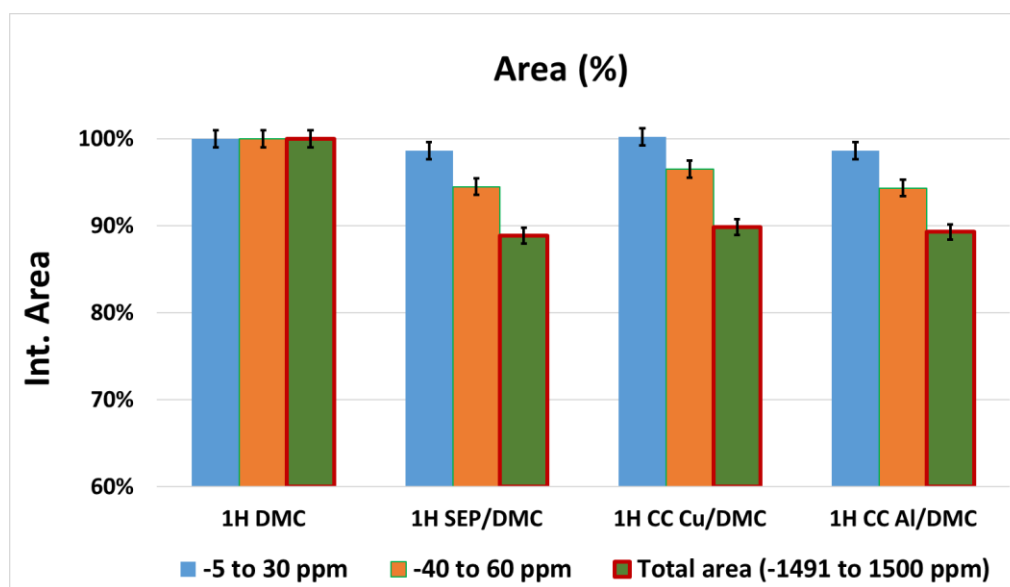


Figure 5-24 Effect of non-electrochemically active battery components on the integration area of the DMC ^1H spectra.

The integration value of the ^1H DMC signal for all components were calculated for the full spectral width going from -1491 to 1500 ppm (range 1) and shorter ranges including -40 to 60 ppm (range

2) and -5 to 30 ppm (range 3). As for paramagnetic materials, the area under the ^1H NMR spectra is smaller in range 1 compared to ranges 2 and 3, due to the baseline distortion. Given the complex shapes of the distorted NMR spectra, we chose to keep the baseline distortion, aiming to maintain a consistent comparison approach for all spectra.

5.6.1.6 Effect on longitudinal relaxation of the DMC ^1H spectrum

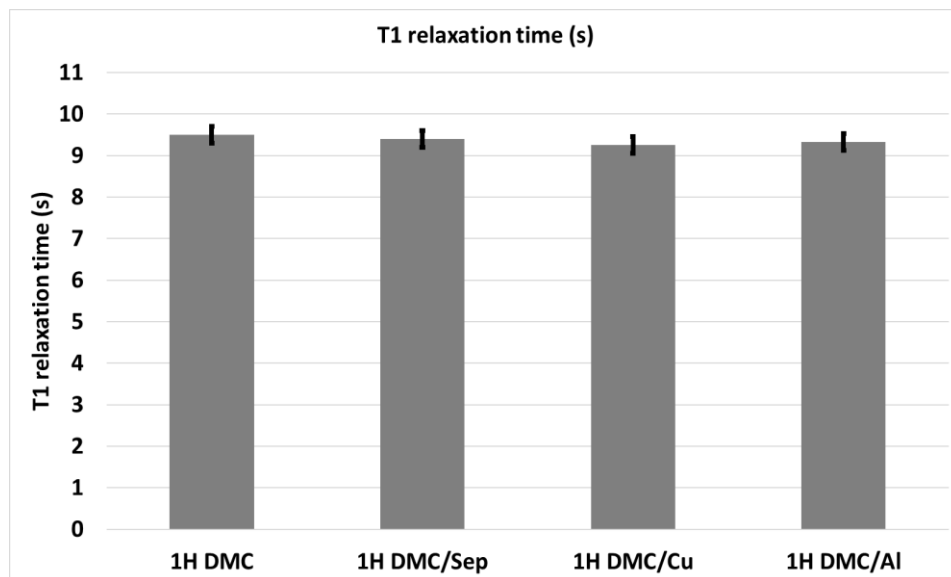


Figure 5-25 Effect of non-electrochemically active battery components on the T_1 relaxation time of the 200 μl DMC.

As mentioned earlier the proton T_1 measurements of DMC in contact with different pellets were recorded using a saturation-recovery sequence. The measured areas were then fitted with a single exponential. The resulting relaxation constants T_1 are reported in Figure 5-25. We are aware that this is an approximation as there is probably a distribution of T_1 depending on the distance to the non-electroactive material.

Figure 5-25 illustrates how, in the case of aluminum and copper current collectors as well as separators, the relaxation time constant of protons within the DMC solvent slightly decreases. The differences in relaxation time constants are small and fall within the range of our measurement uncertainty.

After evaluating the effect of non-electrochemically active battery components by monitoring the changes in the ^1H NMR of the DMC solvent using the introduced descriptors, we conclude that

their effect is minimal. Therefore, we will now examine the impact of electrochemically active battery components, including the graphite (anode) and NMC 111 (cathode) electrodes.

5.6.2 Effect of electrodes

5.6.2.1 Pristine graphite electrode

Herein the effect of a pristine graphite electrode composed of 96% graphite (C6) as the active material, coated on one side of a copper foil, on the ^1H spectra of DMC was studied to determine the effect of graphite active materials itself as we know the effect of Cu current collector. Therefore, a 5mm-diameter graphite electrode was placed in 200 μl of DMC in a 10mm glass NMR tube and the ^1H NMR of DMC was measured.

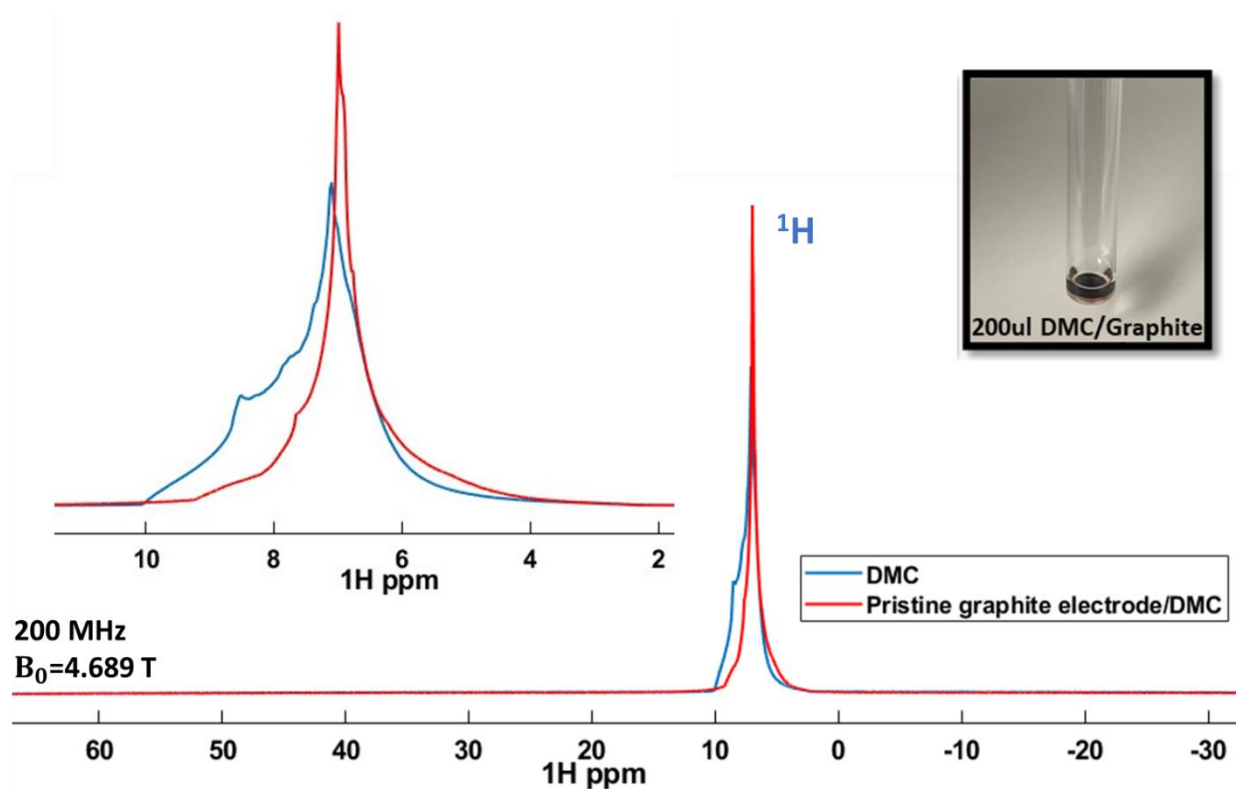


Figure 5-26 ^1H signal of DMC in the presence of 5mm pristine graphite electrode (Cu current collector).

The graphite electrode introduces local magnetic field gradients, resulting in variations in the magnetic field homogeneity near the electrode. This disrupted field can also create a blind zone where the NMR signal is distorted or attenuated. In the context of a graphite electrode, which is typically diamagnetic (and has a highly anisotropic susceptibility), a blind zone may arise due to the susceptibility mismatch between the graphite and the surrounding medium (DMC, in our case). The size and extent of the blind zone around the graphite pellet depend on factors such as the dimensions of the pellet, and the magnetic susceptibility difference between the graphite and the surrounding DMC solvent.^{146,207,211,214,215}

Graphite does not generate significant demagnetizing fields^{146,207} and its influence on the shape of the ^1H NMR signal of DMC (as shown in Figure 5-26) is minimal. Figure 5-27 reports the shift and width values. First, Additionally, the presence of graphite in 200 μL of DMC shifts its ^1H spectra slightly, approximately by 0.4 ppm.

Then, we observe that both in the spectra and the width values, the line width of the ^1H NMR spectra of DMC in contact with the graphite electrode narrows to approximately 1.7 ppm compared to the ^1H signal of 200 μL pure DMC solvent. This may seem counter-intuitive, as one expects a broadening from the addition of the electrode. However, the most shifted/broadened parts of 200 μL DMC may be the interfaces with the glass of the NMR tube. These may disappear with the addition of the graphite electrode, resulting in a narrower spectrum.

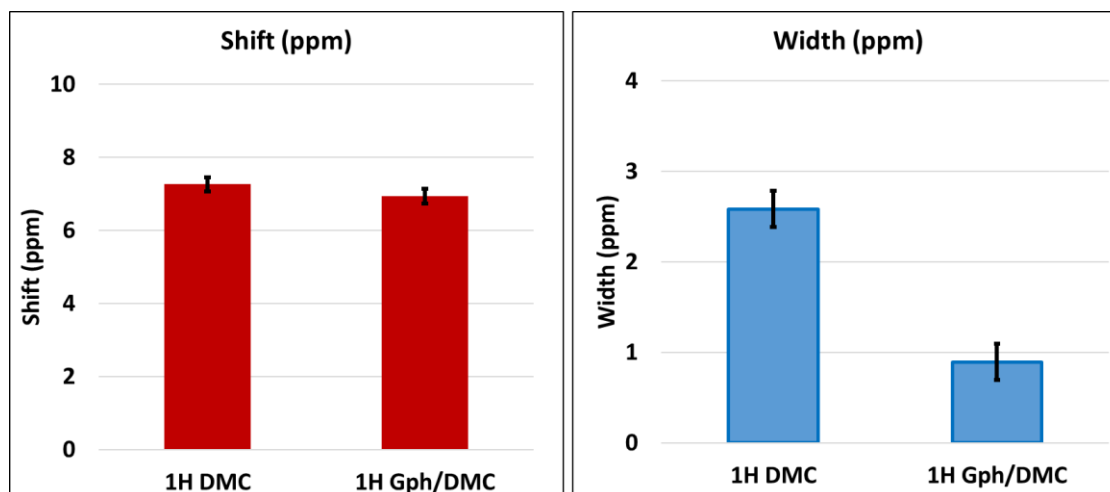


Figure 5-27 Effect of graphite electrode on the weighted average shift and width (FW30%HWAS) of the DMC ^1H spectra.

Figure 5-28 displays the area of the proton signal for pure DMC and the graphite/DMC sample at various integration ranges. In range 1, where the graphite electrode is present within the DMC solvent, there is an approximately 24% decrease in the integration value. This implies that around 24% of the proton signal of DMC was not detected in our measurement. This phenomenon can be attributed to a blind zone around the graphite electrode.

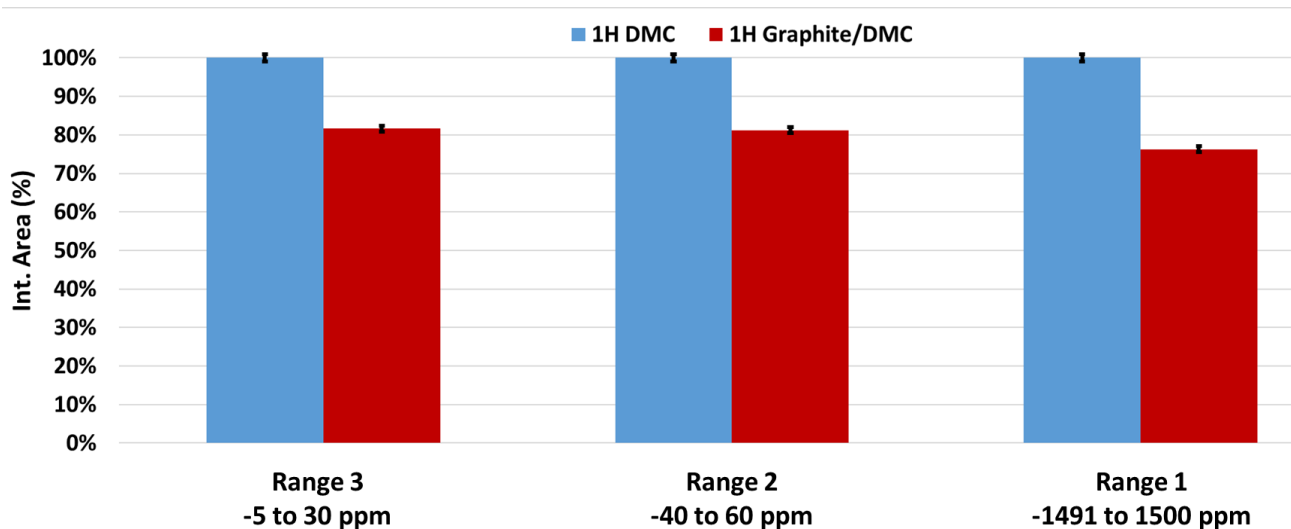


Figure 5-28 Effect of graphite electrode on the integration area of the DMC ^1H spectra.

5.6.2.2 Effect of NMC 622 electrode

In this experiment, we used $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) electrode materials coated on one side of an Al foil and provided by the manufacturer, as the last battery components. Herein, we observe the effect of NMC622 electrode on the ^1H NMR of DMC.

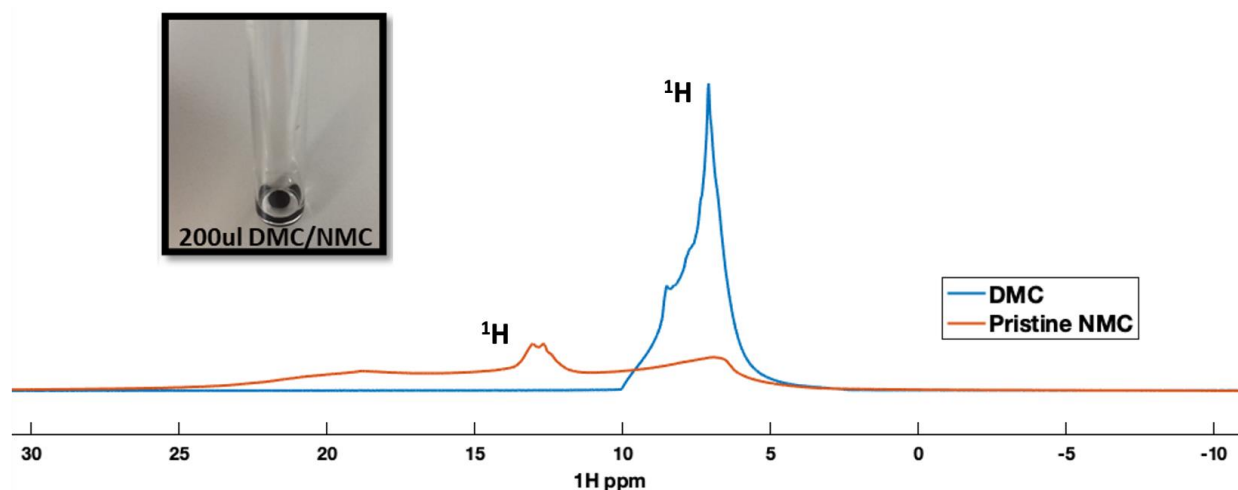


Figure 5-29 ^1H signal of DMC in the presence of pristine NMC (622) electrode.

In Figure 5-29, it is evident that the presence of the NMC electrode in the vicinity of the DMC solvent leads to a significant broadening of approximately 13 ppm (as shown in Figure 5-30) compared to the reference DMC solvent. The results also show that the presence of the NMC electrode in the vicinity of the DMC results in an approximate 5 ppm shift compared to the ^1H signal of the reference DMC.

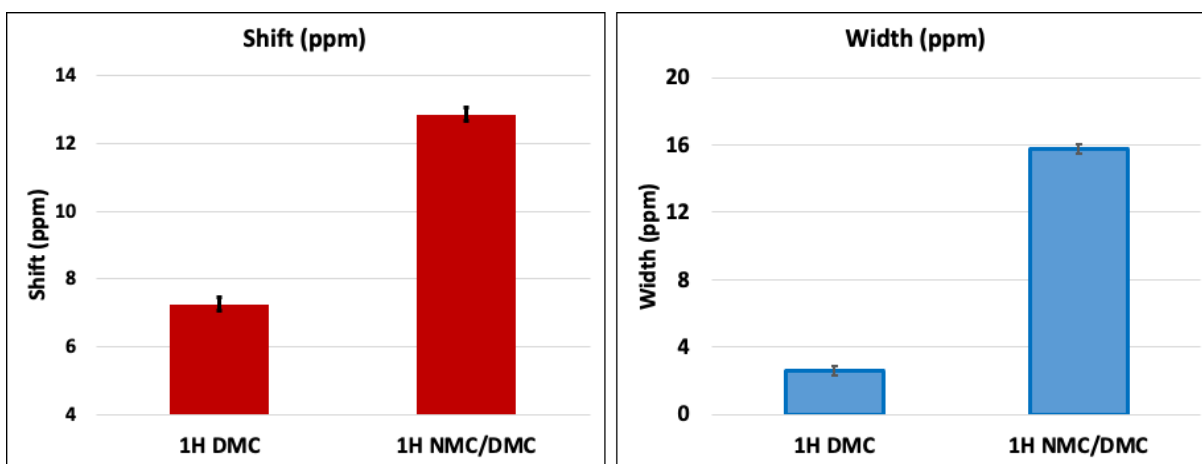


Figure 5-30 The effect of pristine NMC (622) electrode on the WAS and width (FW30%HWAS) of the ^1H signal of DMC.

In Figure 5-31, regarding the area integration, the effect of NMC results in approximately a 15% loss in the proton signal over the total range under the proton NMR signal of DMC. As for graphite, this is assigned to a blind zone at the interface with the NMC622 electrode.

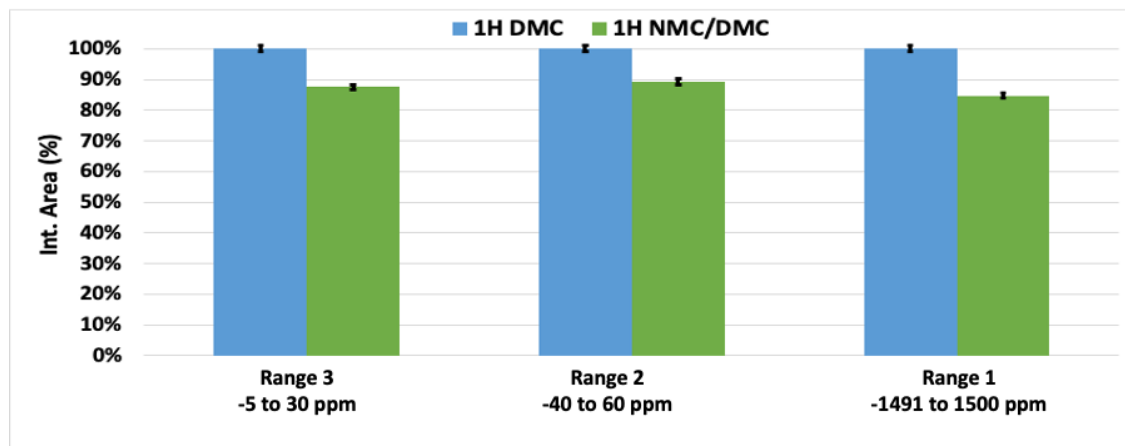


Figure 5-31 The effect of pristine NMC (622) electrode on the integration area of ^1H signal of DMC at different range.

5.6.2.3 Effect on longitudinal relaxation

Figure 5-32 illustrates the T_1 relaxation time constants for DMC in contact with both graphite and NMC622 electrodes. The presence of the paramagnetic NMC electrode in contact with DMC shortens the relaxation time constant of the DMC solvent by 2.2 seconds. On the other hand, in the case of the graphite electrode, the relaxation time of the DMC solvent decreased by approximately 0.7 seconds. This difference in relaxation times indicates that the paramagnetic properties of the NMC622 electrode will be dominant for the relaxation effects on DMC.

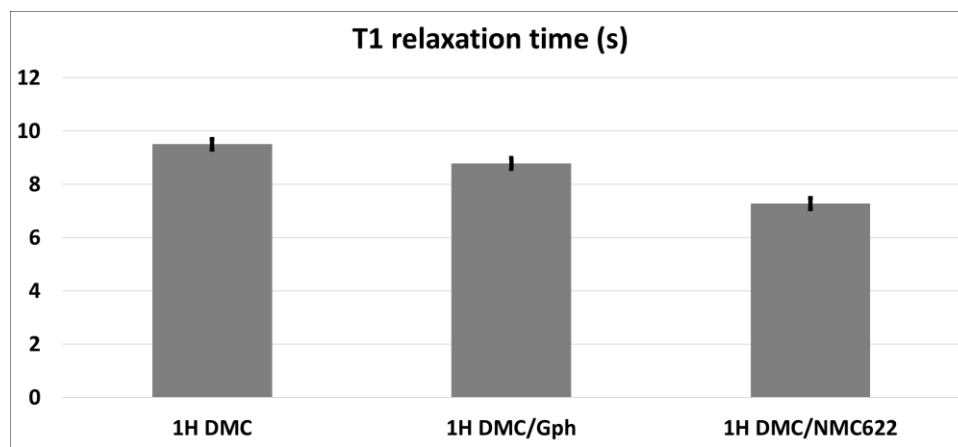


Figure 5-32 Effect of NMC622 and graphite electrodes on the T_1 relaxation time of the 200 μl DMC.

5.6.2.4 Comparison of the effect of NMC 622 electrode and NMC 111 pellet

In this part, we compare the effect of NMC 622 electrode (including the current collector) with that of the NMC 111 pellet shown earlier. By doing this, we can determine how altering the electrode paramagnetism affects the ^1H NMR spectra and to what extent our approach is sensitive to this change.

Figure 5-33 displays the ^1H NMR signal of DMC in contact with NMC 622 electrode and NMC 111 pellet. It should be noted that the mass and shapes of the NMC 622 electrode and NMC 111 pellet are not the same. We can see that the ^1H signal of DMC influenced by NMC 622 electrode and NMC 111 pellet are distorted and show different lineshape distortions. This disparity in shape distortion can be attributed to different structures and corresponding magnetic susceptibility of the two active materials and to a smaller extent, to the presence of aluminum current collector in NMC 622 electrode (however it is shown to have a minor effect on ^1H signal of DMC).

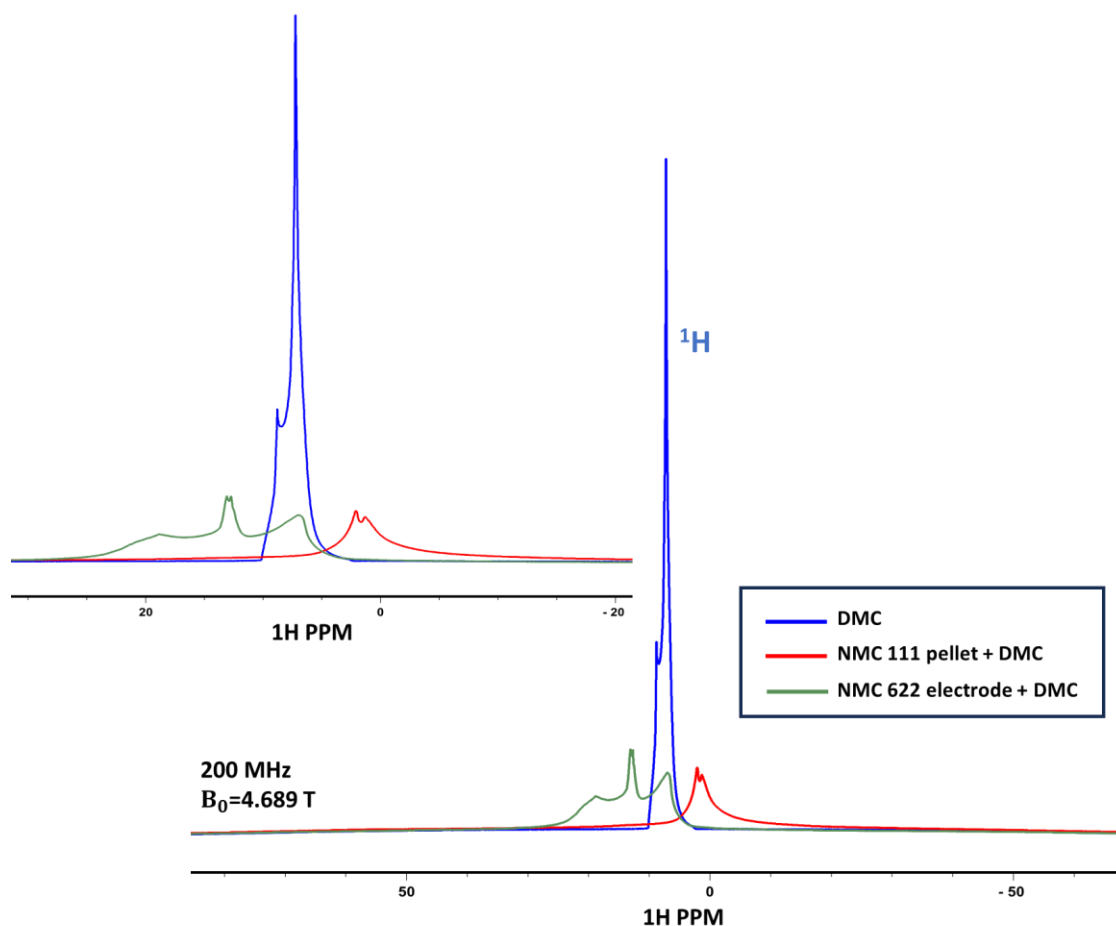


Figure 5-33 ^1H signal of DMC in the presence of pristine NMC 622 electrode and NMC 111 pellet.

As shown in Figures 5-35 and 5-34, the presence of the NMC 622 electrode in the vicinity of DMC leads to a significant broadening and shift of approximately 13 and 6 ppm, respectively, compared to the reference DMC solvent. On the other hand, the effect of the NMC 111 pellet in the vicinity of the DMC solvent results in a smaller broadening of 6 ppm compared to the reference DMC solvent. Nevertheless, the resulting shift in the ^1H signal of DMC due to the effect of the NMC 111 pellet remains of the same order of magnitude as that from the NMC 622 electrode.

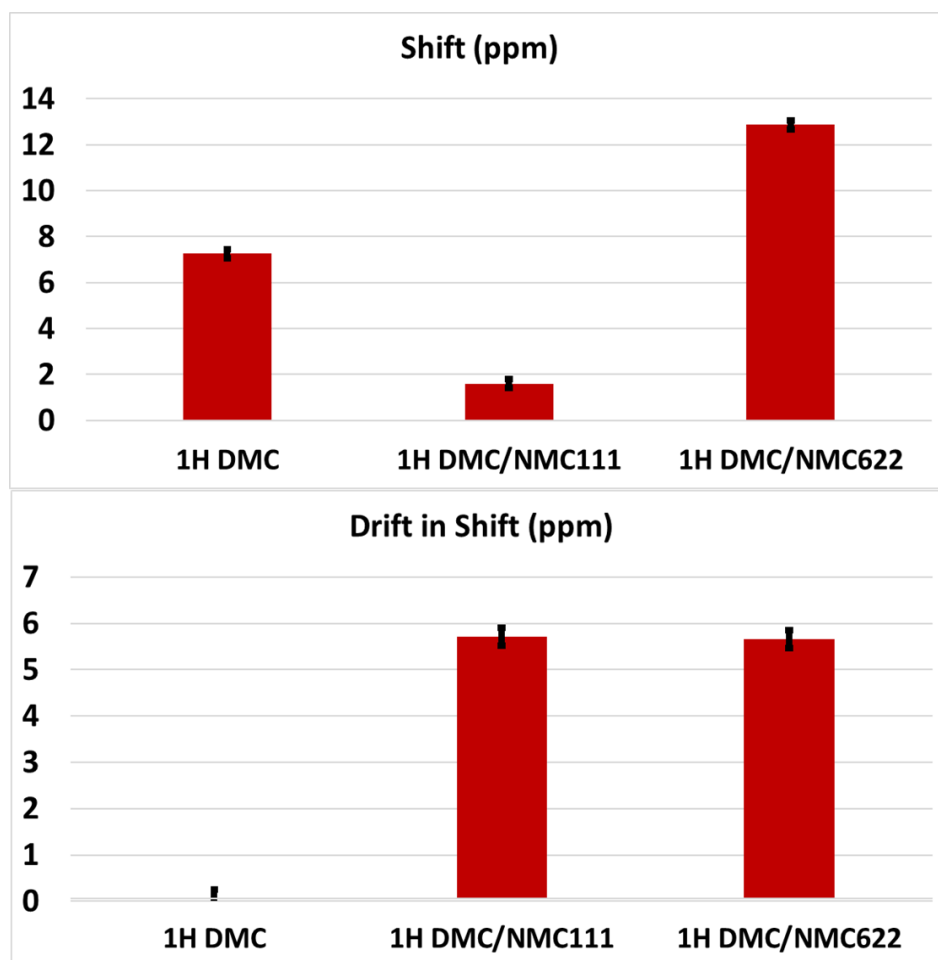


Figure 5-34 The effect of pristine NMC 622 electrode and NMC 111 pellet on the WAS of ^1H signal of DMC and absolute drift in shift.

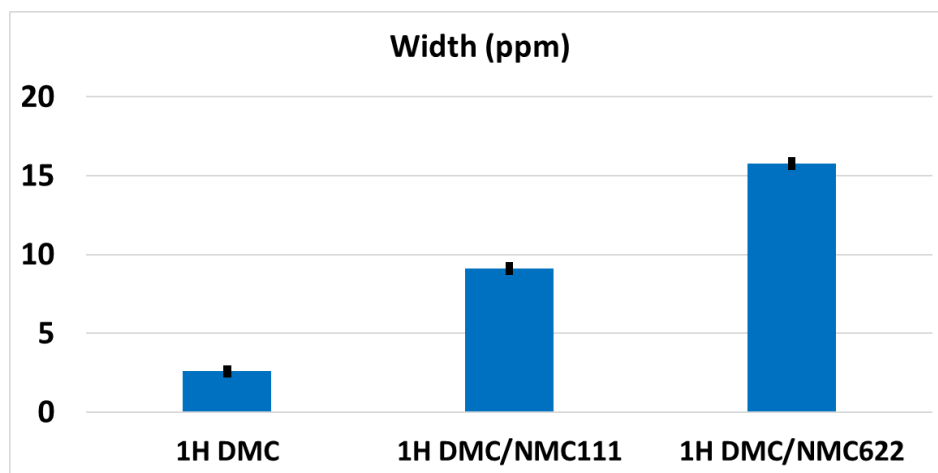


Figure 5-35 The effect of pristine NMC 622 electrode and NMC 111 pellet on the width (FW30%HWAS) of ^1H signal of DMC.

The more pronounced distortion in the ^1H signal of DMC due to the presence of the NMC 622 electrode (with a stronger magnetic susceptibility) in proximity to the DMC solvent compared to the NMC 111 pellet seems to indicate that the magnetic susceptibility of NMC 622 electrode is stronger than that of NMC 111. The stronger effect of the NMC 622 electrode is also evidenced in the faster relaxation of the ^1H signal of DMC (Figure 5-36).

This should however be confirmed by measuring more similar samples (both deposited as electrode slurries on a current collector, for example) and by magnetic susceptibility measurements.

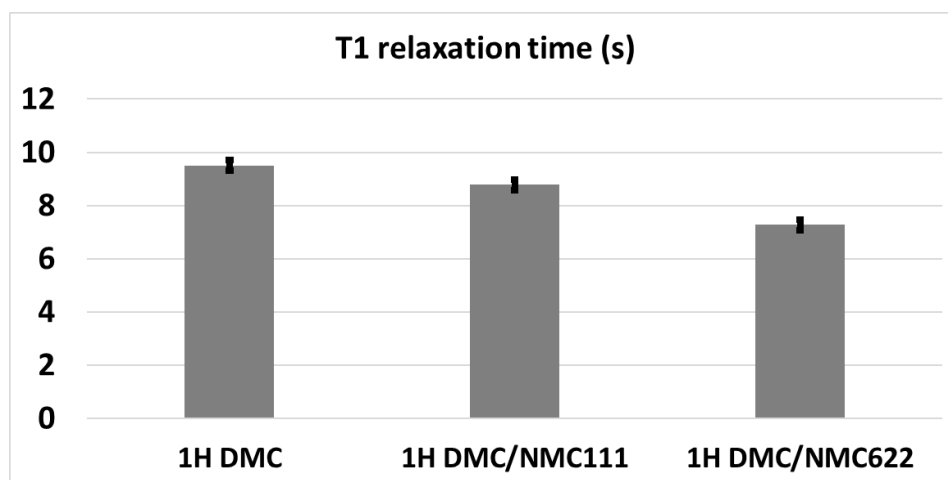


Figure 5-36 Effect of pristine NMC 622 and NMC 111 pellet on the T_1 relaxation time of the 200 μl DMC. It should be noted that the saturation recovery experiment was fitted with a single exponential when there is probably a distribution of T_1 s depending on the distance to the electrode or pellet.

5.6.3 Summary

Figure 5-37 displays the ^1H signal of DMC in contact with all battery components, revealing the most substantial distortion in the ^1H DMC signal from the NMC 622 electrode compared to other battery components.

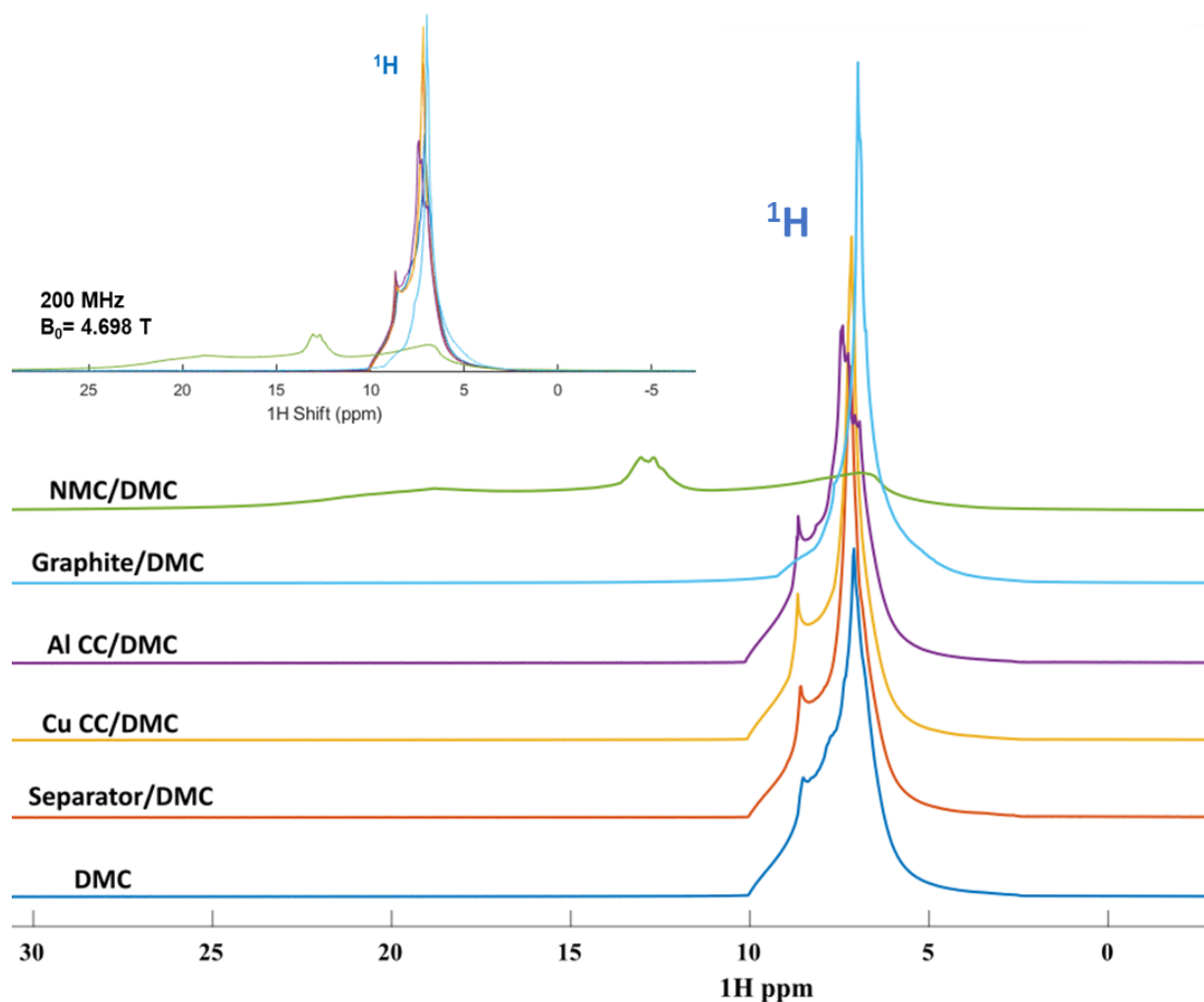


Figure 5-37 ^1H signal of DMC in the presence of all battery components.

Figures 5-38 and 5-39 quantify the impact of all battery components on the shift and width of the DMC ^1H spectra, respectively. The NMC electrode exerts the most pronounced influence on the ^1H signal of DMC, compared to all other battery components, in terms of spectral shift and broadening.

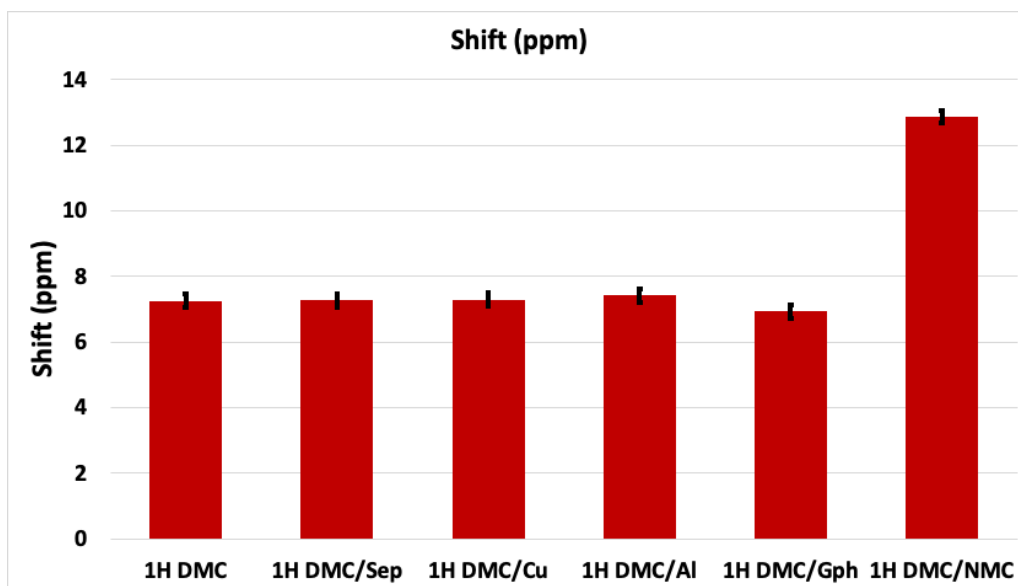


Figure 5-38 Effect of all battery components on the WAS shift of the DMC ^1H spectra.

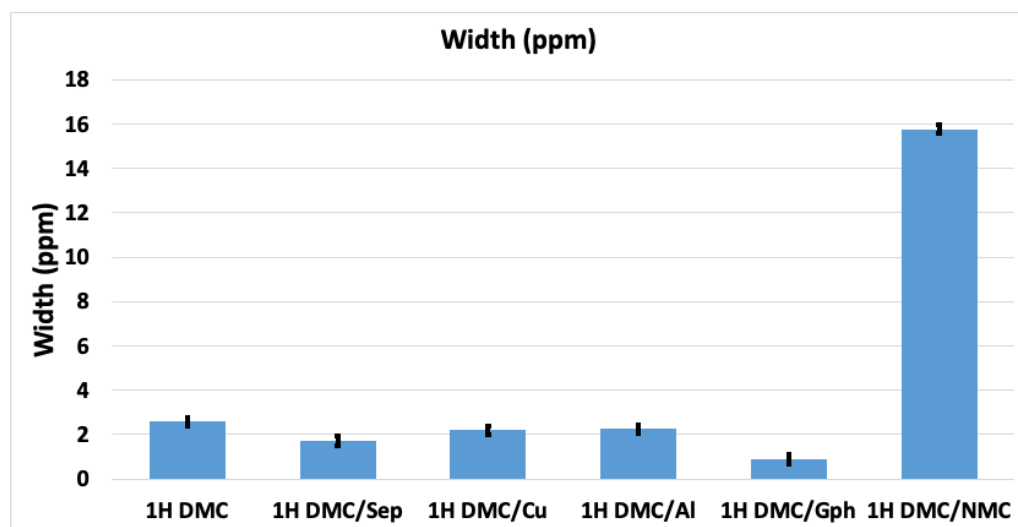


Figure 5-39 Effect of all battery components on the width (FW30%HWAS) of the DMC ^1H spectra.

In Figure 5-40, the area of the ^1H signal of DMC in proximity to all components is presented, with different integration ranges. Notably, for the graphite/DMC sample (as discussed in section 6.2.1), the integral value is lower compared to the other components, including the paramagnetic NMC. This is likely attributed to the presence of a blind zone around the graphite electrode. Conversely, in the case of NMC/DMC, we observe a 15% reduction in the ^1H signal, which is less pronounced than the effect observed with graphite.

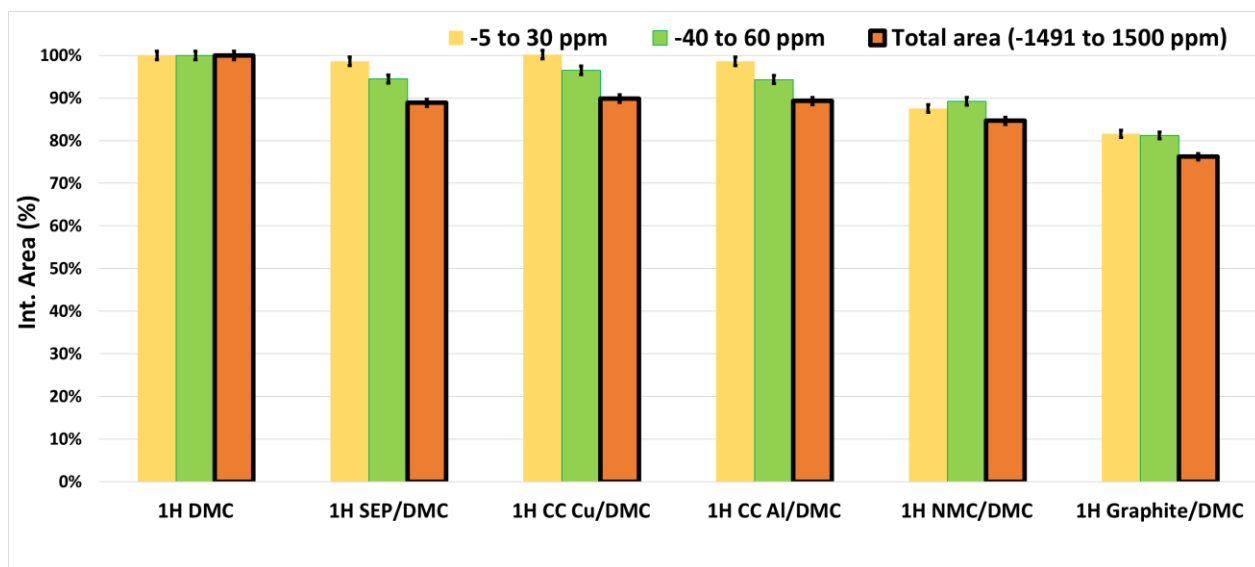


Figure 5-40 Effect of all battery components on the integration area of the DMC ^1H spectra.

Figure 5-41 displays the relaxation time constants of ^1H in DMC in contact with various battery components. Among these components, the most significant effect is observed for the paramagnetic NMC electrode in contact with the DMC solvent, with a faster relaxation.

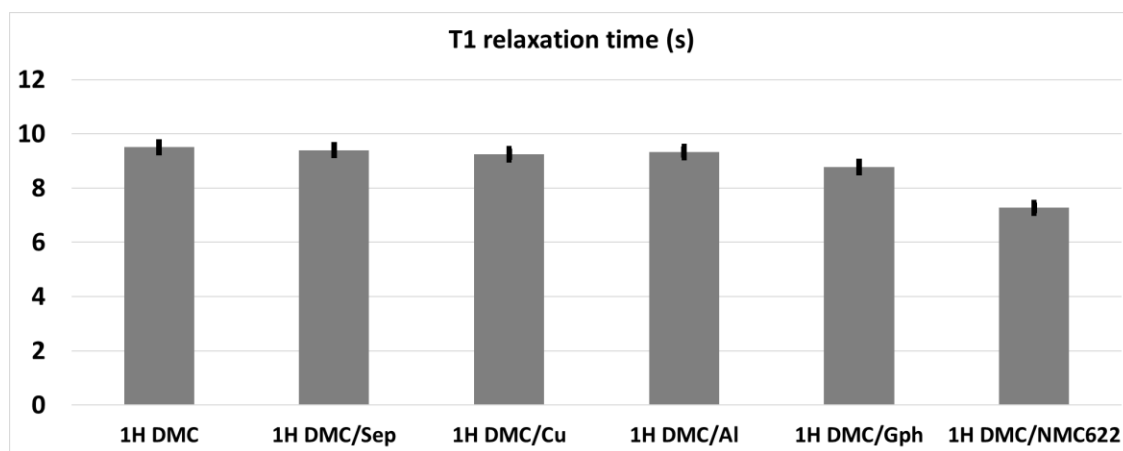


Figure 5-41 Effect of all battery components on the T_1 relaxation time constant of the DMC ^1H .

Figure 5-42 displays the full width at various heights of WAS shifts in the ^1H NMR spectrum of DMC in the presence of battery components. These results demonstrate the higher sensitivity of width to the positive NMC622 electrode.

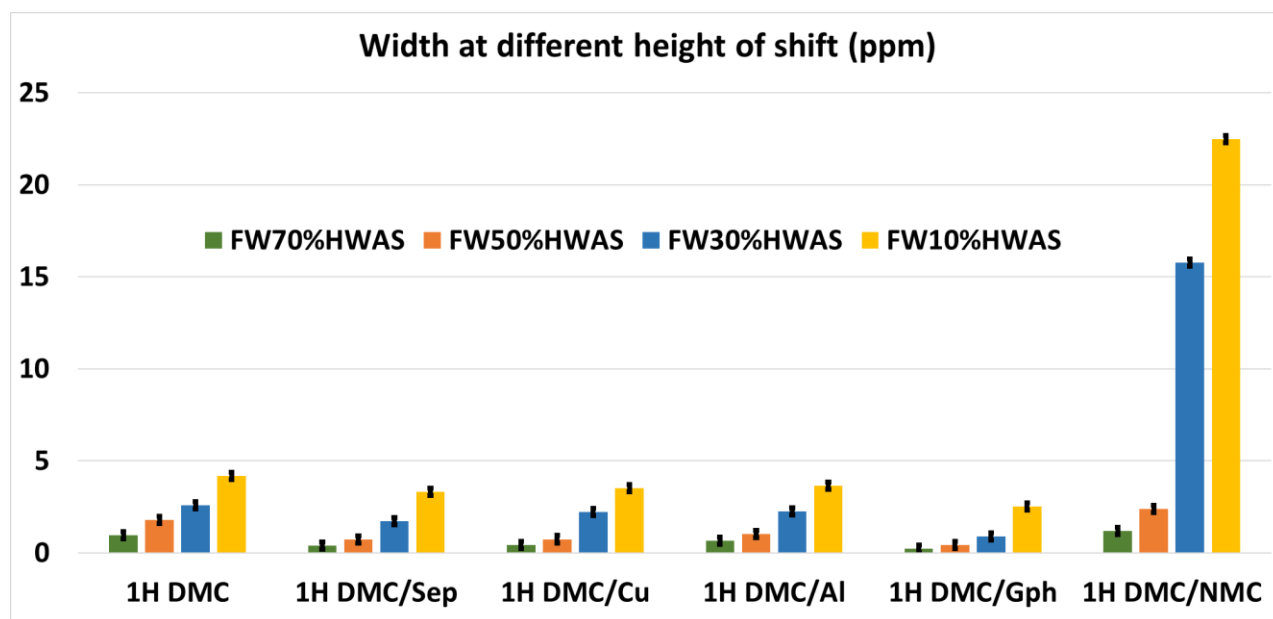


Figure 5-42 Effect of battery components on the width of the ^1H DMC spectra at different heights of Shift.

Figure 5-43a displays the proton signal of DMC in contact with the pristine graphite electrode. Linewidths at various heights of shift have been specified. As demonstrated these linewidth values do not change much at different heights of shift showing a negligible effect of the graphite electrode on the symmetry of the ^1H DMC spectrum. However, in the case of paramagnetic pristine NMC electrode, the linewidth value changes considerably from 50% height to 30% height of shift (Figure 5-43b).

Therefore, for the subsequent quantification in our study, the linewidth at 30% height of the shift has been chosen for comparison between samples. This decision was made because the width at 50% height considers a small width, making it an unreliable representative of the actual spectrum distortion.

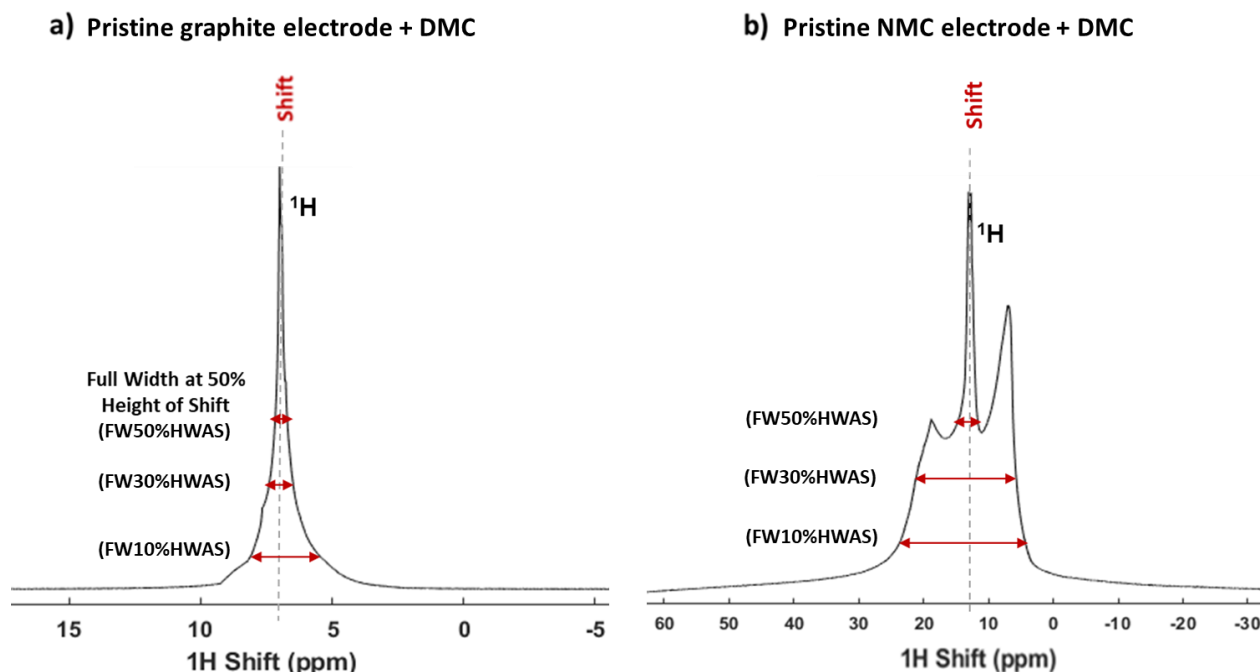


Figure 5-43 Width of the ^1H signal of DMC in contact with (a) pristine graphite and (b) pristine NMC electrodes at different heights of Shift.

5.6.4 Conclusion

In conclusion, we observed that the most notable effect on the ^1H signal of DMC is attributed to the paramagnetic NMC electrode among all battery components. This effect was clearly evident in terms of shift, width, and T_1 . As a result, for subsequent measurements, we will use these descriptors for comparing the effect of different samples on the ^1H signal of DMC solvent.

5.7 Identifying the contribution in the distorted spectrum (part of the 1D spectrum that is close to the electrodes)

As explained earlier, the 1D spectrum is a superposition of all the DMC environments in the tube, including bulk, interface with the tube walls and with the electrode. Herein, we aim to identify the parts of the 1D spectrum that are in proximity to the electrode by employing localized spectroscopy (chemical shift imaging, CSI). By doing so, we can discriminate molecules located at different positions within the liquid and track the spatial (along the vertical axis) dependence of the magnetic susceptibility effects on the ^1H NMR spectrum of DMC.

Electrode materials (e.g., NMC or LFP) typically exhibited a non-planar morphology after punching the 5mm-electrode from the electrode sheet. The surface of these electrodes may have variations and irregularities due to the manufacturing process and the nature of the material, or the constraints on the dried electrode are too strong for the electrode to resist the process of punching.

5.7.1 NMR Peek tube

Given that we are unable to control the flatness of the electrode (active materials film on current collector foil) within the liquid DMC and glass tube and knowing the impact of the electrode shape on the ^1H signal of the DMC electrolyte, we developed a novel NMR tube (Figure 5-44) with a diameter of 10 mm using Polyether ether ketone (PEEK).

PEEK is a colorless organic thermoplastic polymer in the polyaryletherketone family which has been known as a good candidate for electrochemical holders due to its combination of chemical resistance, high temperature stability, good mechanical properties, and electrical insulation.²¹⁶ Using a PEEK tube not only ensures airtight sealing during NMR measurements but also enables better control of the electrode's orientation by maintaining a constant pressure at the edge of the electrodes. Therefore, employing a PEEK tube instead of an NMR glass tube results in a flat surface shape for all the samples, solving issues with curled electrodes and minimizing variability and uncertainty in our measurements, especially when we want to compare several materials.

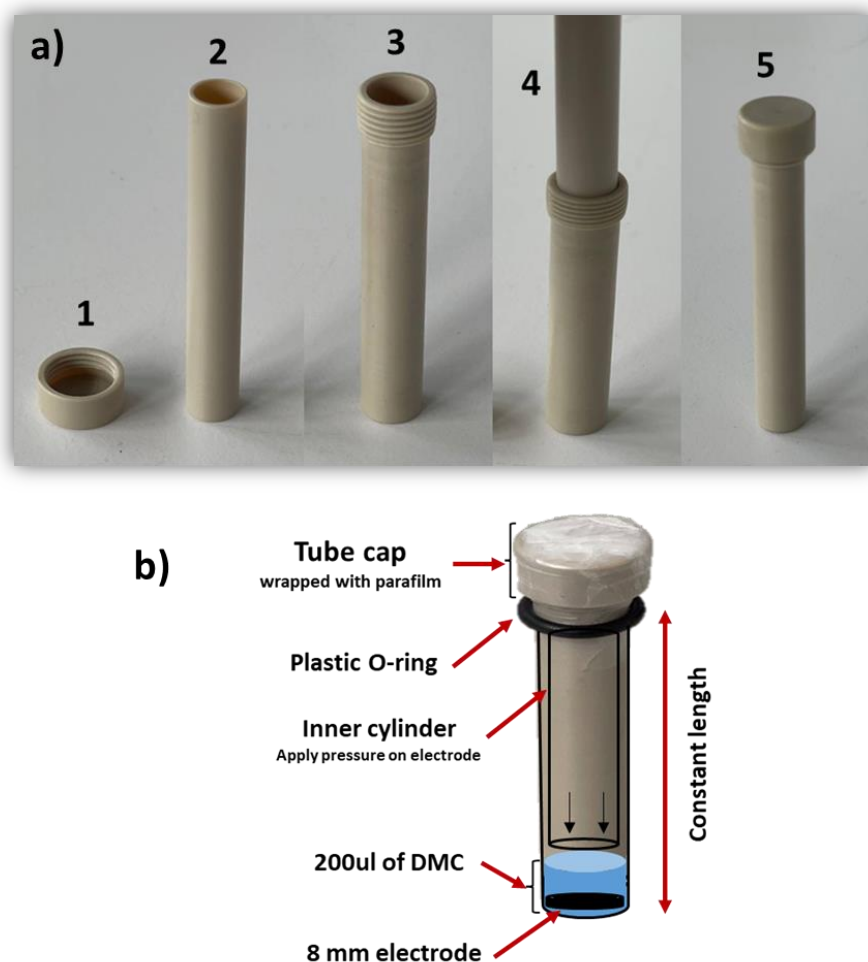


Figure 5-44 (a) 10 mm NMR PEEK tube is composed of a PEEK tube container (3), a cylindrical tube (2) that applies pressure on the electrode (4), and a screwed cap (1) to ensure the airtightness of the tube (5) (b) schematic illustration of PEEK tube.

Figure 5-44 displays both the components and a schematic illustration of the 10 mm NMR PEEK tube. In this setup, the cylindrical tube applies pressure on the electrode edge at the bottom of the PEEK tube, ensuring a flat surface. Simultaneously, a screw cap at the top applies pressure on the inner cylinder and maintains airtightness during NMR measurements.

5.7.2 200 μL DMC Inside PEEK tube

5.7.2.1 CSI (Most quantitative, $d_1=45$ s)

To study the effect of electrodes interface and their flatness on the ^1H spectrum of DMC, we evaluate the presence and distribution of ^1H in 200 μl DMC filled inside a 10 mm NMR PEEK tube using chemical shift imaging (CSI). This technique provides spatially resolved ^1H NMR spectra of slices within the 200 μl of DMC. Figure 5-45 shows the ^1H CSI of 200 μl DMC placed in this PEEK tube with a recycle delay of 45 s, sufficient for full relaxation. The Y axis gives the position along the vertical of the tube and each Hz corresponds to $1\mu\text{m}$. The projection of all the spectra along the vertical axis provides a 1D profile of protons.

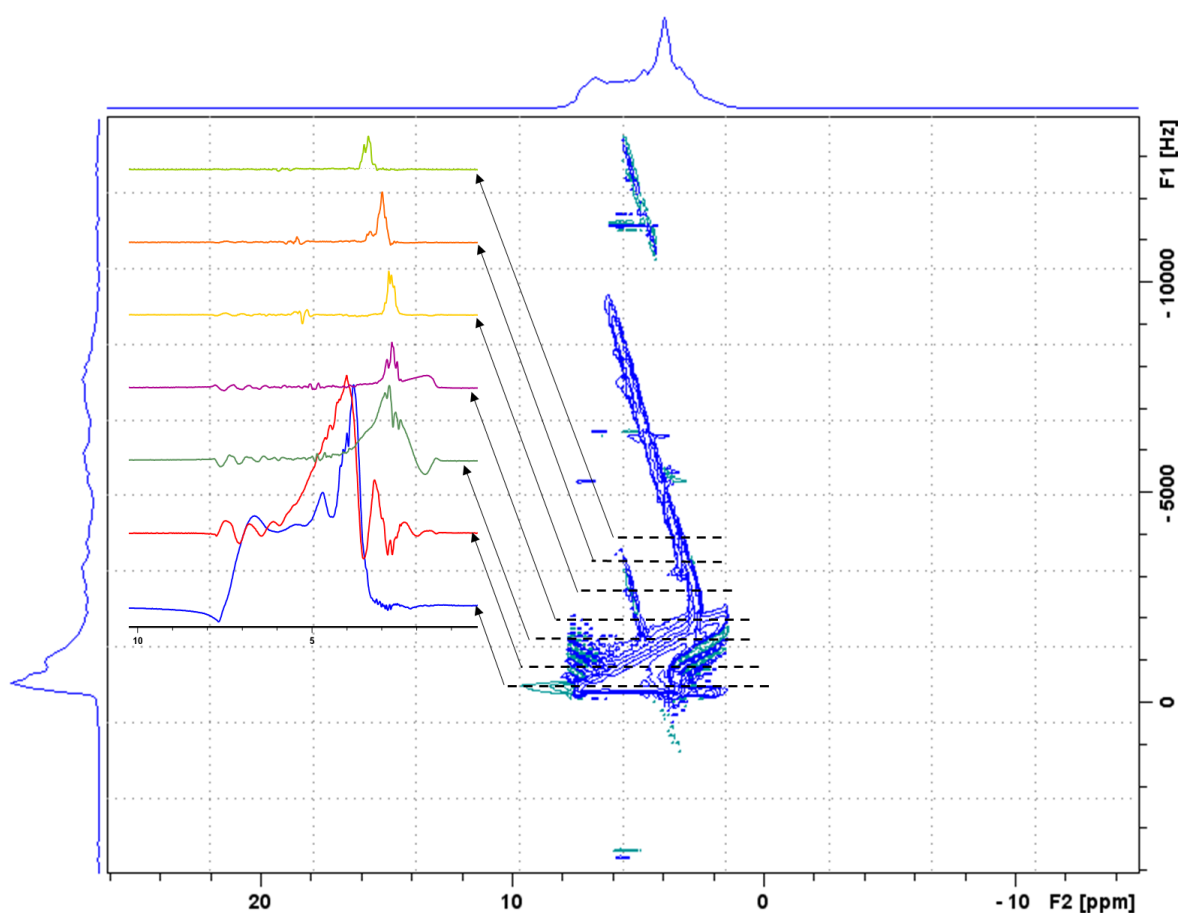


Figure 5-45 ^1H CSI of 200 μl DMC in PEEK tube with recycle delay of 45 s (bottom part of the tube). FOV: 2.5 cm; Number of slices: 256, gradient maximum value: 117.98 G/cm. The vertical axis is in Hz, which corresponds to μm in this case.

Figure 5-45 also displays ^1H NMR spectra of slices extracted from the CSI measurement, with the corresponding position indicated by the vertical axis on the side (in μm). We observe a distortion in the signal at the bottom of the tube, corresponding to the interface between PEEK and DMC. This distortion may be due to the interfaces of the liquid with the bottom part of the PEEK tube and the inner cylindrical insert. Starting from the bottom of the tube up to 2 mm height (2000 Hz, purple spectrum), the spectrum shifts to the right (~ 2 ppm) and becomes narrower. This is probably the region containing the most DMC.

Upon examining the spectra (Figure 5-45), it is evident that as we move higher in the tube (above 2 mm), the distortion in the signal reduces, and the signal intensity does not change significantly; it remains relatively constant (up to 5 mm). These signals are tentatively assigned to the presence of liquid DMC between the PEEK tube and the cylindrical insert, which would rise due to capillarity (up to approximately 5 mm). Here, the signals tend to slightly shift to the left (~ 3 ppm), which might be due to imperfection in the shims. It is important to note that we can only observe signals that survive the length of the echo in the CSI ($754.5 \mu\text{s}$).

It should be noted that the 200 μL of DMC in a standard NMR glass tube would rise approximately 4 mm up the tube. However, with the introduction of an inner cylinder in PEEK tube that results in a decreased area, the DMC should ideally rise to a height of 5.1 mm. However, the ^1H CSI results above show that the DMC solvent reaches a height closer to 8 mm due to capillarity effects.

In Figure 5-46, we extracted slices corresponding to the upper part of the PEEK tube. Beyond 5 mm, the signals continue shifting to the left, and their intensity increases (up to an 8 mm height). However, above 8 mm height, we noticed a significant decrease in signal intensity, indicating the absence of DMC above.

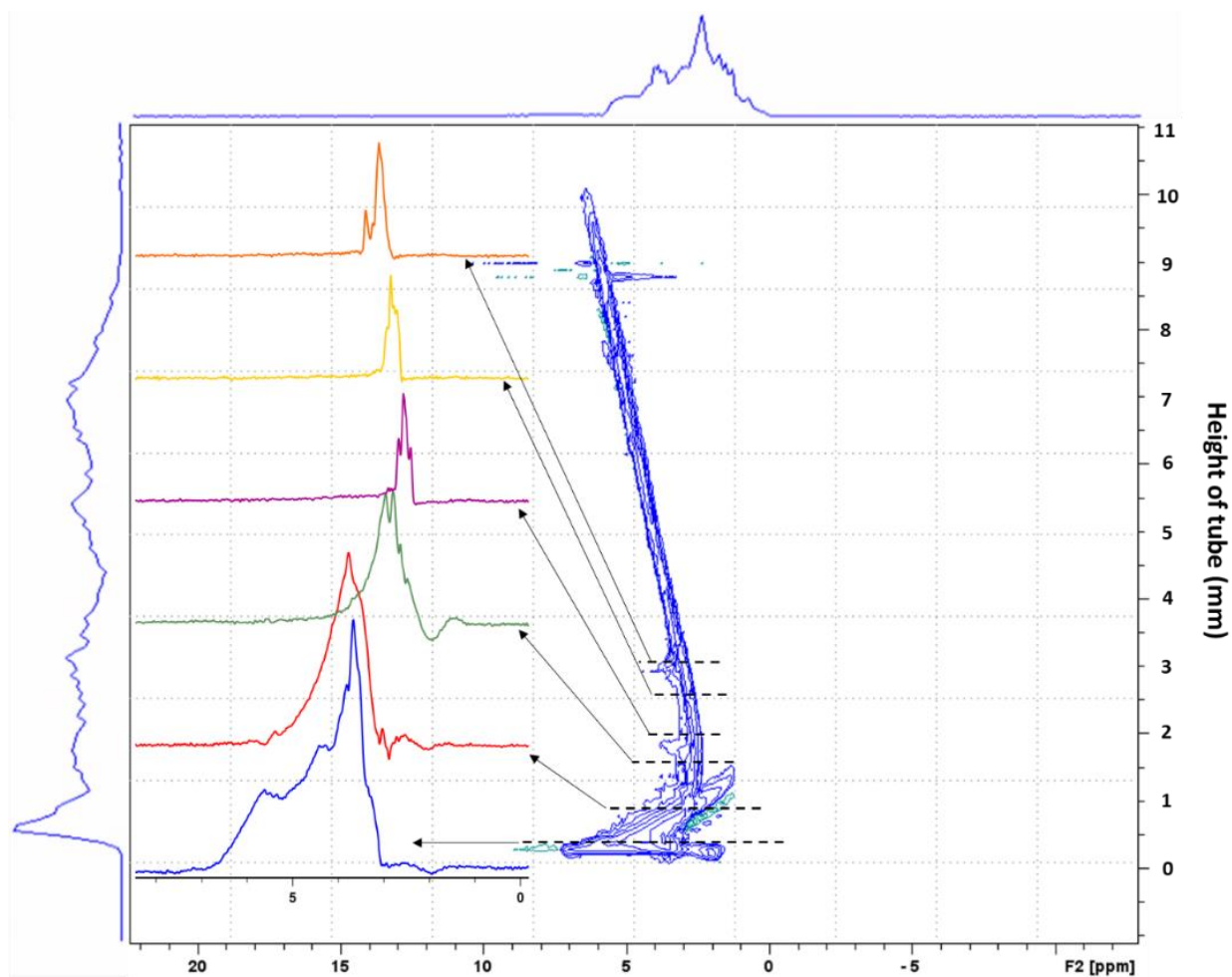


Figure 5-47 ^1H CSI of 200 μl DMC in PEEK tube with recycle delay of 1 s (bottom part of the tube).

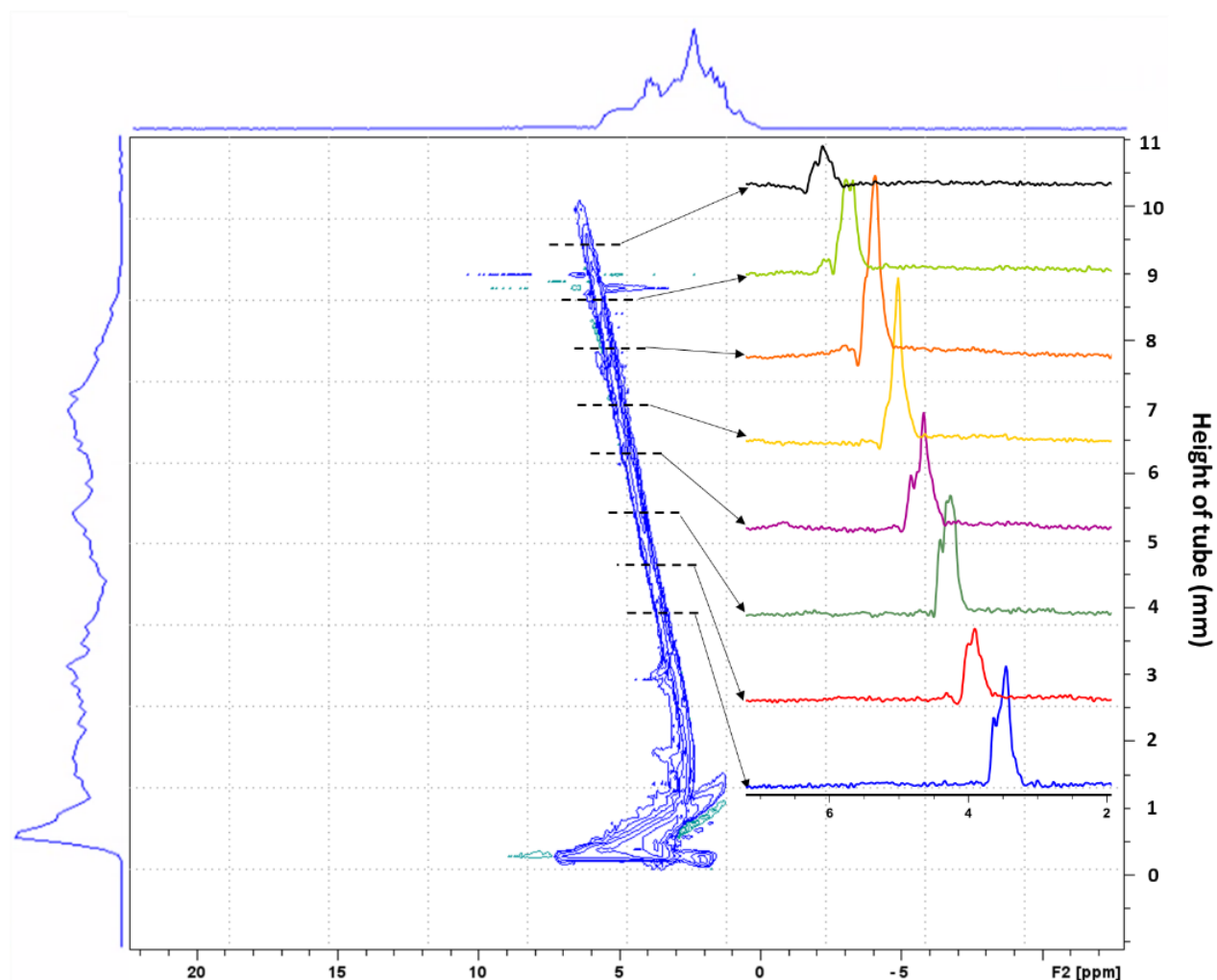


Figure 5-48 ^1H CSI of 200 μl DMC in PEEK tube with recycle delay of 1 s (upper part of the tube).

Figure 5-49 presents the comparison between ^1H CSI of 200 μl of DMC with two different recycle delays (1 s and 45 s). The measurement with a short recycle delay shows a significant loss of signal in the region that contains bulk DMC liquid (0 to 2 mm from the bottom. This is due to the saturation of the signals with longer relaxation time, mostly coming from the bulk liquid.

Furthermore, we do not observe a significant change at different recycle delays in the signal from the top part of the tube, assigned to the DMC solvent driven up by capillarity (from 5 mm to 9 mm). This indicates that the signal from this region has a relatively short recycle delay, and it is not fully saturated when reducing the recycle delay to 1 second.

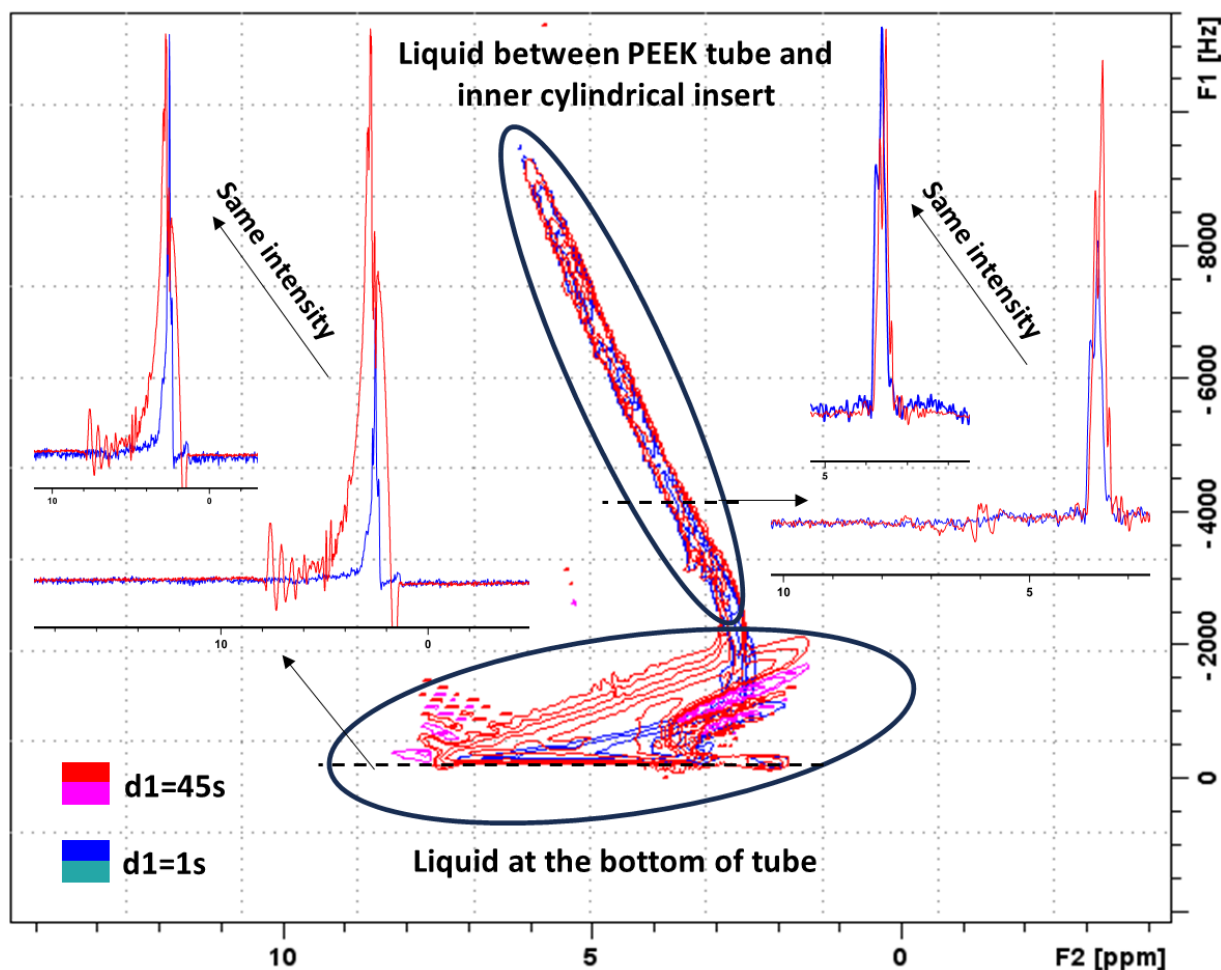


Figure 5-49 ^1H CSI of pure 200 μl DMC in PEEK tube with recycle delay of 45 s (red and purple) and 1 s (blue and green).

5.7.3 200 μl DMC with LFP electrode

After evaluating the distribution of the ^1H signal of DMC in 200 μL of DMC in the PEEK tube, we proceeded to study the effect of the LFP electrode soaked in the 200 μL of DMC inside the PEEK tube. This allowed us to study the effect of the interface and flatness of LFP electrodes on the ^1H spectrum of DMC.

5.7.3.1 LFP electrode

Herein, we used double-sided LiFePO_4 (LFP) obtained from LiFUND technology commercial dry pouch cells. The LFP was coated over Al foil at 96.5% active material and a loading of 16 mg/cm^2 . The LFP active materials from one side of the electrode were removed and then punched into 8mm

diameter. The punched electrodes were dried under vacuum at 80 °C overnight to eliminate any moisture.

5.7.3.2 Quantitative 1D spectrum

Figure 5-50 shows the ^1H signal of 200 μL of DMC in contact with an LFP pellet and LFP electrode with a recycle delay of 45 seconds (fully quantitative for both). The proton signal of DMC (red) in contact with the LFP electrode (in the PEEK tube) shows two relatively sharp components centered at 4.6 and 17 ppm. Meanwhile, the proton signal of DMC (blue) in contact with the LFP pellet (in a standard NMR glass tube) is significantly broadened.

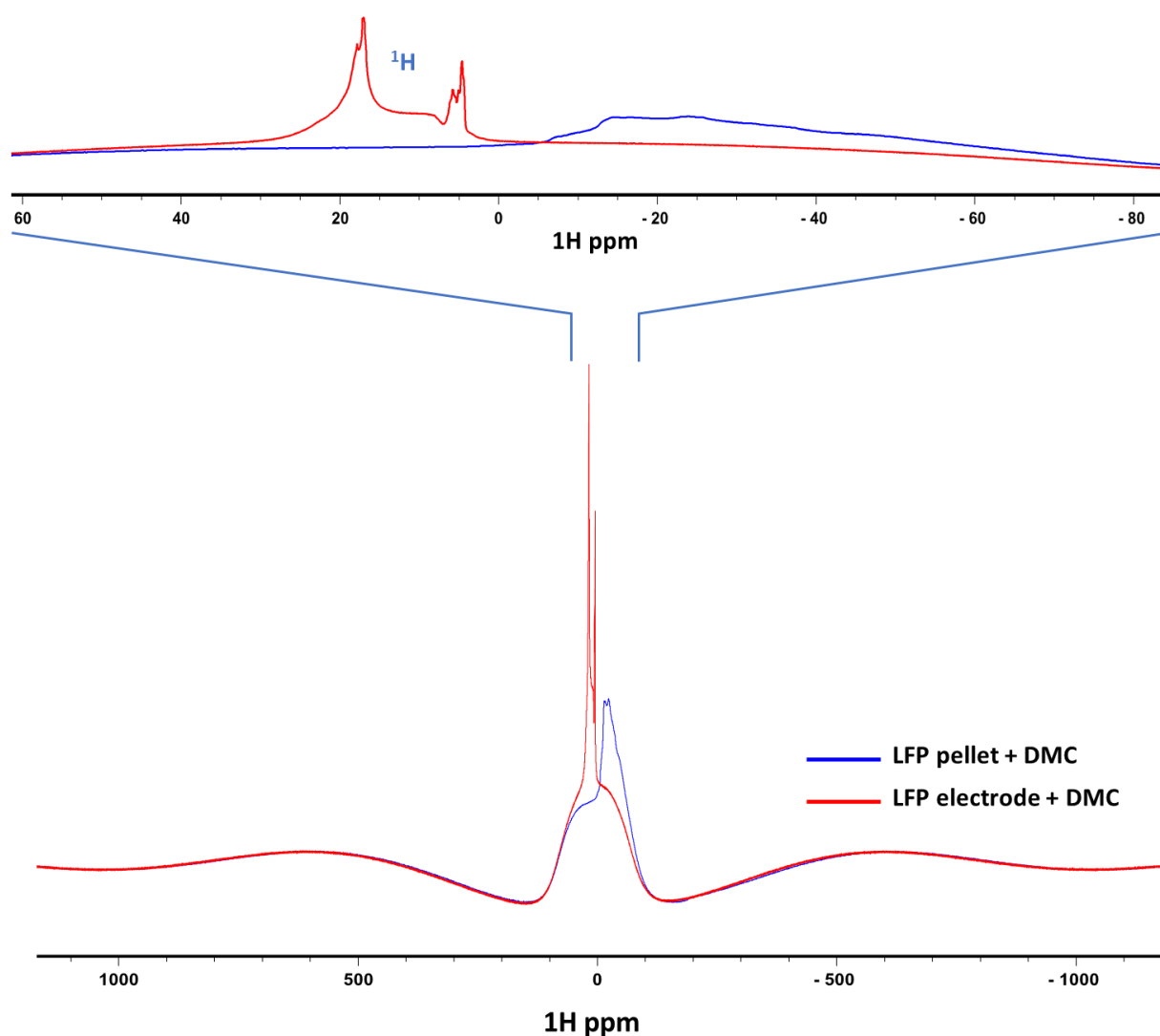


Figure 5-50 ^1H signal of DMC in the presence of LFP pellet and LFP electrode.

The difference in the shape of the signal can be attributed to the slightly different composition of the active materials used in the electrode and pellet, the effect of the aluminum current collector present in the LFP electrode, and also the differences in tubes used for the measurement.

Figure 5-51 shows the proton signal of DMC in contact with the LFP electrode for recycle delays of 1 s (blue) and 45 s (red). As shown in the figure, the intensity of the spectrum is lowered, but all the signals remain even after decreasing the recycle delay to 1 s (indicating they all have quite fast relaxation time).

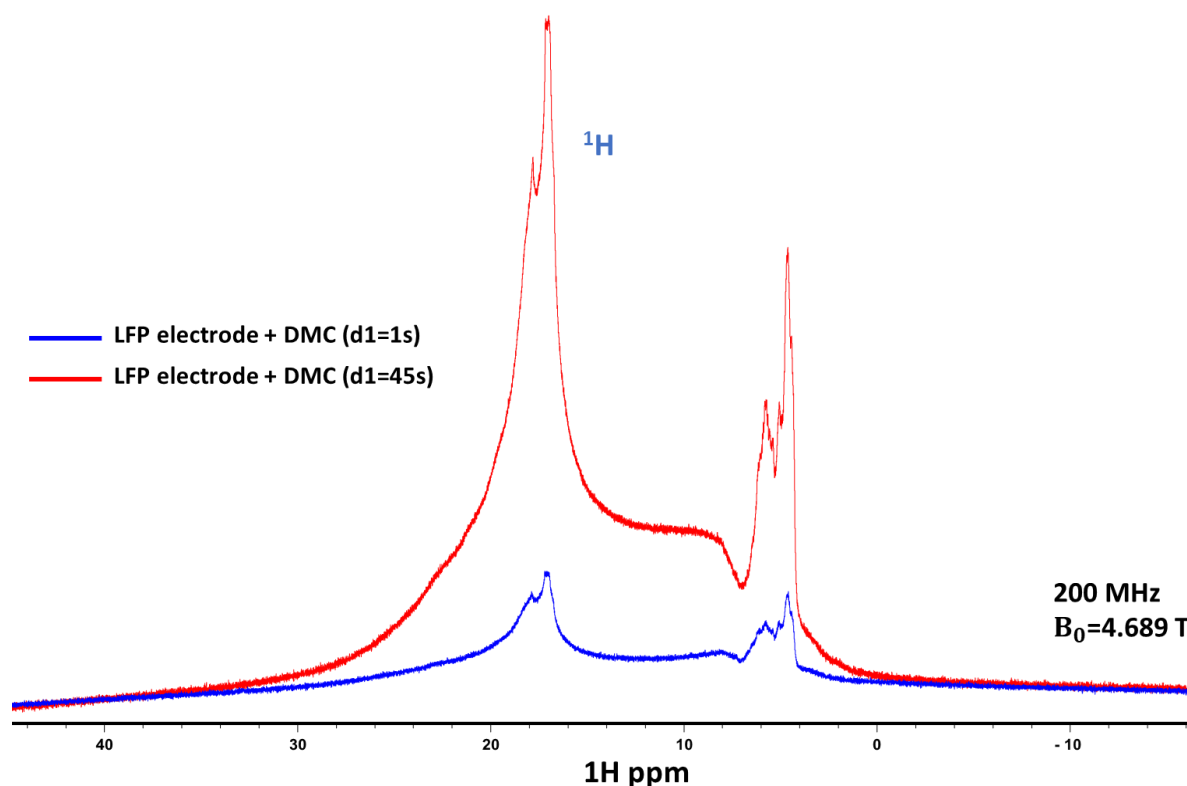


Figure 5-51 ^1H signal of DMC in the presence of LFP electrode with recycle delay of 1 s (blue) and 45 s (red). One pulse experiment with saturation with 64 scans for both.

Figure 5-52 displays the same spectra, scaled to have the same intensity for the 8 ppm peak. The peaks on the left-hand side lost more intensity compared to the peaks on the right-hand side. The peaks on the left can be assigned to the signals from bulk DMC in contact with the LFP electrode at the bottom of the tube, while the peaks on the right can be attributed to the DMC solvent trapped between the PEEK tube and the cylindrical insert. The signals from the trapped DMC show faster

relaxation compared to the signals from bulk DMC, as by decreasing d_1 , they experience more signal loss.

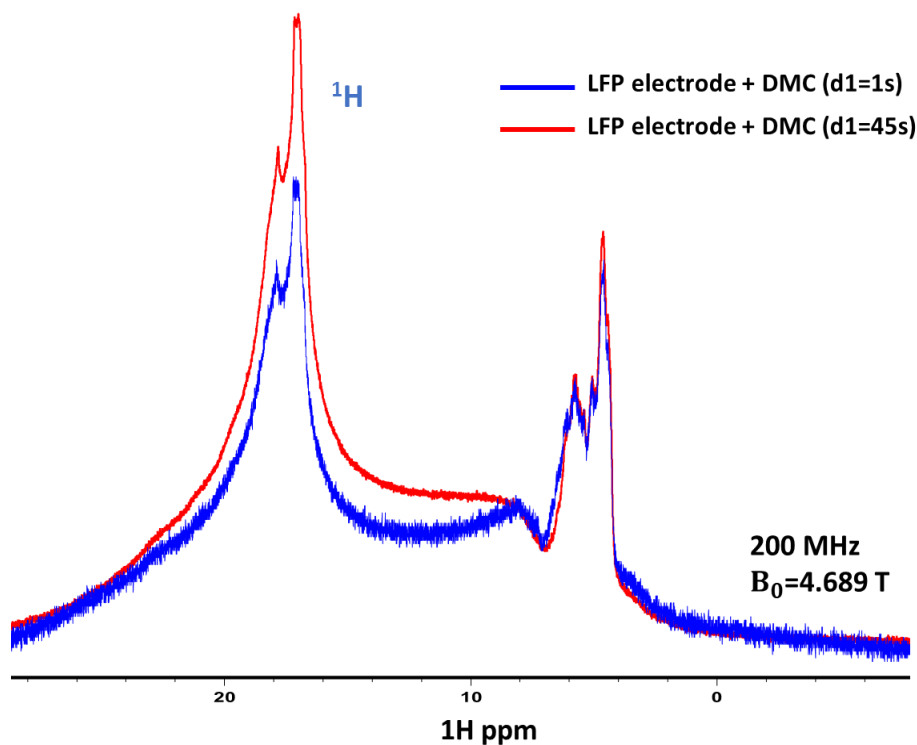


Figure 5-52 ^1H signal of DMC in the presence of LFP electrode with recycle delay of 1 s (blue) and 45 s (red) plotted with same intensity.

5.7.3.3 CSI with a long recycle delay

In Figure 5-53, the ^1H CSI signal of 200 μL of DMC in contact with an LFP electrode is presented, utilizing a quantitative recycle delay of 45 seconds. Upon comparing Figure 5-53 with Figure 5-51, it becomes evident that the significant broad hump observed in Figure 5-51 is effectively attenuated. We assign this to a T_2 filtering effect in the ^1H signal of DMC in contact with LFP electrode.

As for Figure 5-45, the signal from the bottom of the tube (up to 2 mm height) shows a significant distribution due to the interfaces between the LFP electrode or the interior wall of the PEEK tube and DMC. As we move from the bottom to the upper part of the tube, up to 2 mm, the distortion decreases, and the signals become narrower, shifting to the right by around 15 ppm (from the first to the last spectra).

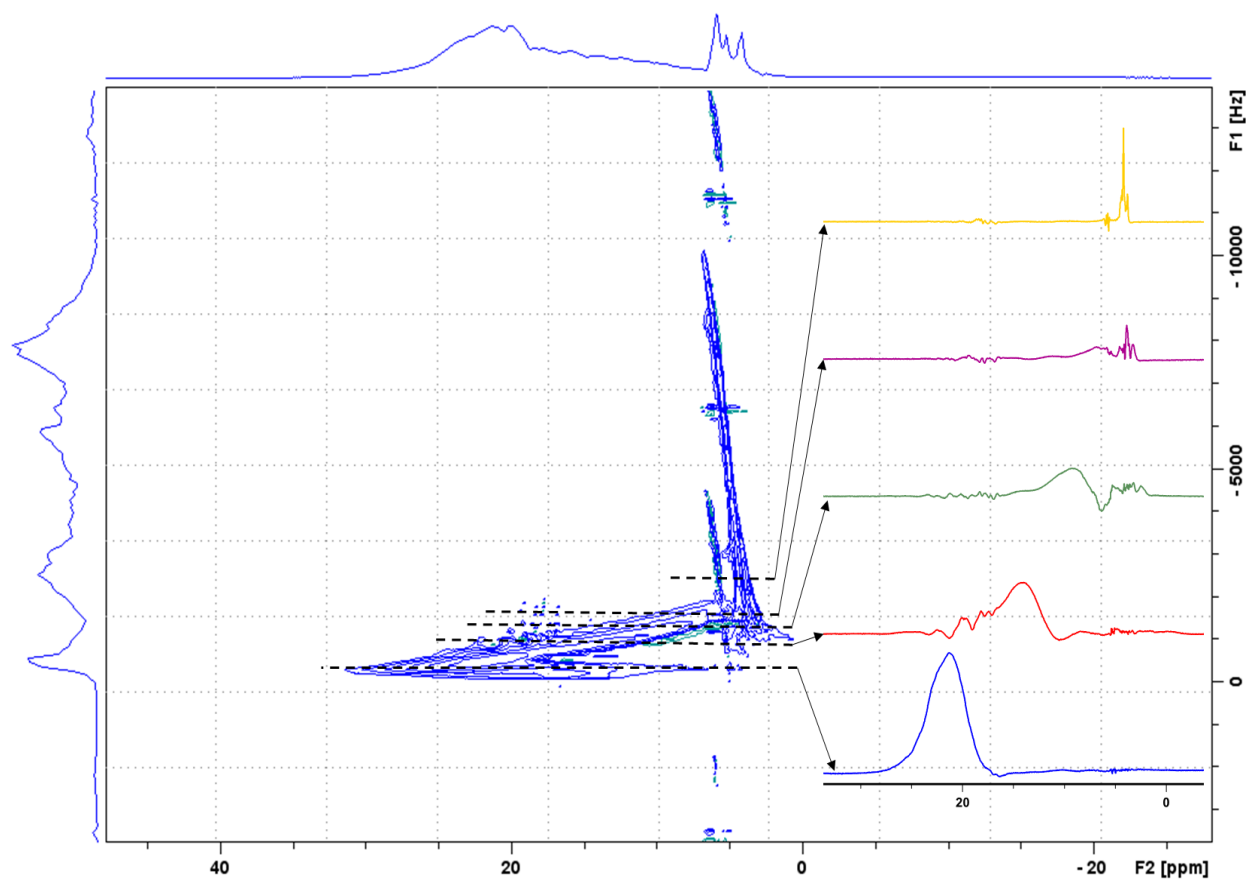


Figure 5-53 ^1H CSI of 200 μl DMC in contact with LFP electrode in the PEEK tube with recycle delay of 45 s (bottom part of the tube).

Moving from 2mm to 10mm height of tube (Figure 5-54), the proton signals (coming from the trapped DMC solvent between walls) intensities are slightly changed and shift to the left around 2 ppm.

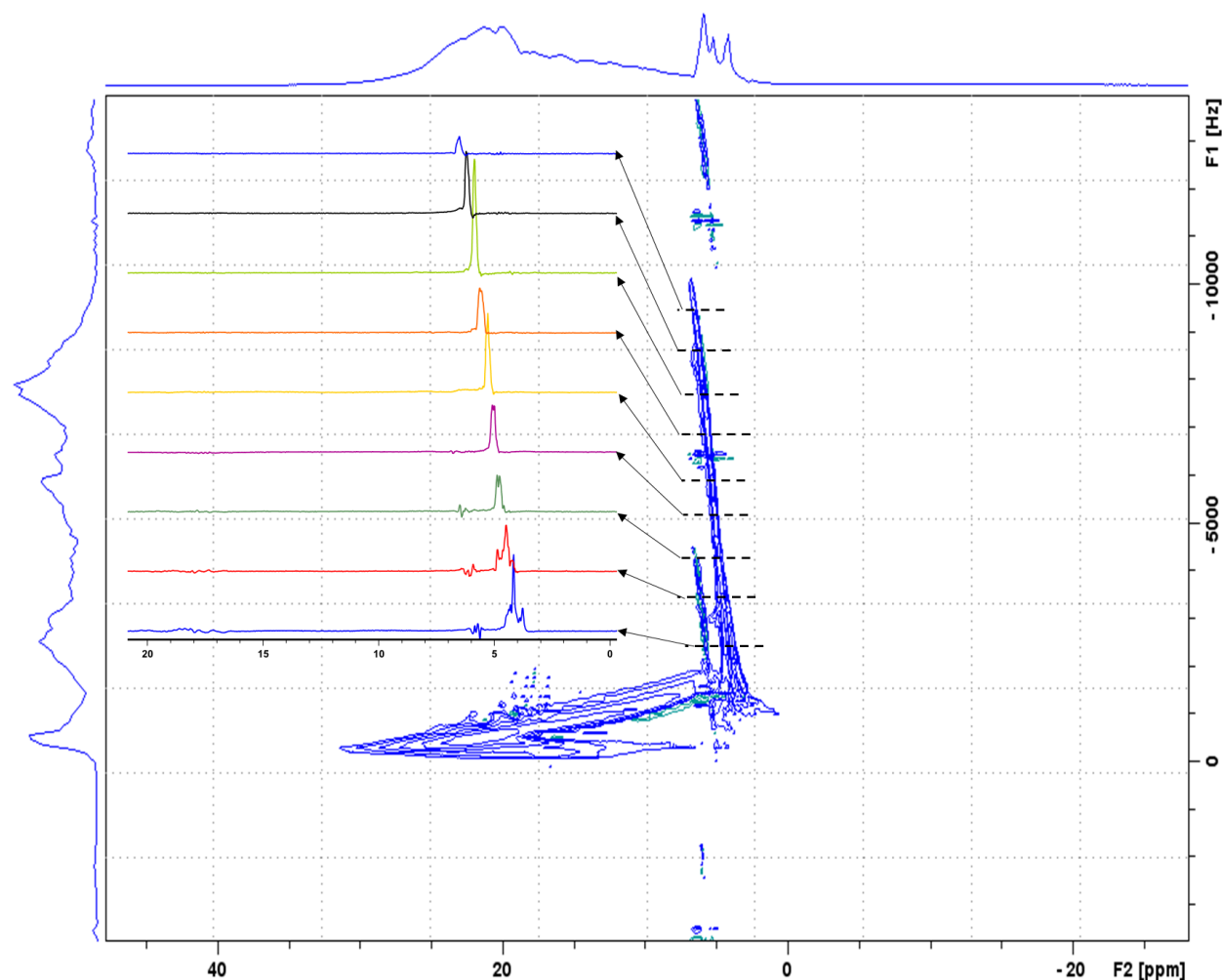


Figure 5-54 ^1H CSI of 200 μL DMC in contact with LFP electrode in the PEEK tube with recycle delay of 45 s (upper part of the tube).

5.7.3.4 Comparison with “quantitative” CSI of DMC

By comparing the ^1H CSI of pure 200 μL DMC and 200 μL DMC in contact with an LFP electrode in the PEEK tube with a recycle delay of 45 s (Figure 5-55), we can observe how the paramagnetic LFP electrode affects the signal from the bulk DMC area, where the DMC solvent and LFP are in contact with each other. The LFP electrode induces a significant distortion in the proton signals from this area (from the bottom to a 2 mm height of the tube), resulting in broader and more shifted signals (Figure 5-53), compared to those observed in pure DMC (see Figure 5-45). For instance, the proton signal of DMC from the bottom of the tube in the presence of the LFP electrode shows a width that is double in comparison to the proton signal of pure DMC.

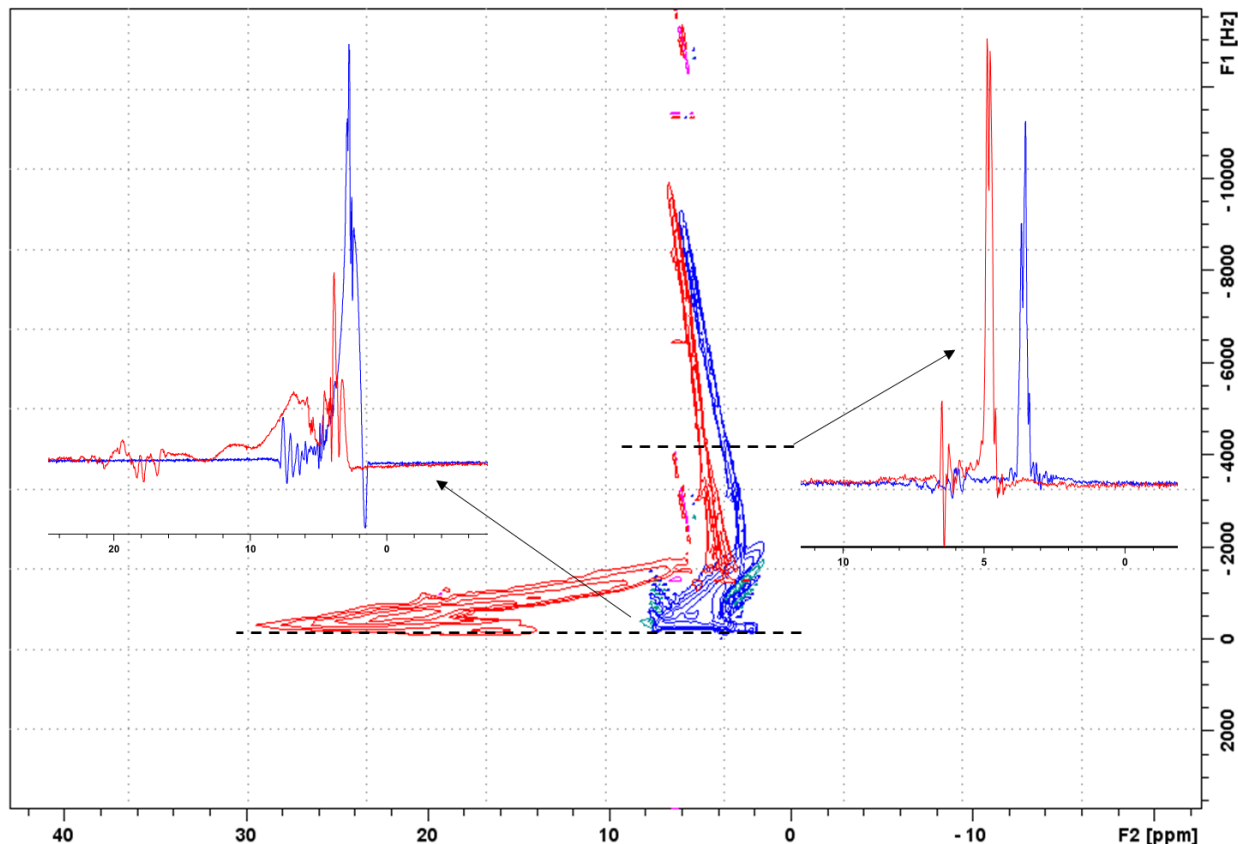


Figure 5-55 ^1H CSI of pure 200 μl DMC in PEEK tube (blue and green) and ^1H CSI of 200 μl DMC in contact with LFP electrode in the PEEK tube (red and purple) with recycle delay of 45 s.

The signals from the capillarity part in both cases show roughly the same width, with just a slight shift. The signal intensity for DMC in contact with LFP electrode in this region is surprisingly more intense than the pure DMC signal. This may be due to a better tuning of the probe, or to the longer stay of the sample (LFP+DMC) inside the magnet, allowing more DMC to go up by capillarity.

5.7.3.5 Effect of shorter recycle delay

Herein, we aim to compare the effect of changing the recycle delay on the ^1H CSI of DMC and of DMC in contact with an LFP electrode and compare the results. Therefore, we will start by examining the effect of a short recycle delay (1 s) on the ^1H CSI of DMC in contact with an LFP electrode (Figures 5-56 and 5-57).

In Figure 5-56, the proton signal from DMC at the bottom of the tube, shows significant broadening, as expected. As we move higher in the tube (up to 2mm), the signal narrows and experiences a shift of approximately 12 ppm.

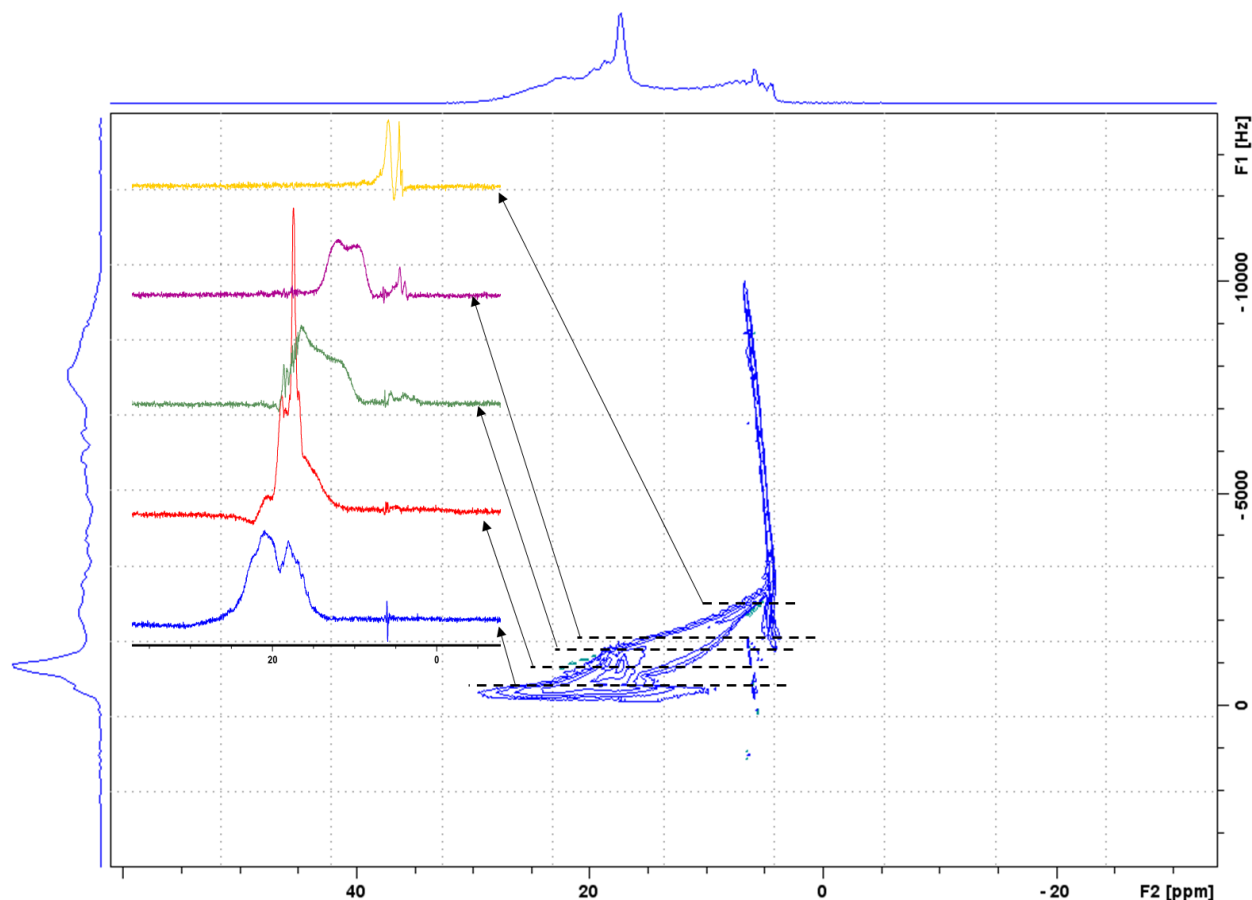


Figure 5-56 ^1H CSI of 200 μl DMC in contact with LFP electrode in the PEEK tube with recycle delay of 1 s (bottom part of the tube).

The signal from the capillarity part (2 mm to 10 mm) does not show a significant change, and the width of the signal remains roughly the same but slightly shifted to the left (2 ppm).

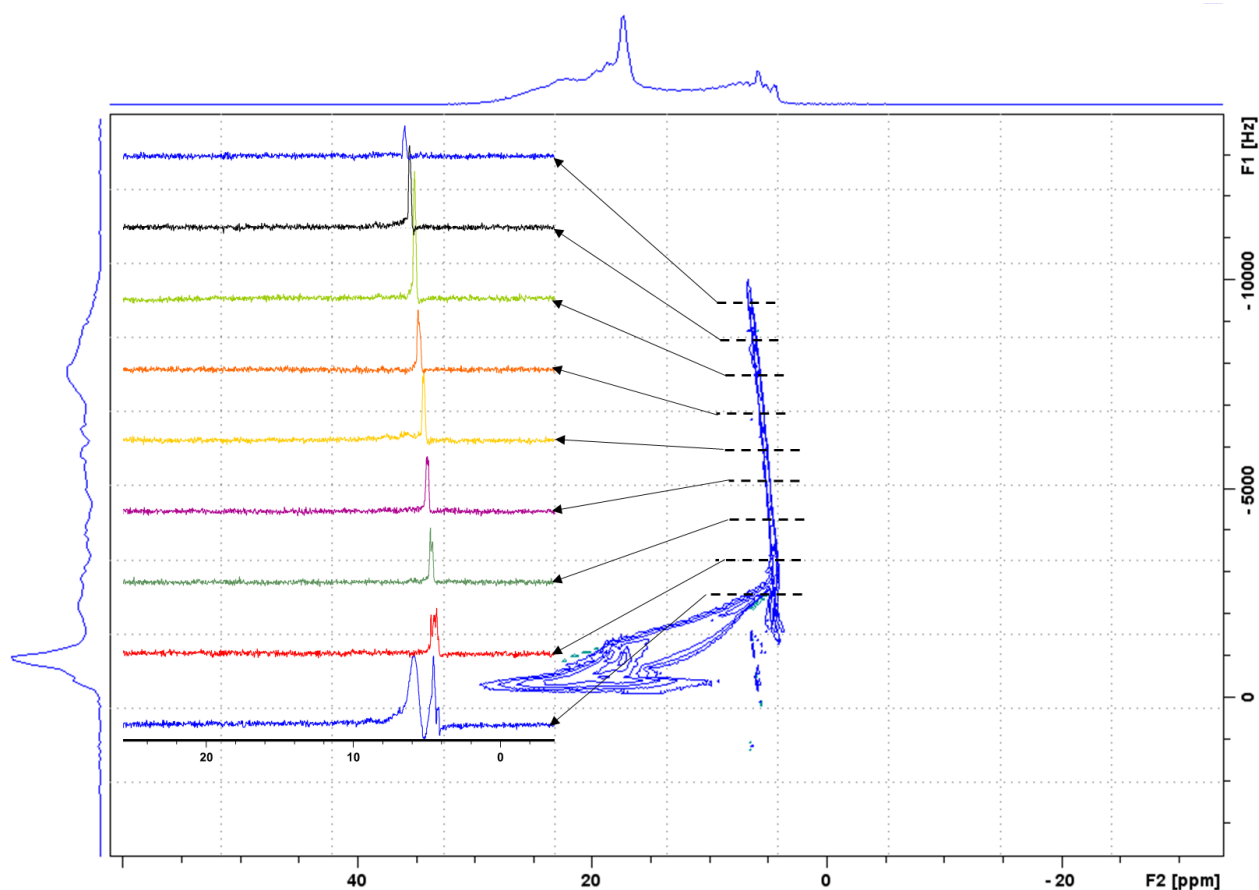


Figure 5-57 ^1H CSI of 200 μl DMC in contact with LFP electrode in the PEEK tube with recycle delay of 1 s (top part of the tube).

Figure 5-58 shows a comparison of the ^1H CSI of 200 μL of pure DMC and 200 μl of DMC in contact with a paramagnetic LFP electrode with a short recycle delay of 1 second. Due to the effect of the LFP electrode, the ^1H signal from the bottom of the tube is shifted to the left by approximately 16 ppm and exhibits a broadening that is four times larger compared to the ^1H signal from the bottom of pure DMC.

At a height of 1.6 mm in the tube, the distortion due to LFP and interfaces still persists but is decreased as we move to higher parts of the tube. The signals from the trapped DMC at a height of 4mm are still under the effect of the LFP electrode, as we observe a significant loss in signal intensity compared to the pure DMC signal from this region.

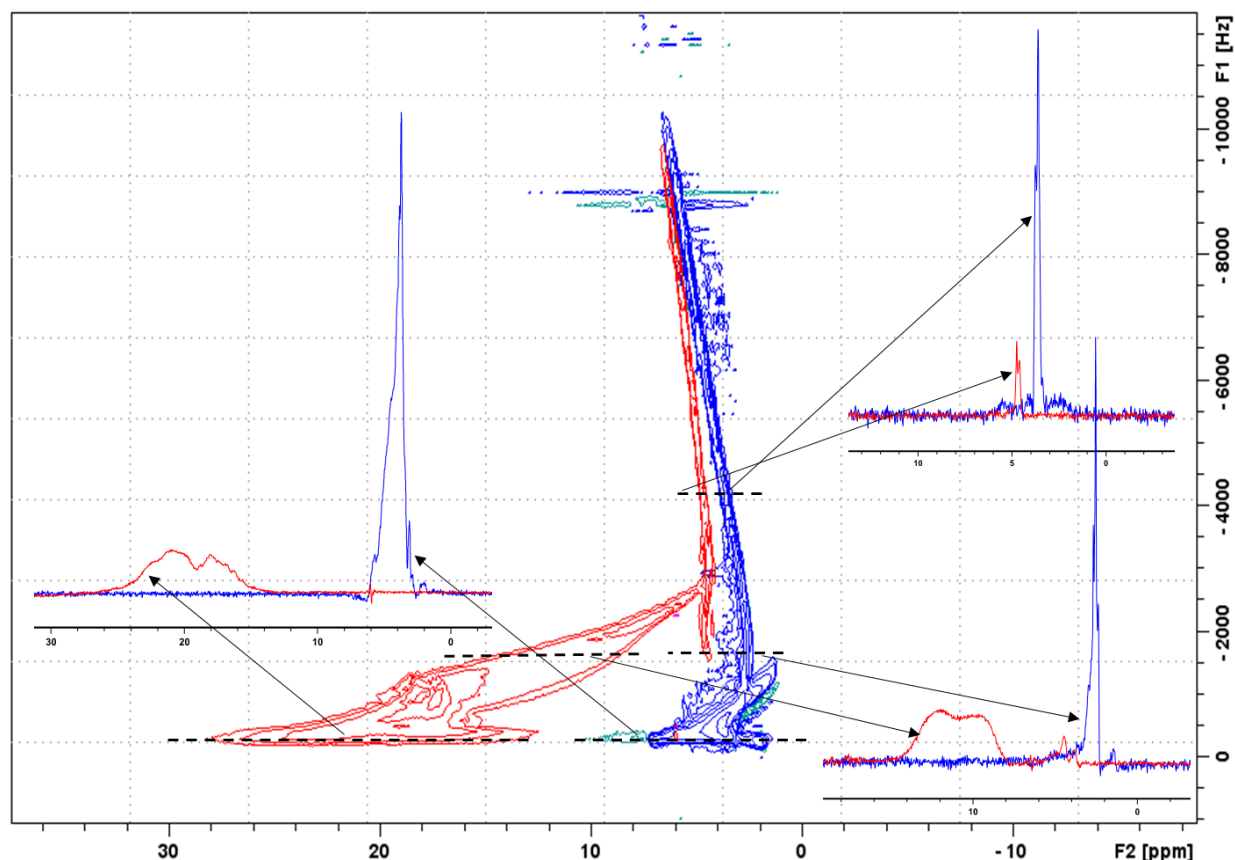


Figure 5-58 ^1H CSI of pure 200 μl DMC in PEEK tube (blue and green) and ^1H CSI of 200 μl DMC in contact with LFP electrode in the PEEK tube (red and purple) with a recycle delay of 1 s. Insets show an overlay of slices from the two CSI.

Figure 5-59 presents a comparison of the ^1H CSI of 200 μL DMC in contact with a paramagnetic LFP electrode at recycle delays of 1 and 45 seconds. When examining the signals from the bottom of the tube with a long recycle delay, we observe a sharp and broad spectrum. However, with $d_1=1$ s, we notice a significant loss in signal intensity, as for pure DMC. This can be assigned to the longer T_1 of the DMC molecules in that region. Due to the short recycle delay, these signals were effectively attenuated by saturation.

The same behavior is observed in the upper part of the tube at 4.2 mm, where we have a sharp signal corresponding to trapped DMC with $d_1=45$ s (blue), and a less intense signal with $d_1=1$ s (red). Here, the magnetic susceptibility effect of the LFP electrode and interfaces effect are the same in both cases, and the difference only arises from the distribution of T_1 relaxation constants, since the sample remains the same for both measurements. When comparing the shift and shape of

the signal from the two measurements at the same intensity, we observe negligible alteration from changing the relaxation delay in the capillarity part. However, this results in a significant intensity difference between the two measurements due to partial signal saturation in the measurement with $d1=1$ s. For the “bulk” part at the bottom of the tube; the spectrum is slightly broader (FWHH of 2521 Hz (12.6 ppm) for $d1=45$ s to 3002 Hz (15 ppm) for $d1=1$ s). The short recycle delay exerts a filtering that enhances the components of the spectrum closer to LFP, hence the increase in the contribution of broader components.

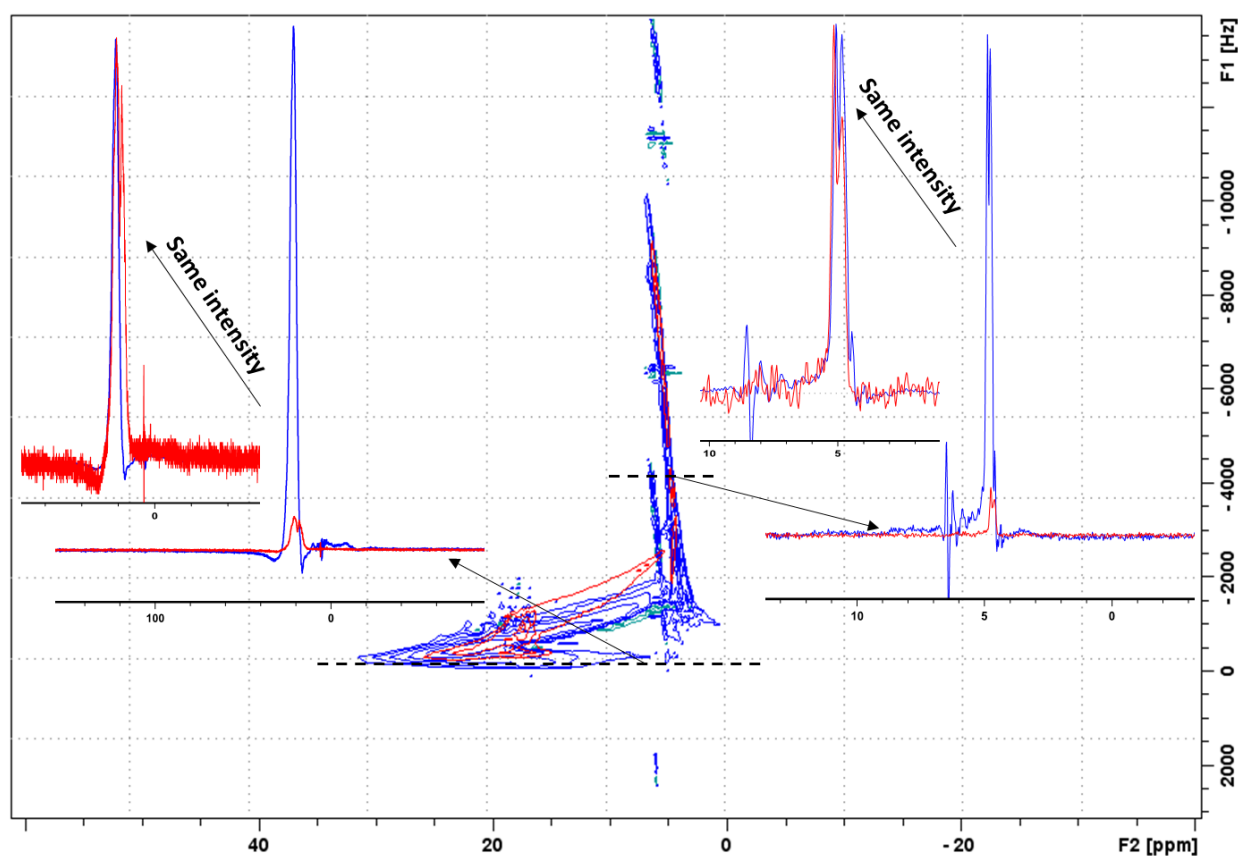


Figure 5-59 ^1H CSI of 200 μL DMC in contact with LFP electrode in the PEEK tube with recycle delay of 45 s (blue and green) and 1 s (red and purple). Insets show an overlay of slices from the two CSI, in which the spectra have been scaled to the same maximum intensity.

5.7.4 Summary/conclusion

In this chapter, we used the CSI technique to spatially resolve the distribution of ^1H NMR spectra of 200 μL of DMC inside a specifically designed NMR PEEK tube. To further investigate the

influence of electrodes on the ^1H spectrum of DMC, we introduced a paramagnetic LFP electrode in contact with the DMC solvent within the PEEK tube. Additionally, we explored the impact of T_1 on our measurements by collecting data at two recycle delays, allowing the discrimination of the signals with the longest/shortest relaxation rates.

We observed significant distortion in the proton signals coming from DMC near the LFP electrode, at the bottom of the PEEK tube. This distortion led to a significant shift and broadening of the ^1H signal. Moving away from the electrode, we noticed a reduction in the observed signal distortion. The magnetic susceptibility effect of the paramagnetic LFP electrode was prominent in the signal from the “bulk” DMC zone (0 to 2 mm from the bottom). However, the susceptibility effect was less evident, in terms of broadening, in the signals from the capillary part (2 mm to 10 mm). This part is narrower and is located on the low ppm side of the spectrum, so that localized spectroscopy is not absolutely needed to follow magnetic susceptibility effects from the electrode.

Finally, decreasing the recycle delay from 45 s to 1 s resulted, as expected, in a reduction in the ^1H signal throughout the tube. With a shorter recycle delay, we lost the portion of the signals with the longest T_1 , allowing us to focus more on the electrolyte close to the LFP electrode and enhance slightly broader signals.

5.8 General conclusion

In order to meet our final goal which is studying the change in the SOC of the battery through the magnetic susceptibility variations of the battery electrodes in an *operando* setup (upon cycling of the battery), we started by evaluating the effect of each pristine battery components. Doing so not only simplifies the experimental measurement but also benchmarks the effect of each component for a full cell study.

We initially investigated the effect of the pristine active materials for batteries on the ^1H spectrum of DMC, used as a reference protonated liquid. Doing this, we proved the feasibility of detecting variations in the magnetic susceptibility of paramagnetic pellets by measuring ^1H NMR spectrum of the reference liquid in which it is soaked. Then the effect of non-electroactive battery components such as current collectors and separators on the liquid electrolyte ^1H signal was demonstrated to be negligible compared to the NMC 622 positive electrode. The negative graphite electrode was also shown to generate a smaller broadening and shift, even though the loss of signal was stronger.

This chapter benchmarked the effect of each pristine battery component on the liquid electrolyte ^1H signal. The next step is to determine the sensitivity of this approach to the SOC of an electrode, in order to apply it on a full cell with an *operando* NMR measurement.

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Chapter 6 Effect of state of charge and discharge on different battery systems

6.1 Introduction

In this chapter, we investigate how the redox state of the positive electrodes in the charging battery can be tracked indirectly, through the distortion of the ^1H NMR spectrum of the electrolyte near the positive electrode. In the previous chapter, specific descriptors have been defined to track the changes in the ^1H NMR spectrum of DMC, due to the magnetic susceptibility effect. The magnetic susceptibility of the electrodes changes as the battery is charged and discharged, hence the change in oxidation state of the positive electrode should be detectable by NMR. The ultimate goal is to enable measuring, *operando*, the redox state of positive electrodes in batteries, even when their NMR signals cannot be detected. Consequently, exact knowledge of the redox state will contribute to better exploitation of the electrochemical curves in full batteries.

The electronic structure of positive active materials such as NMC 622, one of the widely used positive electrodes, undergoes changes from redox activity during cycling in a cell (NMC 622//LiPF₆//Graphite). These changes are related to the SOC, defined as the percentage of advancement in the charge of the battery. During the charging process, lithium ions are extracted from the NMC 622 electrode, leading to an increase in the redox state of the transition metals and a decrease in the degree of lithiation of the material. A potential challenge arises from partial transition metal dissolution in the electrolyte for high voltages, which varies the relative abundance and redox states of transition metal ions in the electrode, leading to variations in the electrode's electrochemical properties, performance, and local magnetic susceptibility.^{188,217}

Understanding of the changes in the electronic structure of electrodes during cycling and their relationship to the SOC is crucial for optimizing the design and performance of LIBs. Following the experimental strategy developed in the last chapter, herein we investigate the sensitivity of the distortions of DMC ^1H NMR spectra to the redox state of cathode materials during the cycling of the cell. A variety of cells (NMC 622//LiPF₆//Graphite) were assembled and then cycled using a specific charge-discharge protocol. Cells were halted at specific SOC, and the positive and negative electrodes were extracted from the cells then prepared for *ex situ* NMR analysis.

Finally, the ^1H *operando* NMR measurements of the electrolyte inside an operating battery composed of NMC//LiPF₆//Gph full cell has been conducted and the *operando* results of the 5th cycle (following the initial 4 formation cycles) were discussed.

6.2 Experimental (Materials and electrode)

6.2.1 Negative electrode

A commercially available negative electrode was used, composed of 96% graphite (C6) as the active material. The electrode was coated on one side of a copper foil. Graphite has a theoretical specific mass capacity of 372 mAh·g⁻¹. Starting from the theoretical capacitance values ($C_{th,m}$) and considering the manufacturer's percentage of active material in the electrode (96% of graphite), we obtain a specific theoretical capacity of 357 mAh·g⁻¹ ($0.96 * C_{th,m}$) for the graphite electrode.

Table 6-1 displays the graphite characteristics provided by the manufacturer, which have been optimized for high energy density applications, specifically for applications requiring long-range batteries. The available parameters include the surface capacity $C_{cons,s}$ (in mAh·cm⁻²), percentage of active ingredient MA_{cons} (in %), surface density $\rho_{cons,s}$ (in mg·cm⁻²), and density d_{cons} (in g·cm⁻³).

While surface capacity is commonly used for balancing the electrodes of full cells, the specific mass capacity $C_{cons,m}$ in mAh·g⁻¹ can be useful when the exact area of the electrode is unknown. The specific mass capacity can be calculated as:

$$C_{cons,m} = \frac{C_{cons,s}}{\rho_{cons,s}}$$

The manufacturer-provided value ($C_{cons,m}$) of 336 mAh·g⁻¹ reflects the practical capacity that can be obtained after the formation cycles of the battery, as estimated by the manufacturer.

Table 6-1 Commercial NMC 622 and Graphite electrodes characteristics reported by manufacturer.

Characteristics	NMC 622	Graphite
Surface capacity (mAh.cm ⁻²)	3.52	3.92
Active material (%)	90	96
Porosity (%)	35	37
Surface density (mg.cm ⁻²)	24.45	11.67
Electrode thickness with porosity (μm)	81	83
Density (g.cm ⁻³)	3.01	1.41
Manufacturer specific capacity (mAh.g ⁻¹)	144	336

6.2.2 Positive electrode

Coated LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC 622) on aluminum foil containing 90 wt% active material, 8 wt% PVDF binder, and 2 wt% Carbon Black was used as a positive electrode. Ni-enriched NMC electrodes (specifically NMC 622), are known to give access to higher redox states (more lithium ions extraction) without destructuring the material (unlike LCO electrodes, which are limited to 0.5 Li per Co except in very specific cases).

The specific theoretical capacity of the electrode is 149 mAh.g⁻¹, assuming that 0.6 Li per transition metal atom can be extracted from the active material, with 90% active material in the electrode.⁸¹ A practical specific mass capacity of 144 mAh.g⁻¹ is expected from the manufacturer data, after the formation cycles. The full characteristics of NMC electrodes can be found in Table 6-1.

6.2.3 Separator and electrolyte

Whatman grade GF/D glass microfiber filter with a thickness of 670 μm used a separator. The electrolyte is supplied by Solvionic (99.9% purity) and is composed of a salt of lithium hexafluorophosphate (LiPF₆) of concentration 1 mol.L⁻¹, dissolved in an organic solvent consisting of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a 1:1 volume ratio.

6.2.4 Cell assembly

The electrodes are usually punched as 10 mm-diameter disks and assembled in a Swagelok cell. The 10 mm inner diameter of the NMR glass tube creates a constraint, which prevents us from using 10 mm-diameter electrodes for *ex-situ* ^1H solution-state NMR. We tried to punch the electrodes into 8 mm disks after cycling, but the inherent brittleness of the electrodes, particularly graphite, led to active material losses at the edges. Therefore, to address these challenges, we decided to use 8 mm-diameter electrodes for the Swagelok assembly instead of the original 10 mm-diameter electrodes. Therefore, the positive and negative electrode sheets (high energy graphite and NMC 622) and glass microfiber separator were punched respectively using an 8 mm and 9 mm diameter punch in the ambient atmosphere.

Subsequently, they were heat-treated and dried overnight in a BUCHI® ball furnace at 140°C under vacuum conditions for a minimum of 8 hours. The dried electrodes were then transferred to an argon-filled glove box without introducing any air (in a closed vacuum vial), where the final assembly took place. The Teflon-made Swagelok cell and its components such as stainless-steel rods and spring were dried in an oven at 60°C for at least one night. To minimize exposure time outside the controlled environment, the transition between leaving the oven and entering the glove box was done rapidly.

For the *ex situ* measurements, Swagelok cells (Figure 6-1) were assembled inside a glovebox with an argon atmosphere. The assembly process involved placing an 8 mm diameter NMC cathode disk onto a nickel plate as the current collector. Subsequently, a small drop of electrolyte was carefully applied onto a 9 mm glass microfiber separator using a micro pipette. The soaked separator was gently positioned on top of the NMC cathode. Finally, the 8 mm graphite anode was placed onto the soaked separator, and the cell was securely sealed by screwing on the cap. It is important to note that the screwing pressure should be controlled to ensure proper contact between the battery components and good reproducibility.

6.2.5 Swagelok cell modification

In order to enhance the alignment of the 8 mm-diameter electrodes inside the 10 mm-diameter body of the cell and reduce reproducibility issues during battery assembly, the design of the Swagelok

cells was modified. This modification involved the incorporation of a cylindrical tube made with Polyethylene terephthalate (PET), as shown in Figure 6-1 into the cell design. PET (commercially sold as Ertalyte) is a thermoplastic polymer known for its good mechanical properties, chemical resistance, and mechanical stability. The introduction of the PET tube inside the polypropylene body, on the surface of the current collector plate (stainless steel or nickel), facilitates the alignment of the electrodes and the separator in between.

Consequently, cycled electrodes can be extracted from the cell and easily placed within a 10 mm NMR glass tube for *ex situ* measurements.

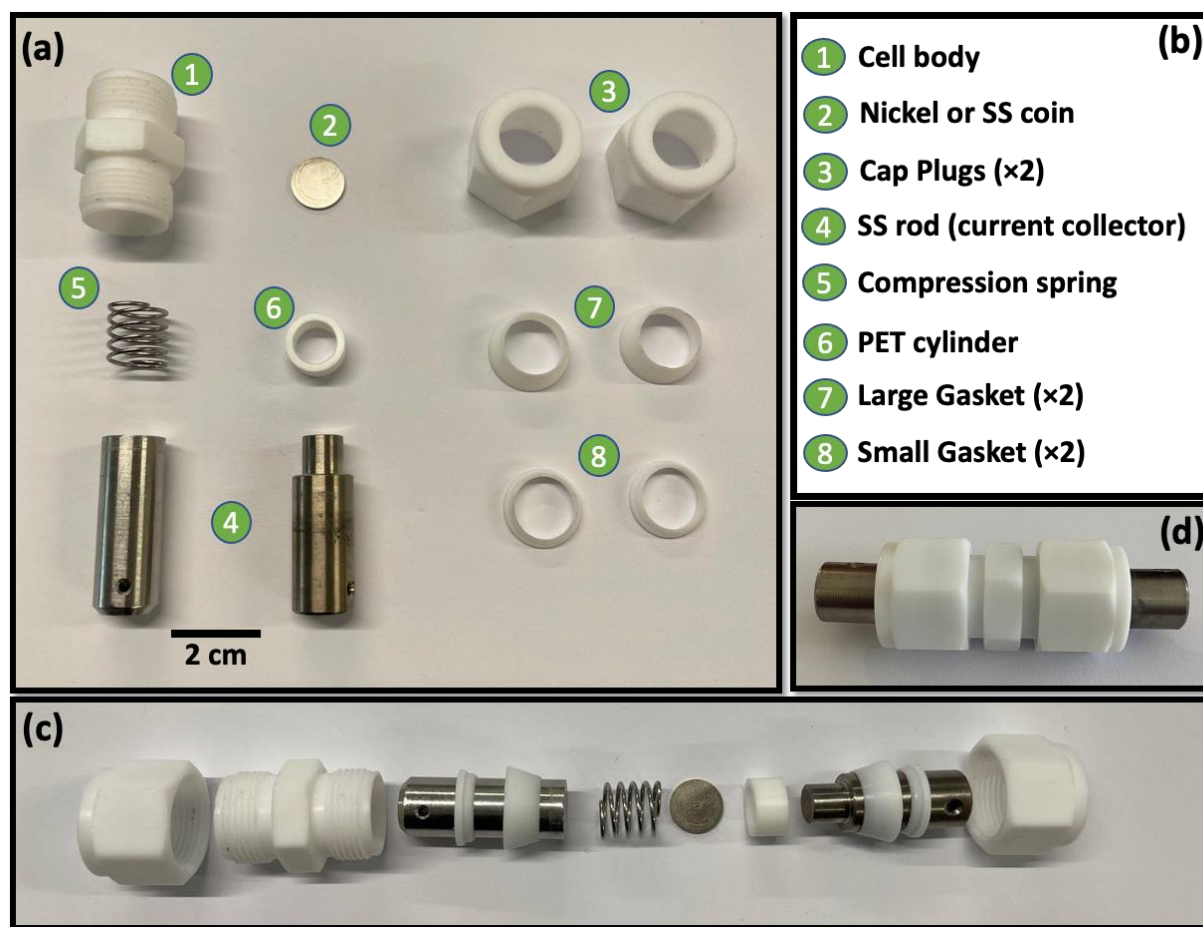


Figure 6-1 Presentation of the modified Swagelok cell: (a) photos of components, (b) legend, (c) Cell Pre-assembly, (d) Assembled cell.

6.2.6 Cycling procedure

To avoid overcharging or over-discharging, and to approximate real-life conditions,⁷⁶ we cycled complete cells between 2.7 V and 4.2 V (Figure 6-2). NMC 622/graphite cells typically have a nominal voltage of around 3.6-3.7 V, and they are considered fully charged when their voltage reaches approximately 4.2 V. Similarly, they are considered fully discharged when the voltage drops to around 2.7 V.²¹⁸ It is worth mentioning that the specific voltage range for cycling can vary depending on the battery chemistry, manufacturer recommendations, and application requirements.

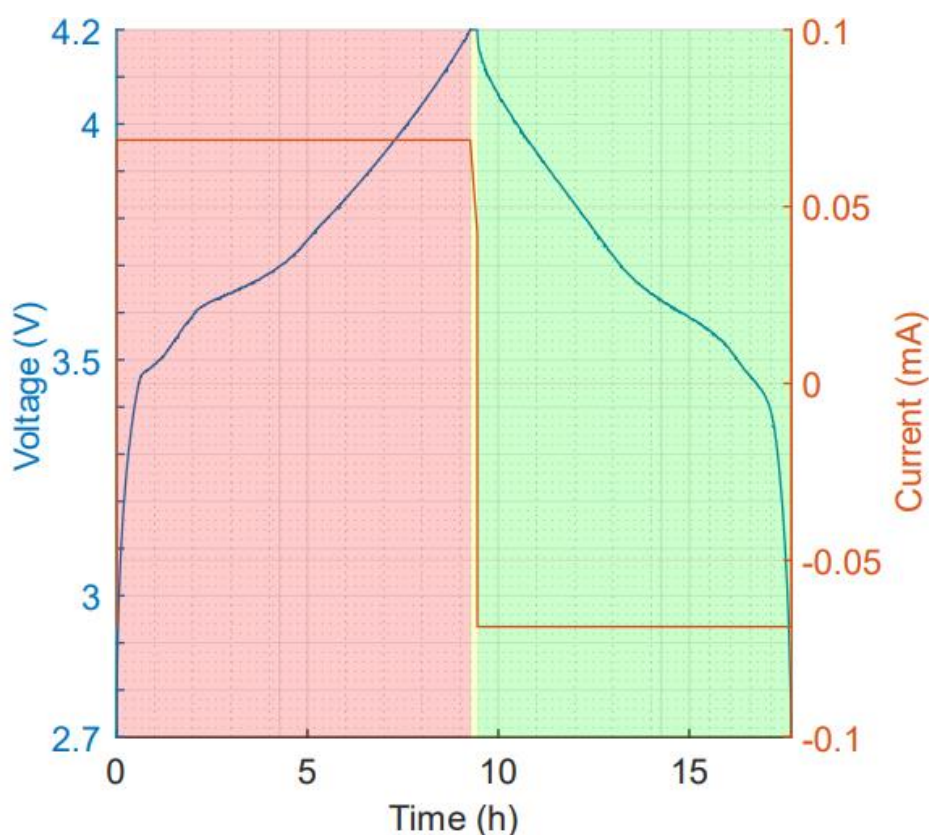


Figure 6-2 Example of a cycle on a complete NMC/Graphite cell, charging on red background, discharging on green background.

In this study, electrochemical cycling was carried out using a Biologic galvanostat (VSP), controlled using EC-Lab software (V 11.30). Cells (NMC 622//LiPF₆//Graphite) were cycled at room temperature and four formation cycles were performed.

Prior to being introduced into the market, commercial batteries undergo a cycling process known as formation to achieve a stable and advertised capacity. This formation stage corresponds to cycling the batteries to stabilize the passivating layers on the surface of the electrodes, namely the SEI (Surface Electrolyte Interface) and CEI (Cathode Electrolyte Interface).

Furthermore, specific charging stop criteria are implemented to minimize the risk of lithium metal deposition resulting from overcharging. Consequently, voltage limits are applied when the battery is undergoing constant current (CC) charging stages as well as constant voltage (CV) charging stages, which serve to address the issue of excessive voltage. It is crucial to acknowledge that depending on the N/P balance of the battery, the CV phases can potentially result in overlithiation. For calculation of current, we take the value of the manufacturer's capacity computed from the graphite mass ($C_{cons,abs}$).

The usual criterion for stopping CV phases (cut-off current) is that the current becomes lower than the current corresponding to a 50 h load ($I < C/50$). The purpose of employing CV during formation cycles is to ensure the continued lithiation of the graphite electrode, even in the presence of overvoltage phenomena. This approach aims to achieve optimal capacity utilization of the battery.

In the case of 8 mm electrodes (Swagelok cells) for the ex-situ NMR measurement, we cycled NMC/graphite batteries between 2.7 V and 4.2 V and perform four formation cycles at a rate of C/20, with each charge maintaining the voltage at 4.2 V in CV with a cut-off current of C/50. We therefore apply 4 formation cycles to our cells and then on the fifth cycle we proceed to stop them at different SOC. We consider as experimental capacity $C_{exp,abs}$ the value of the fourth formation charge in milliamp-hours (mAh). For the in-situ cells, we cycled the batteries between 2.7 V and 4.2 V and performed four formation cycles at a rate of C/10, with each charge maintaining the voltage at 4.2 V in CV with a cut-off current of C/50.

6.2.7 Determination of the charging current

In the case of NMC/graphite batteries, it is traditional to assess capacity based on the electrode's surface area. However, due to the inherent brittleness of graphite, we observed material losses of up to 0.6 mg from the edges of the electrodes during the die-cutting process, even for 8 mm-

diameter fresh electrodes. Consequently, the electrode surface varies, rendering inaccurate the direct calculation of expected capacity from surface capacity. To obtain the most accurate estimation of the available capacity in the punched electrode, we employed the same weighing method as in Araujo de Afonso's thesis.⁸¹ We weighted the coated electrode together with its current collector and then subtracted the mass of the collector. The mass of the collector was determined by averaging the weights of 10 to 15 individual current collector discs. Finally, by multiplying the obtained mass with the manufacturer's specified capacity, we estimated the capacity of the punched electrode.

In terms of equation:

$$m_{weighted} = m_{electrode} + m_{collector}$$

$$C_{cons,abs} = m_{electrode} \cdot C_{Cons,m}$$

Where:

$m_{weighted}$: the weighted mass of the electrode plus the current collector in the glovebox in grams (g). The negative electrode is generally between 4.4 and 4.9 mg and the positive electrode ranges between 5.9 and 6.1 mg.

$m_{electrode}$: the mass of the single electrode (active material, binder, and additives) in grams (g) i.e., **$m_{el,Gph}$** for the negative and **$m_{el,NMC}$** for the positive, typically between 1.86 and 2.36 mg for the graphite-based electrode, and between 4.91 and 5.11 mg for the NMC 622-based one.

$m_{collector}$: the mass of the current collector in grams (g), i.e., **m_{cu}** for the copper collector and **m_{Al}** for the aluminum current collector, typically for 8 mm-diameter disks: 6.43 mg for copper and 2.57 mg for aluminum. For 5 mm-diameter disks: 2.54 mg for copper and 0.99 mg for aluminum.

$C_{cons,abs}$: the capacity expected from the manufacturer's data in milliampere-hours (mAh).

By considering the expected capacities and the desired charge regimes, we can calculate the appropriate current intensity for cycling of the cell. This calculation is performed by considering the capacity calculated from the NMC manufacturer.

$$i_{charge} = \frac{C_{cons,abs}}{t_{charge}}$$

With i_{charge} : the current intensity to be applied for a C/n charging regime in amperes [A], typically for a C/20 charging regime for 8 mm diameter electrodes, we have current intensities ranging from 100 to 120 μ A. Furthermore, when employing a C/10 charging regime for 5 mm diameter electrodes, we observe current intensities on the order of approximately 60 to 80 μ A.; t_{charge} : the expected charging time required to reach full charge in hours [h], i.e., n for a C/n regime.

Table 6-2 summarizes the names given to the capacities in this manuscript and what they represent.

Table 6-2 Summary of capacity descriptions in this manuscript.

Given name	Abbreviation	Our specific definition
Theoretical specific capacity	$C_{theo,m}$	Calculated from molar masses and mobility of Li ions.
Constructor specific capacity	$C_{cons,m}$	Manufacturer's estimation
Constructor capacity of our electrodes	$C_{cons,el}$	Calculated from values given by manufacturer.
Experimental capacity	C_{exp}	Recorded during the last charge of formation cycle (4 th charge).

6.2.8 Cells disassembly and rinsing

The cells were stopped at different SOC and state of discharge (SOD) after the formation cycles, during the 5th cycle. Subsequently, the cells were transferred inside the Argon-filled glove box to ensure an inert atmosphere for NMR sample preparation. The cells were then disassembled, and each cycled electrode was retrieved and placed into an NMR glass tube.

The electrodes were rinsed to avoid side-reactions and slow down their evolution (if any) while waiting for the NMR measurement. They were soaked and shaken in roughly twice their volume of pure DMC. The cleaning DMC was then removed from the NMR tube. This procedure was

reproduced several times until the electrode was considered clean. The NMR glass tube containing the clean electrode was then subjected to vacuum conditions for 30 minutes inside the glovebox prechamber to facilitate drying of the remaining DMC solvent. The dried electrode was stored in the closed NMR tube until the next NMR measurement time. It is important to highlight that the use of metallic tools was prohibited to avoid accidental discharge.

6.2.9 Preparing for *ex situ* ^1H solution NMR

The carefully planned procedure for the *ex-situ* ^1H NMR measurement of the cycled electrode in contact with DMC solvent is illustrated in Figure 6-3. The dried electrode was placed inside a standard 10 mm NMR glass tube, containing 200 μL of liquid DMC. To ensure cleanliness, the NMR tubes underwent a washing step with acetone, followed by overnight storage in an inverted position within a fume hood. Subsequently, the tubes were transferred to the glovebox environment. To enable accurate comparison and quantification between samples, the amount of DMC solvent was precisely weighed before introducing the electrode into the tube. A strip of Parafilm was wrapped around the joint between the NMR tube and cap to minimize the risk of solvent evaporation. Additionally, to ensure that DMC was positioned at the center of the NMR coil for each measurement, a plastic O-ring was positioned around the NMR tube at 4.7 cm from the bottom to maintain the same distance from the upper part of the coil for each sample.

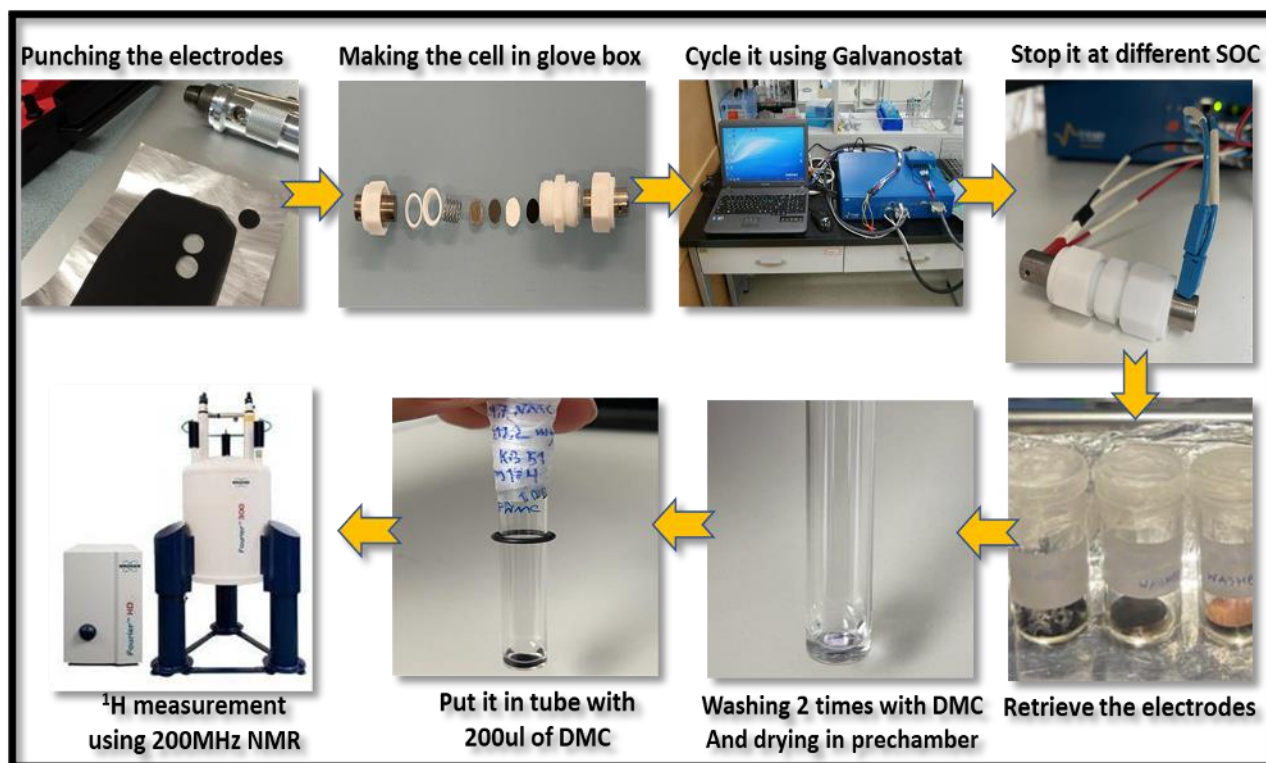


Figure 6-3 Ex situ ^1H solution NMR Preparation of DMC/electrodes.

6.2.10 NMR measurements

^1H NMR spectra were acquired at room temperature in a Nitrogen-filled (N_2) environment using a Bruker 200MHz spectrometer equipped with a narrow bore BST, diff-30 Bruker probe, and a micro-5 gradient insert. A standard one-dimensional ^1H $\pi/2$ -acquisition NMR sequence was employed, utilizing a 90° pulse length of approximately $15\ \mu\text{s}$ for each sample. The spectral width was set to 2997.7 ppm (corresponding to a frequency range of 598429 Hz). To ensure accurate referencing, the ^1H NMR spectra were externally referenced to a 2 M aqueous solution of Gadolinium-doped water ($\text{Gd}(\text{NO}_3)_3(\text{H}_2\text{O})_5$), set at a chemical shift of 4.8 ppm.

For each sample, ^1H T_1 measurements of DMC in contact with the electrodes were conducted separately. The NMR spectra were acquired and processed using the Bruker Topspin 3.6.2 software application. Data analysis and plotting were carried out by employing home-written MATLAB scripts.

6.3 Sensitivity of magnetic susceptibility to the redox state of Gph and NMC electrodes in NMC//LiPF₆//Gph system

6.3.1 Charged NMC cathode in NMC 622//LiPF₆//Gph system

Figure 6-4 shows the effect of paramagnetic NMC 622 cathodes stopped at different SOC on the ¹H NMR signal of reference DMC, with a global shift and broadening. Following the change in the redox state of the Ni, Co, and Mn transition metals in NMC 622 during electrochemical charging, the magnetic susceptibility of the electrode varies. However, other parameters such as the shape of the electrodes can participate in the distortion of the DMC signal since the shape may change the interface between the liquid and the NMC pellet.

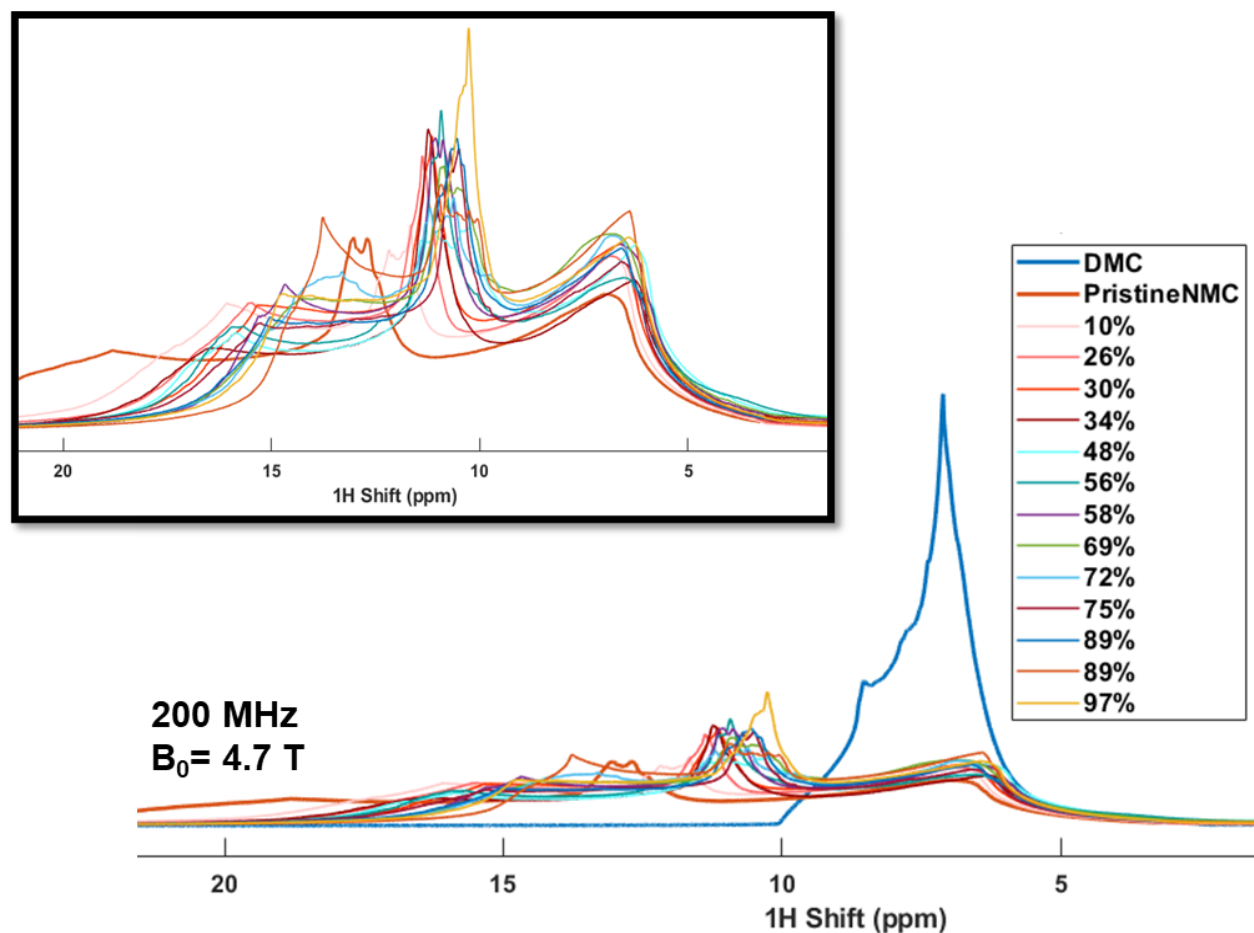


Figure 6-4 ¹H signal of DMC in the presence of NMC 622 cathodes at different SOC.

6.3.1.1 Effect on shift

To quantify the effect of different redox states of the NMC cathodes on the DMC signal, the corresponding shift and width were plotted in Figures 6-5 and 6-6. In Figure 6-5 the shift shows a clear downtrend line upon higher SOC, corresponding to oxidation of NMC 622 and removal of lithium ions (delithiation process). Though, the second half charge shows less sensitivity to the redox state compared to the first half charge. This indicates the higher sensitivity of shift to the change in the magnetic susceptibility at the beginning of delithiation.

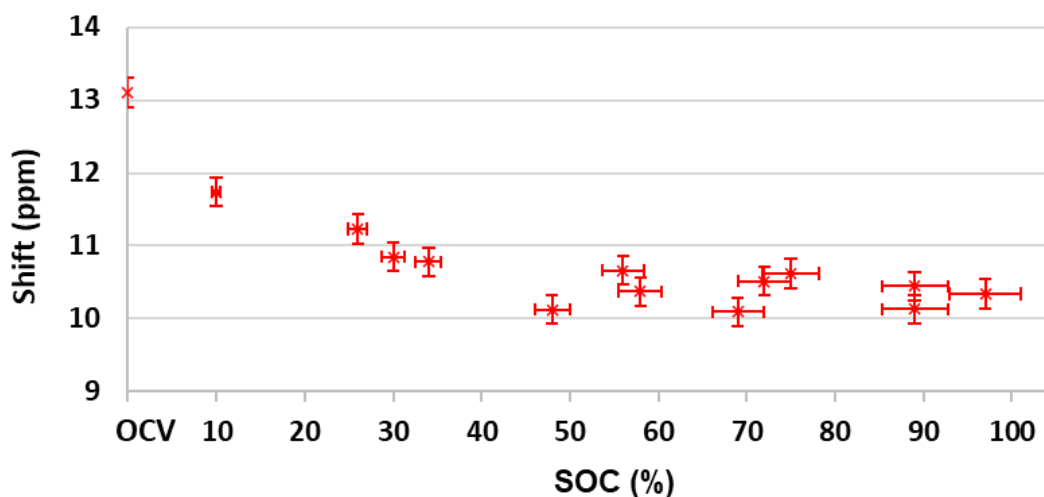


Figure 6-5 Effect of varying SOC of NMC cathodes on the WAS shift of the DMC ^1H spectra.

6.3.1.2 Effect on width

A downtrend line was also seen for width upon the oxidation of NMC 622 (delithiation process); however, it was clear in the second part of the charge this time. In the first half of the charge, it shows an accident in the decrease of width. This needs to be reproduced to identify if it arises from the uncertainty in the measurement or if it is real.

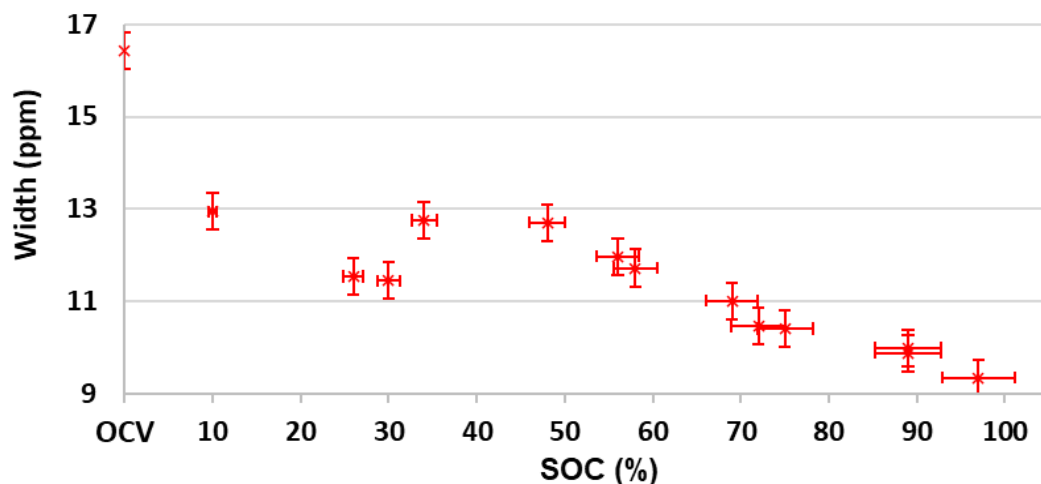


Figure 6-6 Effect of varying SOC of NMC cathodes on the width (FW30%HWAS) of the DMC ^1H spectra.

6.3.1.3 Effect on area

Figure 6-7 displays the areas under the proton signal of DMC in the presence of NMC cathodes at various SOC.

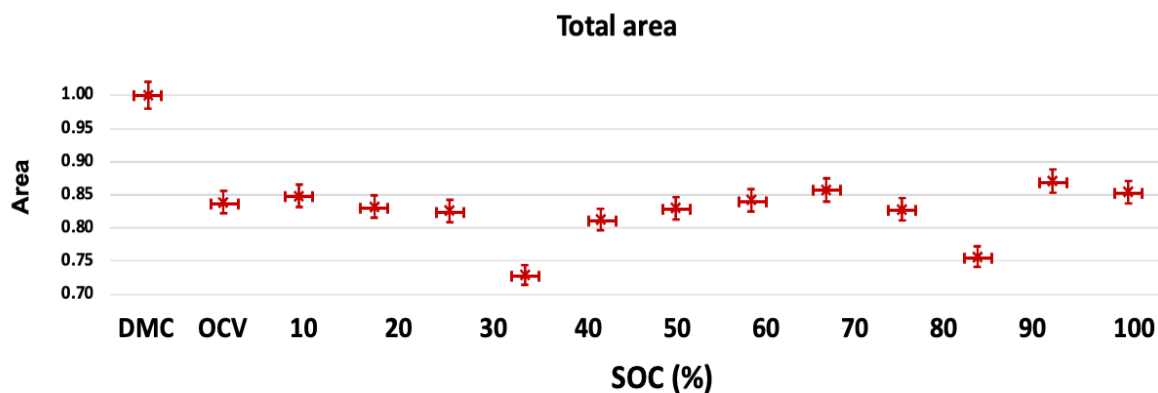


Figure 6-7 Effect of varying SOC of NMC cathodes on the area under ^1H signal of DMC (Integration range: ± 1500 ppm).

The areas show random variations at different redox states, suggesting that the area is not sensitive enough to be a proper descriptor in this context. However, it is important to note that this variability may arise from uncertainties during sample preparation and NMR measurements.

6.3.2 Charged graphite anode in NMC//LiPF₆//Gph system

The effect of SOC of graphite anode on the ¹H signal of DMC is shown in Figure 6-8.

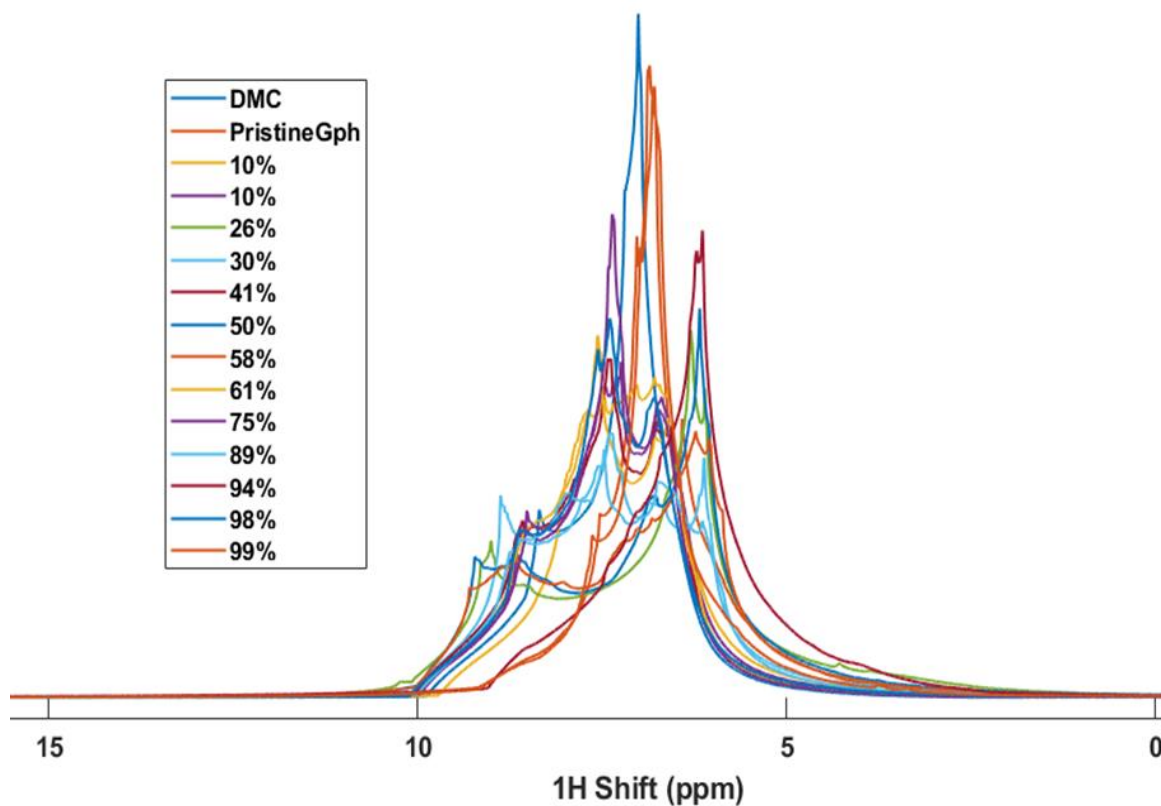


Figure 6-8 ¹H signal of DMC in the presence of graphite anodes at different SOC.

6.3.2.1 Effect on shift

Results for shift (Figure 6-9) show a much smaller variation by changing the SOC compared to the effect of the NMC 622 cathode. This indicates the relatively low dependency of ¹H NMR spectra on the redox state of the graphite anode, possibly because the magnetic susceptibility does not change enough.

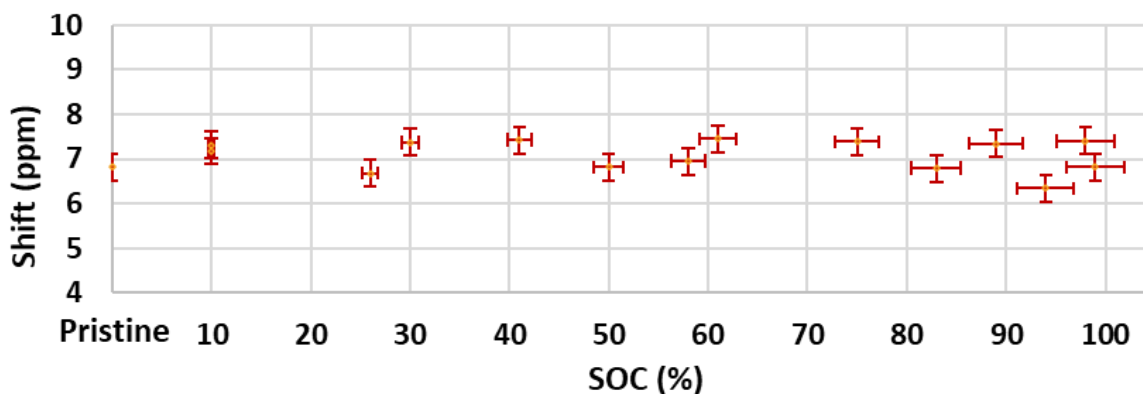


Figure 6-9 Effect of SOC of graphite anodes on the shift of the DMC ^1H spectra.

6.3.2.2 Effect on width

As shown in Figure 6-10, a relatively random variation was observed for the width. Again, we do not know if this comes from the uncertainty in the redox state of the electrode or from an intrinsically low sensitivity.

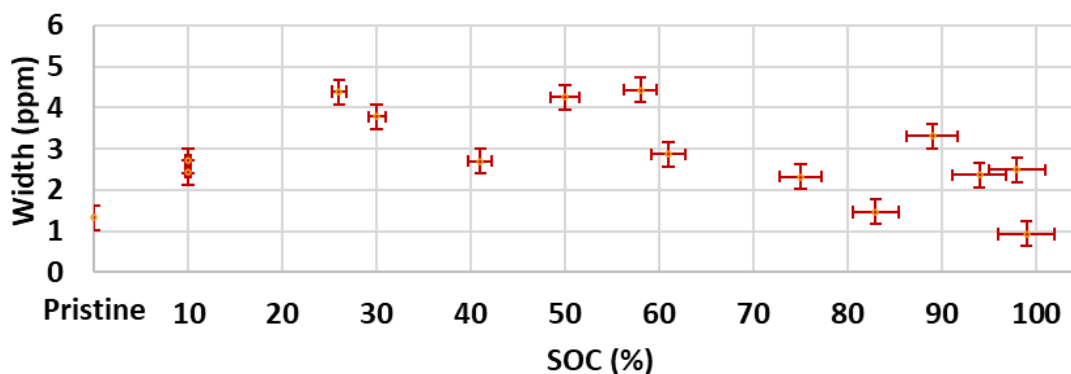


Figure 6-10 Effect of SOC of graphite anodes on the shift and width of the DMC ^1H spectra.

6.3.2.3 Effect on area

Figure 6-11 displays the areas under the proton signal of DMC in the presence of graphite anodes extracted at different SOC. Similar to what was observed in Figure 6-7 with NMC cathodes, the areas in this case also exhibit random variation with the redox states. This pattern suggests that the

area is not a highly sensitive descriptor. Therefore, in the following study of the discharge behavior of NMC 622//LiPF₆//graphite battery system, we will not report the areas.

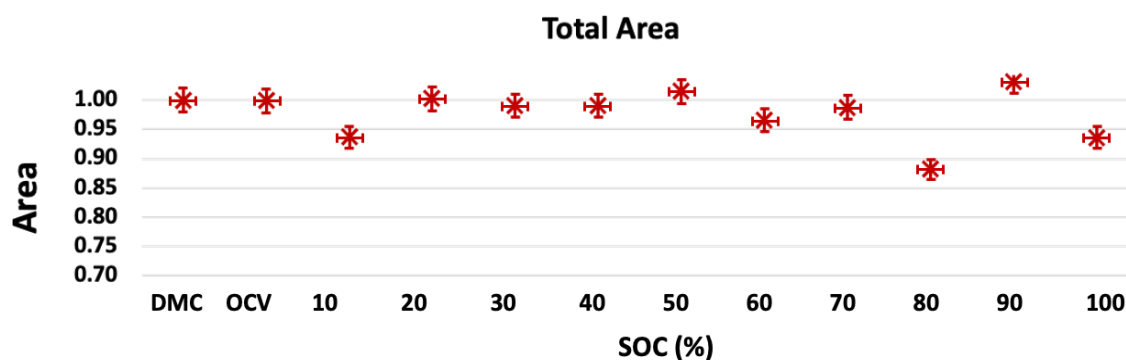


Figure 6-11 Effect of varying SOC of graphite anodes on the area under ¹H signal of DMC (Integration range: ± 1500 ppm).

6.3.3 Discharged NMC electrode in NMC//LiPF₆//Gph system

The same protocol was performed for discharging the cells, extracting the electrodes, and measuring the ¹H NMR spectrum. The results are shown in Figure 6-12.

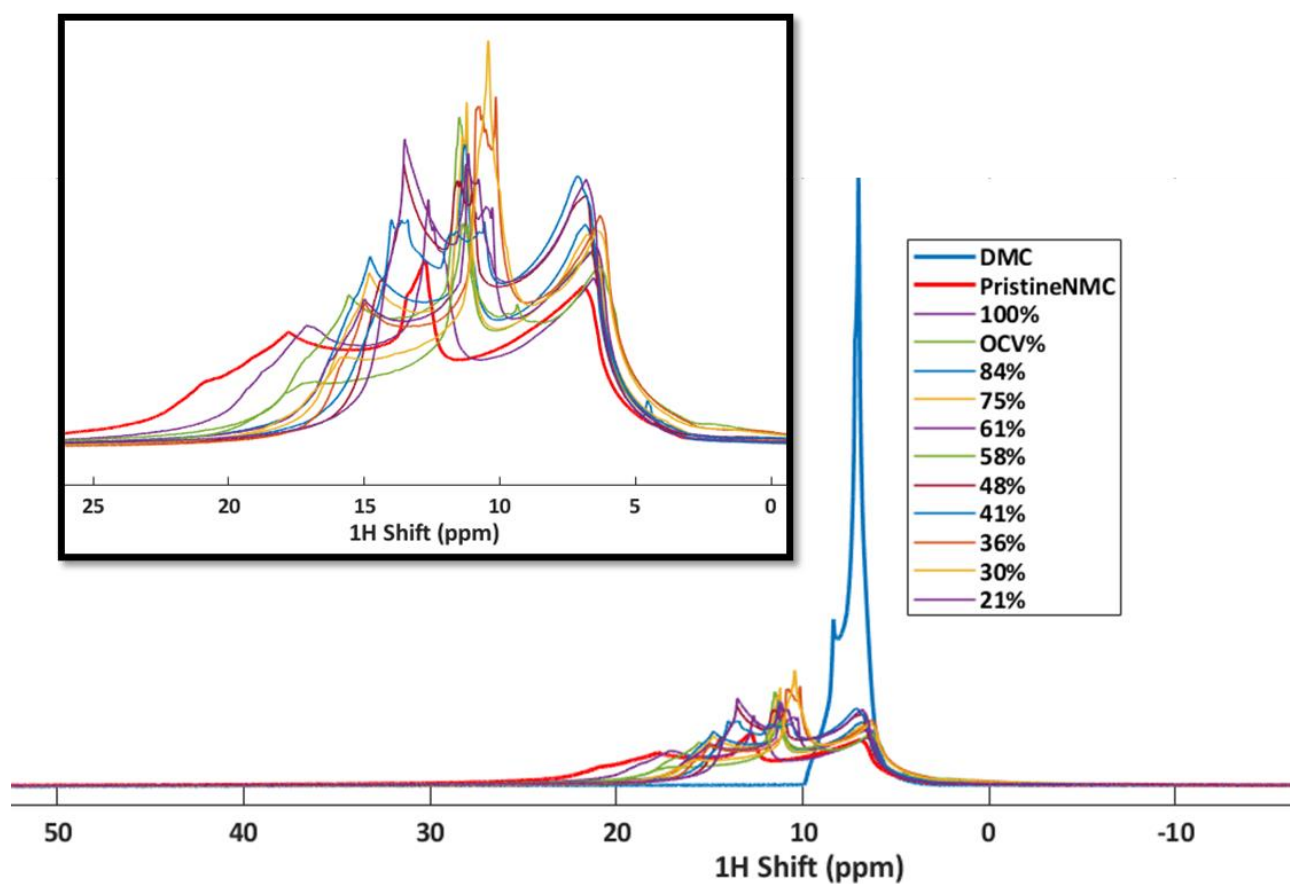


Figure 6-12 ^1H signal of DMC in the presence of NMC cathodes with different SOD. SOD-100% corresponds to fully discharged (SOC-0%).

6.3.3.1 Effect on shift

As expected, the proton NMR signal of DMC indicates a shift in the presence of discharged NMC cathodes in Figure 6-13. The average shift decreases as SOD increases, in agreement with the reduction and lithiation of the NMC 622 cathodes. Two accidents are observed at 75%SOD and 30%SOD.

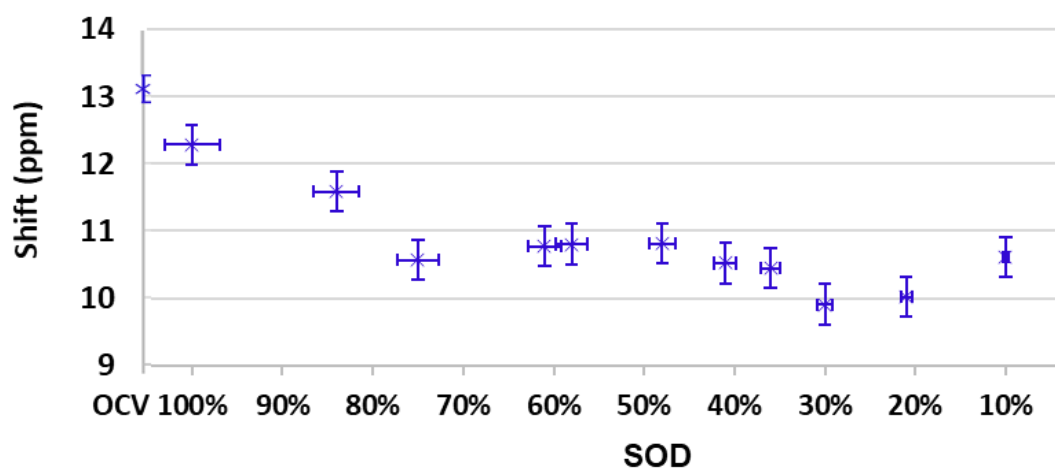


Figure 6-13 Effect of SOD of NMC cathodes on the WAS shift of the DMC ^1H spectra.

6.3.3.2 Effect on width

The same decreasing behavior was observed in Figure 6-14 regarding the broadening of the ^1H signal of DMC in contact with NMC 622 electrodes at varying states of discharge.

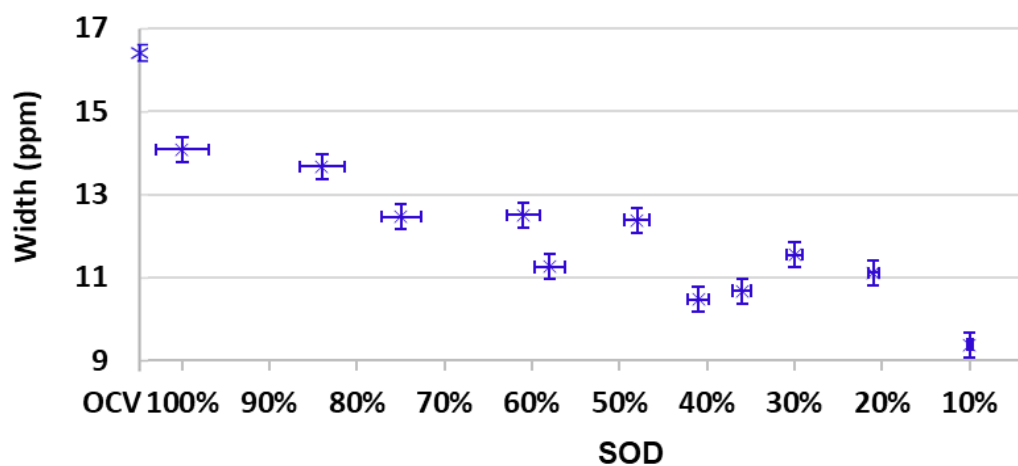


Figure 6-14 Effect of SOD of NMC cathodes on the width of the DMC ^1H spectra.

To conclude, it seems that the changes in the magnetic susceptibility of the NMC electrodes due to their redox state are large enough for monitoring it with the ^1H signal of DMC, through shift and width measurements.

6.3.4 Discharged graphite anode in NMC//LiPF₆//Gph system

We followed the same protocol as previously for discharging the cells, extracting the graphite electrodes, and conducting NMR measurements. The ^1H NMR results are presented in Figure 6-15.

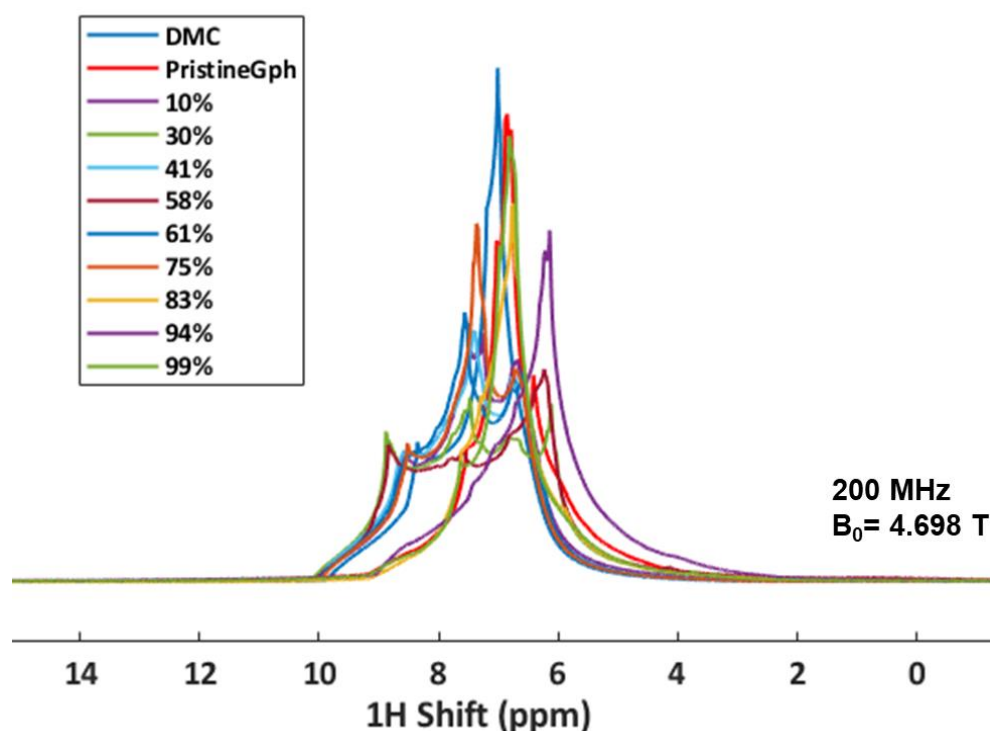


Figure 6-15 ^1H signal of DMC in the presence of discharged graphite anodes.

6.3.4.1 Effect on shift

Similar to the observations in charged graphite, the shift variations of the ^1H signal for discharged graphite (Figure 6-16) also shows a minor and relatively random variation upon changes in the SOD. This variation exhibits a significantly lower amplitude compared to the effect observed in

the NMC 622 cathode. These findings suggest a minimal dependence of the NMR measurement to the redox state for the conductive graphite anode, either because magnetic susceptibility does not change enough or because the NMR measurement does not manage to capture it due to the large blind zone.

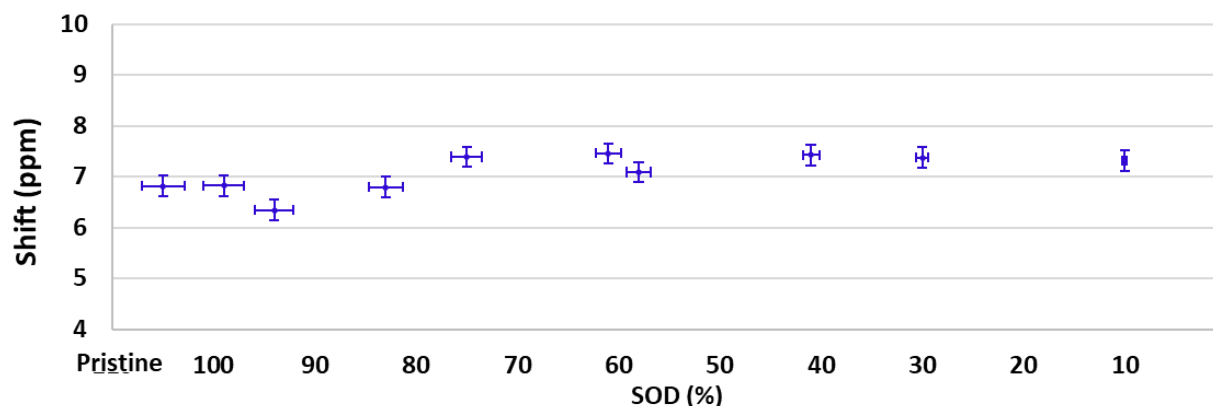


Figure 6-16 Effect of variation of the SOD of Gph anodes on the shift of the DMC ^1H spectra.

6.3.4.2 Effect on width

As shown in Figure 6-17, we observe again a relatively random variation in the width of the proton signal of DMC when changing between graphite electrodes extracted at different SOD. This could potentially stem from low sensitivity of the graphite or uncertainties during both sample preparation and NMR measurements.

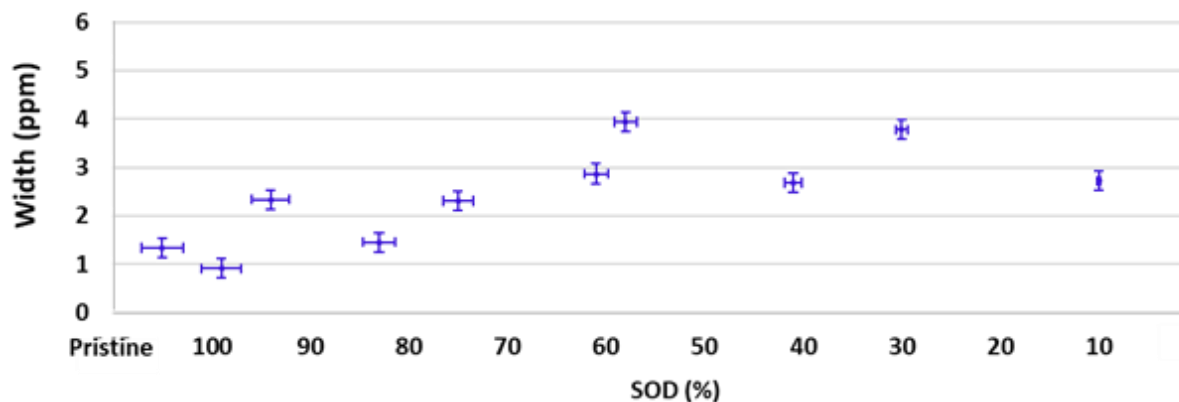


Figure 6-17 Effect of variation of the SOD of graphite anodes on the width of ^1H signal of DMC.

The ^1H NMR spectrum of DMC in contact with graphite electrodes exhibits very low sensitivity to changes in their SOC or SOD. Therefore, we can consider that the ^1H NMR measurement of DMC will inform us mainly on the positive electrode redox state.

6.3.5 Uncertainties

In this chapter, we aim to link the redox state of the electrode to its signature on the DMC ^1H NMR spectrum. The redox state can be derived from the quantity of charge passed through the battery. Often, the quantity of charge is given as a SOC for the battery, the percentage of capacity over the total capacity of the battery. This total capacity can however fluctuate over cycles and be difficult to predict precisely. Usually, formation cycles are used to stabilize the battery capacity, which is then considered as reproducible. We therefore assumed that the expected total capacity in 5th cycle would be the same as in 4th cycle.

In the following, SOC is therefore calculated as:

$$\text{SOC (5}^{\text{th}} \text{ charge)} = \text{experimental capacity (5}^{\text{th}} \text{ charge)} / \text{expected total capacity}$$

The exact redox state of the electrode depends on the capacity and the quantity of the active material, assuming no side-reaction.

In our experimental approach, several sources of uncertainty could affect the accuracy and reliability of our determination of the electrode redox state.

The process of washing the electrodes after retrieving them from the Swagelok cell, with DMC and drying them in the glovebox prechamber may modify slightly the electrode redox state. We tried to perform the same approach for all the samples but variations in the amount of DMC, the washing time and the effectiveness of the cleaning process may also slightly impact the results. The duration and conditions of the drying process, including temperature and level of remaining liquid, may introduce uncertainties in the DMC content of the electrodes. However, in our study, we consistently treated all samples under the same conditions, minimizing potential variations. Therefore, we anticipate that any uncertainty arising from disassembling of the cell and subsequent washing and drying procedures will be extremely negligible.

After drying the electrode and during the preparation of the sample in NMR glass tube, it is crucial to achieve a completely airtight seal on the tube in order to prevent any exchange of gas between the sample and the surrounding environment. However, attaining a perfect seal can be difficult, and there may be some uncertainty in maintaining the airtight condition. To assess and measure the level of airtightness in our measurement protocol, we conducted repeated ^1H NMR measurements on a sample filled with 200 μl of DMC inside an NMR tube. These measurements were performed at different time period after placing the tube inside the NMR magnet under a nitrogen atmosphere.

Nitrogen gas is commonly used in NMR measurements to create an inert environment inside the NMR magnet to prevent oxidation and maintain sample integrity, especially in the case of moisture and air sensitive samples. Therefore, employing nitrogen gas can effectively prevent unwanted reactions and maintain the reliability and accuracy of the NMR measurements.

Figure 6-18 illustrates the resulting changes in the ^1H NMR spectra of the liquid DMC after 3-hours, revealing an extremely small and negligible alteration in the integration area. This finding demonstrates that by wrapping the NMR tube cap with parafilm and rapidly transferring the sample into the magnet under a nitrogen environment, we can effectively prevent the evaporation of DMC.

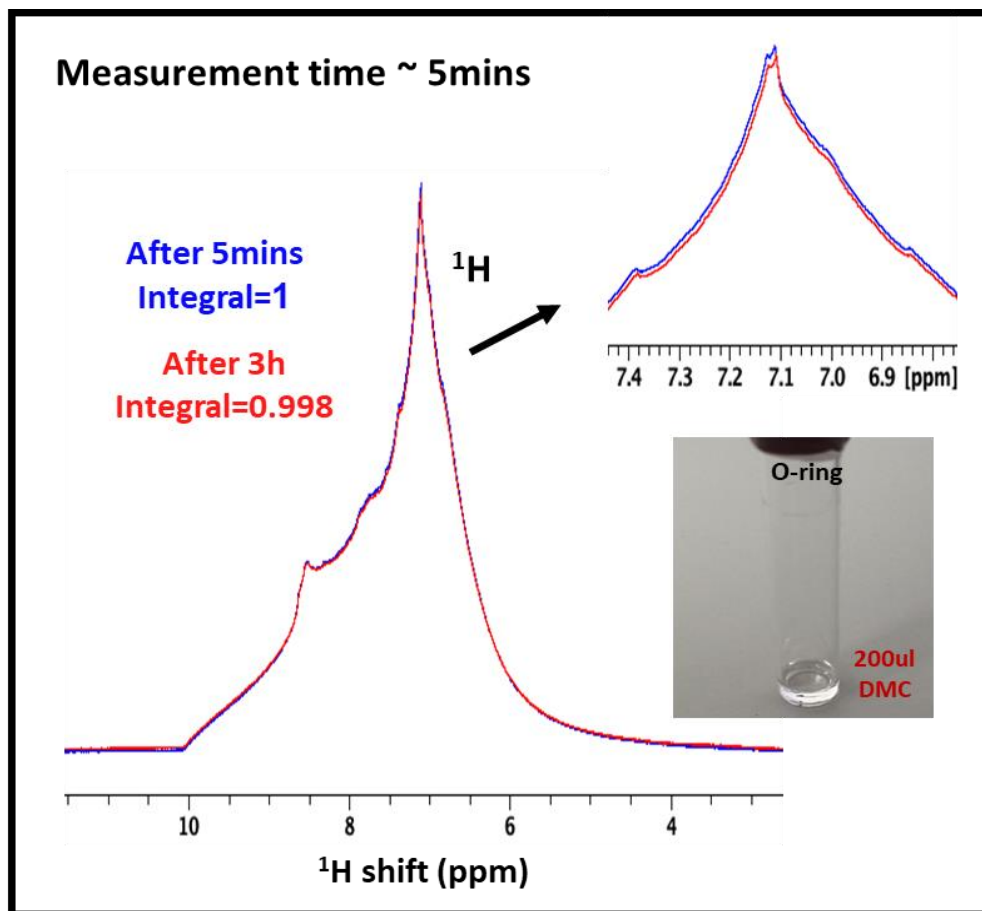


Figure 6-18 ^1H NMR on 200 μl of DMC: blue, 5 minutes after preparation of the sample under nitrogen. Red, after 3 hours under nitrogen.

In Figure 6-19, we further examine the change in the ^1H signal of the liquid DMC near the graphite electrode. These measurements were performed after 5 minutes (right after transferring the sample from glovebox into the NMR) and 16 hours of preparation of the sample, under air. The results indicate a noticeable 0.8 percent decrease in the proton signal when the sample is exposed to air. This finding emphasizes the importance of wrapping the NMR tube and preserving it in a nitrogen atmosphere after preparation in the glovebox. It demonstrates that maintaining an inert nitrogen atmosphere is crucial for ensuring reliable and accurate measurements. Therefore, all subsequent measurements were carried out under an inert nitrogen atmosphere in magnet.

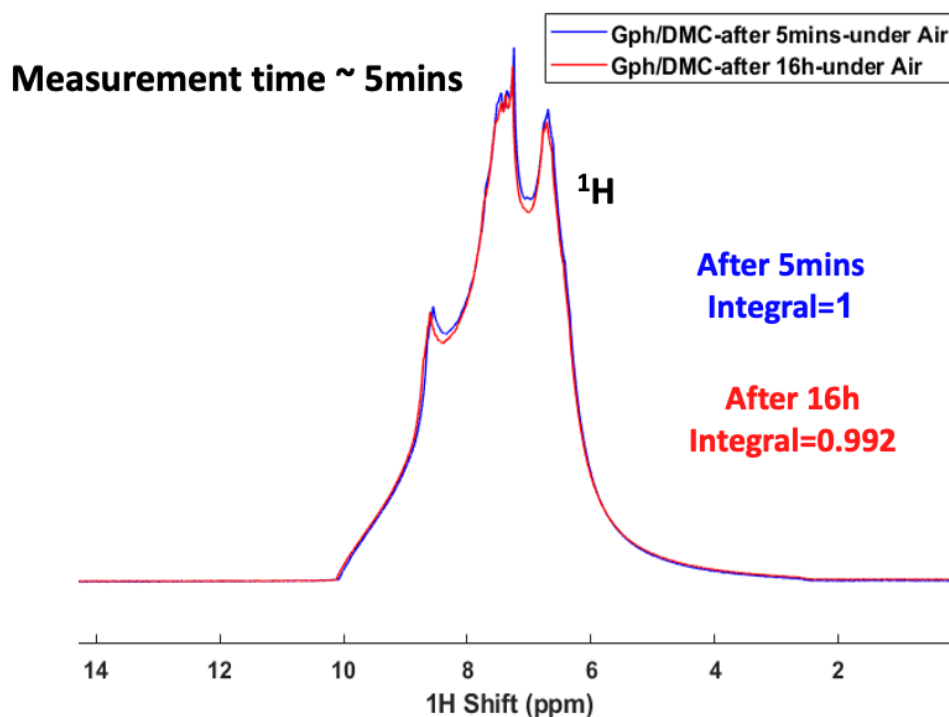


Figure 6-19 ^1H NMR on Graphite/DMC sample: blue, 5 minutes preparation of the sample (after transferring from glove box to NMR magnet) under nitrogen. Red, after 16 hours in magnet under air.

The accuracy and precision of our NMR measurement can introduce uncertainty which includes factors such as signal-to-noise ratio, calibration accuracy, and variations in the NMR instrument's performance. The uncertainty associated with NMR measurements can typically be estimated using the standard deviation of replicate measurements or through calibration using known standards.

Stopping the batteries at different states of charge during the 5th cycle introduces uncertainty in the exact SOC values achieved. Factors such as variations in the charging and discharging currents, measurement errors in monitoring the SOC, and the battery's internal resistance can affect the accuracy of the targeted SOC values.

6.3.6 Comparison of the shift and width values of the ^1H NMC/DMC upon varying SOC and SOD

The comparison between the different SOC and SOD of NMC cathodes is shown in Figures 6-20 and 6-21. There is a similar behavior for both shift and width, in good agreement with the reversibility of the charge-discharge processes in these cells. The correlation between variation in

shift and variation in SOC and SOD is stronger than width, highlighting the ^1H NMR average shift of DMC as the best descriptor for inferring the redox state of the electrode.

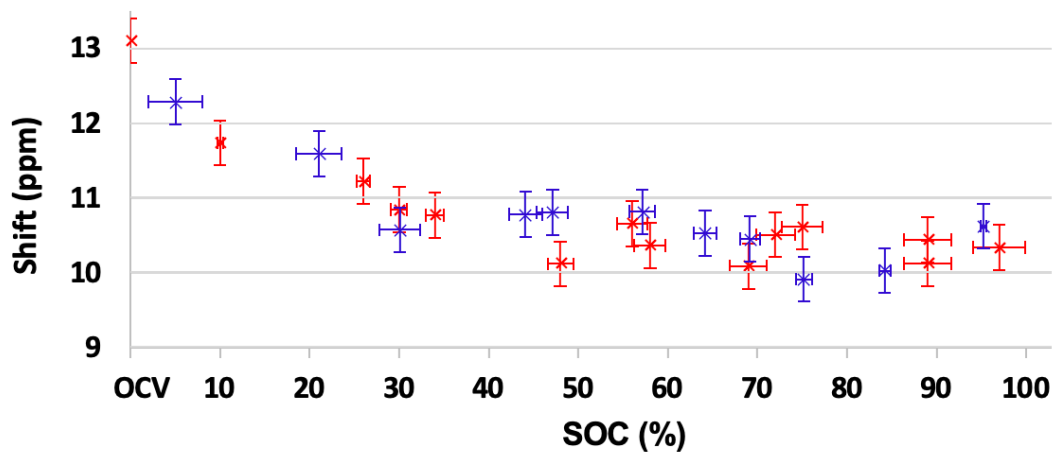


Figure 6-20 Comparing the effect of NMC cathodes on the shift of the ^1H signal of DMC at different SOC and SOD.

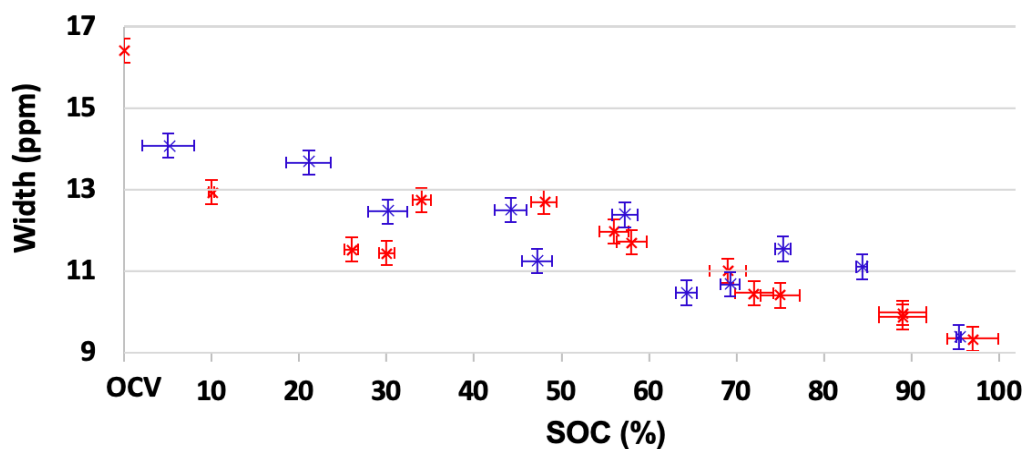


Figure 6-21 Comparing the effect of NMC cathodes on the width of the ^1H signal of DMC at different SOC and SOD.

6.3.6.1 Difference between commercial and modified Swagelok

As previously mentioned in the experimental section, modifications were implemented on the commercial Swagelok cells to enhance the alignment of electrodes and minimize uncertainty during battery assembly across different cells.

Cycling in the modified cell results in a lower irreversible capacity loss in the first charge–discharge cycle and lower capacity fade through 4th cycle, compared to cycling in a standard Swagelok cell where a more significant irreversible capacity loss in the first charge–discharge cycle and capacity fades after 4 cycles has been seen.

The results demonstrate an approximate 7% increase in capacity retention after the 4th cycle when utilizing the modified Swagelok cell in comparison to the standard Swagelok cell. Consequently, for subsequent cell cycling, we utilized the modified Swagelok cells, which yielded improved electrochemical performance.

In the following, we extend our approach to LiFePO₄ (LFP)//LiPF₆//graphite battery system.

6.4 Sensitivity of magnetic susceptibility to the redox state of LFP electrodes in LFP//LiPF₆//Gph system

6.4.1 Materials

Double-sided LiFePO₄ (LFP) and artificial graphite (AG) electrodes were obtained from LiFUND Technology commercial dry pouch cells. The LFP electrode was coated over an Al foil at 96.5% active material and 16 mg/cm², while the AG electrode was coated over a Cu foil with a loading of 95.7% active material and 7.72 mg/cm². As mentioned in Chapter 5 (Section 7.3.1), the LFP active material from one side of the (double-sided) electrode was removed using ethyl acetate and then punched into 8 mm diameter disks. These punched electrodes were dried under vacuum at 80°C overnight to eliminate any remaining moisture. The same separator and electrolyte, as mentioned in Section 2.3, were used for the cell assembly.

6.4.2 Cell assembly

For the cell assembly, like the NMC//LiPF₆//graphite battery system (section 2.4), we utilized 8 mm negative and positive electrodes and a 9 mm separator. It is important to note that all cells were assembled in the modified Swagelok cell.

6.4.3 Cycling procedure

Electrochemical cycling was carried out using a Biologic galvanostat (VSP), controlled using EC-Lab software (V 11.30). Cells (NMC//LiPF₆//Graphite) were cycled at a rate of C/5 at room temperature while the operational voltage window was set to 2.5-3.65 V. The cells were stopped at different SOC and SOD after the formation cycle, specifically during the 5th cycle. Subsequently, the cells were transferred and securely stored inside an Ar-filled glove box. Following this, the cells were disassembled, and each cycled LFP and Graphite electrodes was retrieved, placed into an NMR glass tube, and rinsed using the same approach as explained in section 2.5.

6.4.4 Charged LFP cathode

Figure 6-22 shows the effect of paramagnetic LFP cathodes stopped at different SOC on the ¹H signal of DMC, with a significant shift and broadening.

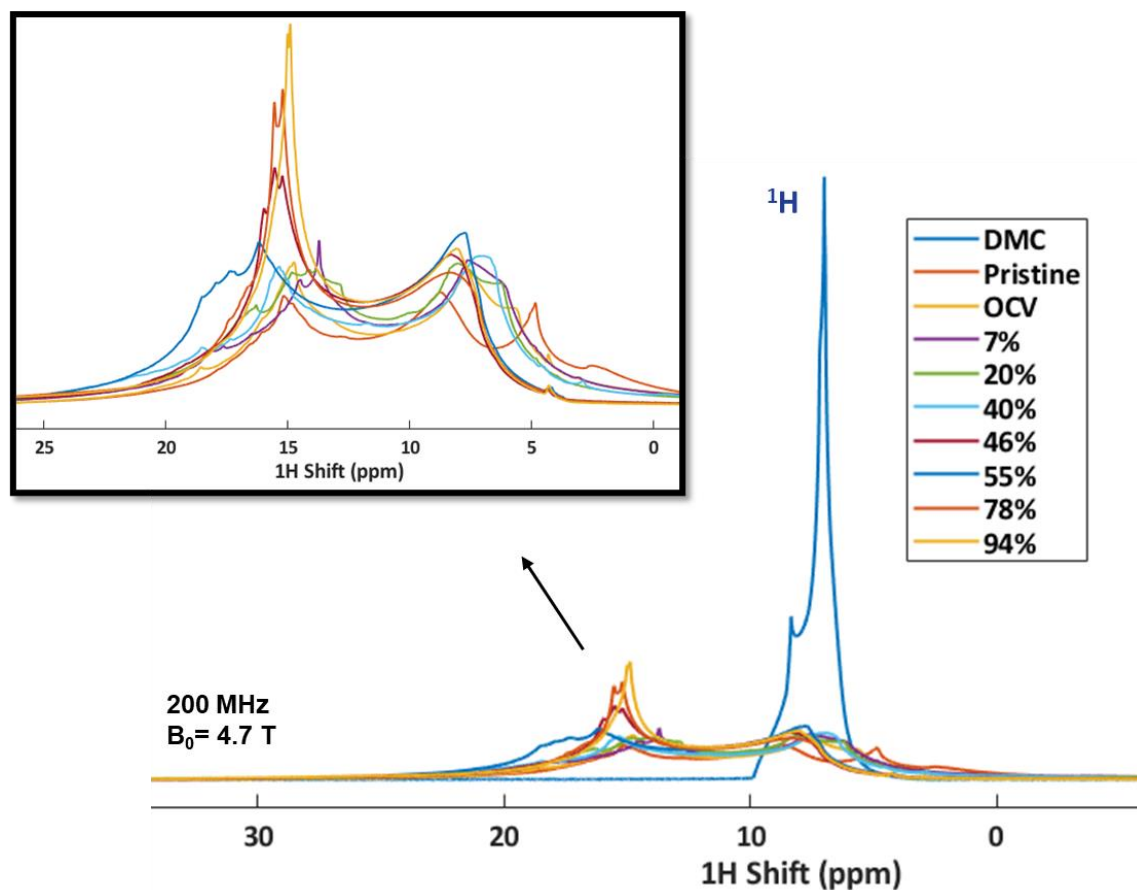


Figure 6-22 ¹H signal of DMC in the presence of LFP cathodes at different SOC.

LiFePO₄ oxidation happens through a biphasic reaction, so the magnetic susceptibility behavior is expected to be more complex. It will notably depend on the morphology of the biphasic material (the relative position of the FePO₄ and the LiFePO₄ phases).²¹⁹ In the following we test the sensitivity of ¹H NMR of DMC to probe these changes in magnetic susceptibilities.

6.4.4.1 Effect on shift

To quantify the effect of varying SOC of the LFP cathodes on the proton signal of DMC, we plotted the corresponding shift and width in Figures 6-23 and 6-24, respectively. The results for the shift display a clear upward trend with higher SOC upon removal of lithium from LFP cathodes, making the ¹H NMR shift of DMC a good descriptor of the redox variations.

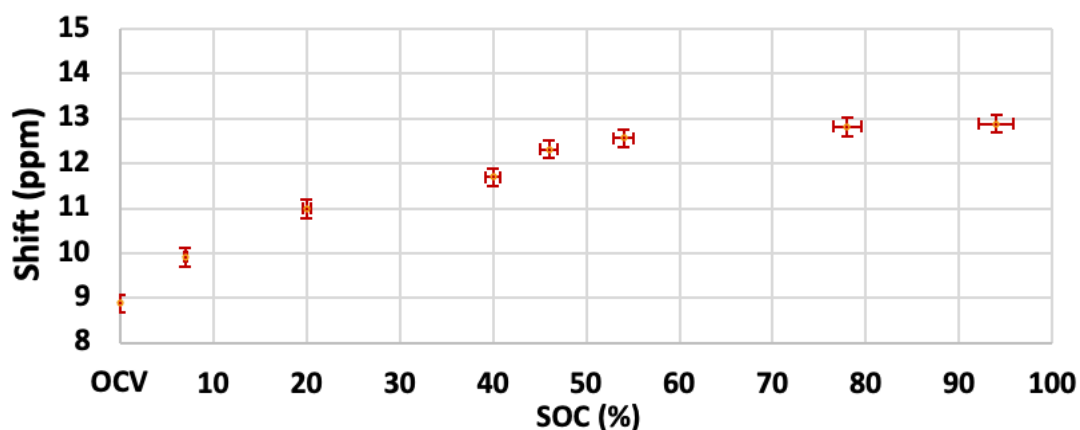


Figure 6-23 Effect of variation in SOC of LFP cathodes on the shift of the DMC ¹H spectra.

6.4.4.2 Effect on width

A downtrend line was seen for width upon the removal of lithium from LFP electrode. However, the width values exhibit less sensitivity to redox state for the second half. The width seems less sensitive to the redox state of the electrode compared to the shift, as seen for NMC 622.

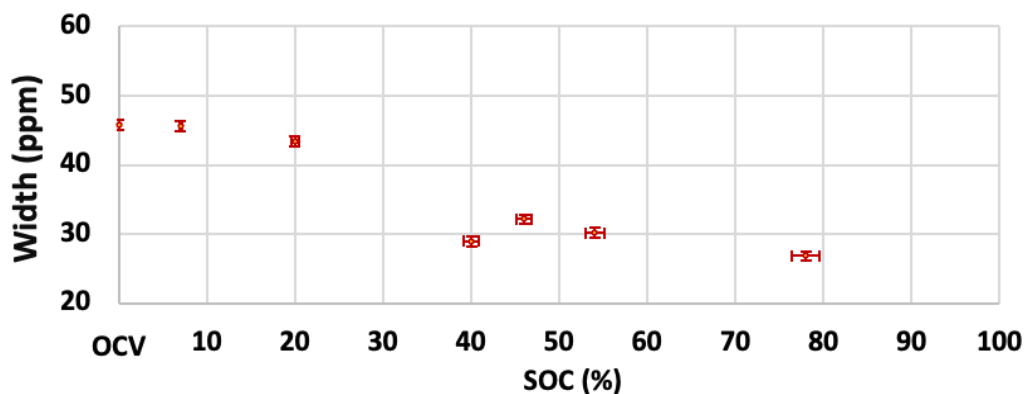


Figure 6-24 Effect of variation in SOC of LFP cathodes on the width of ^1H signal of DMC.

6.4.4.3 Effect on area

In contrast to the observations in the area integration values under the ^1H signal of DMC (full area) with NMC and graphite electrodes, in the case of LFP electrode at various SOC, the area integration values present a clear upward trend (Figure 6-25), with an increase in area as more and more FePO_4 is formed.

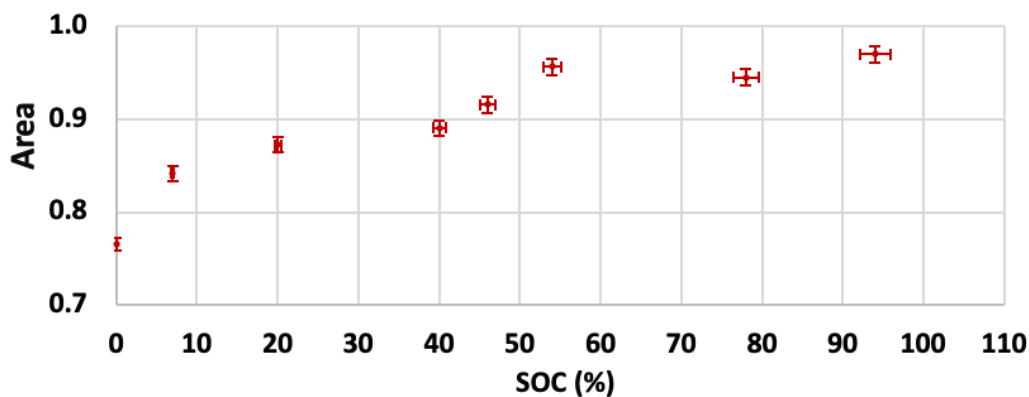


Figure 6-25 Effect of variation in SOC of LFP cathodes on the area under the ^1H signal of DMC.

6.4.5 Discharged LFP cathodes

Figure 6-26 illustrates the impact of paramagnetic LFP cathodes at various SOC on the ^1H signal of DMC. This figure evidences notable shifts and broadening in the ^1H signal of DMC compared to the signal of pure DMC.

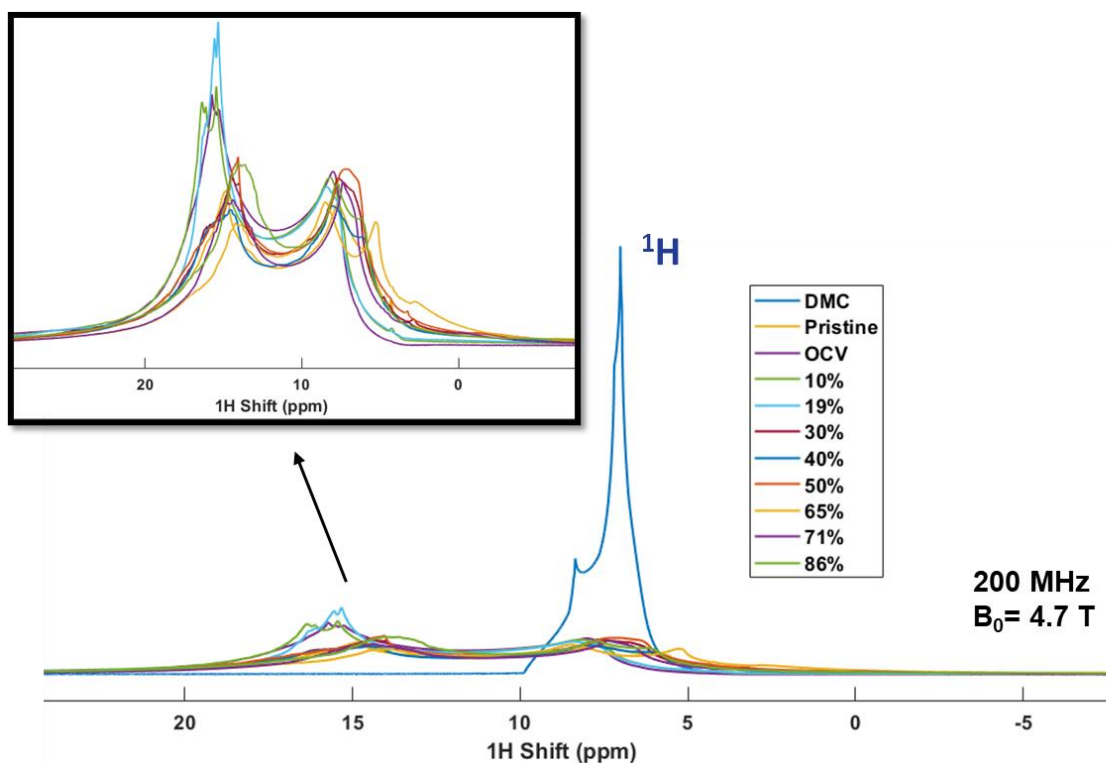


Figure 6-26 ^1H signal of DMC in the presence of LFP cathodes with varying SOD.

6.4.5.1 Effect on shift

As shown in Figure 6-27, the results for the shift values of the ^1H signals of DMC under the influence of LFP cathodes at various SOD reveal a clear upward trend and demonstrate its significant sensitivity to alterations in the magnetic susceptibility of the LFP electrodes.

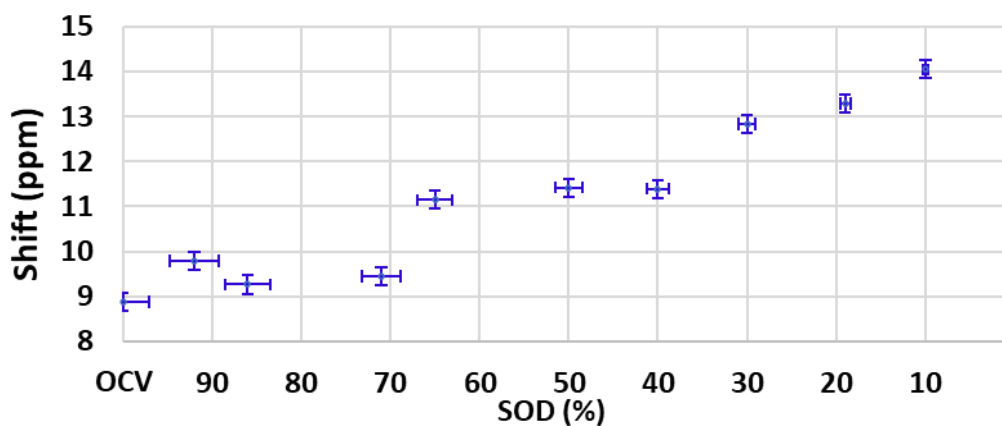


Figure 6-27 Effect of variation in SOD of LFP cathodes on the shift of the DMC ^1H spectra.

6.4.5.2 Effect on width

The results regarding the width values of the ^1H signals of DMC influenced by LFP cathodes at varying SOD (Figure 6-28) reveal a trend resembling a 'W' shape. It is currently uncertain whether this pattern is a result of measurement uncertainties or an inherent characteristic. Thus, further repetitions of the measurement are necessary to have a more definitive and conclusive understanding.

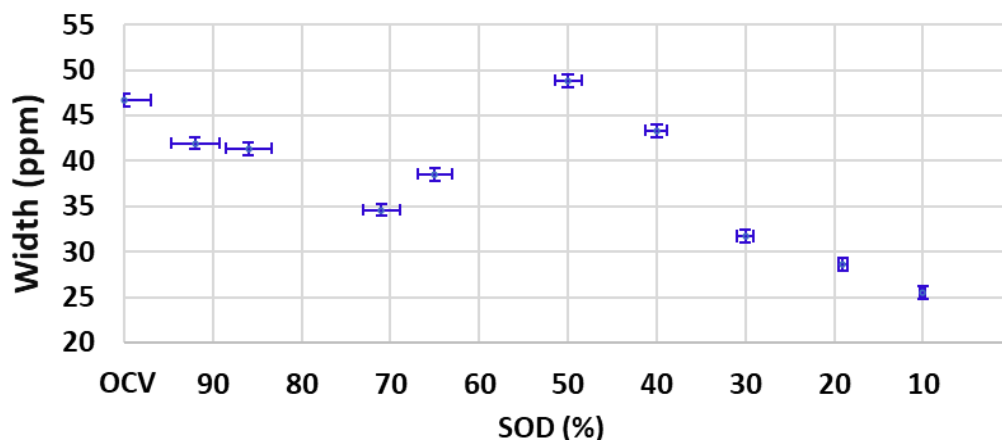


Figure 6-28 Effect of variation in SOD of LFP cathodes on the width of the DMC ^1H spectra.

This section expands the applications of Na-ion batteries. Detection with ^1H NMR of the electrolyte is even more advantageous in that case, as ^{23}Na is less sensitive than ^7Li and presents broadening in the solid-state and enhanced relaxation from its quadrupolar character.

6.5 ^1H Operando measurement of NMC//LiPF₆//Gph full cell

This section presents the final step of our proof of concept: ^1H NMR measurement of the electrolyte solvent inside an operating battery.

6.5.1 Materials and electrode

Operando measurements were conducted using *in situ* cells fabricated from Kel-F material (Figure 6-29), specifically designed in the CEMHTI laboratory for NMR measurement.¹⁰ The assembly of these cells was performed inside an Ar-filled glovebox with water and oxygen levels maintained below 1 ppm. The cell configuration included a 5 mm diameter NMC 622 cathode, graphite anode, 6 mm diameter glass fiber separator, and 200 μl of LiPF₆ 1M in ED/DMC electrolyte.

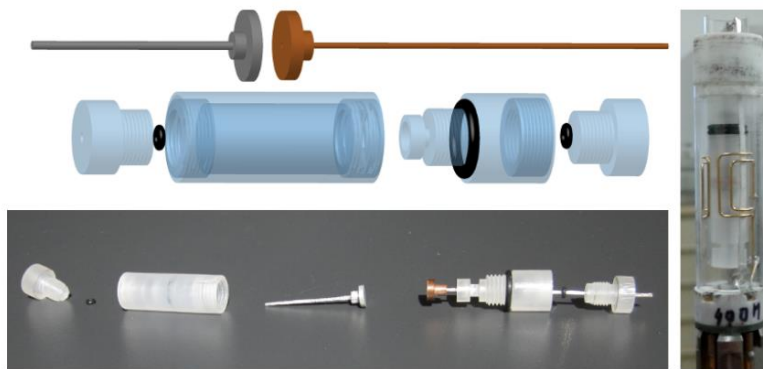


Figure 6-29 The electrochemical Kel-F in situ cell, Copyright 2014 American Chemical Society.¹⁰

6.5.2 Cell assembly

The protocol is the same as for the Swagelok cell. The commercial electrode sheets were punched in ambient air using a 5 mm diameter puncher. Subsequently, they were heat-treated and dried overnight in a BUCHI® ball furnace at 140°C under vacuum conditions for a minimum of 8 hours. The dried electrodes were then transferred to an argon-filled glove box without breaking the vacuum, where the final assembly took place.

The Kel-F® cell and metallic collectors were dried separately in an oven at 60°C for at least one night. To minimize exposure time outside the controlled environment, the transition between leaving the oven and re-entering the glove box was performed swiftly. Special care was taken when removing the metal collectors from the oven, as they had an oxide layer that required sanding and subsequent cleaning in an ethanol sonic bath to ensure a clean surface. Before entering the glove box, a pre-assembly of the NMR cell was carried out, resulting in two separate parts: the body with a collector on one side and the cap with the second collector on the other.

In accordance with the cell assembly protocol, the first step involves placing a 5 mm NMC electrode on the upper part of the aluminum current collector, aligning the two aluminum surfaces to face each other. Subsequently, a precise amount of LiPF₆ electrolyte is dropped onto a 6 mm glass microfiber separator using a micropipette. The wet separator is then positioned on the top surface of the NMC electrode, effectively covering all its exposed areas. Following this, a 5 mm graphite anode is carefully positioned on top of the separator. To ensure optimal alignment, both electrodes must be centered within the in-situ cell (as illustrated in Figure 6-30). It is of utmost

importance to settle and place the separator smoothly, avoiding any crumpling that could lead to contact between the electrodes, subsequently increasing the risk of short circuits. Finally, the cell can be sealed by placing the upper part and securely screwing the cap.

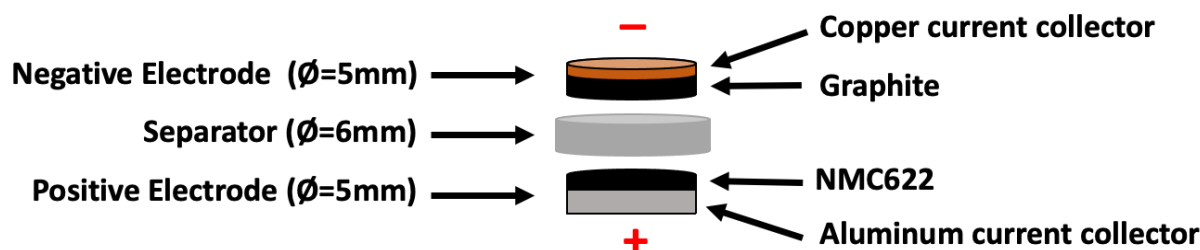


Figure 6-30 Illustration of electrodes and separator with dimensions.

6.5.3 Cycling procedure

The in-situ cells were subjected to cycling at a rate of C/10, with room temperature and N₂ atmosphere, operating between voltage limits of 2.7 V and 4.2 V. Same voltage window as Swagelok cell cycling was chosen for cycling of in-situ cell. The voltage was held during CV periods until the current dropped below C/50.

6.5.4 Battery setup optimization

During the setup preparation of the battery inside the magnet, certain factors are essential for optimal signal detection.

Every magnet possesses what is referred to as a magnetic center (sweet spot). This denotes the region within the magnetic field where the intensity is at its highest and homogeneity is optimal as shown in Figure 6-31. In NMR probes, this magnetic center aligns with the center of the coil. The probe is designed by the manufacturer in such a way that the coil is positioned at the magnetic center of the magnet it is intended for.

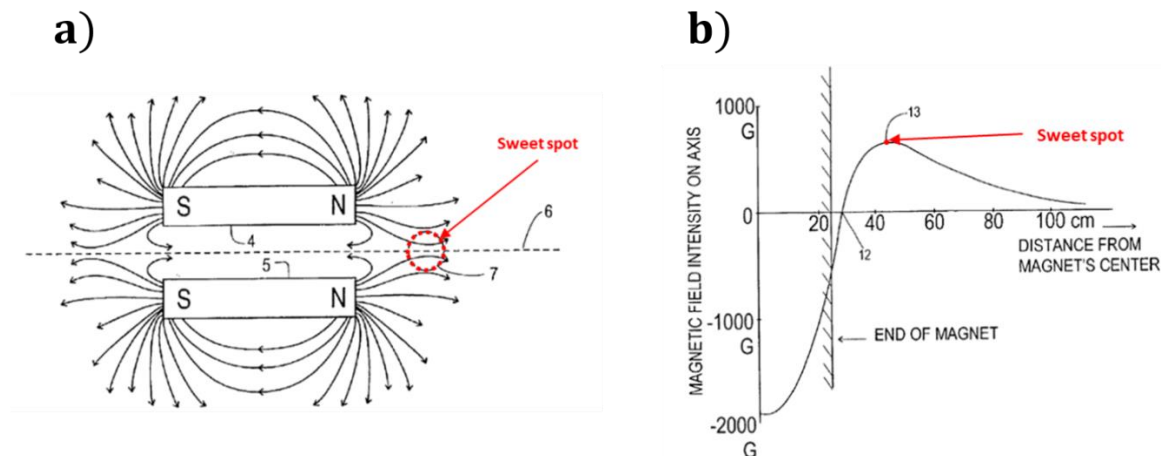


Figure 6-31 (a) Example of the magnetic center (sweet spot) on two identical parallel bar magnets, (b) Magnetic field strength as a function of distance from magnet center.^{81,220}

For optimal signal detection, it is therefore necessary to position battery within the homogeneous zone of the magnet (magnetic center). Sample homogeneity is also important, which must minimize parasitic effects and fit within the choice of magnet, probe, and coil to the sample and the form under which it is being studied.

Furthermore, skin effect needs to be considered in the case of in-situ NMR/MRI of the battery for metallic collectors such as copper, aluminum, etc. Therefore, the metallic collectors were oriented parallel to the direction of the RF field provided by the coil.

In an *in situ* NMR study of a battery, temporal resolution can be a limiting factor. It necessitates the optimization of acquisition parameters to obtain the necessary sensitivity for the studied process.⁸¹

6.5.5 NMR parameters of the experiment

The *operando* ^1H measurement was performed using a Bruker 200MHz spectrometer equipped with a narrow bore BST, diffusion 30 probe, and micro 5 gradient insert. The electrochemical cycling process was conducted under a Nitrogen-filled environment. Successive ^1H NMR spectra with a 90° pulse length of $15\ \mu\text{s}$ were acquired throughout the cycling process to observe the proton signals in the LiPF_6 electrolyte.

Spectra were acquired with a recycling delay of 1 s and 40 s between acquisitions. Chemical shift referencing was achieved using a $\text{Gd}(\text{NO}_3)_3(\text{H}_2\text{O})_5$ solution, with the peak having the highest intensity in the ^1H spectrum set as the reference at 4.8 ppm. The spectral width was set to 2997.7 ppm, corresponding to a frequency range of 598429.08 Hz. The acquired NMR spectra were processed using the Bruker Topspin 3.6.2 software application. Data analysis and plotting were performed using home-written MATLAB scripts.

6.5.6 NMR measurement and electrochemical cycling

The electrochemical cycling and NMR measurements were initiated simultaneously, and data were collected over multiple cycles. However, the *operando* results presented here are specifically related to the 5th cycle, following the initial 4 formation cycles. Figure 6-32 shows the formation cycles of the NMC//LiPF₆//Graphite NMR cell with different colors, each corresponding to a different mode (Section 4.1.1 Chapter 2).

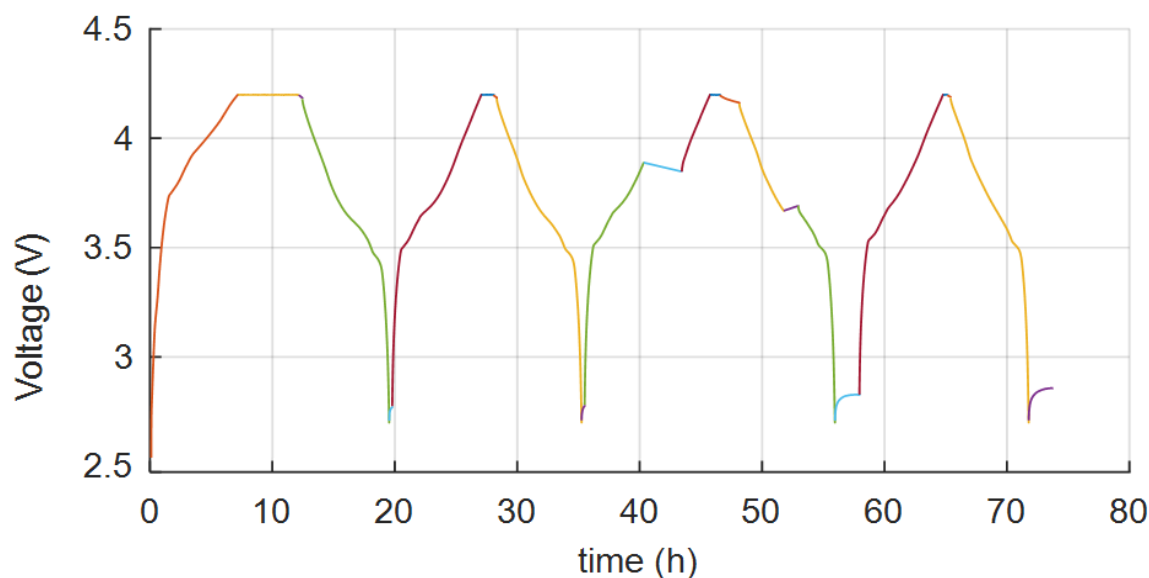


Figure 6-32 Formation cycles of NMC//LiPF₆//Graphite cell (cell KB229).

The sudden drop in the voltage profile is attributed to pauses during cycling, which were necessary for implementing changes in the acquisition parameters of NMR for different measurements.

6.5.7 Operando NMR results

Figure 6-33 shows a zoomed version of the voltage profile, which corresponds to the 5th cycle and the *operando* NMR study.

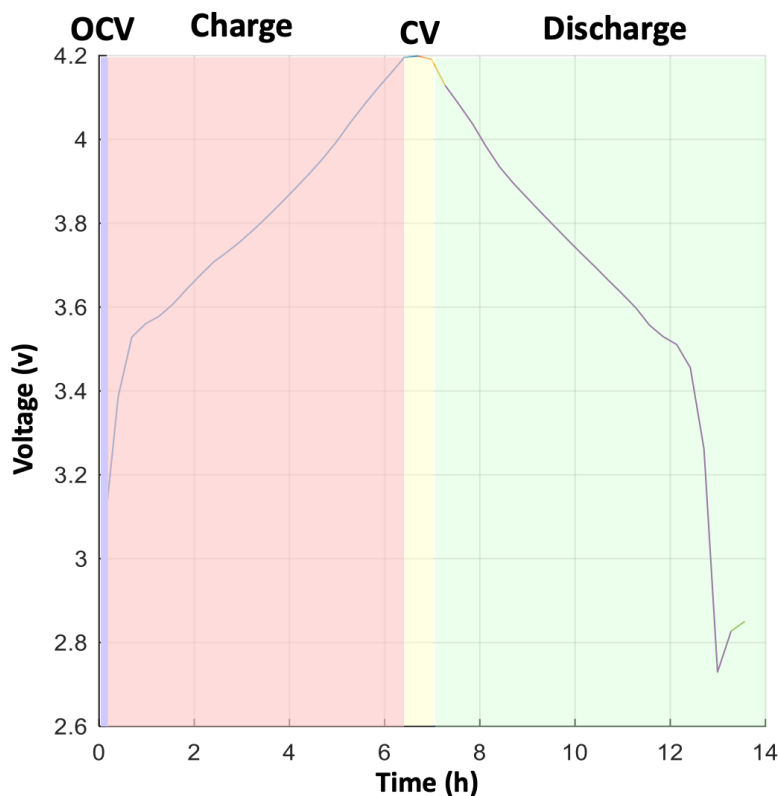


Figure 6-33 Voltage profile of NMC//LiPF₆//Graphite cell (cell KB229) upon 5th cycle with illustration of different mode.

Figure 6-34 shows the corresponding pseudo-2D (contour map) ¹H NMR spectrum from the NMR cell KB229 in the 5th cycle, plotted using MATLAB. In this plot, the X-axis represents the shift of the ¹H signal of the electrolyte (in ppm), while the Y-axis represents the time axis. The proton NMR spectrum intensity is represented as contours. Each horizontal line in the plot corresponds to a specific ¹H NMR spectrum at a given point in time.

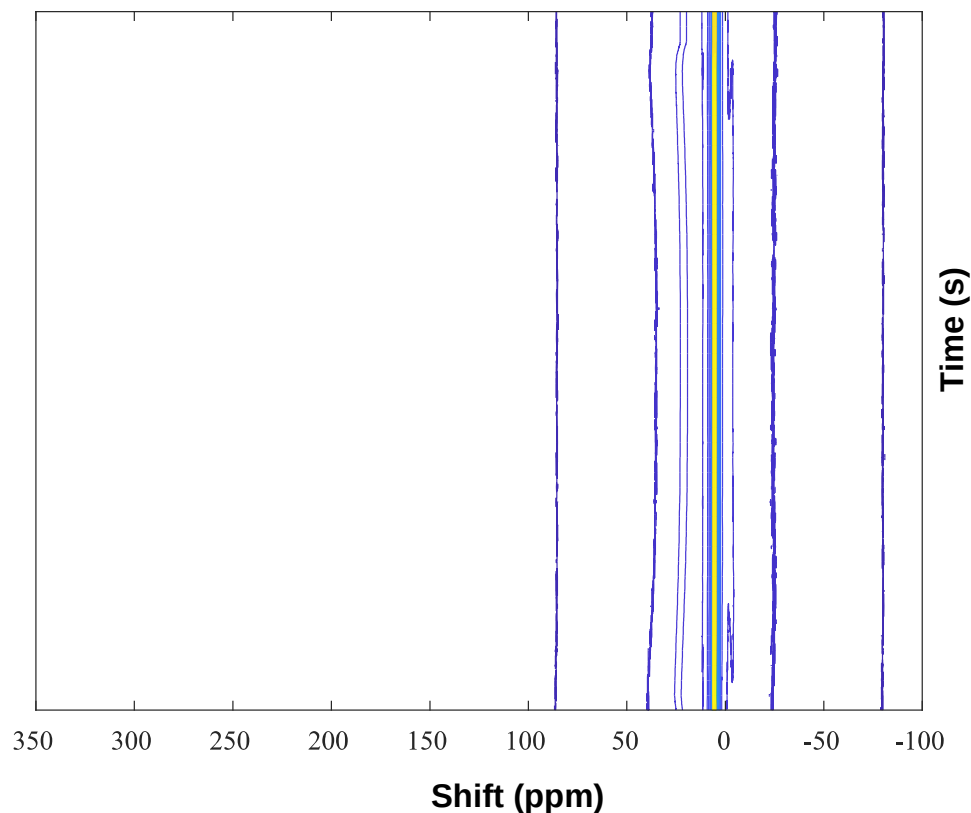


Figure 6-34 Contour map of ^1H NMR spectra from the NMR cell KB229 upon 5th cycle.

The complex nature of the data, as illustrated in the contour plot of Figure 6-34, makes interpretation and analysis challenging. Consequently, in Figure 6-35, we present a stacked plot of ^1H NMR data, where each spectrum corresponds to one line (each lasts 18 mins and 54 s) and is associated with a specific point on the cycling plot (Figure 6-37). In Figure 6-35, a slight shift of the peak positions is observed upon cycling. Describing properly the signal modifications poses a challenge, especially for small variations.

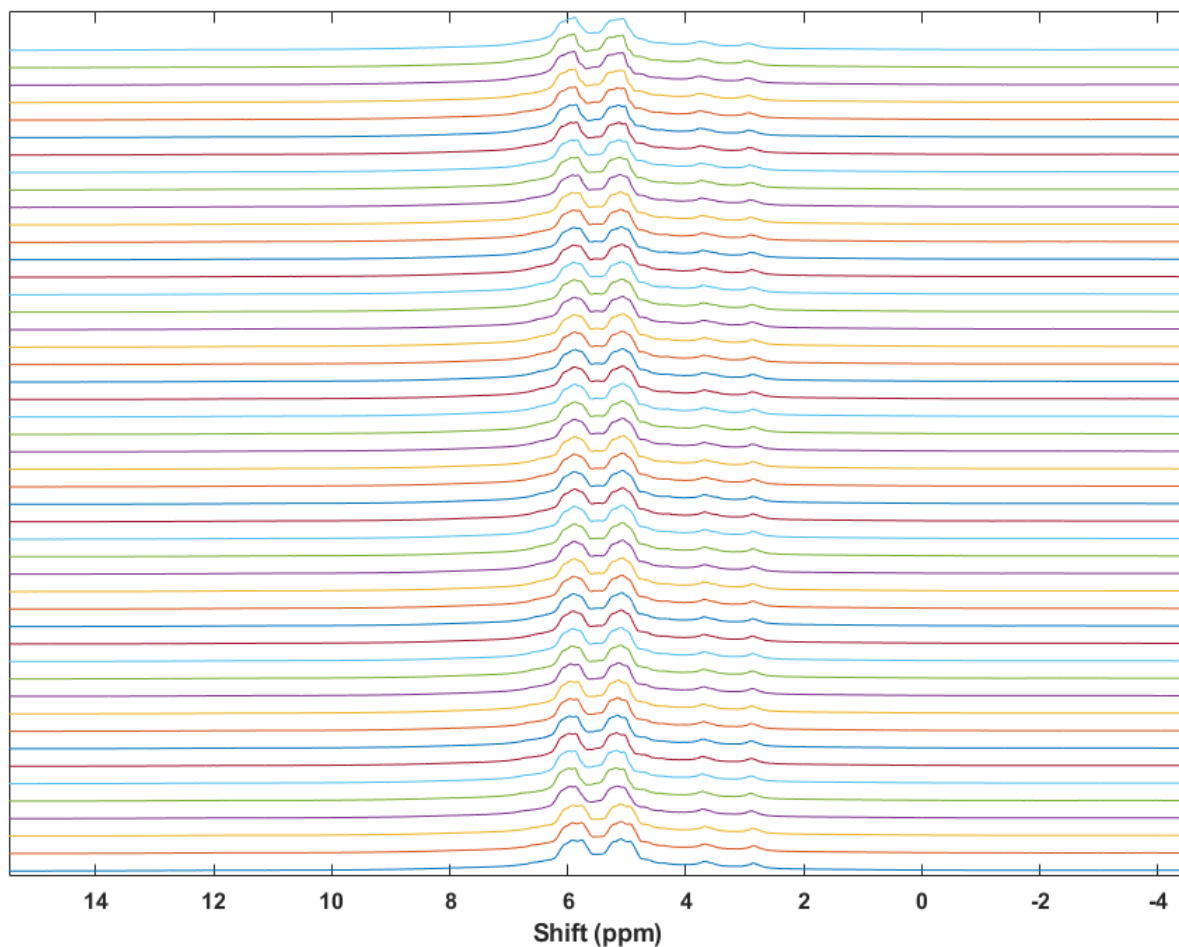


Figure 6-35 Stacked plot of ^1H signal of electrolyte in cell KB229 upon 5th cycle.

Consequently, a difference map was created through subtracting each ^1H spectrum from the initial ^1H spectrum (Figure 6-38). This results in the appearance of a horizontal line instead of the initial spectrum. Changes in the subsequent spectra compared to this reference spectrum are easier to spot in this way.

This approach enables an easier monitoring and analysis of the evolution of the ^1H spectrum of the electrolyte right from the start of the measurement.

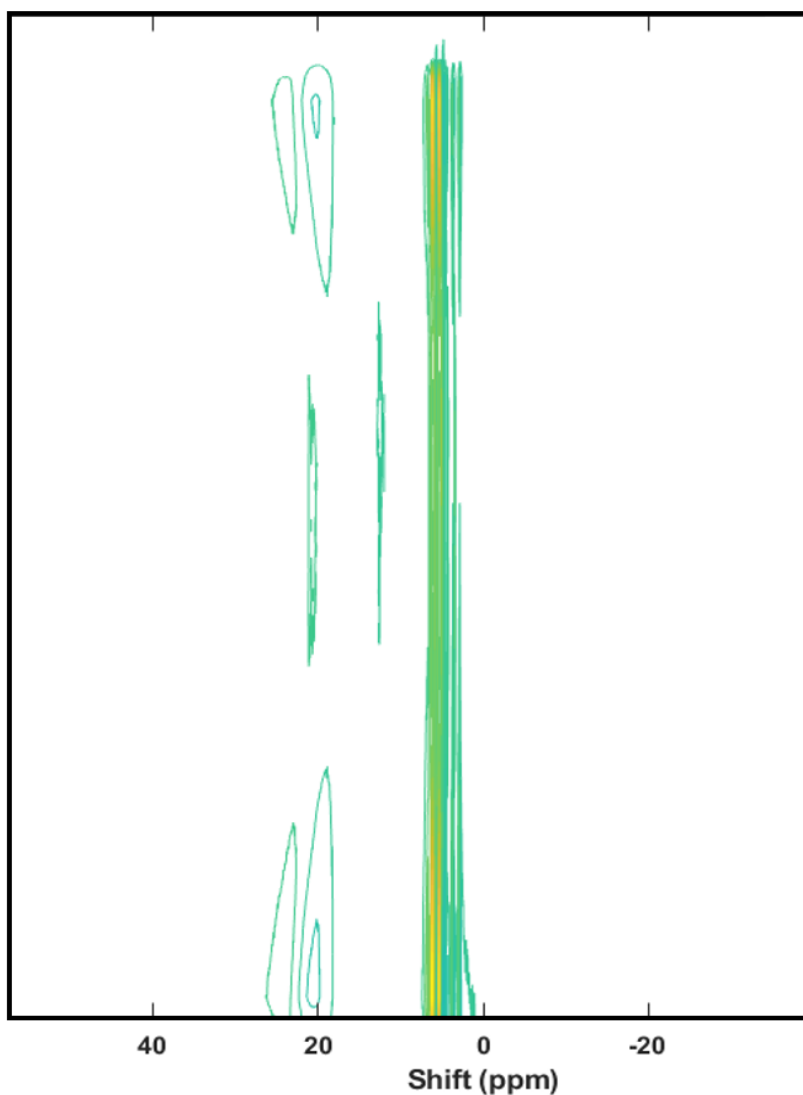


Figure 6-36 Contour map of ^1H NMR spectra from the NMR cell KB229 upon 5th cycle subtracted from first spectrum.

In this contour map, noticeable alterations in the proton signal are observed during the onset of charging and delithiation of NMC, gradually diminishing as we approach the constant voltage (CV) step in the middle. Furthermore, during the discharging and lithiation of NMC, these alterations in the ^1H signal reemerge and intensify until the end of the discharge process. These signal alterations should be related to the changes in the magnetic susceptibility of the positive NMC cathode, as determined before.

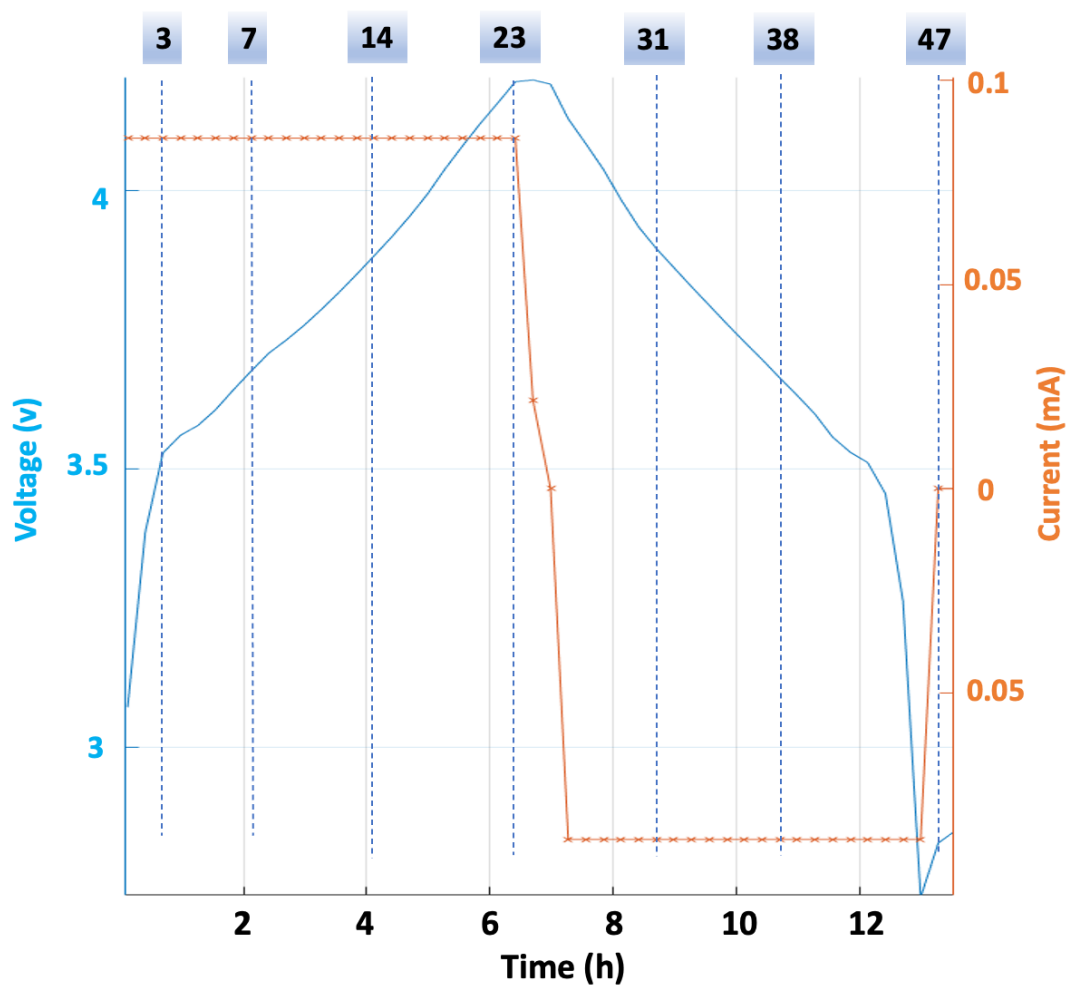


Figure 6-37 Voltage profile of NMC//LiPF₆//Graphite cell (cell KB229) upon 5th cycle with NMR data acquisition point appearing as red crosses. The numbers are corresponded to the spectrums, recorded during specified voltage-time.

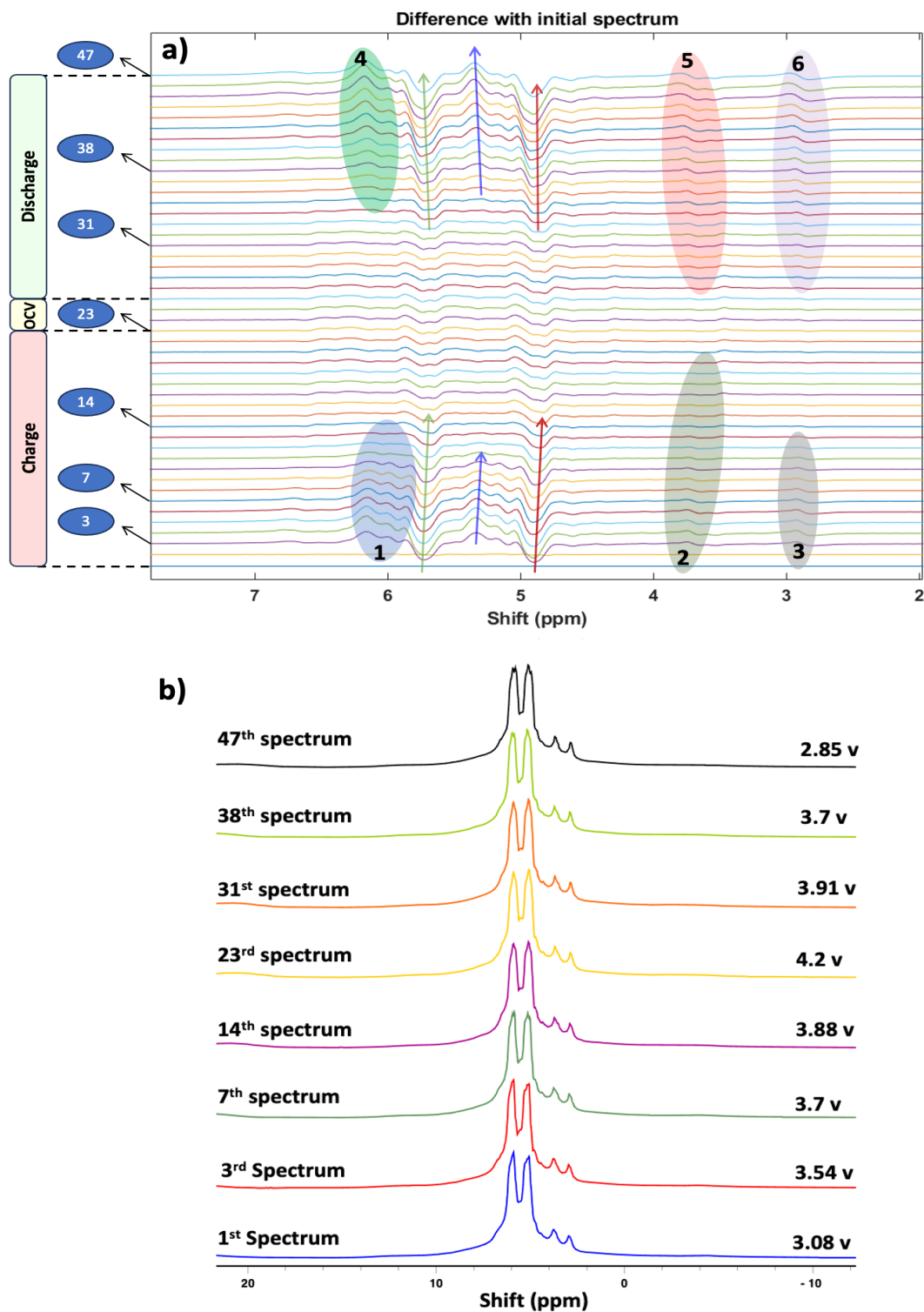


Figure 6-38 Stacked plot of ^1H signal of electrolyte (in the cell KB229 upon 5th cycle) subtracted from the 1st spectrum for (a) all signals and (b) selected signals.

In the corresponding stacked plot (Figure 6-38a), all the successive ^1H signals from the electrolyte inside the cell are presented, with each spectrum recorded during cycling. These points are indicated on the current values (cross signs) in Figure 6-37.

As shown in Figure 6-38, starting from spectrum 3 (~ 3.54 V), a notable alteration (distortion) in the ^1H signal, primarily observed in the two main peaks at 5.1 and 5.9 ppm, becomes evident. We assume that this signal alteration is due to a significant change in the local magnetic susceptibility of the battery, mainly assigned to the alteration in the redox state of the NMC electrode. This peak distortion also remains in the subsequent spectra during the charging process until approximately 3.8 V, although it gradually diminishes and exhibits a slight rightward shift at the end (as denoted by the arrow at the bottom of the figure).

Between 3.8 V to 4.2 V upon charging, the CV step, and from 4.2 V to 3.9 V upon discharging, the alterations in the spectra are minimal. However, the alteration (distortion) intensifies as the voltage decreases to around 2.8 V during the lithiation of the NMC cathode, displaying a slight leftward shift, as highlighted by the colorful arrow at the top of the figure. This is in line with a magnetic susceptibility effect arising from the redox state, as it is reversible.

Additionally, we observe slight alterations in the ^1H spectra on both the left and right sides of the main peaks, highlighted by colored ellipses numbered 1, 2, and 3 (4, 5 and 6 on discharge). These changes, except for zone number 1 and 4, are tiny and tend to diminish as the voltage increases during charging. In zone 1, however, this alteration is more significant, with a slight rightward shift during charging.

During the discharging phase, these alterations in the ^1H spectra reappear, being more pronounced and noticeable in zone 4. Zone 4 exhibits an increasing distortion and a leftward shift as the voltage decreases during discharge.

Again, these variations are symmetrical with respect to the top of charge and validate our hypothesis that ^1H in the electrolyte signal are sensitive to changes in the redox states of the positive electrode. However, the state at the end of discharge is not strictly identical to the state before charge, which is expected given that coulombic efficiency is not 100%.

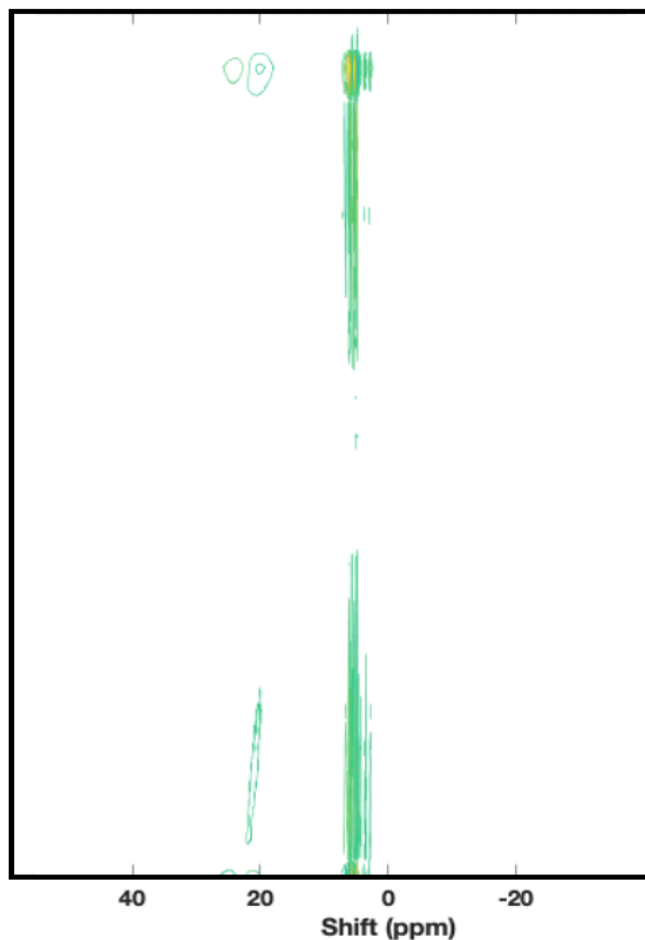


Figure 6-39 Contour map of ^1H NMR spectra from the NMR cell KB229 upon 5th cycle deviated from the previous spectrum.

Figures 6-39 and 6-40 present the dOp²²¹ contour map and stacked plot of the ^1H signal of LiPF_6 electrolyte, respectively. In these figures, each individual line was subtracted from the preceding one. This approach provides a clearer understanding of how the ^1H spectra of the electrolyte undergo changes at each step compared to the previous spectrum.

In both figures, the change into the proton signal of electrolyte is evident at the beginning of the charge and toward the end of discharge.

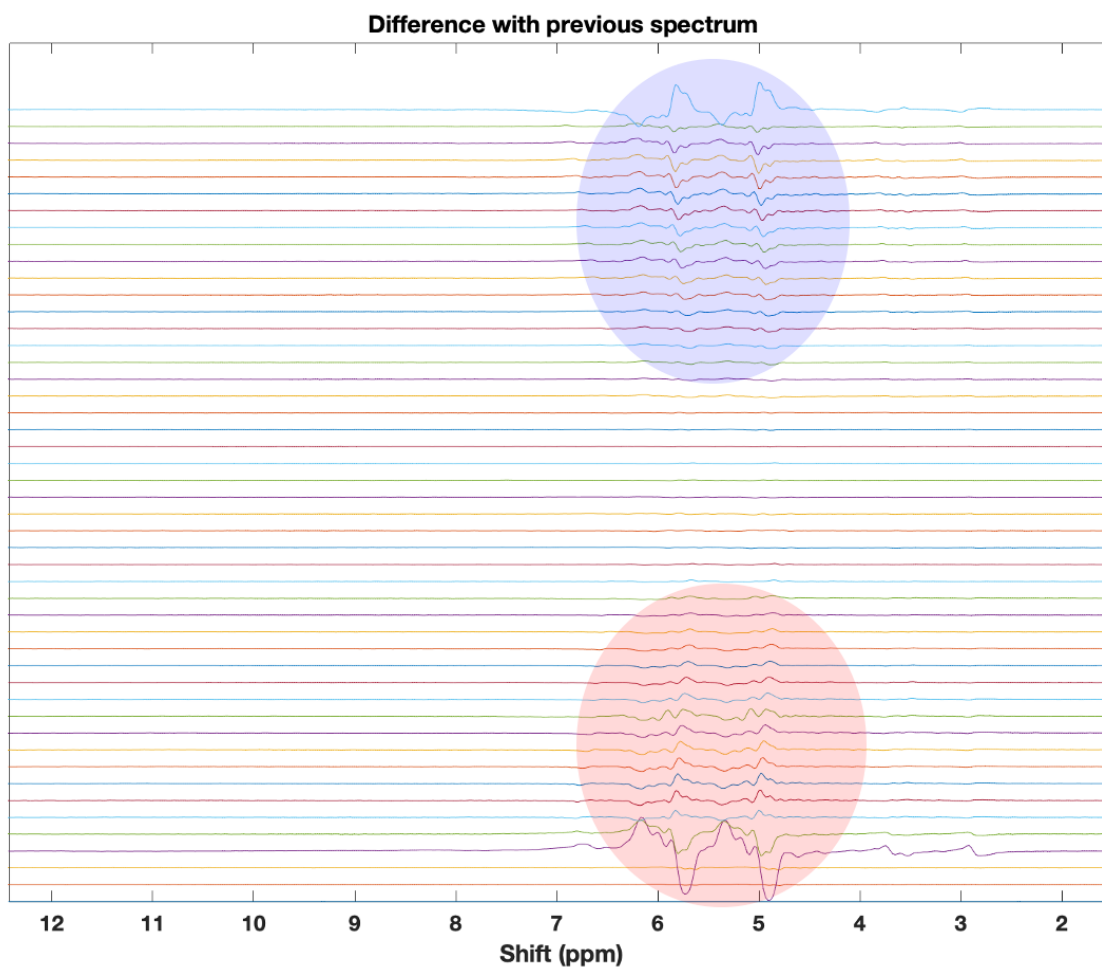


Figure 6-40 Stacked plot of ^1H signal of electrolyte deviated from the previous spectrum in the cell KB229 upon 5th cycle.

6.6 Conclusion

The results show that we can indirectly measure changes in the magnetic susceptibility of the electrodes by observing their impact on the electrolyte solvent. These changes can be correlated with the oxidation state of the electrodes. We demonstrate that alterations in the redox state and consequent magnetic susceptibility of positive electrodes are reflected in the highly sensitive ^1H NMR signal of the DMC solvent in contact with them. This observation is supported by the discernible trend in the shift and width of the ^1H signal of the DMC solvent when electrodes with different states of charge are present.

The ^1H NMR spectrum of DMC in contact with NMC electrodes demonstrates notable sensitivity to variations in their SOC or SOD. Conversely, when interacting with graphite electrodes, the sensitivity to changes in SOC or SOD is considerably low. Consequently, ^1H NMR measurements of DMC primarily provide valuable insights into the redox state of the positive electrode. Comparing various SOC and SOD of NMC cathodes reveals a consistent behavior in both shift and width which aligns well with the reversible nature of the charge-discharge processes in these cells. The correlation between variations in shifts and variation in SOC and SOD is notably stronger compared to the correlation with width. This emphasizes that the average shift of ^1H NMR in DMC serves as a more effective descriptor for determining the redox state of the electrode.

Additionally, when examining the ^1H NMR spectrum of DMC in proximity to LFP electrodes, a notable sensitivity to changes in their SOC or SOD is observed. The resulting changes in their magnetic susceptibility are large enough to be followed effectively through both shift and width measurements of the ^1H signal of DMC. Analyzing the shift values of the ^1H signals of DMC influenced by paramagnetic LFP cathodes at various SOC and SOD reveals a distinct and clear trend. On the contrary, the width values display a lesser sensitivity to the redox state of LFP cathodes. In general, the width appears to exhibit lower sensitivity to the redox state of the electrodes when compared to the shift. However, contrary to the observations regarding area integration values under the ^1H signal of DMC with NMC and graphite electrodes, the area integration values for LFP electrodes at various SOC demonstrate a discernible trend.

These findings clearly show that our approach can be extended to Na-ion batteries. Utilizing ^1H NMR to detect changes in the electrolyte is particularly advantageous in this case since ^{23}Na is less sensitive compared to ^7Li , and it displays broadening in the solid-state, besides enhanced relaxation resulting from its quadrupolar character.

The operando ^1H NMR results of the LP30 electrolyte within an operating NMC//LP30//Gph full cell during the 5th cycle reveal sensitivity to alterations in the redox state of electrodes and the consequent local magnetic susceptibility of the cell. This sensitivity, although reduced, shows trends in signal shift and width in agreement with *ex situ* measurements.

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3. General conclusion

Estimating the state of charge (SOC) of batteries is crucial for defining the actual available energy in the battery and providing information on the remaining working time and device lifetime. However, the direct determination of SOC within batteries remains challenging. This challenge necessitates the improvement in the design of the battery management system, as current strategies, and techniques for determining SOC often face drawbacks. In our study, we aim to evaluate the capability of *operando* NMR to detect changes in the magnetic properties of batteries upon cycling, serving as an indicator for SOC.

The *in situ* and *operando* conventional ^7Li NMR analysis of batteries faces limitations in temporal and spectral resolution, particularly when dealing with paramagnetic and conductive electrodes. This reduced capability to identify specific Li-ion species or compounds can pose challenges when studying the complex chemistry and dynamics occurring within an operating battery. *Operando* NMR analysis of Na-ion batteries also suffers from the low sensitivity of ^{23}Na NMR due to its lower gyromagnetic ratio, quadrupolar nature, and rapid relaxation. Consequently, *in situ* NMR spectra of both LIBs and SIBs typically experience significant spectral overlap during cycling, necessitating combination with *ex situ* measurement for interpretation. Moreover, the reduction of their recording time is restricted due to the lack of sensitivity of ^7Li and ^{23}Na .

To overcome these challenges, we came up with an approach in which we focus on the local magnetic susceptibility changes within the operating cell which is influenced by the material's electronic configuration. Consequently, as redox reactions occur inside the battery and alter the electronic structure of electrodes, the magnetic susceptibility of the cell also undergoes changes. In our approach, instead of directly examining lithium atoms within the electrodes, we concentrate on the ^1H signal of the liquid electrolyte solvent. This signal is correlated with the oxidation state of the electrodes and provides detailed information about electrochemical processes. This information is crucial for identifying the sources of capacity loss in full batteries.

Through a comprehensive investigation of the impact of pristine active materials like LMO, NMC, LCO, and LFP on the ^1H spectrum of DMC, used as a reference protonated liquid, we observed that the LFP pellets induce more distortion on the ^1H signal of DMC compared to LMO, NMC, and LCO pellets. This higher distortion is attributed to the higher magnetic susceptibility values of LFP.

The resulting distortion of the ^1H signal was quantified based on its shift, spectral width, T_1 relaxation time, and the area under the spectrum. The results clearly demonstrate that the presence of LFP pellets induces a more significant shift and signal broadening in the ^1H spectrum and results in a faster relaxation of the bulk DMC solvent. Through this analysis, we successfully established the feasibility of detecting variations in the magnetic susceptibility of paramagnetic pellets by measuring the ^1H NMR signal of the reference liquid DMC in their vicinity.

Furthermore, an investigation into the influence of various battery components, including current collectors, separators, NMC 622, and graphite electrodes, on the ^1H signal of DMC revealed their negligible impact compared to the effect induced by the paramagnetic NMC 622 positive electrode.

Moreover, utilizing a specially designed NMR PEEK tube, we assessed the impact of the flatness and shape of the paramagnetic electrode on the ^1H NMR signal of DMC. Through a comparison between the ^1H CSI of pure 200 μL DMC and 200 μL DMC in contact with an LFP electrode within the PEEK tube, we observed a notable distortion in the proton signals near the electrode. This distortion led to broader and more shifted signals compared to those observed in pure DMC. The observed effects can be attributed to the magnetic susceptibility effect of the LFP electrode and interface effect, which ultimately causes faster relaxation of the ^1H signals of DMC near the electrode.

The *ex situ* NMR results demonstrate that the proton signal of DMC in contact with positive electrodes is sensitive to variation in their redox state and the subsequent alterations in magnetic susceptibility. This sensitivity was observed by analyzing the behavior of the shift and width of the ^1H signal of liquid DMC in the presence of electrodes at various states of charge.

The ^1H NMR spectrum of DMC in contact with NMC electrodes demonstrates a strong sensitivity to changes in their SOC and SOD. On the contrary when in contact with graphite electrodes, there is a notably low sensitivity to alterations in their SOC or SOD. As a result, ^1H NMR measurements of DMC predominantly provide insights into the redox state of the positive electrode. When comparing different SOC and SOD of NMC cathodes, both shift and width exhibit a similar behavior, aligning well with the reversibility of the charge-discharge processes in these cells. The correlation between variations in shift and alterations in SOC and SOD is stronger than that with width, highlighting the average shift of ^1H NMR of DMC as the most effective descriptor for deducing the redox state of the electrode.

The results concerning the shift values and area integration of the ^1H signals of DMC under the influence of paramagnetic LFP cathodes at various SOC and SOD display a distinct trend. However, the width values demonstrate less sensitivity to the redox state of LFP cathodes.

The ^1H *operando* NMR results of the electrolyte (1 mol. L^{-1} LiPF_6 in EC:DMC) within an operating NMC// LiPF_6 //Graphite full cell during the 5th cycle shows sensitivity to changes in the redox state of the electrodes and their corresponding magnetic susceptibility. The preliminary *operando* measurement results highlight a noticeable trend in the variation of the shift and width of the ^1H signal of the electrolyte, consistent with observations in the *ex situ* NMR measurements.

An essential advantage of our approach is the substantial enhancement in sensitivity achieved by utilizing ^1H instead of the conventional ^7Li , making it applicable to a wide variety of battery systems, particularly Na-ion batteries. Furthermore, the rapid measurements facilitated by the ^1H NMR method present a significant advantage in terms of time resolution over other existing NMR methods. This advantage will be crucial in investigating various cycling behaviors in an *operando* mode, especially those occurring within very short timescales.

Our approach has the potential to identify the origin of capacity losses (for a given system) and to correlate the SOC of the electrodes with electrochemical markers such as voltage, capacity retention or coulombic efficiency. They could be integrated into a better model for the battery management system to better predict the future capacity of a battery and its potential failures.

4. Perspectives

1. *Ex situ* measurement

In this thesis we optimized a Swagelok cell design for cycling 8mm-diameter electrodes. This modification yields more reproducible electrochemical performance and provides electrodes at various states of charge that are compatible with measurements in a liquid-state NMR tube. Measurements in the future will lead to experimental results with reduced uncertainty on the state-of-charge of the battery.

Regarding the ^1H NMR measurement of DMC in the vicinity of electrode materials at various state of charge, the utilization of the newly-designed PEEK tube provides enhanced control over the geometry of the electrode-DMC interface. As the shape of the electrode can change slightly from sample to sample and hence SOC to SOC, using a controlled electrode geometry for the NMR measurement will increase the precision of the comparison between similar electrodes at different redox states.

We demonstrated a trend in the ^1H NMR shifts with state of charge of the battery. In the future, we should extend the state-of-charge study with the modified Swagelok cell and PEEK tube on additional battery chemistries like LiFePO_4 (LFP)// LiPF_6 //Graphite and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF)// NaPF_6 //hard carbon (HC) to provide better statistics with a broader range of states of charge and discharge for each battery system.

Furthermore, we should perform VSM or SQUID magnetometry to evaluate the magnetic susceptibility of electrodes with specified redox states to correlate them with the ^1H *ex situ* NMR measurements of liquid DMC spectra. In this case, it is crucial to handle the sample retrieval from the NMR tube with great care and precision, ensuring careful preparation for subsequent magnetometry measurements. By doing so, we will be able to correlate the results obtained from magnetometry with the *ex situ* NMR data.

Finally, we could extend the T_1 study of ^1H DMC in contact with different active materials with localized measurements to identify the distribution in T_1 relaxation of ^1H DMC at different

distances from the electrodes. By doing so, we could gain information regarding the local magnetic field experienced by the DMC electrolyte at varying distances.

2. Data analysis

We could develop an analytical model to better quantify the distortion of the NMR signal caused by the magnetic susceptibility effect of positive active materials. This effect often leads to substantial broadening and distortion of the signal. This new model would not only account for alterations in the weighted average shift and width at different heights of shift, but it would also evaluate the overall change in the signal's shape.

Interpreting changes in the ^1H signal of LiPF_6 electrolyte, characterized by two sharp peaks, through shifts and widths presents challenges. Hence, we utilized only DMC, which exhibits a single sharp peak. As highlighted earlier, by establishing a relationship between the overall shape of the ^1H signal of LiPF_6 and the battery's redox state, we may be able to develop a model for signals at different states of charge.

3. *Operando* measurement

In the future we could extend our *operando* measurement approach (including T_1 and spatial filtering) to study other battery systems such as LFP// LiPF_6 //Graphite. A very interesting possibility is the extension to Na-ion batteries, for which it is notably difficult to record ^{23}Na *in situ* NMR. Additionally, we could play with the recycling delay during the *operando* measurement to select specific environments in DMC, closer to the electrodes for example. Furthermore, we could perform chemical shift imaging (CSI) with selected recycle delays to select spatially and relaxation-wise the parts closest to the electrodes.

So far, we demonstrated that this approach was sensitive enough to follow changes in the state-of-charge in one cycle of charge-discharge. The next steps are *operando* measurements on batteries to follow the changes upon many cycles, especially the evolution of the redox state of the positive electrode that may differ from the state-of-charge inferred from the galvanostatic measurements and coulombic efficiency. This is highly promising for the investigation of the impregnation of the

electrodes by the electrolyte, as well as the parasitic reactions occurring between the electrode and the electrolyte in batteries. Furthermore, we should be able to analyze the effect of different additives in the electrolyte.

Khashayar BAGHERI

Spectroscopie et imagerie RMN ex situ et in situ pour le stockage électrochimique de l'énergie

La résonance magnétique nucléaire (RMN) est une technique de caractérisation prometteuse pour l'étude des systèmes de stockage électrochimiques de l'énergie. Cette thèse porte sur le développement d'une nouvelle approche RMN pour caractériser l'ensemble du dispositif pendant son fonctionnement (in situ/operando) et suivre l'état de charge des électrodes dans les batteries Li-ion et Na-ion. Le potentiel de la RMN du ^1H est exploré pour suivre l'évolution des électrodes par le biais de changements de susceptibilité magnétique. Les modifications du signal RMN ^1H du solvant de l'électrolyte sont corrélées avec les états d'oxydoréduction des électrodes positives pour une batterie de type Li-ion, NMC622//LiPF₆//graphite et une de type Na-ion, NVPF//NaPF₆//carbone dur. Ces développements fournissent une perspective unique sur l'état de charge des électrodes positives dans des batteries en fonctionnement et offrent une sensibilité accrue pour les mesures RMN operando sur les batteries.

Mots clés : Spectroscopie RMN, Batterie Li-ion, Matériaux, Stockage électrochimique de l'énergie, Susceptibilité magnétique, Batterie Na-ion

Ex situ and in situ NMR spectroscopy and imaging for electrochemical energy storage

Nuclear Magnetic Resonance (NMR) stands as a promising characterization technique for studying electrochemical energy storage systems with complex interactions. This thesis reports on the development of a new NMR approach for characterizing the entire device during operation (in situ/operando) and tracking the state of charge of the electrodes in Li-ion and Na-ion batteries. We explore the potential of ^1H NMR to monitor the evolution of the electrodes through changes in magnetic susceptibility. The alterations in the ^1H signal of the electrolyte solvent is demonstrated to correlate with the positive electrode redox state. Preliminary results are obtained for a functioning Li-ion battery, NMC622//LiPF₆//graphite and a Na-ion battery, NVPF//NaPF₆//hard carbon. This approach should provide a unique perspective into the state of charge of positive electrodes for functioning batteries. These developments also offer an enhanced sensitivity for operando NMR measurements in batteries.

Keywords: NMR spectroscopy, Li-ion battery, Materials, Electrochemical energy storage, magnetic susceptibility, Na-ion batteries



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