Parallel-Plate RF Probe for Magnetic Resonance and Magnetic Resonance Imaging

Studies of Lithium-Ion Batteries

by

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ABSTRACT

Magnetic Resonance (MR) and Magnetic Resonance Imaging (MRI) have become essential techniques to interrogate Lithium-Ion Batteries (LIBs). They are non-destructive and non-invasive techniques that can be employed to study internal processes in LIBs during *ex situ*, *in situ* and *in operando* experiments. The ability to interrogate different chemical species inside the battery, has proven to be essential to study important processes such as lithium intercalation, lithium plating and solid electrolyte interface formation. Improving MR hardware is vital for better investigation leading to performance optimization of LIBs.

The presence of conductive materials in the LIB, such as electrodes, and the thickness of these materials, poses challenges to the MR experiment. Signal attenuation during RF excitation and reception is one of the critical issues. In this thesis, Parallel-Plate Resonator (PPR) RF probes are presented and optimized for LIB studies. The PPR, with magnetic field **B**₁ parallel to the plates avoids RF attenuation due to the presence of the conductive electrodes. The **B**₁ homogeneity of the probe was improved with distributed capacitance in the corners of the probe.

The PPR was first designed and optimized for thin-film imaging. With improved homogeneity and a nominal resolution of 10 μ m, the PPR proved to be ideal for the study of flat cuboid samples. Bulk T_1 - T_2 relaxation correlation measurements of LIBs were introduced in this thesis. A PPR combined with a cartridge-like LIB cell was employed in the measurement. The T_1 - T_2 relaxation correlation detected lithium intercalated into graphite in addition to other Li species. The versatility of the PPR was also explored. The RF probe

was tested over a wide range of frequencies from 8 MHz to 500 MHz. The PPR performed well in all situations with no change in the quality factor after sample insertion. Finally, the PPR was combined with a variable field superconducting magnet to perform multinuclear studies on a LIB. This preliminary study showed good sensitivity to the three nuclei under study. These results open the door to the development of new methods for detection and quantification of MR data from LIBs.

DEDICATION

To my Parents, ZENAIDA and LUIS ROBERTO: For their endless love, support, and encouragement.

To my wife, BEATRIZ:

You have been my inspiration, my support.

To my teachers and professors:

Whose teachings and encouragement took me to this point.

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The journey I started a few years ago as a Ph.D candidate is coming to an end. This amazing journey was not an individual experience. Along the way, I met and shared the path with several great individuals. Without their encouragement, help, support, and advice, the work presented here would not be possible. To them, I would like to express here my deepest gratitude.

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To Prof. Bruce J. Balcom, I wish to express my sincerest gratitude and appreciation for giving me the opportunity of working under his supervision at the UNB MRI Centre. Without his guidance and unwavering support, none of the work presented herein would have been possible. He was always interested in my progress and patiently read all my drafts and provided me with inspiring questions and new ideas to improve my research and papers. With his immense knowledge, he has been an inspiration to me and other members of the MRI group. His passion for seeking new insight and ways to comprehend the reality around us never fades, especially regarding Magnetic Resonance. I also would like to thank him for being always attentive to my family well being and mine as well.

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List of Symbols, Nomenclature or Abbreviations

| \mathbf{B}_0 | Static magnetic field, magnetic flux density |
|----------------|--|
| \mathbf{B}_1 | Radiofrequency magnetic field |
| CPMG | Carr-Purcell-Meiboom-Gill |
| DEC | Diethyl carbonate |
| DMC | Dimethyl carbonate |
| DHK | Double half k-space |
| EC | Ethylene carbonate |
| ESL | Equivalent Series Inductance |
| ESR | Equivalent Series Resistance |
| FID | Free Induction Decay |
| FOV | Field of View |
| G_x | Magnetic field gradient strength along x direction |
| G_y | Magnetic field gradient strength along y direction |
| G_z | Magnetic field gradient strength along z direction |
| Q | Quality Factor |
| LIB | Lithium-Ion Battery |
| MR | Magnetic Resonance |
| MRI | Magnetic Resonance Imaging |
| PCB | Printed circuit board |

| PEM | Polymer electrolyte membrane |
|---------|--|
| PPR | Parallel-Plate Resonator |
| RF | Radiofrequency |
| ROI | region of interest |
| SEI | Solid electrolyte interface |
| SNR | Signal-to-noise ratio |
| SPRITE | Single Point Ramped Imaging with T_1 Enhancement |
| T_1 | Spin-lattice relaxation time constant |
| T_2 | Spin-spin relaxation time constant |
| T_2^* | Effective spin-spin relaxation time constant |
| TE | Echo Time |
| TEM | Transverse electromagnetic |
| TR | Repetition Time |
| SE | Spin Echo |
| SPI | Single Point Imaging |
| Ω | Ohm |

Chapter 1

Introduction

1.1 Research motivation and objectives

The ever increasing demand for Electric Vehicles (EV) [1] and the global surge in electrochemical energy storage [2] are driving research into Lithium-Ion Battery (LIB) performance optimization [3]. Performance optimization of LIBs relies on the improvement of existing battery materials (anodes, cathodes, electrolytes) [4], a clear understanding of their interaction [5] and a better assessment of the dynamic processes within the LIB [6]. Better characterization techniques, capable of detecting and quantifying these interactions are essential.

Magnetic Resonance (MR) and Magnetic Resonance Imaging (MRI) have proven to be excellent tools to gain insight into a range of important processes inside LIBs [7–9] and other electrochemical devices [10]. The ability of MR/MRI for non-destructive testing [11] and their ability to interrogate different nuclei of the sample under study [12, 13] has widened their application to LIB studies.

However, there are still inherent features of LIBs that preclude the use of MR to its full potential. The conductive electrodes present in the Li-ion cell limit RF excitation and MR signal reception [14], making it difficult to design a RF probe with high sensitivity and good homogeneity for LIB studies. Limited RF penetration also precludes the use of realistic LIB geometries. The small separation between the electrodes reduces the sample volume and thus experiment sensitivity, leading to studies at higher static magnetic fields. The design of RF probes capable of accommodating larger realistic LIBs, with high magnetic field homogeneity and high sensitivity while avoiding RF attenuation is essential for efficient

interrogation of LIB structures.

This thesis focuses on the design and application of Parallel-Plate Resonator (PPR) RF probes for LIB studies. Previous work at UNB showed that the PPR RF probe was a good choice for MR studies of fuel cells [10]. With the B_1 magnetic field parallel to the electrodes, avoiding RF attenuation, and with a geometry that can naturally accommodate a flat sample, the PPR is an ideal choice for LIB studies. However, due to its inhomogeneous B_1 magnetic field it has not previously been employed for LIB studies.

For this thesis we proposed four objectives.

First, to design and optimize a PPR at 100 MHz for ¹H thin film imaging (Chapter 3). The RF probe was optimized to have maximum \mathbf{B}_1 magnetic field and was tested for sensitivity.

Second, based on the results presented in Chapter 3, a similar PPR was optimized for ⁷Li studies at 38 MHz (Chapter 4). Custom-built Li-Ion cells, both uncharged and charged were tested. Lithium intercalated into graphite was expected to be observed.

Third, to test the range of applicability of the PPR (Chapter 5). Different sizes of PPR was tested at different resonance frequencies from 8 to 500 MHz.

Fourth, to test the PPR for multinuclear MR/MRI studies of LIBs (Chapter 6).

1.2 Thesis outline

The thesis is organized as follows:

Chapter 1 provides an introduction as well as an outline of the thesis work.

Chapter 2 establishes the background information relevant to this thesis. The chapter is divided into three sections. The first section presents a brief introduction to the LIB.

The main components of LIBs are described and their influence on the MR resonance experiment is outlined. The second section introduces relevant MR/MRI background to better understand the content of this thesis. The emphasis of this section is placed on the RF probe features and their importance for RF excitation and MR signal acquisition. The last section is devoted to RF probes for LIB studies. The main types of RF probes for LIB studies are described as well as the challenges presented in their design and construction.

Chapter 3 presents the Parallel-Plate Resonator RF probe for high resolution imaging in the direction perpendicular to the electrodes. The PPR was optimized for strength and uniformity of the B_1 magnetic field through simulation. The chapter is largely based on a paper published in the journal *Concepts in Magnetic Resonance Part A* [15]. The author of the thesis performed the simulations, experiments, and data analysis of the corresponding chapter. The experiments were designed with the assistance of Prof. Bruce J. Balcom and Dr. Bryce MacMillan. The manuscript was written by the author of the thesis with the assistance of Prof. Bruce J. Balcom, Dr. Bryce MacMillan and Prof. Gillian R. Goward. Dr. Bryce MacMillan assisted with the experiments.

Chapter 4 introduces the Parallel-Plate Resonator RF probe for LIB studies. The probe was employed along with a new removable cartridge-like electrochemical cell. For the first time, T_1 - T_2 relaxation correlation experiments were performed in a Lithium-Ion cell. This chapter is largely based on an article published in the *Journal of Magnetic Resonance* [16]. The author of the thesis performed the experiments, data analysis and simulations presented in this chapter. The experiments were designed with the assistance of Prof. Bruce J. Balcom. The manuscript was written by the author of the thesis with the assistance of Prof. Bruce J. Balcom, Prof. Gillian R. Goward, Prof. C. Adam Dyker, Dr. Bryce MacMillan, Dr. Sergey Krachkovskiy and Dr. Kevin J. Sanders. Dr. Fahad Alkhayri, assisted with the preparation and assembly of the Lithium-Ion cells Chapter 5 explores the use of the Parallel-Plate Resonator RF probe for the study of thin cuboid samples over a wide range of frequencies, from tens to hundreds of MHz. This chapter emphasizes the versatility of the PPR for MR experiments. Both horizontal and vertical bore magnet systems were employed in these studies. The chapter is largely based on a paper submitted for publication to the journal *Magnetic Resonance Letters*. The manuscript was written by the author of the thesis with the assistance of Prof. Bruce J. Balcom, Dr. Kevin J. Sanders and Prof. Gillian R. Goward. Prof. Bruce J. Balcom, assisted with the experimental design. Dr. Kevin J. Sanders also assisted with the experiments and data analysis.

Chapter 6 describes a multinuclear MR/MRI study of LIBs. This chapter is a preliminary study which lays a path for further development. The author performed the data analysis and wrote the first draft of the corresponding study. Prof. Bruce J. Balcom assisted with the experimental design and with writing the reports which are the basis of the chapter. Dr. Florin Marica assisted with operating the variable field magnet, setting the optimal parameters, and analysing MR/MRI data. Dr. Kevin J. Sanders, Prof. C. Adam Dyker and Prof. Gillian R. Goward also assisted in the experimental design. Md Al Raihan assisted with the preparation and assembly of the Lithium-Ion cells.

Chapter 7 concludes and summarizes the main contributions of the thesis, and provides recommendations for future work.

This thesis is written in the form of chapters as papers. The content has been structured so that successive topics build on each other and flow naturally between successive chapters. The format of the references in all the chapters have been standardized. They all follow Elsevier's reference style format for the *Journal of Magnetic Resonance*. Note that British spelling of English has been employed throughout the thesis. Consequently, all the Chapters have had minor spell changes.

References

- E. M. Szumska, R. S. Jurecki, Parameters influencing on electric vehicle range, Energies 14 (2021) 4821–4843. doi:10.3390/en14164821.
- [2] J. B. Goodenough, Electrochemical energy storage in a sustainable modern society, Energy and Environmental Science 7 (2014) 14–18. doi:10.1039/c3ee42613k.
- [3] S. M. Arif, T. T. Lie, B. C. Seet, S. Ayyadi, K. Jensen, Review of electric vehicle technologies, charging methods, standards and optimization techniques, Electronics (Switzerland) 10 (2021) 1910–1932. doi:10.3390/electronics10161910.
- [4] M. Tang, V. Sarou-Kanian, P. Melin, J. B. Leriche, M. Ménétrier, J. M. Tarascon, M. Deschamps, E. Salager, Following lithiation fronts in paramagnetic electrodes with *in situ* magnetic resonance spectroscopic imaging, Nature Communications 7 (2016) 13284–13292. doi:10.1038/ncomms13284.
- [5] S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, D. L. Wood, The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling, Carbon 105 (2016) 52–76. doi:10.1016/j. carbon.2016.04.008.
- [6] M. B. Pinson, M. Z. Bazant, Theory of SEI formation in rechargeable batteries: Capacity fade, accelerated aging and lifetime prediction, Journal of The Electrochemical Society 160 (2013) A243–A250. doi:10.1149/2.044302jes.
- [7] A. Ilott, M. Mohammadi, H. Chang, C. Grey, A. Jerschow, Real-time 3D imaging of microstructure growth in battery cells using indirect MRI, Proceedings of the National Academy of Sciences 113 (2016) 10779–10784. doi:10.1073/pnas.1607903113.

- [8] S. P. Rangarajan, Y. Barsukov, P. P. Mukherjee, In operando signature and quantification of lithium plating, Journal of Materials Chemistry A 7 (2019) 20683–20695. doi:10.1039/C9TA07314K.
- [9] K. Märker, C. Xu, C. P. Grey, Operando NMR of NMC811/graphite lithium-ion batteries: Structure, dynamics, and lithium metal deposition, Journal of the American Chemical Society 142 (2020) 17447–17456. doi:10.1021/jacs.0c06727.
- [10] Z. Zhang, J. Martin, J. Wu, H. Wang, K. Promislow, B. J. Balcom, Magnetic resonance imaging of water content across the Nafion membrane in an operational PEM fuel cell, Journal of Magnetic Resonance 193 (2008) 259–266. doi:10.1016/j. jmr.2008.05.005.
- [11] S. Benders, M. Mohammadi, C. A. Klug, A. Jerschow, Nuclear magnetic resonance spectroscopy of rechargeable pouch cell batteries: beating the skin depth by excitation and detection via the casing, Scientific Reports 10 (2020) 13781–13787. doi:10.1038/s41598-020-70505-0.
- [12] C. Wan, S. Xu, M. Y. Hu, R. Cao, J. Qian, Z. Qin, J. Liu, K. T. Mueller, J.-G. Zhang, J. Z. Hu, Multinuclear NMR study of the solid electrolyte interface formed in lithium metal batteries, ACS Applied Materials and Interfaces 9 (2017) 14741–14748. doi: 10.1021/acsami.6b15383.
- [13] B. M. Meyer, N. Leifer, S. Sakamoto, S. G. Greenbaum, C. P. Grey, High field multinuclear NMR investigation of the SEI layer in lithium rechargeable batteries, Electrochemical and Solid-State Letters 8 (2005) A145–A149. doi:10.1149/1.1854117.
- [14] A. J. Ilott, S. Chandrashekar, A. Klöckner, H. J. Chang, N. M. Trease, C. P. Grey, L. Greengard, A. Jerschow, Visualizing skin effects in conductors with MRI: ⁷Li MRI

experiments and calculations, Journal of Magnetic Resonance 245 (2014) 143–149. doi:10.1016/j.jmr.2014.06.013.

- [15] A. R. Aguilera, B. MacMillan, G. R. Goward, B. J. Balcom, Optimization of a parallel-plate RF probe for high resolution thin film imaging, Concepts in Magnetic Resonance Part A 47A (2018) e21465–e21470. doi:10.1002/cmr.a.21465.
- [16] A. R. Aguilera, B. MacMillan, S. Krachkovskiy, K. J. Sanders, F. Alkhayri, C. A. Dyker, G. R. Goward, B. J. Balcom, A parallel-plate RF probe and battery cartridge for ⁷Li ion battery studies, Journal of Magnetic Resonance 325 (2021) 106943– 106950. doi:10.1016/j.jmr.2021.106943.

Chapter 2

Magnetic Resonance and Magnetic Resonance Imaging in Lithium-Ion Batteries Research

This thesis is devoted to the design, optimization, and application of the Parallel-Plate Resonator (PPR) RF probe for MR/MRI studies of Lithium-Ion Batteries (LIBs). This chapter is divided into three sections to provide relevant background information for a better understanding of the work presented in the thesis.

The first section presents a brief overview of the LIB. The general working principle of the LIB is established. Then, the main components of the LIB are discussed, emphasizing the possible challenges they may introduce in the MR experiment. This is followed by a brief description of important processes such as lithium intercalation, solid electrolyte interface, and lithium plating, which can have a significant impact on LIB performance. A more in depth description and analysis of LIBs can be found in many reference books [1, 2].

The second section introduces relevant MR and MRI background that is fundamental for this thesis. Due to the presence of several metallic components in the LIBs, concepts such as eddy currents and magnetic susceptibility are also described. Additionally, an overview of RF probe design and characterization is presented. Basic MR theory and RF probe design, which is well described in many reference books is not repeated here. For general MR theory, several books can be consulted, for both quantum and classical descriptions [3–5]. For general design of RF probes, several good reference books have also been written [6, 7].

The final section discusses the main types of RF probes for MR and MRI studies of LIBs. Their limitations and the challenges in their design and construction are discussed.

The chapter finishes with a short conclusion where the challenges faced in MR studies of LIBs are summarized. We also state the reasons why the development of an alternative RF probe design is required for better interrogation of LIBs.

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2.1 Lithium-Ion Batteries

2.1.1 General Overview

A Lithium-Ion Battery (LIB) is a combination of one or multiple electrochemical cells, that utilize lithium ions as the main component of their electrochemistry. The simplest LIB consists of four main parts, cathode, anode, separator, and electrolyte, as shown in Fig. 2.1. Generally, the cathode is coated on an aluminium foil (aluminium current collector) and the anode is coated on a copper foil (copper current collector). Both the anode and the cathode can be coated either on one side or on both sides.

During the charging (green arrows) and discharging (red arrows) cycles of a LIB, Li ions move back and forth between the cathode and the anode converting electrical energy into chemical energy and *vice versa*. During charging cycles of a LIB, Li atoms in the cathode are ionized and separated from their electrons. This is achieved by the application of voltage across the current collectors attached to the electrodes. Then, the Li ions move from the cathode and pass through the separator, soaked with electrolyte, until they reach the anode where they are again united with the electrons. During discharging cycles, the reverse process occurs. A negative voltage is applied to the current collectors. The basic principle for reversible lithium intercalation was first established by Steele in 1973 [8].

The LIB can be cycled using two different schemes, constant current (CC) and constant

2.1. Lithium-Ion Batteries



Fig. 2.1. Schematic of a simple lithium-ion cell. Each lithium-ion cell consists of an anode and a cathode, electrically separated by a porous separator. The separator is soaked in an electrolyte containing dissociated lithium salts, which enables the transfer of lithium ions between the two electrodes

voltage (CV). They can be used independently or they can be combined for a more efficient cycling of the LIB. In the CV mode, the cycler (power supply) behaves as a voltage source, it holds the voltage constant across the current collectors of the LIB while the current varies. In the CC protocol, the cycler varies the voltage across the current collectors of the LIB while it holds the current constant.

In the CV mode, the charging of the LIB is faster. However, the current may be excessive which can lead to excessive heating of the LIB. CC mode is more efficient and generally employed on the first charging stage of the LIB. A two-stage charging protocol CC-CV, is generally employed. The CC mode is employed until the cell reaches its preset voltage. Then the cycler switches to CV mode until the current across the current collector is 3 - 5 % of the initial charging current. In this thesis only the CC mode was employed for Li-Ion cell charging

LIBs have become one of the most widely used types of batteries. With the advantages

of high energy density, long life cycle, and low self-discharge rate, LIBs are the main choice for electric vehicles [9] and energy storage for intermittent renewable energy [10]. However, despite their efficiency and reliability, there are still challenges to overcome to improve and optimize the performance of the LIB.

Improving LIB performance requires new methods and techniques to detect and quantify battery component interaction. MR and MRI have become essential techniques to understand and quantify the interaction between different part of the battery [11, 12]. With MR it is possible to perform nondestructive testing of LIBs during *in-situ*, *ex-situ*, and *in operando* experiments [13–17]. MR is also capable of providing information on different nuclei in the cell, giving it a notable advantage over other methods to interrogate LIBs [18, 19].

2.1.2 Cathodes

The cathode is the most important component of the LIB [16]. The capacity, energy density and working voltage of the battery depend heavily on the cathode capacity. Cathodes are generally layered transition metal (TM) oxides, coated on aluminium foil (aluminium current collector) (see Fig. 2.1). They act as a reservoir for the Li ions in the cell. During the charging process, Li ions move from the cathode and insert in the anode (generally graphite). Selecting the appropriate cathode material depends on factors, such as, capacity, cell voltage, power, life cycle, etc.

Several cathode materials have been proposed to achieve high energy density, reduce the cost of the LIB and improve their safety. The layered oxide $\text{LiNi}_x \text{Mn}_y \text{Co}_{1-x-y} \text{O}_2$ (0 $\leq x, y \leq 1, x + y \leq 1$) (NMC) has proven to be one of the best candidates [20]. LIBs containing the layered oxide NMC are typically high energy cells due to the material high specific capacity (>200 mAhg⁻¹). Aiken *et al.* [20] have proven that $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532) can be a superior alternative to other cathodes electrodes, such as, LiFePO₄. In this thesis, all cells assembled utilize NMC532 as the cathode [20-22].

MR has proven to be a great tool to understand the structure and function of LIB cathodes [16]. However, due to the paramagnetic nature of the cathode materials, the T_2 relaxation lifetime is very short. This can be challenging for the MR experiment. RF probes with short deadtimes, brief RF pulses, shorter echo times and larger magnetic field gradients are necessary to successfully interrogate the cathode material. Also, the quadrupolar coupling in these solid materials containing Li ions is not averaged out by rapid molecular tumbling, as in liquids, thus causing large chemical shifts. This makes the MR experiments even more difficult. For a more detailed description of MR of paramagnetic cathode materials see [12, 16].

Due to the very short MR signal lifetime of the paramagnetic cathodes, no signal from the cathodes is expected to be observed in any of the battery experiments performed in this thesis.

2.1.3 Anodes

The anode in the LIB is a layered material, coated on copper foil (copper current collector). The principal function of the anode is to host Li ions during cell charging. A good anode should have good porosity and high conductivity for the insertion of the Li ions. Moreover, it should have good durability, low cost and be light weight [23].

Graphite is by far the most widely use anode material in LIBs [23]. It has good porosity, good electrical conductivity and can deliver a specific capacity of 375 mAhg⁻¹, without significant volume change [24]. Surface reactions of the graphite with the liquid electrolytes is a key factor in the performance of the battery. During these reactions, a stable protective layer, conductive to Li ions but electronically insulating is formed. This protective

layer, the solid electrolyte interface (SEI), is critical to ensure high coulombic efficiency and safety for the battery [25, 26]. However, if the formation of the SEI is nonuniform, it can result in nonuniform lithium deposition and formation of lithium dendrites [26, 27]. This can be detrimental to the performance of the battery, and it can be a safety hazard [27].

Pristine graphite is a diamagnetic material. However, when Li ions are intercalating into graphite, a transition from diamagnetic to paramagnetic gradually takes place [28]. The magnetic properties of the graphite can make the detection and quantification of the different phases in lithium-graphite intercalated compounds challenging. The magnetic transition from diamagnetic to paramagnetic that gradually takes place in the graphite emphasizes the need for better and faster *in operando* techniques to capture and quantify these transient processes [29].

Another important aspect of graphite is its conductivity. Graphite is considered a semimetal, it is a conductor in the direction parallel to the graphite layers and an insulator in the direction perpendicular to the graphite layers [30, 31]. For MR experiments, selecting the direction perpendicular to the layers is advantageous to maximize RF penetration (see Section 2.2.6). Even if the RF excitation is perpendicular to the graphite layers, full RF penetration into the graphite cannot be guaranteed. Excellent work evaluating the orientationdependence of RF penetration into metal sheets has been presented by Ilott *et al.* [32] and Vashaee *et al.* [33]. They proved that the maximum penetration of the RF excitation happens when the metal strip is parallel to the RF magnetic field orientation. In Appendix A, an electromagnetic simulation is reported to better understand RF penetration into graphite.

The thickness of the graphite electrode plays an important role in maximizing the energy density and reducing the cost of the LIB. The anode is generally 60 - 65 μ m thick, but thicker graphite anodes are desirable. However, thicker graphite anodes lead to underutilization of the capacity due to cell polarization [34]. Thicker graphite anodes are advantageous for the MR experiment, as long as full RF penetration is achieved. The sample volume will increase, thus increasing experiment sensitivity and reducing the experiment time.

The graphite anode will be the most important battery component under study in this thesis (see chapter 4). Detection and quantification of the Li intercalated into graphite is an essential step for future experiments involving more complex processes such as the SEI formation and lithium plating detection.

2.1.4 Non-aqueous Liquid Electrolytes

The electrolyte is an indispensable component of every LIB [35]. It serves as a transport medium for the Li ions, as they transit between the electrodes. Selecting the ideal electrolyte is key for battery performance. The vast majority of electrolytes for LIB are non-aqueous electrolytes [35]. These electrolytes can be classified into three different groups: liquid, solid, and polymer. In this thesis only non-aqueous liquid electrolytes are employed.

Electrolytes must meet some minimum requirements to be employed in LIBs. They should be good ionic conductors to permit an easy flow of Li ions between the electrodes. Higher ionic conductivity of the electrolyte reduces the rate of self-discharge of the cell as well as increasing its life cycle. Good electrolytes also need to have a wide electro-chemical stability window to avoid electrolyte degradation during cell operation. Lastly, the electrolytes must show great stability against the electrode surfaces.

Non-aqueous liquid electrolytes consist of a lithium salt dissolved in a mixture of organic solvents. Choosing the right ratio between lithium salts and organic solvents is very important. The ionic conductivity and the stability window of the electrolyte depend on their concentration and the type of solvent. A compromise between viscosity and concentration of the charge carriers is needed it to achieve the best conductivity and electrochemical properties of the electrolyte.

Most commercial LIBs employ lithium hexafluorophosphate (LiPF₆) as the lithium salt [36]. LiPF₆ shows high ionic conductivity, good electrochemical stability and protects the aluminium current collector against corrosion when dissolved in organic solvents [37]. However, its thermal stability at high temperatures is poor [38]. Many other lithium salts have been considered to improve LIB performance [37, 39]. They include lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), LiC₂F₆NO₄S₂, [40] which is consider a safer alternative to commonly used LiPF₆ [41]. LiTFSI is highly soluble in the commonly used organic solvents but severely corrodes aluminium [42].

All lithium cells employed in this thesis either utilize LiPF_6 or LiTFSI salts for their electrolytes. They are always mixed with two organic solvents in a 1:1 volume ratio. In all cases 1M salt concentration electrolyte was employed.

Organic solvents also play an important role in the optimum performance of the LIB. Ethylene carbonate (EC), $(CH_2O)_2CO$, based liquid electrolytes are widely employed in LIBs because the decomposition compounds of EC form a good protective layer on the surface of the anode, in the early stages of the first reduction. This layer prevents excessive Li ion consumption during the intercalation process. However, pure EC-based electrolytes are not employed due to high viscosity. Mixtures of EC with low viscosity solvents such as dimethyl carbonate (DMC), $OC(OCH_3)_2$, and diethyl carbonate (DEC), $OC(OCH_2CH_3)_2$, are commonly employed.

Liquid electrolytes are flammable, often toxic, and with relatively low ionic conductivity. Flammability of the liquid electrolyte is one of the major safety hazard of LIBs. To avoid this safety hazard, researcher are looking for suitable solid electrolytes [43, 44]. The relatively low conductivity of the liquid electrolyte causes the battery to have a high internal resistance which is detrimental for the optimum performance of the battery. This problem
is minimized by reducing the thickness of the electrolyte layer, so that the Li ions travel a shorter distance between the electrodes [45]. A smaller separation between the electrodes in the cell means a thinner separator, which will also play an important role in the battery performance (see section 2.1.5).

Liquid electrolytes contain many MR active nuclei (See Table 2.1). Therefore, MR techniques are a natural choice to interrogate liquid electrolytes [46, 47]. Electrolyte degradation and SEI formation during electrochemical operation are two of the most active areas of LIBs research [18, 47–49]. Liquid electrolytes are facile to interrogate. However, for a relatively small amount of electrolyte, less than 500 μ L, experiments such as, T_1 - T_2 relaxation correlation, 2D images and high resolution 1D images, may be time consuming. This is especially true for nuclei with low gyromagnetic ratios and/or low natural abundance (see Table 2.1). Another shortcoming of non-aqueous liquid electrolytes is their relatively long relaxation times T_1 and T_2 . Long relaxation times T_1 lead to a longer repetition time TR (TR = ~ 5 T_1), thus increasing the experiment time. On the other hand, long relaxation time T_2 , may lead to an increase in the number of echoes for echo-based MR experiments. This may be an issue in MR experiments of LIBs where components with short and long relaxation lifetimes coexist. The solution to this problem is the employment of variable echo time sequences (see section 2.2.4).

Some MR active nuclei in the electrolyte solution are quadrupolar. However, due to the fast isotropic tumbling of the molecules in the electrolyte solution, the impact of the quadrupolar interaction is significantly reduced.

2.1.5 Separator

LIB separators are essential to the function and performance of batteries. The separator is a thin, porous layer that electronically isolates the cathode from anode avoiding cell short circuit. The separator also allows the Li ions to move freely between electrodes.

Optimum separators for LIB have to meet a large list of requirements [50, 51]. Some essential requirements of the separator are related to thickness, porosity, and pore size. The thickness of the separator adversely affects the performance of the LIB [45]. A thick separator leads to a large separation between the electrodes, thus increasing the path length for Li ions transiting between the electrodes, increasing the resistance of the cell. This will also limit the current during cell charging and increase the self-discharge rate of the cell once it has been charged. Thicker separators will also lead to a reduction of the energy density of the LIB. Most commercial separators for LIBs have a thickness less than 50 μ m, with a typical thickness of 25 μ m (e.g. Celgard 2325 separator). Thinner separators are also employed for higher energy density batteries [50].

Porosity is another crucial property of separators because the absorption of the liquid electrolyte depends on their porosity. Typical porosity values for separators have been reported between 40%-60% [52, 53]. Besides having an optimal porosity for lithium ion transport, separators need to have a small pore size and a homogeneous pore size distribution. The average pore size for separators is below 1 μ m [50, 53], to maintain electrical insulation and ensure homogeneous cell charging.

All cells assembled for this thesis have one or more layers of Whatman[®] GF/F paper filter as the separator. This glass fibre (GF) separator has a thickness of ~ 250 μ m. These are much thicker than commercial separators and have not been adopted for commercial applications because their thickness reduces the battery energy density. However, Whatman separators have a faster wetting time than other commercial separators. This is a result of a larger porosity [54].

In our cell, the Whatman separator will dictate the separation between the electrodes. Also, we expect all the electrolyte to be absorbed by the paper filter. So, we do not expect a significant quantity of free electrolyte. Relaxation times T_1 and T_2 will depend on the pore size distribution of the paper filter. Thus different Li population may be found in the paper filter (see Chapters 4 and 6)

2.1.6 Lithium Intercalation

Lithium intercalation is the process of the Li ions intercalating into the anode host structure. This is a complex process that is essential for LIBs [55]. In the case of the graphite anode, intercalation mechanisms have been well described [29, 55]. Four different stages of the lithium intercalation have been detailed. As, explained in Section 2.1.3, these phase changes produces a transition from diamagnetic to paramagnetic of the graphite electrode.

Lithium intercalation species have been widely studied by MR [24, 29, 56, 57]. However, a detailed mechanism of the lithiation and the transition between the stages remains to be elucidated [55]. Understanding lithium intercalation is essential in order to employ thicker anode materials.

2.1.7 Solid Electrolyte Interface

As discussed in Section 2.1.3, the interaction between the anode and the electrolyte is vital for the LIB performance. During the first charging cycle, a protective layer called the SEI is formed. The SEI is composed of multiple inorganic and organic products from electrolyte decomposition [25, 26] .The stability and thickness of the SEI depends on the type of anode and the electrolyte formulation. The thickness of the SEI in the graphite electrode has been reported to be 20-50 nm [25]. The employment of the organic solvent EC, as an electrolyte base, has proven to lead to the formation of a uniform SEI.

The relative minimal thickness of the SEI limits the quantification and characterization of the different components of the SEI. This limits understanding the dynamics of the SEI [58].

Multinuclear MR has proven to be a valuable tool to study the composition of the SEI [18, 19]. However, the complexity of the SEI makes difficult the quantification of the different species in the SEI during *in situ* and *in operando* LIB studies. In this thesis, the signal from the SEI was not detected.

2.1.8 Lithium Plating and Dendrite Formation

Lithium plating is detrimental for the performance of the battery. It can cause capacity loss in the cell due to irreversible consumption of Li ions [59]. Lithium plating can also trigger dendrite formation [27]. Dendrite formation poses safety hazards for the LIB. If dendrites grow large enough, they may puncture the separator causing a cell short circuit.

Lithium plating is the formation and deposition of metallic lithium on the surface of the graphite electrode. Research into lithium plating and dendrite formation is an active field of study [60]. Understanding the behaviour of lithium plating is crucial for optimizing charging protocols. So far, two lithium plating criteria have been suggested, plating potential and concentration saturation of Li ions [61].

MR has been a valuable tool for detection and quantification of lithium plating [14, 62, 63] and dendrite formation [27]. However, in this thesis neither lithium plating nor dendrites were observed because all cells were cycled at low charging rates to avoid lithium plating.

2.2 Magnetic Resonance Background

Since 1946 [64, 65], MR techniques have been continually evolving and improving, widening their range of applications. MR and MRI are commonly employed in clinical imaging, material science (organic and inorganic), food science, as well as in the study of electrochemical devices. The versatility of MR is based on the following advantages: 1) ability to perform non-destructive testing, 2) capability of multinuclear studies, and 3) ability to provide spatially resolved information. In addition, the technological improvement of the equipment employed in MR experiments has helped to widen even more the application of MR.

2.2.1 Magnetic Susceptibility and Bulk Magnetization

The central idea of the MR phenomenon is; when a large number of magnetic moments (the sample) are placed in a static magnetic field, \mathbf{B}_0 (in the +z direction), the magnetic moments will tend to align with the applied \mathbf{B}_0 . Some magnetic moments will align antiparallel to \mathbf{B}_0 and a slightly larger quantity will tend to align parallel to \mathbf{B}_0 . This alignment of the magnetic moments will produce a net macroscopic magnetization, M_0 . The magnitude of the magnetization will be proportional to the static magnetic field strength \mathbf{B}_0 and the magnetic susceptibility χ of the material,

$$M_0 = \chi B_0 \tag{2.1}$$

The magnetic susceptibility is a physical quantity that measure the degree to which a material can be magnetized in a external magnetic field and can be expressed as,

$$\chi = \frac{N_s \gamma^2 \hbar^2 I(I+1)}{3k_B T_s} \tag{2.2}$$

where *I* is the spin quantum number, γ is the gyromagnetic ratio, N_s is the number of spins at resonance per unit volume, k_B is Boltzmann's constant, \hbar is the Planck's constant divided by 2π , and T_s is the sample temperature.

All materials can be classified into three different groups depending on the value of their magnetic susceptibility:

- diamagnetic materials: $-1 < \chi \leq 0$,
- paramagnetic materials: $0 < \chi \leq 1$,
- ferromagnetic materials: $\chi > 1$

The first two groups of materials are relevant in the development of this thesis. The cathodes and anodes in the LIB assembly are paramagnetic and diamagnetic materials respectively.

The final expression for the net magnetization is given by,

$$M_0 = \frac{N_s \gamma^2 \hbar^2 I (I+1) B_0}{3k_B T_S}$$
(2.3)

The net magnetization will be parallel to the direction of the static magnetic field and will precess with a Larmor frequency which is given by,

$$\omega_0 = -\gamma B_0 \tag{2.4}$$

The Larmor frequency will depend on static magnetic field \mathbf{B}_0 and the gyromagnetic ratio of the nuclei, see Table 2.1.

The aim of any MR experiment is to detect and quantify the net macroscopic magnetization with different methods and/or under different conditions, to get relevant information about the sample under study. However, under this established equilibrium the magnetization cannot be detected. The magnetization has to be manipulated, rotated away from the

| Isotope | Ι | N.A (%) | $Q.M (fm^2)$ | F.R (%) | γ (MHz T ⁻¹) |
|------------------|---------------|---------|--------------|---------|---------------------------------|
| $^{1}\mathrm{H}$ | $\frac{1}{2}$ | 99.99 | - | 100.00 | 42.577 |
| ¹³ C | $\frac{1}{2}$ | 1.07 | - | 25.25 | 10.7084 |
| ¹⁹ F | $\frac{1}{2}$ | 100 | - | 94.09 | 40.078 |
| ³¹ P | $\frac{1}{2}$ | 100 | - | 40.48 | 17.235 |
| ⁶ Li | 1 | 7.59 | - 0.081 | 14.72 | 6.265 |
| ⁷ Li | $\frac{3}{2}$ | 92.41 | - 4.01 | 38.86 | 16.546 |
| ¹⁷ O | $\frac{5}{2}$ | 0.04 | - 2.55 | 13.56 | -5.772 |
| ²⁷ Al | $\frac{5}{2}$ | 100 | 14.66 | 26.06 | 11.103 |
| | | | | | |

Table 2.1: MR Properties of Selected Isotopes

I, spin quantum number; N.A, natural abundance; Q.M, quadrupole moment in units of $fm^2 = 10^{-30} m^2$; F.R, frequency relative to hydrogen; γ , gyromagnetic ratio

equilibrium position on the z-axis.

2.2.2 MR signal detection

The basic underlying principles of the MR phenomenon can be explained using several different approaches, such as, Matrix Density, Product Operator, Quantum Mechanics and Classical Mechanics. All approaches are consistent, within their degree of approximation. However, in this thesis the classical approach is preferred. It has been shown that the net macroscopic magnetization can be treated according to simple laws of classical mechanics [65].

As mentioned in the previous section, the sample magnetization must be displaced from equilibrium in order to be detected. This is accomplished by employing a time-varying RF magnetic field \mathbf{B}_1 (RF excitation), perpendicular to the main static magnetic field \mathbf{B}_0 . The \mathbf{B}_1 magnetic field, also oscillating at the Larmor frequency, will force the sample magnetization to rotate off the z-axis. The nutation or flip angle α of the magnetization, for on-resonance RF excitation, is given by the following equation,

$$\alpha = -\int_0^t \gamma \mathbf{B}_1(t) \, dt \tag{2.5}$$

The magnetization can be decomposed in longitudinal (M_z) and transverse (M_{xy}) components. However, only the transverse magnetization can be detected. At equilibrium, where $M_z = M_0$ and $M_{xy} = 0$, no MR signal can be detected. After the application of a flip angle α , a non-zero transverse magnetization exists $(M_z = M_0 \cos(\alpha), M_{xy} = M_0 \sin(\alpha))$ and can be detected after the action of the RF magnetic field **B**₁ is removed.

The time-varying magnetic field produced by the precession of the transverse magnetization will induce an electromotive force (*emf*), ξ , in the RF probe (see section 2.2.5). The *emf* induced by the transient motion of the M_{xy} can be obtained using the Reciprocity Principle [66]. The MR signal induced in the RF probe will be,

$$\xi = -\int_{sample} \frac{\partial}{\partial t} \left\{ \mathbf{B}_1 \cdot \mathbf{M}_0 \right\} \, dV_s \tag{2.6}$$

If the sample magnetization \mathbf{M}_0 is tilted an angle α away from the equilibrium position and \mathbf{B}_1 is considered homogeneous in the whole sample volume, the induced voltage in the RF probe is given by,

$$\xi = \omega_0 (B_1)_{xy} M_0 \sin(\alpha) V_s \cos(\omega_0 t)$$
(2.7)

where $(B_1)_{xy}$ is the transversal component of the **B**₁ magnetic field, perpendicular to **B**₀. The induced voltage in the RF probe is maximum when in the equation 2.7, the flip angle $\alpha = 90^{\circ}$ where $M_z = 0$ and $M_{xy} = M_0$.

Substituting equations 2.4 and 2.3 into 2.7, shows that the voltage induced in the RF probe is proportional to \mathbf{B}_0^2 . However, the final magnitude of the MR signal depends on the quality factor of the RF probe (see section 2.2.5).

2.2.3 Relaxation mechanisms

After RF excitation, the magnetization will return to equilibrium. The longitudinal magnetization M_z , will recover until all the magnetization is parallel to **B**₀. On the other hand, the transverse magnetization M_{xy} , will decay to zero. The rate of regrowth of M_z and the rate of decay of M_{xy} , depend on the properties of the sample. The return to equilibrium of the magnetization components is described by the Bloch equations [65],

$$M_{xy}(t) = M_0 \sin(\alpha) \exp\left(-i(\omega_0 t + \phi)\right) \exp\left(-\frac{t}{T_2}\right)$$
(2.8)

$$M_z(t) = M_0 \cos(\alpha) \, \exp\left(-\frac{t}{T_1}\right) + M_0 \left(1 - \exp\left(-\frac{t}{T_1}\right)\right) \tag{2.9}$$

The relaxation time T_1 , is the time required for the longitudinal magnetization to reach 63 % of its final value. T_1 is known as the spin-lattice relaxation time. The relaxation time T_1 depends on the the molecular environment and its dynamics. The translational, vibrational, and rotational motion of the nuclei will influence the relaxation time T_1 .

 T_2 describes the rate at which the spins lose phase coherence and is known as the spin-spin relaxation time. T_2 is the time for the transverse magnetization irreversibly decay to e^{-1} of the initial value. The relaxation time T_2 will be affected by the random tumbling of the molecules, perturbations of the magnetic field due to the magnetic dipoles, quadrupolar interactions (I > 1/2), as well as local inhomogeneities in the magnetic field.

When local inhomogeneities of the magnetic field are important, an effective transverse relaxation time, T_2^* , is often employed. The relation between T_2 and T_2^* is given as,

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B_0 \tag{2.10}$$

 T_2^* may be measured in a FID experiment, which is the simplest MR experiment possible.

Another important relaxation mechanism to consider is related to the quadrupolar interaction. In quadrupolar nuclei, multiple energy transitions are possible, therefore multiple relaxation components can be present. We will focus only in the quadrupolar interaction of the nuclei with spin 3/2. This is relevant because the most important nucleus interrogated in this thesis is ⁷Li, which has spin 3/2. In the particular case of nuclei with spin 3/2, the relaxation times are characterized by a slow and a fast relaxation process [67]

$$\frac{1}{T_{1,s}} = \left(\frac{e^2 q Q}{10}\right) \left(1 + \frac{\eta^2}{3}\right) \tau_c \left(\frac{1}{1 + \omega_0^2 \tau_c^2}\right)$$
(2.11)

$$\frac{1}{T_{1,f}} = \left(\frac{e^2 q Q}{10}\right) \left(1 + \frac{\eta^2}{3}\right) \tau_c \left(\frac{1}{1 + 4\omega_0^2 \tau_c^2}\right)$$
(2.12)

$$\frac{1}{T_{2,s}} = \left(\frac{e^2 q Q}{20}\right) \left(1 + \frac{\eta^2}{3}\right) \tau_c \left(\frac{1}{1 + \omega_0^2 \tau_c^2} + \frac{1}{1 + 4\omega_0^2 \tau_c^2}\right)$$
(2.13)

$$\frac{1}{T_{2,f}} = \left(\frac{e^2 q Q}{20}\right) \left(1 + \frac{\eta^2}{3}\right) \tau_c \left(1 + \frac{1}{1 + 4\omega_0^2 \tau_c^2}\right)$$
(2.14)

where τ_c is the correlation time and η is given by,

$$\eta = \frac{\frac{\partial V_{xx}}{\partial x^2} - \frac{\partial V_{yy}}{\partial y^2}}{\frac{\partial V_{zz}}{\partial z^2}}$$
(2.15)

where V is the electric potential of the molecule complex, eQ is the quadrupolar moment and eq is the field gradient.

For the ⁷Li electrolyte experiment, the quadrupolar interaction is greatly diminished due to the fast isotropic tumbling of the molecules. However, for the solid material containing ⁷Li the quadrupolar interaction has significant impact on the relaxation times T_1 and T_2 . There will be three possible energy transitions. The central transition, which is not affected by the first order quadrupolar moment, is more likely to be observed.

2.2.4 Pulse Sequences

Two types of MR pulse sequences were employed in this thesis. Pulse sequences were employed for bulk MR measurements of relaxation times T_2^* , T_2 and T_1 , and pulse sequences for MRI (DHK SE SPI and Spiral SPRITE). Pulse sequences for bulk MR experiments are all well described in most MR books. Thus, we will not describe these methods here, except for the T_2 measurement where modifications were introduced to optimize the experiment.

Bulk T_2 measurements are generally performed using a constant TE. However, when in the sample, short and long T_2 lifetimes are present, selecting a constant TE can be troublesome. If a short TE is selected, a very large number of echoes will be necessary to acquire the entire T_2 decay. This will increase the RF amplifier duty cycle. If a long TE is selected it will be impossible to detect the short T_2 lifetimes components.

In Chapter 4, to acquire both short and long T_2 lifetimes components of Li populations in LIBs, a CPMG sequence with a variable TE was employed [68]. The TE was changed following a sigmoidal variation expressed by equation 2.16.

$$TE_n = TE_{min} + \frac{TE_{max} - TE_{min}}{1 + \exp(-R \times (n - \frac{n_{max}}{2}))}$$
(2.16)

where *n* is the echo number, n_{max} the maximum echo number, TE_n is the echo time, TE_{min} the minimum echo time, TE_{max} the maximum echo time, and *R* is the rate of change of the echoes. *R* was chosen to be small, so that the first 200 echoes are equal to TE_{min} and the last 200 echoes are equal to TE_{max} , as shown in Fig. 2.2. The maximum echo number n_{max} , was selected in order to acquire at least $5 \times T_2$ of the CPMG decay.



Fig. 2.2. Sigmoidal echo time variation for detecting Li populations with short and long T_2 lifetime components in LIB

The TE_n curve was selected to be symmetric around the middle echo number $(n_{max}/2)$. However, the symmetry can be changed by choosing a transition point that is different from $n_{max}/2$. All MRI experiments were performed using pure phase encoding MRI pulse sequences. The k-space is mapped by changing the magnetic field gradient value, **G**, and keeping the encoding time, t_p constant (see equation 2.18). Pure phase encoding techniques are well known to be less affected by **B**₀ inhomogeneities and susceptibility variations than frequency encoding techniques. This leads to images with fewer artefacts.

Double half k-space (DHK) spin echo (SE) single point imaging (SPI) [69] for the 1D T_2 -weighted image was employed in Chapter 3. In this pulse sequence the use of two phase encoding gradients, of opposite polarity, permits a decreased encoding time, t_p . The reduction of the encoding time is of great importance because it reduces the TE by a factor of 2, which permits us to image samples with shorter relaxation times T_2 , and also to reduce the image acquisition time. Another advantage of the DHK SE SPI sequence, is the possibility of acquiring multiple T_2 -weighted images.

The signal at any point in k-space is given by

$$S(k_y) = \int \rho(y) \, \exp\left(-\frac{TE}{T_2}\right) \, \exp\left(-i2\pi k_y \cdot y\right) \, dy \tag{2.17}$$

$$k_y = \frac{\gamma}{2\pi} G y t_p \tag{2.18}$$

where G_y is the magnetic field gradient and t_p the encoding time. After Fourier transforming the acquired T_2 -weighted signal, the image intensity, $\rho(y)$, is given by

$$\rho(y) = \rho_0 \, \exp\left(-\frac{TE}{T_2(y)}\right) \tag{2.19}$$

Because the signal amplitude of the image is dictated by the signal at $k_y = 0$, the image will not suffer from attenuation due to diffusion.

The other phase encoding technique employed in thesis is Spiral-SPRITE [70, 71]. This

is a modification of the SPRITE pulse sequence that was introduced by Balcom *et al.* [72]. In Spiral-SPRITE the magnetic field gradients are sinusoidally changed through a set of discrete gradient steps [71]. The observed image intensity at any k-space location is given by

$$S = \rho_0 \, \exp\left(-\frac{t_p}{T_2^*}\right) \sin(\alpha) \tag{2.20}$$

where ρ_0 is the local proton density, α is the flip angle and t_p the encoding time. This pulse sequence has the advantage of reducing gradient duty cycle, reducing the image acquisition time and increasing SNR.

2.2.5 RF probes

As outlined in Section 2.2.2, the RF probes play an important role in the MR experiment. They have two functions: 1) the excitation of the MR active nuclei in the sample and/or 2) the reception of the MR signal produced by the net spin magnetization after the RF excitation has ceased. These two functions can be performed using a single RF probe, working as transmitter and receiver or two separated RF probes, one for RF excitation and the other for signal reception. The former is most common.

The design and optimization of an RF probe generally depends on the type of application [6]. However, they are generally classified in different subgroups, such as, microcoils [73], surface coils [74], volume coils [75] and Transverse Electromagnetic (TEM) Resonator Coils [76]. A good description of these types of RF probes can be found in many reference books [6, 7]

2.2.5.1 Tuning and Matching

For optimal excitation and reception, the RF probe must be tuned and matched at the Larmor frequency. Tuning the RF probe is essential to be able to flip the magnetization to the transverse plane and later to detect the voltage induced by the precessing magnetization in the probe. The frequency at which the RF probe can be efficiently tuned will depend on the inductance of the coil,

$$\omega_0 = \frac{1}{\sqrt{L_c C_T}} \tag{2.21}$$

 L_c is the inductance of the coil circuit and C_T is the capacitance of the coil circuit. An external capacitor is usually added to the coil create the resonant condition of Eq. 2.21. This is illustrated in Fig. 2.3.

The best efficiency of the probe is obtained when all the power delivered by the transmitter is entirely dissipated in the probe resistance. To achieve optimum energy transfer between the probe and the transmitter, the RF probe impedance must match the 50 Ω impedance of the spectrometer.

Tuning and matching cannot be done independently. A resonant circuit is always employed to simultaneously tune and match the RF probe. Fig. 2.3 shows the two commonly employed resonant circuits to tune and match the RF probe. The parallel tuned/series matched circuit presented in Fig. 2.3a is generally preferred because only the losses of the tuning capacitor, due to its resistance, R_T , are included in the resonant circuit. In Fig. 2.3b the losses due to the resistance of the tuning capacitor (C_T) and matching capacitor (C_M), R_T and R_M respectively, are both included in the total losses of the RF probe, thus reducing its efficiency.

Impedance matching is a fundamental aspect of RF probe design. If the RF is not



Fig. 2.3. Parallel tuned/series matched (A) and series tuned/parallel matched (B) circuits

matched, signal reflections caused by the mismatched impedance can lead to serious problems, even damaging the power amplifier. The parameter used to express the quality of a matching is called the reflection coefficient, Γ . This represents the ratio of the amplitude of the reflected and the incident RF powers. The lower the reflection coefficient the better the matching of the RF probe.

2.2.5.2 **RF** probe characterization

The RF probe must be sensitive. The probe must produce the highest possible \mathbf{B}_1 magnetic field, at a specific frequency, with a homogeneous \mathbf{B}_1 in the sample volume. The quality factor, Q, is the first parameter employed to evaluate the sensitivity of the probe,

$$Q = 2\pi f_0 \frac{L_c}{R} \tag{2.22}$$

R the resistance of the RF probe circuit. Generally, the larger the Q of the probe the shorter the 90° pulse duration and higher the signal-to-noise ratio (SNR) of the signal detected. However, after the sample is inserted into the RF probe, the Q of the probe may change. The change will depend on the properties of the sample. Conductive samples generally result in a decrease of the Q of the RF probe.

One commonly employed metric to evaluated the sensitivity of the RF probe is the ratio between the unloaded quality factor (no sample inserted), Q_u and the loaded quality factor (with the sample), Q_L . However, this metric is often misleading when the **B**₁ magnetic field has substantial magnitude in lossy samples beyond the homogeneous region of interest. [77]. Also, this metric has limited value if the conservative electric field is not minimized.

A better figure of merit for the RF probe is a related to the SNR equation,

$$\frac{S}{N} \propto \frac{V_s}{\tau_{90} \sqrt{P}} \tag{2.23}$$

where τ_{90} is the 90° degree pulse duration, over the whole sample volume V_s for a constant power P. For the same sample, with the same applied RF power, the RF probe with the shorter 90° degree pulse duration is the most sensitive probe.

Significant effort has been devoted to a theoretical description of the SNR [66, 78]. A full description and all the parameters influencing the SNR are described in [66, 78].

2.2.5.3 Losses

Several loss mechanisms contribute to the degradation of SNR. Losses are well described elsewhere [6]. Here, a simplified description of those losses is presented.

Depending on the magnitude of the noise of the sample and the probe, the SNR of the experiment can be classified into one of three noise regimes. If the losses of the sample are larger than the losses of the RF probe, the SNR is in a sample-noise-dominated regime. In this regime improving the Q of the RF probe will have little to no effect on the SNR [79].

On the other hand, if the losses are dominated by the RF probe, the SNR is in a coilnoise-dominated regime. Improving the quality factor of the RF probe may lead to an improvement of the SNR. If the losses of the probe and the sample are comparable then the SNR is in a transition regime. Several approaches, may be taken to improve the SNR [78].

This classification is generally performed on the basis of the losses of the RF probe and the losses of the sample. However, Doty et al. [77] suggested a better approach considering the product fd, where d is the diameter of the RF probe and f is the working frequency. Based on this classification, RF probes with a product fd < 4 MHz·m are in the coil-noisedominant regime. This is important for the work presented in Chapter 5.

2.2.6 **RF** penetration into conductive materials

It is important to consider the conductivity of the sample when performing an MR experiment. When a conductive material is inserted inside the RF probe, the RF excitation is attenuated at the surface of the conductor. How deeply the RF excitation can penetrate into the material, will depend on the frequency as well as the properties of the material. The skin depth or extent of RF penetration is described by the following equation,

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \tag{2.24}$$

where δ is the penetration depth (m), f is the frequency (Hz), μ is the absolute magnetic permeability of the material (H/m), and σ is the electrical conductivity of the material (S/m). μ has the same value, 1.26×10^{-6} H/m, for both copper and aluminium. For copper, with a conductivity $\sigma = 5.9 \times 10^7$ S/m, the skin depth at room temperature, at frequencies of 38 and 116 MHz is 10.6 μ m and 6.0 μ m, respectively. The typical thickness of a copper current collector is 10 - 15 μ m. In the case of aluminium, with a conductivity $\sigma = 3.7 \times 10^7$ S/m, for the same two frequencies the RF penetration is 13.0 μ m and 7.6 μ m respectively. The aluminium current collector thickness in LIB is typically 15 - 20 μ m.

RF penetration into the graphite electrode is important in MR studies of LIBs. Full RF penetration into graphite will allow a better quantification of lithium intercalation into graphite. Graphite conductivity is much lower than copper and depends on the orientation [30, 31]. If the RF excitation is perpendicular to the basal plane, the conductivity in that direction is $\sigma = 3.3 \times 10^1$ S/m. On the other hand, if the RF excitation is parallel to the basal plane, the conductivity in that direction is $\sigma = 2.0 \times 10^5$ S/m. RF penetration into graphite, at 38 and 116 MHz, in the direction perpendicular to the basal plane is 4472 μ m and 2560 μ m respectively. RF penetration in the direction parallel to the basal plane, for the same frequencies is 182 μ m and 105 μ m respectively.

Considering that the typical thickness of a graphite electrode is 50-55 μ m (excluding the copper current collector), we may consider that full RF penetration is achieved. However, the copper current collector will preclude full RF penetration of the cell. Another point to consider is that RF excitation of the electrodes is generally parallel to the electrodes, and the lateral size of the electrodes is much larger than the skin depth. For example, the typical graphite electrode size is 3×3 cm. So, the question arises: do we have full RF excitation

in the graphite electrode? We explore the answer to this question through simulation in Appendix A.

2.2.7 Eddy Currents

Eddy currents are produced by fast switching of the magnetic field gradients or by the rapidly oscillating magnetic field B_1 of the RF probe. These fast changes of magnetic field induce currents in the surrounding conducting materials. The eddy currents oppose the originating magnetic field. Eddy currents may affect the MR experiment in a negative way. Images acquired in the presence of large eddy currents may suffer from artefacts. Eddy currents may also lead to a faster decay of the MR signal.

Eddy currents can be treated in accordance with Faraday's Law of Induction. In a conductive material, the electromotive force ξ induced by the **B**₁ magnetic field of the RF probe, is proportional to the time variation of the magnetic flux density, given by the equation,

$$\xi = -\frac{\partial \Phi_B}{\partial t} = -\frac{\partial}{\partial t} \int_S \mathbf{B}_1 \cdot \mathbf{n} \, dS \tag{2.25}$$

The induced eddy currents will be a maximum when the conductive surface is perpendicular to the direction of the \mathbf{B}_1 magnetic field. Therefore, placing the conductive surface parallel to \mathbf{B}_1 and reducing the area of the surface will significantly reduce or eliminate eddy currents [33]. This is also true for the eddy currents produced by the fast switching magnetic field gradient. Eddy currents produced by the magnetic field gradients may also be reduced by decreasing the slew rate of the gradient switching.

In MR/MRI studies of LIBs, the electrodes, together with the current collectors, should be parallel to both the \mathbf{B}_1 magnetic field and the imaging gradients in order to minimize eddy currents. In the particular case of MRI, employing phase encoding methods such as SPRITE [72] is also advantageous. SPRITE family sequences are largely immune to eddy currents and \mathbf{B}_0 inhomogeneity effects.

2.2.8 Electromagnetic Simulations

3D electromagnetic software tools are critical for the design and optimization of RF probes. Several electromagnetic simulation packages are available for RF probe simulation, for example CST Microwave Studio, HFSS and XFDTD. Doty *et al.* [77] carried out a detailed evaluation of these three software packages for RF probe simulation and optimization problems. They concluded that Microwave Studio by Computer Simulation Technology (CST) is better suited and more accurate for RF probe simulation.

CST Microwave Studio offers automatic optimization routines, where the models can be parametrized with respect to their geometry or lumped elements. In the particular case of RF probes, it permits one to find the optimum parameters to achieve a given \mathbf{B}_1 homogeneity or \mathbf{B}_1 magnetic field strength.

Time domain (TD) and Frequency domain (FD) solvers are commonly employed in CST Microwave Studio for electromagnetic simulation. The TD solver is highly sensitive to the discretization method. However, it is fast and produces good results in most cases. On the other hand, FD solver also provides good results, but it takes longer and demands more computational power. Thus the TD solver is generally preferred for electromagnetic simulation of **RF** probes.

Several automatic optimization algorithms can be chosen in CST Microwave Studio, both local and global algorithms. However, global optimization algorithms are preferred to avoid the risk of converging to a local minimum, even when this could lead to an increase in calculation time.

2.3 Cell designs and RF Probes for MR studies of LIB

2.3.1 Cell design

Realistic commercial electrochemical cells are generally compact and encased in metallic cases to avoid damage and deformation. This makes it impossible for the RF magnetic field to penetrate inside the cell due to the skin effect (see section 2.2.6). This precludes the MR studies of such commercial cells.

Several cell designs have been proposed for MR studies of LIBs. The main objective of such cells is to allow RF penetration into the cell. However, these cells must satisfy other requirements. One of such requirements is air tightness, to avoid electrolyte contamination to ensure the proper functioning of the cell. Another requirement is to minimize the metallic components to avoid eddy currents and avoid a reduction of the RF probe sensitivity. Otherwise, the metallic components of the cell must be placed so the RF magnetic field is not attenuated during excitation and reception.

The first cell designed for MR studies of LIBs was a coin-like cell [80]. The battery components in this cell were contained in a Teflon housing. One feature of this cell was that the electrode material is mounted directly on the central conductor of the MR detector circuit for optimum signal sensitivity. However, this cell is relatively small and difficult to seal. Also, it is not a common type of cell employed for large battery systems.

Bellcore cells have also been employed in MR studies of LIBs [81]. These cells are flat, and the battery components are sealed inside a special plastic bag covered with a thin aluminium layer to seal the cell. The cell is easy to build, and the size can be easily adjusted. However, this type of cell suffers from poor contact between the separators and the electrodes. Also, electrolyte impregnation is a problem in these cells due to the lack of screws to tighten the cell. This type of cell is commonly employed in MR studies of LIBs due to the reduced amount of conductive material in the cell.

One of the most popular cell for batteries studies is the cylindrical cell [82]. These cylindrical cells are larger than Bellcore cells, thus improving MR sensitivity because of increased active material. They can store up to 4 times more active material than the Bellcore cell. Cylindrical cells are easy to build and to assemble because the are equipped with screw-like caps. Cylindrical cells also allow Magic Angle Spinning (MAS) MR experiments. This can lead to better spectral resolution in MR experiments. Several versions of cylindrical cells have been proposed [83]. Despite the larger volume of this cell, they look like a pencil cell. The increase in volume is due to an increase in the separation between the electrodes, and not due to an increase in the lateral area of the cell which would be preferred. The larger separation between the cell electrodes reduces battery performance. A wider cell with a small separation between the electrodes would be ideal.

An in depth description of these and other types of cell can be found in a recent book from the Royal Society of Chemistry [12].

2.3.2 RF probes for LIB

In MR/MRI studies of LIBs choosing a suitable resonator and battery container avoiding RF attenuation during excitation/reception, while providing high sensitivity, is critical. Several different types of MR RF probe design have been employed in ⁷Li ion battery experiments [34, 82, 84–87].

The first *in situ* LIB studies performed using a toroid coil was presented by Rathke *et al.* [85]. In this study, MR analysis of the electrode–electrolyte interface in lithium polymer-electrolyte battery materials was performed. The toroid RF probe produces a B_1 magnetic field that depends on the distance from the centre of the coil, producing a non-linear RF excitation. The unusual geometry and inherently low signal to noise hindered

widespread use [86].

Solenoidal RF probes and cylindrical cell designs [82] have also been employed for LIB studies. These RF probes produce a homogeneous B_1 magnetic field, but the compatible LIB cell geometries are limited with inherently low MR sensitivity. Solenoidal coils are limited to cylindrical cells for better performance. But as discussed in the previous section, cylindrical pencil-like cells are volume limited with unrealistic gaps between the electrodes, leading to a reduced performance of the cell.

Saddle coils have been widely employed for LIB studies [34, 87]. This probe has also been employed in combination with cylindrical battery containers for MR investigations of batteries. The natural LIB cell geometry with such an RF probe is a pencil-like cell. Quite naturally pencil-like cells resemble an MR tube. In the context of a LIB, this probe is similar to the solenoidal coil. However, the solenoidal coil has a better B_1 magnetic field homogeneity.

2.4 Conclusions

A wide variety of RF probes and battery cell containers, have been employed for MR studies of LIB. The perfect combination of a cell container and RF probe, that maximizes sample volume, with a homogeneous B_1 magnetic field and high sensitivity, is still a challenge. The ideal RF probe must also avoid RF attenuation and minimize eddy currents. As shown in Chapter 3, the PPR RF probe is a natural choice for LIB studies.

References

- C. Julien, A. Mauger, A. Vijh, K. Zaghib, Lithium Batteries: Science and Technology, 1st Edition, Springer, 2016. doi:10.1007/978-3-319-19108-9.
- [2] K. Ozawa, Lithium Ion Rechargeable Batteries: Materials, Technology, and New Applications, 1st Edition, Wiley-VCH, 2009. doi:10.1002/9783527629022.
- [3] A. Abragam, The principles of nuclear magnetism, 1st Edition, Oxford University Press, 1960.
- [4] P. Callaghan, Principles of nuclear magnetic resonance microscopy, 1st Edition, Oxford University Press, 1991.
- [5] M. H. Levitt, Spin Dynamics: Basics of Nuclear Magnetic Resonance, 2nd Edition, John Wiley and Sons, 2008.
- [6] J. Mispelter, M. Lupu, A. Briguet, NMR Probeheads for Biophysical and Biomedical Experiments, 2nd Edition, Imperial College Press, 2006. doi:10.1142/p438.
- [7] J. T. Vaughan, J. R. Griffiths, RF Coils for MRI, 1st Edition, John Wiley and Sons, 2012.
- [8] W. V. Gool, Fast Ion Transport in Solids., 1st Edition, North Holland Publishing Co., 1973.
- [9] C. Iclodean, B. Varga, N. Burnete, D. Cimerdean, B. Jurchiş, Comparison of different battery types for electric vehicles, IOP Conference Series: Materials Science and Engineering 252 (2017) 012058–012060. doi:10.1088/1757-899X/252/1/012058.

- [10] T. Chen, Y. Jin, H. Lv, A. Yang, M. Liu, B. Chen, Y. Xie, Q. Chen, Applications of lithium-ion batteries in grid-scale energy storage systems, Transactions of Tianjin University 26 (2020) 208–217. doi:10.1007/s12209-020-00236-w.
- [11] O. Pecher, J. Carretero-Gonzalez, K. J. Griffith, C. P. Grey, Materials' methods: NMR in battery research, Chemistry of Materials 29 (2017) 213–242. doi:10.1021/acs. chemmater.6b03183.
- [12] Y. Yang, R. Fu, H. Huo, NMR and MRI of Electrochemical Storage Materials and Devices, Royal Society of Chemistry, 2021.
- [13] S. Chandrashekar, N. M. Trease, H. J. Chang, L. S. Du, C. P. Grey, A. Jerschow, ⁷Li MRI of Li batteries reveals location of microstructural lithium, Nature Materials 11 (2012) 311–315. doi:10.1038/nmat3246.
- K. J. Sanders, A. R. Aguilera, J. R. Keffer, B. J. Balcom, I. C. Halalay, G. R. Goward, Transient lithium metal plating on graphite: Operando ⁷Li nuclear magnetic resonance investigation of a battery cell using a novel RF probe, Carbon 189 (2022) 377– 385. doi:10.1016/j.carbon.2021.12.082.
- [15] S. A. Krachkovskiy, M. Reza, A. R. Aguilera, I. C. Halalay, B. J. Balcom, G. R. Goward, Real-time quantitative detection of lithium plating by *in situ* NMR using a parallel-plate resonator, Journal of The Electrochemical Society 167 (2020) 130514–130519. doi:10.1149/1945-7111/abb7ea.
- [16] C. P. Grey, N. Dupré, NMR studies of cathode materials for lithium-ion rechargeable batteries, Chemical Reviews 104 (2004) 4493–4512. doi:10.1021/cr020734p.
- [17] A. R. Aguilera, B. MacMillan, S. Krachkovskiy, K. J. Sanders, F. Alkhayri, C. A. Dyker, G. R. Goward, B. J. Balcom, A parallel-plate RF probe and battery car-

tridge for ⁷Li ion battery studies, Journal of Magnetic Resonance 325 (2021) 106943–106950. doi:10.1016/j.jmr.2021.106943.

- [18] C. Wan, S. Xu, M. Y. Hu, R. Cao, J. Qian, Z. Qin, J. Liu, K. T. Mueller, J.-G. Zhang, J. Z. Hu, Multinuclear NMR study of the solid electrolyte interface formed in lithium metal batteries, ACS Applied Materials and Interfaces 9 (2017) 14741–14748. doi: 10.1021/acsami.6b15383.
- [19] H. Huo, M. Chamas, P. E. Lippens, M. Ménétrier, Multinuclear NMR study of the solid electrolyte interface on the Li-FeSn₂ negative electrodes for Li-Ion batteries, Journal of Physical Chemistry C 116 (2012) 2390–2398. doi:10.1021/jp210017b.
- [20] C. P. Aiken, E. R. Logan, A. Eldesoky, H. Hebecker, J. M. Oxner, J. E. Harlow, M. Metzger, J. R. Dahn, Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O₂ as a superior alternative to LiFePO₄ for long-lived low voltage Li-Ion cells, Journal of The Electrochemical Society 169 (2022) 050512–050524. doi:10.1149/1945-7111/ac67b5.
- [21] J. E. Harlow, X. Ma, J. Li, E. Logan, Y. Liu, N. Zhang, L. Ma, S. L. Glazier, M. M. E. Cormier, M. Genovese, S. Buteau, A. Cameron, J. E. Stark, J. R. Dahn, A wide range of testing results on an excellent lithium-ion cell chemistry to be used as benchmarks for new battery technologies, Journal of The Electrochemical Society 166 (2019) A3031–A3045. doi:10.1149/2.0981913jes.
- [22] T. Taskovic, L. M. Thompson, A. Eldesoky, M. D. Lumsden, J. R. Dahn, Optimizing electrolyte additive loadings in NMC532/graphite cells: Vinylene carbonate and ethylene sulfate, Journal of The Electrochemical Society 168 (2021) 010514–010524. doi:10.1149/1945-7111/abd833.

- [23] P. Nzereogu, A. Omah, F. Ezema, E. Iwuoha, A. Nwanya, Anode materials for lithium-ion batteries: A review, Applied Surface Science Advances 9 (2022) 100233– 100252. doi:10.1016/j.apsadv.2022.100233.
- [24] M. Winter, J. O. Besenhard, M. E. Spahr, P. Novák, Insertion electrode materials for rechargeable lithium batteries, Advanced Materials 10 (1998) 725–763. doi:10. 1002/(SICI)1521-4095(199807)10:10<725::AID-ADMA725>3.0.C0;2-Z.
- [25] M. Nie, D. Chalasani, D. P. Abraham, Y. Chen, A. Bose, B. L. Lucht, Lithium ion battery graphite solid electrolyte interphase revealed by microscopy and spectroscopy, Journal of Physical Chemistry C 117 (2013) 1257–1267. doi:10.1021/jp3118055.
- [26] M. Gauthier, T. J. Carney, A. Grimaud, L. Giordano, N. Pour, H.-H. Chang, D. P. Fenning, S. F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp, Y. Shao-Horn, Electrode–electrolyte interface in Li-Ion batteries: Current understanding and new insights, The Journal of Physical Chemistry Letters 6 (2015) 4653–4672. doi: 10.1021/acs.jpclett.5b01727.
- [27] R. Bhattacharyya, B. Key, H. Chen, A. S. Best, A. F. Hollenkamp, C. P. Grey, *In situ* NMR observation of the formation of metallic lithium microstructures in lithium batteries, Nature Materials 9 (2010) 504–510. doi:10.1038/nmat2764.
- [28] K. Mukai, T. Inoue, Magnetic susceptibility measurements on li-intercalated graphite:
 Paramagnetic to diamagnetic transitions in C₁₂Li induced by magnetic field, Carbon 123 (2017) 645–650. doi:10.1016/j.carbon.2017.08.012.
- [29] J. L. L. Lopez, P. J. Grandinetti, A. C. Co, Enhancing the real-time detection of phase changes in lithium-graphite intercalated compounds through derivative operando

(dOp) NMR cyclic voltammetry, Journal of Materials Chemistry A 6 (2017) 231–243. doi:10.1039/c7ta07521a.

- [30] M. Park, X. Zhang, M. Chung, G. B. Less, A. M. Sastry, A review of conduction phenomena in Li-ion batteries, Journal of Power Sources 195 (2010) 7904–7929. doi:10.1016/j.jpowsour.2010.06.060.
- [31] H. O. Pierson, Handbook of Carbon, Graphite, Diamonds and Fullerenes: Processing, Properties and Applications (Materials Science and Process Technology), William Andrew Publishing, 1993.
- [32] A. J. Ilott, S. Chandrashekar, A. Klöckner, H. J. Chang, N. M. Trease, C. P. Grey, L. Greengard, A. Jerschow, Visualizing skin effects in conductors with MRI: ⁷Li MRI experiments and calculations, Journal of Magnetic Resonance 245 (2014) 143–149. doi:10.1016/j.jmr.2014.06.013.
- [33] S. Vashaee, F. Goora, M. M. Britton, B. Newling, B. J. Balcom, Mapping B₁induced eddy current effects near metallic structures in MR images: A comparison of simulation and experiment, Journal of Magnetic Resonance 250 (2015) 17–24. doi:10.1016/j.jmr.2014.10.016.
- [34] S. A. Krachkovskiy, J. M. Foster, J. D. Bazak, B. J. Balcom, G. R. Goward, Operando mapping of Li concentration profiles and phase transformations in graphite electrodes by magnetic resonance imaging and nuclear magnetic resonance spectroscopy, Journal of Physical Chemistry C 122 (2018) 21784–21791. doi:10.1021/acs.jpcc. 8b06563.
- [35] K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, Chemical Reviews 104 (2004) 4303–4418. doi:10.1021/cr030203g.

- [36] J. B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, Chemistry of Materials 22 (2010) 587–603. doi:10.1021/cm901452z.
- [37] A. Mauger, C. M. Julien, A. Paolella, M. Armand, K. Zaghib, A comprehensive review of lithium salts and beyond for rechargeable batteries: Progress and perspectives, Materials Science and Engineering R: Reports 134 (2018) 1–21. doi: 10.1016/j.mser.2018.07.001.
- [38] H. Yang, G. V. Zhuang, P. N. Ross, Thermal stability of LiPF₆ salt and Li-ion battery electrolytes containing LiPF₆, Journal of Power Sources 161 (2006) 573–579. doi: 10.1016/j.jpowsour.2006.03.058.
- [39] R. Younesi, G. M. Veith, P. Johansson, K. Edström, T. Vegge, Lithium salts for advanced lithium batteries: Li-metal, Li-O₂, and Li-S, Energy and Environmental Science 8 (2015) 1905–1922. doi:10.1039/c5ee01215e.
- [40] J. Dudley, D. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvath, M. Juzkow, B. Denis, P. Juric, P. Aghakian, J. Dahn, Conductivity of electrolytes for rechargeable lithium batteries, Journal of Power Sources 35 (1991) 59–82. doi: 10.1016/0378-7753(91)80004-H.
- [41] J. Kalhoff, D. Bresser, M. Bolloli, F. Alloin, J. Y. Sanchez, S. Passerini, Enabling LiTFSI-based electrolytes for safer lithium-ion batteries by using linear fluorinated carbonates as (co)solvent, ChemSusChem 7 (2014) 2939–2946. doi:10.1002/ cssc.201402502.
- [42] L. J. Krause, W. Lamanna, J. Summerfield, M. Engle, G. Korba, R. Loch, R. Atanasoski, Corrosion of aluminum at high voltages in non-aqueous electrolytes contain-

ing perfluoroalkylsulfonyl imides; new lithium salts for lithium-ion cells, Journal of Power Sources 68 (1997) 320–325. doi:10.1016/S0378-7753(97)02517-2.

- [43] R. Chen, Q. Li, X. Yu, L. Chen, H. Li, Approaching practically accessible solidstate batteries: Stability issues related to solid electrolytes and interfaces, Chemical Reviews 120 (2020) 6820–6877. doi:10.1021/acs.chemrev.9b00268.
- [44] W. Zhao, J. Yi, P. He, H. Zhou, Solid-state electrolytes for lithium-ion batteries: Fundamentals, challenges and perspectives, Electrochemical Energy Reviews 2 (2019) 574–605. doi:10.1007/s41918-019-00048-0.
- [45] D. V. Horváth, R. Tian, C. Gabbett, V. Nicolosi, J. N. Coleman, Quantifying the effect of separator thickness on rate performance in lithium-ion batteries, Journal of The Electrochemical Society 169 (2022) 030503–030510. doi:10.1149/1945-7111/ ac5654.
- [46] S. A. Krachkovskiy, J. D. Bazak, P. Werhun, B. J. Balcom, I. C. Halalay, G. R. Goward, Visualization of steady-state ionic concentration profiles formed in electrolytes during Li-ion battery operation and determination of mass-transport properties by *in situ* magnetic resonance imaging, Journal of the American Chemical Society 138 (2016) 7992–7999. doi:10.1021/jacs.6b04226.
- [47] S. Wiemers-Meyer, M. Winter, S. Nowak, A battery cell for *in situ* NMR measurements of liquid electrolytes, Physical Chemistry Chemical Physics 19 (2017) 4962–4966. doi:10.1039/c6cp08653e.
- [48] B. M. Meyer, N. Leifer, S. Sakamoto, S. G. Greenbaum, C. P. Grey, High field multinuclear NMR investigation of the SEI layer in lithium rechargeable batteries, Electrochemical and Solid-State Letters 8 (2005) A145–A149. doi:10.1149/1.1854117.

- [49] S. Wiemers-Meyer, M. Winter, S. Nowak, Mechanistic insights into lithium ion battery electrolyte degradation-a quantitative NMR study, Physical Chemistry Chemical Physics 18 (2016) 26595–26601. doi:10.1039/c6cp05276b.
- [50] S. S. Zhang, A review on the separators of liquid electrolyte Li-ion batteries, Journal of Power Sources 164 (2007) 351–364. doi:10.1016/j.jpowsour.2006.10.065.
- [51] C. F. J. Francis, I. L. Kyratzis, A. S. Best, Lithium-ion battery separators for ionicliquid electrolytes: A review, Advanced Materials 32 (2020) 1904205. doi:10. 1002/adma.201904205.
- [52] M. F. Lagadec, R. Zahn, V. Wood, Characterization and performance evaluation of lithium-ion battery separators, Nature Energy 4 (2019) 15–25. doi:10.1038/ s41560-018-0295-9.
- [53] C. M. Costa, Y. H. Lee, J. H. Kim, S. Y. Lee, S. Lanceros-Méndez, Recent advances on separator membranes for lithium-ion battery applications: From porous membranes to solid electrolytes, Energy Storage Materials 22 (2019) 346–375. doi:10.1016/ j.ensm.2019.07.024.
- [54] M. Kirchhöfer, J. V. Zamory, E. Paillard, S. Passerini, Separators for Li-ion and Limetal battery including ionic liquid based electrolytes based on the TFSI- and FSIanions, International Journal of Molecular Sciences 15 (2014) 14868–14890. doi: 10.3390/ijms150814868.
- [55] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, D. Bresser, The success story of graphite as a lithium-ion anode material-fundamentals, remaining challenges, and recent developments including silicon (oxide) composites, Sustainable Energy and Fuels 4 (2020) 5387–5416. doi:10.1039/d0se00175a.

- [56] M. Letellier, F. Chevallier, F. Béguin, E. Frackowiak, J. N. Rouzaud, The first *in situ* ⁷Li NMR study of the reversible lithium insertion mechanism in disorganised carbons, Journal of Physics and Chemistry of Solids 65 (2004) 245–251. doi:10.1016/j. jpcs.2003.10.022.
- [57] M. Letellier, F. Chevallier, F. Béguin, *In situ* ⁷Li NMR during lithium electrochemical insertion into graphite and a carbon/carbon composite, Journal of Physics and Chemistry of Solids 67 (2006) 1228–1232. doi:10.1016/j.jpcs.2006.01.088.
- [58] M. Winter, The solid electrolyte interphase the most important and the least understood solid electrolyte in rechargeable Li batteries, Zeitschrift fur Physikalische Chemie (2009). doi:10.1524/zpch.2009.6086.
- [59] P. Gargh, A. Sarkar, Y. H. Lui, S. Shen, C. Hu, S. Hu, I. C. Nlebedim, P. Shrotriya, Correlating capacity fade with film resistance loss in fast charging of lithium-ion battery, Journal of Power Sources 485 (2021) 229360–229366. doi:10.1016/j. jpowsour.2020.229360.
- [60] U. Janakiraman, T. R. Garrick, M. E. Fortier, Review—lithium plating detection methods in Li-Ion batteries, Journal of The Electrochemical Society 167 (2020) 160552–160574. doi:10.1149/1945-7111/abd3b8.
- [61] T. Gao, Y. Han, D. Fraggedakis, S. Das, T. Zhou, C. N. Yeh, S. Xu, W. C. Chueh, J. Li, M. Z. Bazant, Interplay of lithium intercalation and plating on a single graphite particle, Joule 5 (2021) 393–414. doi:10.1016/j.joule.2020.12.020.
- [62] H. Ge, T. Aoki, N. Ikeda, S. Suga, T. Isobe, Z. Li, Y. Tabuchi, J. Zhang, Investigating lithium plating in lithium-ion batteries at low temperatures using electrochemical

model with NMR assisted parameterization, Journal of The Electrochemical Society 164 (2017) A1050–A1060. doi:10.1149/2.0461706jes.

- [63] S. A. Krachkovskiy, M. Reza, A. R. Aguilera, B. J. Balcom, G. R. Goward, Realtime quantitative detection of lithium plating by *in situ* NMR using a parallel-plate resonator, Journal of The Electrochemical Society 167 (2020) 130514–130519. doi: 10.1149/1945-7111/abb7ea.
- [64] E. M. Purcell, H. C. Torrey, R. V. Pound, Resonance absorption by nuclear magnetic moments in a solid, Physical Review 69 (1946) 37–38. doi:10.1103/PhysRev.69. 37.
- [65] F. Bloch, W. W. Hansen, M. Packard, The nuclear induction experiment, Physical Review 70 (1946) 474–485. doi:10.1103/PhysRev.70.474.
- [66] D. I. Hoult, R. E. Richards, The signal-to-noise ratio of the nuclear magnetic resonance experiment, Journal of Magnetic Resonance (1969) (1976). doi:10.1016/0022-2364(76)90233-X.
- [67] C. Constantinides, Magnetic Resonance Imaging: The Basics, 1st Edition, CRC Press, 2014. doi:10.1201/b16628.
- [68] M. J. Dick, D. Veselinovic, D. Green, Reducing Sample Heating During NMR Measurements, Society of Core Analysts Annual Symposium, 2019.
- [69] A. V. Ouriadov, R. P. MacGregor, B. J. Balcom, Thin film MRI high resolution depth imaging with a local surface coil and spin echo SPI, Journal of Magnetic Resonance 169 (2004) 174–186. doi:10.1016/j.jmr.2004.04.015.

- [70] P. Szomolanyi, D. Goodyear, B. Balcom, D. Matheson, SPIRAL-SPRITE: A rapid single point MRI technique for application to porous media, Magnetic Resonance Imaging 19 (2001) 423–428. doi:10.1016/S0730-725X(01)00260-0.
- [71] M. Halse, D. J. Goodyear, B. MacMillan, P. Szomolanyi, D. Matheson, B. J. Balcom, Centric scan SPRITE magnetic resonance imaging, Journal of Magnetic Resonance 165 (2003) 219–229. doi:10.1016/j.jmr.2003.08.004.
- [72] B. J. Balcom, R. P. Macgregor, S. D. Beyea, D. P. Green, R. L. Armstrong, T. W. Bremner, Single-point ramped imaging with T₁ enhancement (SPRITE), Journal of Magnetic Resonance Series A 123 (1996) 131–134. doi:10.1006/jmra.1996.
 0225.
- [73] A. G. Webb, Microcoil nuclear magnetic resonance spectroscopy, Journal of Pharmaceutical and Biomedical Analysis 38 (2005) 892–903. doi:10.1016/j.jpba. 2005.01.048.
- [74] P. A. Narayana, W. W. Brey, M. V. Kulkarni, C. L. Sievenpiper, Compensation for surface coil sensitivity variation in magnetic resonance imaging, Magnetic Resonance Imaging 6 (1988) 271–274. doi:10.1016/0730-725X(88)90401-8.
- [75] J. T. Vaughan, H. P. Hetherington, J. O. Otu, J. W. Pan, G. M. Pohost, High frequency volume coils for clinical NMR imaging and spectroscopy, Magnetic Resonance in Medicine 32 (1994). doi:10.1002/mrm.1910320209.
- [76] T. Vaughan, TEM body coils, eMagRes 1 (2012). doi:10.1002/9780470034590. emrstm1125.

- [77] F. D. Doty, G. Entzminger, J. Kulkarni, K. Pamarthy, J. P. Staab, Radio frequency coil technology for small-animal MRI, NMR in Biomedicine 20 (2007) 304–325. doi:10.1002/nbm.1149.
- [78] F. D. Doty, Probe design and construction, eMagRes (2007) 1-12. .doi:10.1002/ 9780470034590.emrstm0414.
- [79] K. R. Minard, R. A. Wind, Solenoidal microcoil design part II: Optimizing winding parameters for maximum signal-to-noise performance, Concepts in Magnetic Resonance 13 (2001) 190–210. doi:10.1002/cmr.1008.
- [80] R. E. Gerald, R. J. Klingler, G. Sandí, C. S. Johnson, L. G. Scanlon, J. W. Rathke, ⁷Li NMR study of intercalated lithium in curved carbon lattices, Journal of Power Sources 89 (2000) 237–243. doi:10.1016/S0378-7753(00)00435-3.
- [81] M. Letellier, F. Chevallier, M. Morcrette, *In situ* ⁷Li nuclear magnetic resonance observation of the electrochemical intercalation of lithium in graphite; 1st cycle, Carbon 45 (2007) 1025–1034. doi:10.1016/j.carbon.2006.12.018.
- [82] F. Poli, J. S. Kshetrimayum, L. Monconduit, M. Letellier, New cell design for *in-situ* NMR studies of lithium-ion batteries, Electrochemistry Communications 13 (2011) 1293–1295. doi:10.1016/j.elecom.2011.07.019.
- [83] H. J. Chang, A. J. Ilott, N. M. Trease, M. Mohammadi, A. Jerschow, C. P. Grey, Correlating microstructural lithium metal growth with electrolyte salt depletion in lithium batteries using ⁷Li MRI, Journal of the American Chemical Society 137 (2015) 15209–15216. doi:10.1021/jacs.5b09385.
- [84] S. A. Krachkovskiy, J. D. Bazak, P. Werhun, B. J. Balcom, I. C. Halalay, G. R. Goward, Visualization of steady-state ionic concentration profiles formed in elec-
trolytes during Li-Ion battery operation and determination of mass-transport properties by *in situ* magnetic resonance imaging, Journal of the American Chemical Society 138 (2016) 7992–7999. doi:10.1021/jacs.6b04226.

- [85] J. W. Rathke, R. J. Klingler, R. E. Gerald, K. W. Kramarz, K. Woelk, Toroids in NMR spectroscopy, Progress in Nuclear Magnetic Resonance Spectroscopy 30 (1997) 209– 253. doi:10.1016/s0079-6565(96)01037-0.
- [86] N. M. Trease, L. Zhou, H. J. Chang, B. Y. Zhu, C. P. Grey, *In situ* NMR of lithium ion batteries: Bulk susceptibility effects and practical considerations, Solid State Nuclear Magnetic Resonance 42 (2012) 62–70. doi:10.1016/j.ssnmr.2012.01.004.
- [87] S. A. Kayser, A. Mester, A. Mertens, P. Jakes, R. A. Eichel, J. Granwehr, Long-run: *In operando* NMR to investigate the evolution and degradation of battery cells, Physical Chemistry Chemical Physics 20 (2018) 13765–13776. doi:10.1039/c8cp01067f.

Chapter 3

Optimization of a Parallel-Plate RF Probe for High Resolution Thin Film Imaging

This chapter introduces the Parallel-Plate Resonator RF probe for high spatial resolution MR studies of thin films. The B_1 magnetic field homogeneity and strength of the PPR were evaluated and optimized through simulation. This was the first step to evaluate the performance of PPR RF probe which will be employed for MR studies of LIB in the next chapters.

This chapter is largely based on the paper "Optimization of a Parallel-Plate RF Probe for High Resolution Thin Film Imaging" published in the journal *Concepts in Magnetic Resonance Part A*, 47A, e21465–e21470 (2018). The format of the references in this chapter has been changed to Elsevier's reference style format for the *Journal of Magnetic Resonance*.

Abstract

Choosing an MR probe with the correct dimensions and high sensitivity is critical for magnetic resonance imaging, especially high resolution thin film imaging. In this work, a Parallel-Plate Resonator has been optimized for strength and uniformity of the **B**₁ magnetic field. The Parallel-Plate Resonator is designed for high resolution imaging in the direction perpendicular to the plates. The optimization process was undertaken through simulation with CST Microwave Studio, followed by experiment. A 400 μ m capillary tube, filled with doped water, was used for testing the optimized probe in a 2.4 T magnet. It is shown that increasing the width of the copper leads connected to the plates increases the homogeneity

of the \mathbf{B}_1 magnetic field by almost 90%. The best approach to increase the sensitivity and the homogeneity of the probe was to maintain the dimensions of the plates and copper leads but to add additional capacitors at the corners to distribute the current. This approach produces a 40% stronger \mathbf{B}_1 magnetic field and increases the homogeneity by almost 85%. The experimental \mathbf{B}_1 magnetic field of the parallel-plate prototype agrees within 20% of the value found through simulation, for specified power. The experimental MRI results show that it is possible to achieve a nominal resolution of 10 μ m between the plates for suitable samples using the optimized probe. The optimized Parallel-Plate Resonator, combined with a phase encode SE SPI method, may be used for high resolution studies of lithium-ion transport in the electrolyte solution of lithium-ion batteries.

3.1 Introduction

High resolution thin film Magnetic Resonance Imaging (MRI) has been of interest for more than a decade [1–6, 6, 7]. It has been a useful tool to study polymerization of surface coatings [2], water evaporation [4], water content in operational fuel cells [8, 9], and lithium-ion transport in Lithium-Ion Batteries (LIBs) [7, 10, 11]. MRI is a powerful technique to study electrochemical devices because it provides spatially resolved information about species in solution. This permits more precise knowledge of the processes that are occurring inside of the electrochemical devices during operation [10–12]. However, there are several limitations that hinder or limit the use of MRI for high resolution studies, especially in electrochemical devices. The most important is the inherent low sensitivity of MRI, which is always an issue with high resolution studies. Another factor to consider when studying electrochemical devices, is the presence of metal structures, which can reduce image resolution and screen the RF excitation and signal. In the case of LIBs, the low sensitivity of the nuclei under study is of concern. ⁷Li has a gyromagnetic ratio approximately three times smaller than ¹H, resulting in a reduced signal-to-noise ratio (SNR). These limitations for high resolution studies can be greatly reduced if the MRI method and the RF probe are optimized for the sample and the process of interest.

Ouriadov *et al.* [4] have demonstrated that is advantageous to use a spin echo SE single point imaging SPI phase encode method for high resolution thin film depth imaging. This pure phase encoding technique has an inherently high SNR due to the narrow signal bandwidth, and because the lack of gradient at the k-space origin reduces diffusive signal attenuation. In addition, image distortions due to \mathbf{B}_0 inhomogeneity, susceptibility variations, and chemical shift will be greatly reduced.

According to the "principle of reciprocity" [13, 14], the received MR signal from each point in space is proportional to the local \mathbf{B}_1 magnetic field strength per unit excitation current. So, it is important to maximize the \mathbf{B}_1 magnetic field strength in the sample area. One approach to increase the \mathbf{B}_1 magnetic field strength and increase sensitivity is to use a surface coil placing the sample closer to the probe. The drawback of the surface coil is that sensitivity rapidly decreases with distance and the geometry is not conducive to MRI of an electrochemical cell because the \mathbf{B}_1 magnetic field will be heavily attenuated by conductive layers due to RF screening. A better choice, which we explore in this article, is to employ a parallel-plate type resonator, with \mathbf{B}_1 magnetic field that could be oriented parallel to the current collectors of the electrochemical cells reducing the screening of RF excitation and received signal.

The Parallel-Plate Resonator has been previously employed in MRI to study electrochemical cells [8], histological samples [15, 16], liquid crystal properties [6], high resolution thin film imaging [3], and chemical shift resolved capillary flow [5]. Zhang *et al* [3] developed a Parallel-Plate Resonator with perforated plates allowing mass transport through the resonator to the sample for high resolution thin film imaging in a Nafion fuel cell. The Meadowcroft *et al.* [15] design was based on a flat slotted-tube resonator with a capacitor at each corner. They showed that the \mathbf{B}_1 magnetic field for this Parallel-Plate Resonator is very inhomogeneous. They reduced the inhomogeneity of the probe by removing the capacitors and creating a U-shape Parallel-Plate Resonator with a continuous copper strip folded above and below the sample. In addition, they extended the plates over a region filled with dielectric material to form a distributed capacitance. Hoang *et al.* [16] built on Meadowcroft's work to accommodate different sample sizes and to evaluate the gain in sensitivity for different probe sizes.

The Parallel-Plate Resonator presented by Zhang *et al.* [3] increases the sensitivity by using the current collectors of the fuel cell as part of the MR probe, so that the sample is very close to the RF probe. It also reduces the RF screening produced by the metal structure which is a critical problem for a surface coil [3, 4]. However, the parallel-plate resonator has a relatively poor \mathbf{B}_1 homogeneity and low \mathbf{B}_1 magnetic field strength at the corners of the plates, which is a hindrance for high sensitivity high resolution thin film imaging. None of the work presented above focused on optimization of the parallel-plate resonator, to maximize \mathbf{B}_1 magnetic field strength and homogeneity for high resolution MRI.

In this article, we optimize a Parallel-Plate Resonator to undertake high resolution thin film imaging. We investigate strategies to increase the \mathbf{B}_1 homogeneity and the \mathbf{B}_1 field strength of the probe. The optimization process is undertaken using CST Microwave Studio, a powerful 3D electromagnetic field simulation package. A prototype of the parallelplate resonator was built based on the results of the simulation. In this prototype, the plates are connected through a capacitor in each corner. A \mathbf{B}_1 mapping experiment validated the results of the simulation. Finally, a high resolution thin film imaging profile of doped water in a capillary tube was acquired using a SE SPI method designed for high resolution thin film depth imaging [17, 18].

The results of this work are intended to be used to build a similar parallel-plate resonator that may be used as part of a working LIB. The future integrated device is intended to be used to study lithium-ion transport in the electrolyte solution and lithium-ion intercalation into graphite. Insufficient understanding of these complex electrochemical processes inside LIB batteries hinders optimization of performance. Improved understanding would enable researchers to mitigate degradation and materials failure, and allow extended lifetimes [19–22].

3.2 Simulation

The Parallel-Plate Resonator was designed and optimized with CST MicroWave Studio 2017 (CST of America, Framingham, MA, USA) using a PC with a 2.50 GHz AMD A10-5750M APU Processor and 16 GB of RAM installed. The high frequency domain module was employed for numerical calculation of the magnetic field produced by the plates. The transient solver with tetrahedral meshing was used for all the simulations. No symmetry planes were used during the calculations. The initial probe consists of two parallel copper plates and two copper leads attached to each plate. Each plate with the two leads was simulated as an entire structure to avoid losses introduced by the solder joints. The two plates were connected by one fixed ceramic capacitor as shown in Fig. 3.1a. The plates were 5.00 cm long and 3.50 cm wide while the leads were 1.5 cm long and 1.0 cm wide.

To significantly reduce simulation time, the plates and the leads were simulated as copper sheets. The dimensions of the plates were chosen to maximize the sample area inside a variety of magnetic field gradient sets to be employed for possible lithium-ion battery MRI studies. The initial experimental sample, distilled water, was sandwiched between the plates which were 0.35 cm apart in simulation. The probe, in simulation, was fed a pulse of 0.5 W power through a discrete S-parameter port, with a sinusoidal signal at 100 MHz frequency. After calculation, the results were scaled for an input power of 26 W, the same input power that was applied to the parallel-plate prototype in the experiment. The leads shown on the left side of Fig. 3.1 are the feed points in the simulation. All capacitors were assumed nonideal with an Equivalent Series Resistance ESR of 30 m Ω and an Equivalent Series Inductance ESL of 0.05 nH. These values were chosen from the manufacturer-supplied data as representative typical values of ESR and ESL for the ATC-800B capacitor series. Capacitors from this series were employed to build the parallel-plate prototype. Resistances introduced by the solder joints, R_{sol} , were also considered in the simulation with a typical value of 30 m Ω [23].

The optimization process was undertaken with three different variables. In the first case, the dimensions of the plates were held constant while the dimensions of the leads in Fig. 3.1b were optimized. In the second case, the dimensions of the leads were held constant while the dimensions of the plates were optimized. In both cases, the value of the capacitor C was constant with a value of 1000 pF. In the third case, all the dimensions were constant for the plates and the leads and one capacitor was added to each of the four corners of the plates, as shown in Fig. 3.1c. In this case, the values of the capacitors were optimized through simulation. To reduce optimization time and reduce prototype complexity, only five capacitors were used. It was assumed that the three capacitors on the right have equal

value, C_R , and the two capacitors on the left also have equal value, C_L , as illustrated in Fig. 3.1c.



Fig. 3.1. CST geometry model of the Parallel-Plate Resonator showing the position of the capacitors connecting the copper plates. **a**), Only one capacitor C with fixed value of 1000 pF is connecting the plates. **b**), same as **a**) with wider leads. **c**), Five capacitors joining the plates, two with value C_L on the left and three with value C_R on the right side.

In all cases, the design goal is maximization of the homogeneity and strength of the \mathbf{B}_1 magnetic field in the central ZX plane. A \mathbf{B}_1 magnetic field strength variation of <10%, with respect to the \mathbf{B}_1 magnetic field strength at the centre of the central ZX plane, was considered homogeneous. The main static magnetic field is directed in the positive Z direction, so we are naturally interested in the X and Y components of the \mathbf{B}_1 magnetic field produced inside the plates. Calculation of the \mathbf{B}_1 magnetic field takes approximately 3 hours while the optimization process can take much longer depending on the initial conditions chosen.

3.3 Experimental

A prototype of the Parallel-Plate Resonator was built based on of the optimization results of case 3. The optimized probe consisted of two plates, dimensions 5.0×3.5 cm, and two leads, dimensions 1.5×1.0 cm. They were cut from a single-sided blank printed circuit board (PCB). The thickness of the copper layer of the PCB was 35 μ m. The two leads on the right were connected through a capacitor. The plates were also connected through one capacitor in each of the four corners of the sandwich structure, as shown in Fig. 3.2. The three capacitors C_R on the right are 228 pF (150 pF + 68 pF + 10 pF) while the two capacitors C_L on the left are 193 pF (150 pF + 43 pF). The capacitors also act as a support for the probe as depicted in Fig. 3.2. All capacitors are high Q, low noise, Porcelain Multilayer Capacitors with 5 % tolerance from the ATC-800B series (American Technical Ceramics, Huntington Station, NY, USA). Capacitors used have a ESR that varies from 20 to 52 m Ω and a ESL from 0.04 to 0.10 nH. The RF probe was tuned and matched to 100 MHz using a series capacitive matching network [24] with three variable capacitors. The quality factor Q of the probe, loaded and unloaded, was measured with a RF network analyser model 8714B, (Hewlett Packard, Santa Clara, CA, United States) based on the reflection mode method [24], $Q = 2\frac{f_0}{\Delta f}$. f_0 is the resonance frequency and δf is the bandwidth measured at -3 dB level in the reflection curve. Two different samples were used to measure the Q of the loaded probe, a black rubber sheet and a rectangular capillary tube filled with water doped with CuSO₄. The Q was always measured with the probe tuned at the resonance frequency f_0 and matched at 50 m Ω impedance.

All experiments were performed on a Nalorac (Martinez, CA) 2.4T 32 cm i.d. horizontal bore superconducting magnet with a water cooled 7.5 cm Nalorac gradient set (maximum gradient strength 27.6 G/cm, and maximum slew rate 1000 T/m/s) driven by Techron



Fig. 3.2. Photo of the Parallel-Plate Resonator RF probe. A capacitor was placed in each corner of the Parallel-Plate Resonator with another connecting the two leads on the right. The values of the capacitors were 193 pF (150 pF + 43 pF) for the capacitors C_L on the left and 228 pF (150 pF + 68 pF + 10 pF) for the capacitors C_R on the right. The plates, 0.35 cm apart, are 5 cm long and 3.5 cm wide. The leads are 1.5 cm long and 1.0 cm wide

(Elkhart, IN) 8710 amplifiers. The Parallel-Plate Resonator was driven by a 2 kW Tomco RF amplifier (Tomco Technologies, Stepney, Australia). The 90° pulse duration was 17 μ s for a pulse power of 26 W. The console was a Tecmag (Houston, TX) Redstone. The experiments were performed at the magnet bore temperature, approximately 10 °C. Pure phase encode MRI methods were employed because they are largely immune to **B**₀ inhomogeneity, chemical shift, and susceptibility effects. Magnetic field gradient induced eddy currents have minimal effect on image quality [17, 25, 26].

A 2D ZX spiral SPRITE [26] image was acquired for a uniform black rubber phantom, made of Ultra-Soft Polyurethane (McMaster-Carr, Cleveland, OH), of dimensions 4.5 × 3.5×0.33 cm. The bulk relaxation times were $T_2^* = 342 \ \mu s$, $T_2 = 15$ ms and 1.6 ms, and T_1 = 165 ms. The imaging sequence parameters were $G_{max,x} = 27.6$ G/cm; $G_{max,z} = 26.0$ G/cm; FOV = 6.0×6.0 cm; filter width 500 000 Hz, dwell time 1 μ s; 64×64 k-space matrix was acquired, each point with a phase-encoding time of 53 μ s and 256 signal averages for an overall acquisition time of 28 min. The flip angle was 10.6° with an RF pulse duration of 2 μ s. The delay between acquisitions was 1.5 seconds.

3.3.1 B_1 mapping

A pure phase encode \mathbf{B}_1 mapping method [27] was employed to evaluate the \mathbf{B}_1 homogeneity of the Parallel-Plate Resonator. A set of seven images were acquired with the same black rubber phantom with the same imaging parameters outlined above but with different RF pulse duration (0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 μ s). The shortest and longest RF pulse duration correspond to 4.2° and 10.6° flip angles. The phase cycle for both the RF pulses and the receiver was XXYY. The acquisition time for each image was 28 min with 256 averages.

The \mathbf{B}_1 value at each pixel was calculated as described by Vashaee *et al* [27]. Signal intensity of each pixel was plotted *vs* pulse duration. A relative \mathbf{B}_1^2 was obtained from the slope of this plot, spatially resolved. The absolute \mathbf{B}_1 strength at any position in the RF probe was calculated from the absolute \mathbf{B}_1 value at the centre of the probe. This value was measured at the centre of the probe using a small black rubber sample. For a 90° pulse duration of 17 μ s, the \mathbf{B}_1 value at the centre of the parallel-plate was 3.45 G.

3.3.2 High resolution thin film imaging

Double half k-space DHK spin echo SE single point imaging SPI [4, 9], was employed to acquire high resolution profiles of a doped water sample in a rectangular capillary tube.

The water was doped with CuSO₄ to shorten the relaxation times. The bulk relaxation times of the doped water were $T_2^* = 6.5$ ms and $T_2 = 60$ ms with a $T_1 = 91$ ms. The capillary tubes, purchased from VitroCom (Mountain Lakes, NJ, USA), were 400 μ m thick, 8.0 mm wide, and 5.0 cm long.

The magnetic field gradient G_y was chosen to be the principal phase-encoding gradient while gradients G_z and G_x were used to correct misalignment of the sample with respect to the main phase encode gradient [4]. A composite refocusing 180° -pulse $(90^\circ_y - 180^\circ_x - 90^\circ_y)$ was employed to correct for imperfect 180° -pulses. The duration of the 90° -pulse was 15 μ s, 64 k-space data points were acquired, each with an encoding time $t_p = 5.62$ ms and TE = 9.3 ms. Other sequence parameters were: FOV = $600 \ \mu$ m, TR = 500 ms, 16 signal averages, acquisition time of 9.0 min, filter width of 2500 Hz and 16 time domain points around the echo maximum were acquired at intervals of 200 μ s. The phase cycle for the RF 90°-pulse and the receiver was XXYY and XYYX for the 180° -pulse.

3.4 **Results and Discussion**

3.4.1 Simulation results

Fig. 3.1a shows the initial design of the Parallel-Plate Resonator with the plates connected through a capacitor C. Because the Parallel-Plate Resonator is intended to work as part of a functioning lithium-ion cell, this capacitor plays an important role in the design. During the charging/discharging of the battery, the capacitor will exhibit high impedance to direct current, thereby limiting its flow, and allowing normal battery operation. During RF excitation, the same capacitor will exhibit low impedance to high frequency components allowing them either to pass or limit current flow in the circuit, depending on frequency and the value of the capacitor. Given that the conductivity of the electrolyte is much less than the copper, RF current flow will pass through the capacitor and not through the electrolyte keeping the battery safe during the RF excitation. The electrolyte will decompose if the potential difference between electrodes is higher than 5 V. The value of the capacitor C was chosen to be 1000 pF, so as not to limit the RF excitation current flow significantly.

Fig. 3.3 depicts the simulated \mathbf{B}_1 magnetic field distribution in the central ZX plane between the plates, for different configurations of the resonator. Fig. 3.3a illustrates the \mathbf{B}_1 field distribution for the initial configuration. The \mathbf{B}_1 magnetic field distribution is very inhomogeneous with the highest values of \mathbf{B}_1 at the current feed point and at the connection point where the capacitor is located. The \mathbf{B}_1 magnetic field quickly decreases toward the centre and toward the corners of the plates. This observation agrees with results presented by Zhang *et al.* [28]. The asymmetry in the \mathbf{B}_1 magnetic field distribution is caused by the nonideal capacitor located on the right which has a ESR of 30 m Ω . The homogeneous region for this configuration is approximately 51% of the area of the plates. It is well known that severe \mathbf{B}_1 inhomogeneity leads to signal loss and image distortions. Poor \mathbf{B}_1 homogeneity, and the low \mathbf{B}_1 field strength of 3.0 G at the centre of the central ZX plane between the plates render this configuration ill-suited for high resolution thin film imaging.

Fig. 3.3b shows the \mathbf{B}_1 magnetic field distribution for case 1 where the dimensions of the plates are fixed, and dimensions of the leads were changed. As expected, the best result was obtained when the width of leads matched the plate width. The homogeneous region in Fig. 3.3b is approximately 87% of the area of the plates. However, there was no change in \mathbf{B}_1 field strength at the centre of the central ZX plane between the plates when compared with the initial configuration. The significant increase in homogeneity resulted from the current being distributed through the wider area of the leads. This produced a



Fig. 3.3. Simulation of magnetic field distribution produced by the Parallel-Plate Resonator for three different configurations. The direction of the \mathbf{B}_1 magnetic field is along the x axis. The dimensions of the plates are the same in all cases, 5 cm long and 3.5 cm wide. a), the dimensions of the leads, 1.5 cm long and 1.0 cm wide. b), the dimensions of the leads, 1.5 cm long and 3.5 cm wide. c), dimensions of the leads same as a), but with a capacitor added to each corner of the plates. The dashed line delimits the area covered by the plates and the leads.

more uniform distribution of the current along the width of the plates. Although there is a significant increase in the \mathbf{B}_1 homogeneity, and it is possible to do thin film imaging, this configuration is essentially a longer plate in which the central region is chosen for imaging. This result was previously presented by Meadowcroft *et al.* [15] who used a parallel-plate style RF probe to image histological samples. The asymmetry in the \mathbf{B}_1 magnetic field

distribution is also present in case 1 because of the nonideal capacitor, as shown in Fig. 3.3b.

The results of the optimization for case 2 are similar to the results reported for case 1. The homogeneity of the \mathbf{B}_1 magnetic field is maximized when the width of the leads and the plates are equal. Decreasing the width of the plates will reduce considerably the sample area inside the gradient set, reducing the signal-to-noise ratio in the ultimate battery. This result shows that the best way to increase probe sensitivity and \mathbf{B}_1 field homogeneity is to keep the dimensions of the plates constant and optimize the other parameters.

Fig. 3.3c shows the B_1 magnetic field distribution for case 3 where the two plates are connected through a capacitor located at each corner of the plates with one connecting the two leads on the right side of the Parallel-Plate Resonator. Five is the minimum number of capacitors that will produce a relatively high homogeneous magnetic field without introducing significant challenges in the building process of the prototype. The optimum values for the capacitors C_L and C_R , found through simulation, were 185 pF and 210 pF, respectively. As expected, C_R has a higher value than C_L . The current is expected to flow along the plates from left to right in the plates. This configuration produces a relatively homogeneous \mathbf{B}_1 magnetic field distribution, 84% of the sample area has a \mathbf{B}_1 field variation of <10% referenced to the \mathbf{B}_1 field at the centre of the central ZX plane between the plates. Although the homogeneity in case 3 is slightly lower than case 1, the \mathbf{B}_1 field intensity increased by 40%, from 3.0 G in case 1 to 4.3 G in case 3. The relatively high homogeneity and higher intensity in the \mathbf{B}_1 magnetic field is a result of the proper selection of the capacitors C_L and C_R , as shown in the simulation Fig. 3.3c. The capacitors provide an alternative path for the current. Some current is diverted through the capacitors producing a more even distribution of the current in the plates of the Parallel-Plate Resonator. The configuration presented in case 3 produced a higher \mathbf{B}_1 magnetic field per unit current and similar homogeneity to case 1. The results obtained in case 3 suggest that building a Parallel-Plate Resonator with optimized capacitors at the corners of the plates will have a higher sensitivity due to the higher \mathbf{B}_1 magnetic field [13]. Thereby, it will be the most suitable for high resolution thin film imaging.

3.4.2 Experimental results

The Parallel-Plate Resonator is intended to ultimately function as part of a model lithium-ion battery to provide spatial resolution through MRI of the electrolyte and electrodes. It is important for the RF probe to have high sensitivity since high resolution is required. The home-made Parallel-Plate Resonator was fabricated based on optimization explored through simulation. The RF probe with capacitors in each corner was chosen because of the higher **B**₁ magnetic field strength and relatively high homogeneity.

The values of the capacitors used for building the prototype were slightly different from the values determined through simulation. The values of the capacitors C_L and C_R found through simulation were 185 pF and 210 pF, respectively while the experimental values were 193 pF and 228 pF, respectively. There is a good agreement between the optimized and the experimental values with a difference of <10%. This difference arises from several different factors. First, tolerance and standard values of the capacitors. Commercial capacitors exist in a series of standard values and tolerances making it sometimes difficult to match specific values. The tolerance for the ATC-800B series is 5%. Second, asymmetries created during the building process and differences between the parallel-plate RF probe in simulation and the physical prototype. The separation between the plates is, for example, difficult to match exactly to simulation because of the dimensions of the capacitors and the solder joints. The capacitors were modelled as lumped elements in the simulation but, in the physical prototype they are spatially distributed, they are 3 mm thick. Solder joints will introduce significant losses in the circuit and therefore a decrease in the **B**₁ field strength. It has been reported that solder joints can be responsible for up to 15% of the losses in the RF probe circuit [29]. Finally, the plates were assumed to be infinitely thin in simulation, but in the prototype, they are 35 μ m thick on the PC board. Despite these factors, the experimental results are still in good agreement with the simulation.

Measurement of the quality factor of the probe loaded and unloaded, with the rubber phantom and the doped water in the rectangular capillary tube as samples, produced identical values of 165. Even though this probe should be classified as a mid-range probe according to Doty *et al.* [29], where sample, probe, and capacitor losses are all important, the results suggest that the ESR of the capacitors, the number of capacitors, and the solder joints determine the RF probe losses. In simulation, eight capacitors, two capacitors C_L , three capacitors C_R , and three capacitors in the matching network were considered. All capacitors had an ESR of 30 m Ω and the solder joint, attaching it to the plates, had a resistance of $R_{sol} = 30 \text{ m}\Omega$. In the prototype, 15 capacitors were employed. Each capacitor C_R is a combination of three smaller capacitors (150 pF, 68 pF, and 10 pF) and each capacitor that the ESR can be significantly higher for the capacitors with smaller values. In addition, the increased number of capacitors increases considerably the number of solder joints. All these factors will increase the losses in the probe and explain the difference between the values of capacitors obtained through simulation and experiment.

The Parallel-Plate Resonator has a relatively low inductance of 26 nH. Approximately,

30% of the inductance appears on the leads and the capacitors (leads, 5 nH and capacitors, 3.2 nH). The other 70% of the probe inductance is in the plate area which is a good indicator of the efficiency of the probe. The inductance values were determined using a RF network analyser (Hewlett Packard, Santa Clara, CA, USA) through the resonance frequency with the equation $L = \frac{1}{(2\pi f)^2 C}$. Knowing the resonance frequency and the capacitance, the inductance was calculated. The capacitor leads were removed to reduce parasitic inductance. The solder joints were also minimized.

Fig. 3.4 shows a 2D ZX normalized proton density image of a black rubber sample taken with the prototype Parallel-Plate Resonator. The image signal intensity is homogeneous in the central region of the probe. There are also high signal areas near the feed point and near where the plates are connected through the capacitors. The slightly lower signal between the capacitors on the left and the feed point is produced by the opposition of the current diverted through the capacitors and the current on the feed point. Signal intensity reduction occurs because of the current in this area is perpendicular to the Z direction, producing a \mathbf{B}_1 magnetic field parallel to the Z direction that is ineffective for MR/MRI. The results agree closely with the simulation shown in Fig. 3.3c.

The image presented in Fig. 3.4 is not a direct map of the \mathbf{B}_1 magnetic field distribution. The image intensity is proportional to the square of the \mathbf{B}_1 intensity, accentuating the differences in the \mathbf{B}_1 magnetic field distribution [27]. Fig. 3.5 shows a 2D ZX \mathbf{B}_1 map for the parallel-plate resonator at 2.4 T. The image shows that the \mathbf{B}_1 magnetic field distribution is homogeneous except in regions close to the capacitors and the feed points. The \mathbf{B}_1 field strength at the centre of the plates is 3.5 G. This value is 20% lower than the value of Fig. 3.3c. As explained above, this difference is mainly due to the difference in the number of capacitors, the higher ESR of the smaller capacitors and the number of solder joints. The



Fig. 3.4. 2D ZX normalized proton density image of the black rubber sample $4.5 \times 3.5 \times 0.35$ cm, acquired with 2D Spiral SPRITE with the Parallel-Plate Resonator at a $t_p = 53 \mu$ s. The image was acquired with 256 scans with an acquisition time of 28 min. The FOV was 6×6 cm with a nominal resolution of 0.9 mm in both directions laterally. The image is averaged over the sample thickness.

lower \mathbf{B}_1 strength in the corner is produced by the presence of the capacitors and the solder joints producing an inhomogeneous \mathbf{B}_1 magnetic field in that area. The relatively high homogeneity of the \mathbf{B}_1 magnetic field between the plates and the higher \mathbf{B}_1 strength make this RF probe suitable for high resolution thin film imaging.

The sensitivity of the parallel-plate RF probe was compared with that of a flat surface coil [9]. The flat surface coil was chosen for comparison because it was previously used to study water content in Nafion membranes [8]. In this previous study, a nominal resolution of <10 μ m was obtained with the 2 cm diameter probe and a quality factor of 155. The



Fig. 3.5. Calibrated 2D ZX **B**₁ map for the Parallel-Plate Resonator at 2.4 T using the black rubber sample, $4.5 \times 3.5 \times 0.35$ cm. The FOV was 6×6 cm

90°-pulse duration was determined with an RF amplifier pulse power of 26 W. A black rubber sample, centred 0.5 cm above the probe, was employed to measure the 90°-pulse duration. The duration of the 90°-pulse for the parallel-plate RF resonator was 17 μ s and for the surface coil it was 20 μ s. The 90°-pulse length for fixed power is a good indicator of the probe sensitivity as advocated by Doty [30]. The Parallel-Plate Resonator was more sensitive, than the surface coil.

Nonorthogonality of the sample and the main phase encode magnetic field gradient is problematic for high resolution thin film imaging. Nonorthogonality can lead to significant resolution loss. Fig. 3.6 shows a depth profile of the doped water sample in a thin film

capillary tube of 400 μ m thickness after correcting the nonorthogonality of the sample with the main magnetic field gradient G_y . The two complementary magnetic field gradients G_x and G_z were employed to correct the nonorthogonality as reported by Ouriadov *et al.* [4]. The capillary tube was nonorthogonal with respect to the Y axis by 0.8° in the X direction and 1.5° in the Z direction. The nominal image resolution was 10 μ m. The voxel volume was 2.8 mm³ but note we are averaging over the sample size in X and Z to achieve a high sensitivity depth profile. 64 k-space points were acquired with a field of view of 600 μ m.

As shown in the Y profile of Fig. 3.6, there is a degradation in the edges of the image profile corresponding to the top and bottom of the capillary tube. This could be because the sample does not have a perfectly flat surface, or more likely because of residual nonorthog-onality of the sample and phase-encoding gradient. The degradation of the image profile will result in a degradation of the true image resolution. This resolution can be significantly improved if a near perfect orthogonality between the sample and the main gradient is achieved, as explained by Ouriadov *et al.* [4].

Although the results presented in this work were obtained at a frequency of 100 MHz with ¹H samples in a 2.4 T magnet, the final goal of this work was to use a similar design of the Parallel-Plate Resonator, tuned to a frequency of 116 MHz for ⁷Li samples in a 7 T magnet. The optimization process must be repeated when the components of the LIB are placed inside the parallel-plate. This will change the values of the capacitors and the strength of the **B**₁ magnetic field. However, we are confident that the basic premise of the optimization process will still be valid. This confidence is based on previous work with the Parallel-Plate Resonator to study water transport in a Nafion-based fuel cell [8]. We believe that the optimized Parallel-Plate Resonator combined with the SE SPI method will be very useful in the study of lithium-ion transport in the electrolyte solution and lithium-



Fig. 3.6. Depth profile of the doped water sample in the rectangular capillary tube. The profile was acquired in 16 scans with an acquisition time of 9 min and a $t_p = 5.6$ ms.

ion intercalation into graphite inside a LIB.

3.5 Conclusion

A Parallel-Plate Resonator design was optimized using distributed capacitance increasing the **B**₁ homogeneity and increasing the **B**₁ magnetic field strength. A prototype parallelplate resonator was built based on the optimized design. 2D images and **B**₁ maps showed that the experimental results agree with the simulation. It is possible to achieve high resolution thin film imaging with a resolution <10 μ m. A similar prototype will be tested as part of a functional lithium-ion battery. The parallel-plate RF probe design may be readily adapted for ⁷Li imaging in lithium ion battery studies.

References

- [1] P. M. Glover, P. S. Aptaker, J. R. Bowler, E. Ciampi, P. J. McDonald, A novel highgradient permanent magnet for the profiling of planar films and coatings, Journal of Magnetic Resonance 139 (1999) 90–97. doi:10.1006/jmre.1999.1772.
- [2] T. Dikić, S. J. Erich, W. Ming, H. P. Huinink, P. C. Thüne, R. A. van Benthem, G. de With, Fluorine depth profiling by high-resolution 1D magnetic resonance imaging, Polymer 48 (2007) 4063–4067. doi:10.1016/j.polymer.2007.05.017.
- [3] Z. Zhang, A. E. Marble, R. P. MacGregor, J. Martin, H. Wang, B. J. Balcom, Zero-mode TEM parallel-plate resonator for high-resolution thin film magnetic resonance imaging, Canadian Journal of Chemistry 89 (2011) 745–753. doi:10.1139/ v11-018.
- [4] A. V. Ouriadov, R. P. MacGregor, B. J. Balcom, Thin film MRI high resolution depth imaging with a local surface coil and spin echo SPI, Journal of Magnetic Resonance 169 (2004) 174–186. doi:10.1016/j.jmr.2004.04.015.
- [5] J. Zhang, B. J. Balcom, Parallel-plate RF resonator imaging of chemical shift resolved capillary flow, Magnetic Resonance Imaging 169 (2010) 174–186. doi:10.1016/ j.mri.2010.03.033.
- [6] J. Zhang, R. P. MacGregor, B. J. Balcom, Liquid crystal diffusion in thin films investigated by PFG magnetic resonance and magnetic resonance imaging, Chemical Physics Letters 461 (2008) 106–110. doi:10.1016/j.cplett.2008.06.090.
- [7] S. Klamor, K. Zick, T. Oerther, F. M. Schappacher, M. Winter, G. Brunklaus, ⁷Li *in situ* 1D NMR imaging of a lithium ion battery, Physical Chemistry Chemical Physics 17 (2015) 4458–4465. doi:10.1039/c4cp05021e.

- [8] Z. Zhang, J. Martin, J. Wu, H. Wang, K. Promislow, B. J. Balcom, Magnetic resonance imaging of water content across the Nafion membrane in an operational PEM fuel cell, Journal of Magnetic Resonance 193 (2008) 259–266. doi:10.1016/j. jmr.2008.05.005.
- [9] Z. Zhang, A. E. Marble, B. MacMillan, K. Promislow, J. Martin, H. Wang, B. J. Balcom, Spatial and temporal mapping of water content across Nafion membranes under wetting and drying conditions, Journal of Magnetic Resonance 194 (2008) 245–253. doi:10.1016/j.jmr.2008.07.011.
- [10] S. A. Krachkovskiy, J. D. Bazak, P. Werhun, B. J. Balcom, I. C. Halalay, G. R. Goward, Visualization of steady-state ionic concentration profiles formed in electrolytes during Li-Ion battery operation and determination of mass-transport properties by *in situ* magnetic resonance imaging, Journal of the American Chemical Society 138 (2016) 7992–7999. doi:10.1021/jacs.6b04226.
- [11] S. A. Krachkovskiy, J. M. Foster, J. D. Bazak, B. J. Balcom, G. R. Goward, Operando mapping of Li concentration profiles and phase transformations in graphite electrodes by magnetic resonance imaging and nuclear magnetic resonance spectroscopy, Journal of Physical Chemistry C 122 (2018) 21784–21791. doi:10.1021/acs.jpcc. 8b06563.
- [12] S. Chandrashekar, N. M. Trease, H. J. Chang, L. S. Du, C. P. Grey, A. Jerschow, ⁷Li MRI of Li batteries reveals location of microstructural lithium, Nature Materials 11 (2012) 311–315. doi:10.1038/nmat3246.
- [13] D. I. Hoult, R. E. Richards, The signal-to-noise ratio of the nuclear magnetic resonance experiment, Journal of Magnetic Resonance (1969) 24 (1976) 71–85. doi: 10.1016/0022-2364(76)90233-X.

- [14] D. I. Hoult, The principle of reciprocity in signal strength calculations a mathematical guide, Concepts in Magnetic Resonance 12 (2000) 173–187. doi:10.1002/1099-0534(2000)12:4<173::AID-CMR1>3.0.C0;2-Q.
- [15] M. D. Meadowcroft, S. Zhang, W. Liu, S. P. Bu, J. R. Connor, C. M. Collins, M. B. Smith, Q. X. Yang, Direct magnetic resonance imaging of histological tissue samples at 3.0T, Magnetic Resonance in Medicine 57 (2007) 835–841. doi:10.1002/mrm. 21213.
- [16] D. M. Hoang, E. B. Voura, C. Zhang, L. Fakri-Bouchet, Y. Z. Wadghiri, Evaluation of coils for imaging histological slides: Signal-to-noise ratio and filling factor, Magnetic Resonance in Medicine 71 (2014) 1932–1943. doi:10.1002/mrm.24841.
- [17] S. Gravina, D. G. Cory, Sensitivity and resolution of constant-time imaging, Journal of Magnetic Resonance, Series B 104 (1994) 53-61. doi:10.1006/jmrb.1994. 1052.
- [18] P. J. Prado, B. J. Balcom, I. V. Mastikhin, A. R. Cross, R. L. Armstrong, A. Logan, Magnetic resonance imaging of gases: A single-point ramped imaging with T₁enhancement (SPRITE) study, Journal of Magnetic Resonance 137 (1999) 324–332. doi:10.1006/jmre.1998.1674.
- [19] M. Winter, The solid electrolyte interphase the most important and the least understood solid electrolyte in rechargeable Li batteries, Zeitschrift fur Physikalische Chemie 223 (2009) 1395–1406. doi:10.1524/zpch.2009.6086.
- [20] M. B. Pinson, M. Z. Bazant, Theory of SEI formation in rechargeable batteries: Capacity fade, accelerated aging and lifetime prediction, Journal of The Electrochemical Society 160 (2013) A243–A250. doi:10.1149/2.044302jes.

- [21] J. Zhao, L. Wang, X. He, C. Wan, C. Jiang, Determination of lithium-ion transference numbers in LiPF₆-pc solutions based on electrochemical polarization and NMR measurements, Journal of The Electrochemical Society 155 (2008) A292–296. doi:10.1149/1.2837832.
- [22] K. Xu, A. V. Cresce, Interfacing electrolytes with electrodes in Li ion batteries, Journal of Materials Chemistry 21 (2011) 9849–9864. doi:10.1039/c0jm04309e.
- [23] A. Kumar, W. A. Edelstein, P. A. Bottomley, Noise figure limits for circular loop MR coils, Magnetic Resonance in Medicine 61 (2009) 1201–1209. doi:10.1002/mrm. 21948.
- [24] J. Mispelter, M. Lupu, A. Briguet, NMR Probeheads for Biophysical and Biomedical Experiments, 2nd Edition, Imperial College Press, 2006. doi:10.1142/p438.
- [25] M. Halse, D. J. Goodyear, B. MacMillan, P. Szomolanyi, D. Matheson, B. J. Balcom, Centric scan SPRITE magnetic resonance imaging, Journal of Magnetic Resonance 165 (2003) 219–229. doi:10.1016/j.jmr.2003.08.004.
- [26] P. Szomolanyi, D. Goodyear, B. Balcom, D. Matheson, SPIRAL-SPRITE: A rapid single point MRI technique for application to porous media, Magnetic Resonance Imaging 19 (2001) 423–428. doi:10.1016/S0730-725X(01)00260-0.
- [27] S. Vashaee, B. Newling, B. MacMillan, B. J. Balcom, Mapping with a pure phase encode approach: Quantitative density profiling, Journal of Magnetic Resonance 232 (2013) 68–75. doi:10.1016/j.jmr.2013.04.012.
- [28] Z. Zhang, A. E. Marble, R. P. MacGregor, J. Martin, H. Wang, B. J. Balcom, Zero-mode TEM parallel-plate resonator for high-resolution thin film magnetic reso-

nance imaging, Canadian Journal of Chemistry 89 (2011) 745–753. doi:10.1139/ v11-018.

- [29] F. D. Doty, G. Entzminger, J. Kulkarni, K. Pamarthy, J. P. Staab, Radio frequency coil technology for small-animal MRI, NMR in Biomedicine 20 (2007) 304–325. doi:10.1002/nbm.1149.
- [30] F. D. Doty, Probe design and construction, eMagRes (2007) 1-12. .doi:10.1002/ 9780470034590.emrstm0414.

Chapter 4

Parallel-Plate RF Probe and Battery Cartridge for ⁷Li Ion Battery Studies

The PPR RF probe, which was introduced in Chapter 3, proved to be an excellent choice to interrogate flat planar samples. The RF probe can be optimized for both B_1 magnetic field strength and B_1 magnetic field homogeneity, thus increasing the probe sensitivity. In this Chapter, building on the results presented in the Chapter 3, we optimized a PPR RF probe for MR studies of LIBs. We also introduced a battery cartridge that maximized sample volume and avoided RF attenuation during RF excitation and MR signal reception. Combining the PPR RF probe with the battery cartridge we reported the first T_1 - T_2 relaxation correlation experiment on LIBs. We also, successfully detected and quantified lithium intercalated into graphite.

This chapter is largely based on the paper "A parallel-plate RF probe and battery cartridge for ⁷Li ion battery studies" published in the *Journal of Magnetic Resonance*, 325, 106943-106950 (2021). To avoid content repetition, the introduction of this chapter has been reduced. The content removed was added to section 2.3.

In this chapter we follow the notation for variables and equations recommended by the *Journal of Magnetic Resonance*.

Abstract

A new Parallel-Plate Resonator for ⁷Li ion cell studies is introduced along with a removable cartridge-like electrochemical cell for lithium-ion battery studies. This geometry separates the RF probe from the electrochemical cell permitting charge/discharge of the cell outside the magnet and introduces the possibility of multiplexing samples under test. The new cell has a geometry that is similar to that of a real battery, unlike the majority of cells employed for MR/MRI studies to this point. The cell, with electrodes parallel to the **B**₁ magnetic field of the probe, avoids RF attenuation during excitation/reception. The cell and RF probe dramatically increase the sample volume compared to traditional MR compatible battery designs. *Ex situ* and *in situ* 1D ⁷Li profiles of Li ions in the electrolyte solution of a cartridge-like cell were acquired, with a nominal resolution of 35 mm at 38 MHz. The cell and RF probe may be employed for spectroscopy, imaging and relaxation studies. We also report the results of a T_1 - T_2 relaxation correlation experiment on both a pristine and fully charged cell. This study represents the first T_1 - T_2 relaxation correlation experiment performed in a Li ion cell. The T_1 - T_2 correlation maps suggest lithium intercalated into graphite is detected by this methodology in addition to other Li species.

4.1 Introduction

Magnetic Resonance (MR) has proven to be a valuable tool to investigate, *in operando*, Lithium-Ion Batteries (LIBs), providing invaluable insight into battery structure and function. MR and Magnetic Resonance Imaging (MRI) studies have been undertaken to better understand internal battery behaviour to aid improvements in battery performance [1–5]. Lithium intercalation into graphite [3, 5, 6] and lithium plating on the surface of the electrodes [2, 7, 8] are of great scientific and practical interest for reasons of performance, capacity loss and safety. However, the presence of highly conductive materials in the Liion cell, screening the RF signal, and the lack of dedicated MR probes for these studies hinders the use of MR/MRI methods for realistic cell geometries. The ideal cell geometry will be flat with parallel electrodes separated by electrolyte. This geometry is naturally achieved with a parallel-plate RF probe.

To date, most ⁷Li MR studies of LIBs have employed spectroscopic methods with pencil-like cells [9-11]. This type of cell design has been extremely successful because it permits ex situ magic angle spinning (MAS) techniques to be employed, resulting in high-resolution spectra [9, 10]. In situ ⁷Li MAS studies in LIBs are challenging, mainly due to the inability to perform sample spinning during an *in situ* MR experiment. However, in situ ⁷Li MAS of a full electrochemical LIB cell was recently reported [11]. In the study, a novel jelly roll cell design was employed, permitting observation of metallic lithium plating and formation of the solid-electrolyte interface SEI through the acquisition of high resolution spectra. However, one common objection to cell designs employed for ⁷Li studies is that they do not represent the most favourable LIBs geometries, which are often flat planar structures [12]. There is a natural merit in an MR approach to the study of electrochemical cells where the RF probe is integrated into an operational cell. This was achieved in full cell studies [13] with a parallel-plate structure where the plates functioned as the electrodes and RF probe elements. Recently, Jerschow and coworkers [14] have employed copper pads, exterior to a pouch cell, to resonate the metal elements of the pouch cell for magnetic resonance.

A natural RF probe choice for ⁷Li LIB studies is a parallel-plate type resonator [13]. This geometry naturally accommodates a parallel electrode cartridge-like LIB cell. With the \mathbf{B}_1 magnetic field oriented parallel to the plates, RF attenuation during excitation/reception due to the electrodes is greatly reduced. The Parallel-Plate Resonator has been previously employed in ¹H MR/MRI to study fuel cells [13]. In the current work we separate the

electrochemical cell from the resonator to improve performance and permit multiplexing samples. Recently an optimized Parallel-Plate Resonator was presented for ¹H high resolution thin film imaging [15]. The optimized parallel-plate resonator increases B_1 magnetic field strength, B_1 homogeneity and experiment sensitivity by attaching capacitors to the corners of the plates. A parallel-plate RF probe, forming part of the LIB cell has recently been employed to investigate metallic lithium plating, using spectroscopic methods [16].

In this work, a Parallel-Plate Resonator [15] with a cartridge-like cell for ⁷Li LIB studies was designed, built and tested. The new cell/RF probe design provides a natural geometry to ensure close contact between electrodes and electrolyte. The cell with electrodes parallel to the \mathbf{B}_1 magnetic field of the probe, reduced RF attenuation during excitation/reception. The large sample volume of the cell improves experiment sensitivity compared to other designs. Simulated and experimental values of the \mathbf{B}_1 magnetic field agree to within 25%. To demonstrate the utility of the Parallel-Plate Resonator combined with the cartridge LIB cell, several MR/MRI experiments were undertaken. Ex situ (cell disconnected from the charge/discharge circuit) and in situ (cell connected to the charge/discharge circuit) 1D ⁷Li profiles of Li ions in the electrolyte solution of a cartridge LIB cell were acquired, with a nominal resolution of 35 μ m using a pure phase encoding SE technique [5]. A T_1 - T_2 relaxation correlation experiment in both an uncharged pristine and fully charged cell was also performed. To the best of our knowledge, this study represents the first ⁷Li T_1 - T_2 relaxation correlation experiment performed in a LIB cell. The T_1 - T_2 correlation maps suggest it is possible to identify lithium intercalation into graphite with this approach. The Parallel-Plate Resonator and battery cartridge were developed in this work for use in lithium-ion battery studies, but they may be adapted for other battery types and other battery studies. Similarly, the T_1 - T_2 measurement is well suited to probing behaviour of other nuclei in LIB studies and in studies of other battery types.

4.2 **RF probe design and simulations**

The ⁷Li parallel-plate resonator was designed and optimized with CST Microwave Studio 2017 (CST of America, Framingham, MA) using a PC with a 2.1 GHz AMD RYZEN 5 Processor and 24 GB of installed RAM. The high frequency module was employed for numerical calculation of the magnetic field produced by the probe. The transient solver with tetrahedral meshing was used for the simulations. The Parallel-Plate Resonator design and simulation were based on the optimized ¹H Parallel-Plate Resonator previously reported [15]. The probe consisted of two copper plates, 7 mm apart, with lateral dimensions of 50 mm \times 35 mm. The plates were connected through five capacitors acting as supports for the sandwich structure, as shown in Fig. 4.1. The plates were simulated as sheets to reduce model complexity and calculation time. The capacitor values C_L and C_R were optimized to maximize \mathbf{B}_1 magnetic field homogeneity and strength between the two plates. To better account for the capacitors losses they were assumed nonideal with an equivalent series resistance (ESR) of 30 m Ω , with equivalent series inductance (ESL) of 0.05 nH. The separation between the plates was set to 7.0 mm in order to accommodate a LIB cell with a maximum separation of 2.0 mm between the LIB electrodes. The probe, in simulation, was fed with a Gaussian RF pulse which delivers 0.5 W power to the probe when matched to 50 Ω . The calculation results were scaled for an input power of 115 W, the same input power applied to the parallel-plate prototype in MR experiments. The pulse was applied through a discrete S-parameter port at a frequency of 38 MHz, which is the ⁷Li resonance frequency at 2.4 T. The probe was tuned and matched using a balanced series

capacitive matching network [17] with three variable capacitors. During simulation, the capacitances values C_L and C_R were optimized to maximize the homogeneous \mathbf{B}_1 area between the plates. Deviations in \mathbf{B}_1 homogeneity not exceeding 10% of the \mathbf{B}_1 field strength value at the centre between the plates was considered homogeneous [15].



Fig. 4.1. CST Microwave Studio geometry model of the ⁷Li parallel-plate resonator. The capacitor values C_L and C_R are optimized through simulation to maximize the **B**₁ magnetic field strength and homogeneity between the plates. Capacitors are shown as light blue chamfered disks while the excitation port is shown as a red chamfered disk.

4.3 Experimental

A Parallel-Plate Resonator was built based on the optimized design realized through simulation. The optimized probe consisted of two plates, dimensions 50 mm \times 35 mm, and two leads, dimensions 15 mm \times 10 mm. The plates were cut from a single sided blank printed circuit board (PCB). The thickness of the copper layer of the PCB was 35 μ m. The two leads on the right were connected through a capacitor. The plates were also connected

through one capacitor in each of the four corners of the sandwich structure, as shown in Fig. 4.2. The three capacitors C_R on the right are 201 pF (110 pF + 91 pF) while the two capacitors C_L on the left are 101 pF (68 pF + 33 pF). The capacitors also act as a support for the probe as depicted in Fig. 4.2. All capacitors are high Q, low noise, Porcelain Multilayer Capacitors with 5% tolerance from the ATC-800B series (American Technical Ceramics, Huntington Station, NY). Capacitors used have an ESR that varies from 20 to 52 m Ω and an ESL from 0.04 to 0.10 nH. The RF probe was tuned and matched to 38 MHz using a series capacitive matching network [17] with three variable capacitors. The quality factor Q of the probe, loaded and unloaded, was measured with a RF network analyser model 8714B, (Hewlett Packard, Santa Clara, CA) based on the reflection mode method [17], $Q = 2\frac{\hbar}{\Delta f}$. f_0 is the resonance frequency and is the bandwidth measured at -3 dB level in the reflection curve. The Q was always measured with the probe tuned at the resonance frequency f_0 and matched at 50 Ω impedance.



Fig. 4.2. Photo of the ⁷Li Parallel-Plate Resonator RF probe. The plates, separated by 7.0 mm, are 50 mm long and 35 mm wide. The copper leads are 15 mm long and 10 mm wide. A capacitor was placed in each corner of the Parallel-Plate Resonator with another connecting the two copper leads at right. The **B**₁ magnetic field is aligned along x.

4.3.1 Cell container and electrochemical measurement

The Parallel-Plate Resonator provides an ideal geometry for a removable, cartridge-like, prismatic cell geometry. The cartridge-like cell container was built with two square pieces with a side length of 45 mm. The bottom piece was a copper clad PC board. The top piece was a garolite sheet (McMaster-Carr, Robbinsville, NJ) with an aluminium piece attached to it. The top and bottom pieces were separated by a silicon rubber gasket (McMaster-Carr) to seal the cell and avoid electrolyte spillage. Six brass screws were employed to seal and fasten the cell, as shown in Fig. 4.3. A square area of 900 mm² was cut from the gasket for insertion of the LIB cell.

The LIB cell was assembled with a graphite anode and a Lithium Nickel Manganese Cobalt Oxide cathode, LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ (NMC532), both electrodes with a capacity of ~ 2 mAh/cm² (NEI Corporation, Somerset, NJ). The NMC electrode, with active material loading of 11.83 mg/cm² and a thickness of 70-75 μ m, is coated on an aluminium current collector. The graphite electrode, with a porosity of 35% and a thickness of 60-65 μ m, is coated on a copper current collector. Whatman glass microfibre filters, Grade GF/C, 250 μ m thick (Sigma-Aldrich, Ontario, Canada), were used as separators. The separators were soaked with 1 M LiTFSI in 1:1 (v/v) ethylene carbonate (EC) and diethyl carbonate (DEC) electrolyte solution (Sigma-Aldrich). The electrodes and the separators were cut square with an area 900 mm², to fit in the centre of the rubber gasket in the cartridge container.

The electrodes, the separators, and the cartridge parts were dried prior to assembly. They were dried at 80 °C for 36 h. All LIB cells were assembled inside an argon-filled glove-box (7 ppm oxygen, less than 0.1 ppm water content) as follows: (1) The rubber gasket was placed on top of the copper clad PC board; (2) The graphite electrode was placed at the bottom of the cell, inside the gasket, with the copper current collector in direct contact



Fig. 4.3. The removable cartridge-like Li-ion cell mimics the geometry of the most common Li-ion cells. The square cell can be easily inserted into the RF probe.

with the copper clad PC board; (3) the glass microfibre separator soaked with electrolyte was inserted on top of the graphite electrode; (4) the NMC electrode is then placed on top of the glass microfibre separators; (5) the garolite sheet with aluminium was placed on top of the NMC electrode, in direct contact with the aluminium current collector; (6) the cell was tightly sealed with non-magnetic screws using an adjustable torque screwdriver.

The second cell, with lithium metal as a cathode (MTI Corporation, Richmond, CA) and a graphite anode was assembled as reference cell to test direct detection of lithium metal. Two Li metal disks of 16 mm diameter and 0.6 mm thickness were employed. A rubber gasket with thickness of 2 mm was employed. The electrodes were separated with two Whatman paper filters.

For the ⁷Li MR T_1 - T_2 correlation experiment, a LIB cell with ~ 0.5 mm separation between electrodes (one paper filter separator) and an electrolyte volume of 400 μ L was
assembled. The rubber gasket with a thickness of 1 mm was employed to seal the cell. The screws were tightened with a torque of 0.1 N·m. The same cell was later charged in constant current mode only, with a 2400 Source Meter (Tektronix, Inc., Beaverton, OR) at a low rate of C/35 (500 μ A) up to 4.2 V. For the 1D ⁷Li profile measurements, a different cell, with a separation of ~ 1 mm (four paper filter as separator) between electrodes, and an electrolyte volume of 800 μ L was assembled. The rubber gasket thickness was 2 mm, and the screws were tightened with a torque of 0.5 N·m. In all cases the screws were tightened until the plates contacted the electrodes without displacing electrolyte. The parallel electrodes in the cartridge-like LIB cell ensures close contact of the electrodes and electrolyte.

4.3.2 MR experiments

All experiments were performed on a Nalorac (Martinez, CA) 2.4 T 32 cm i.d. horizontal bore superconducting magnet with a homogeneity of approximately 1 ppm. The magnet is equipped with a water cooled 7.5 cm Nalorac gradient set (maximum gradient strength 27.6 G/cm, and maximum slew rate 1000 T/m/s) driven by Techron (Elkhart, IN) 8710 amplifiers. The Parallel-Plate Resonator was driven by a 2 kW Tomco RF amplifier (Tomco Technologies, Stepney, Australia). The 90° pulse duration for a ⁷Li sample was 30 μ s for a pulse power of 115 W. The ⁷Li resonance frequency was 38 MHz. The console was a Tecmag (Houston, TX) Redstone. MR/MRI experiments were performed at the magnet bore temperature, approximately 10 °C. The bulk relaxation times of the free electrolyte were $T_2^* = 10$ ms with $T_2 = T_1 = 1$ s.

1D ⁷Li depth profiles were acquired using a pure phase encoding SE sequence [18]. The G_y gradient was chosen to be the principal phase encoding gradient. 64 k-space data points

were acquired, each with an encoding time tp = 3.4 ms and TE = 4.6 ms. 32 time domain points were acquired on each echo with a dwell time of 20 μ s. To improve the signal-tonoise ratio, 8 time domain points at the top of the echo were averaged. Other sequence parameters were: FOV = 2 mm, TR = 1 s, 4 signal averages, acquisition time of 22 min, filter width of 2500 Hz. The phase cycle for the RF 90°-pulse and the receiver was $X\bar{X}Y\bar{Y}$ and $\bar{X}\bar{Y}YX$ for the 180°-pulse. *Ex situ* and *in situ* 1D ⁷Li depth profiles were acquired for a pristine LIB cell. The *in situ* profile was acquired while the cell was connected to the 2400 Source Meter (Tektronix, Inc., Beaverton, OR) through two coaxial cables. A 2 MHz low pass filter was employed to prevent noise pick up by the parallel-plate RF probe. The 2400 Source Meter was on during the measurement but was not delivering any current. For the *ex situ* profile, the LIB cell was disconnected from the change/discharge circuit.

The ⁷Li T_1 - T_2 relaxation correlation experiments were performed using a modified inversion-recovery CPMG measurement [19, 20]. A variable echo time was employed to reduce the RF duty cycle. A total of 1024 echoes were acquired with an echo time that incremented non-linearly with the echo number. The echo time variation with echo number was sigmoidal with the midpoint echo time occurring at the 512th echo. 128 echoes were acquired with a minimum echo time of 200 μ s and 128 echoes were acquired with a maximum echo time of 15 ms. During the experiment, 20 inversion-recovery delays t_d , were employed with a minimum value of 1 ms and a maximum value of 9 s. The delay times incremented non-linearly. The acquisition time was approximately 6 h with a relaxation delay of 5 s and 64 scans. Extensive signal averaging was employed to ensure a high quality T_1 - T_2 relaxation correlation experiment. A 2D Fast Laplace Inversion program (Laplace Inversion Software, Schlumberger-Doll Research) written in MATLAB (MathWorks, Natick, MA) was used to construct the 2D MR relaxation correlation maps. The regularization parameter was set to 5 in all T_1 - T_2 data processing.

4.4 **Results and discussion**

4.4.1 **RF probe simulations**

Fig. 4.1 shows the model of the simulated Parallel-Plate Resonator. The lateral dimensions, 50 mm x 35 mm and the separation of the plates, 7.0 mm, were fixed to accommodate a flat LIB cell with a maximum separation between electrodes of 2.0 mm. The optimized values of the capacitors C_L and C_R were 75 pF and 150 pF respectively. Fig. 4.4 depicts the simulated **B**₁ magnetic field distribution in the central slice between the plates, parallel to the x-direction. As previously reported [15], the homogeneity is significantly improved when the optimum capacitor values are chosen. Increasing homogeneity of the RF probe is of great importance for high resolution ⁷Li MRI studies of LIB. For an input power of 115 W in simulation, the magnetic field strength at the centre between the plates was 5.8 G. The theoretical 90-degree pulse duration for the given input power is approximately 26 μ s for a ⁷Li sample.

4.4.2 **RF** probe and battery cartridge

Fig. 4.2 shows a Parallel-Plate Resonator that was built based on the results of the simulations. There is a slight difference between the capacitor values determined through simulation and experiment. The values from simulation were 75 pF and 150 pF for C_L and C_R respectively. The experimental values were 101 pF and 201 pF respectively. The result agrees within 25%, which is consistent with previous results [15]. Discrepancies between



Fig. 4.4. Simulation of magnetic field distribution produced by the ⁷Li parallel-plate resonator with optimized capacitor values C_L and C_R . The dashed line delimits a 30 mm × 30 mm area where the LIB cell resides.

simulation and experiment occur for several reasons. The separation between the plates is difficult to match to simulation because of asymmetries created during the building process. Capacitors were assumed dimensionless in the simulation but in reality, that is not true [15]. In addition, the simulation does not account for the thickness of the copper sheet nor the resistance of solder joints which increases losses in the RF probe circuit.

The sensitivity of the parallel-plate RF probe was compared with a quadrature high pass birdcage coil tuned to the frequency of 38 MHz for ⁷Li. For both RF probes, a 2 mL free electrolyte sample, placed in the centre of the probe was employed to determine the 90°pulse duration. Both RF probes were driven with an input power of 115 W. The birdcage probe, with a diameter of 5 cm and length of 10 cm, and quality factor of 200, produced a 90°-pulse duration of 51 μ s. However, the 90°-pulse duration for the Parallel-Plate Resonator was 30 μ s with a quality factor of 145. The shorter 90°-pulse of the Parallel-Plate Resonator is a good indicator of higher probe sensitivity, as advocated by Doty [21]. The higher sensitivity of the parallel-plate RF probe is due to the favourable geometry of the Parallel-Plate Resonator. The sample space is in close proximity to the plates of the probe, producing a high B_1 magnetic field per unit current as understood by the principle of reciprocity [22, 23]. The birdcage probe diameter of 50 mm was chosen to accommodate the width of the cartridge-like cell.

The experimental sensitivity for LIB studies is very favourable given the cartridge-like LIB cell shown in Fig. 4.3. The sample volume occupies the RF probe sensitive volume in a near ideal fashion. The conductive electrodes and current collectors of the LIB cell are parallel to the **B**₁ magnetic field generated by the Parallel-Plate Resonator limiting probe loading and RF shielding. The skin depth of the graphite electrode at 38 MHz is between 180 μ m and 4500 μ m. Graphite has an orientation dependant conductivity giving the range above [24]. The sample volume of the LIB cartridge-like cell is approximately an order of magnitude greater than the sample volume of typical pencil-like cells employed in vertical bore superconducting magnet studies of LIB cells [25, 26]

The new cell, with large sample volume, can be easily combined with the parallelplate RF probe, allowing multiplexing of different cells. Multiplexing of LIB cells in conventional LIB MR/MRI studies is not possible if the LIB cell is integrated with the RF probe and the entire electrochemical preparation and cycling occurs in the presence of the RF probe. The new RF probe and cell allows more time efficient use of MR/MRI equipment. Multiplexing LIB cells is a considerable advantage, considering that charging/discharging a LIB cell may take days depending on the nature of the experiment and the charging/discharging current.

Separating the RF probe and LIB cell into discrete structures remove a high conduc-

tivity connection across the RF probe. A similar low conductivity connection occurred in previous full cell work [13]. Such a connection reduces the RF sensitivity.

The new RF probe combined with the cartridge-like cell was tested with a series of MR/MRI experiments. *Ex situ* and *in situ* ⁷Li FIDs were acquired for the pristine uncharged cell. No significant difference between the FIDs was found. An MR spectrum was acquired in both cases, however, at 2.4 T the spectral dispersion and the relatively low homogeneity of the magnet does not allow resolution of different Li species inside the LIB cell. Spectroscopy results would be improved with a higher static magnetic field, and a more homogeneous magnet, than that employed here. Our work is primarily MRI and relaxation measurements as reported in this study, which does not require high static magnetic field nor high homogeneity.

A 1D profile of the Li ion concentration in the electrolyte solution was performed on the pristine uncharged LIB cell. Fig. 4.5 shows the 1D *ex situ* and *in situ* intensity profile of the electrolyte solution between the electrodes in a cartridge-like cell. It is observed that there is a minor difference between the intensity profiles. The small difference between *ex situ* and *in situ* intensity profiles was expected. In the *in situ* experiment the RF probe electrically couples with the charging circuit, slightly increasing the losses in the RF circuit. With a nominal resolution of 35 μ m and an imaging time of 22 min, this combination of RF probe and LIB cell is suitable for high resolution studies of electrolyte polarization in LIB cells. We emphasize that these measurements were undertaken at the relatively low field of 2.4 T.

The SE SPI profiling experiment is amenable to detection solely of lithium ions in the electrolyte due to the T_2 restriction of a few milliseconds with SE SPI [25]. The parallelplate RF probe and cell cartridge are however well-suited to other imaging experiments,



Fig. 4.5. 1D ⁷Li intensity profiles, *in situ* (dotted line) and *ex situ* (solid line), for the electrolyte solution between the electrodes. The profiles were acquired using a pure phase encode SE SPI experiment. 4 scans were acquired for an image time of 22 min. The encoding time was $t_p = 3.4$ ms and the field of view was 2.2 mm.

most notably SPRITE [5], for observation and spatial resolution of other Li species. The paramagnetic NMC electrode has significant lithium content, but the signal lifetimes are too short to be observed even with SPRITE MRI methods. The most advantageous use of the new RF probe/cell for LIB studies beyond electrolyte studies is likely to be studies of lithium dendrites formation, lithium plating and lithium intercalation into graphite. We emphasize that the RF probe/cell combination is well suited for use with other battery systems and other electrodes in LIB studies.

4.4.3 T₁-T₂ Relaxation correlation

Relaxation studies are a very advantageous way to discern molecular environments in MR studies. Two-dimensional time correlation techniques are widely employed in MR [19], but they have not been widely used in ⁷Li LIB cell studies [27]. The capability of the parallel-plate RF probe combined with the cartridge-like LIB cell was also demonstrated through T_1 - T_2 relaxation correlation experiments.

A CPMG experiment with non-linearly spaced echo times in T_1 - T_2 correlation experiments was employed [28]. The echo spacing was varied in a sigmoidal way maintaining the TE constant for the first 128 echoes of the sequence with a TE value of 200 μ s. This short TE was necessary to capture the short lifetime T_2 components on the sample. TE for the last 128 echoes was constant with TE value of 15 ms. Employing a CPMG with variable TE greatly reduced the number of echoes acquired while accurately capturing short lifetime T_2 components. The modification was done to limit the RF duty cycle in the presence of both long and short T_2 components. To validate the feasibility of the modified CPMG experiment a long T_2 700 μ L free electrolyte sample was employed. Two different CPMG echo trains were acquired, a regular CPMG with a linear echo time spacing and the modified CPMG with a non-linear echo time spacing. The results showed no significant difference between the relaxation times measured with the different methods. For short lifetime T_2 species the long echo time data is extraneous.

Fig. 4.6a. shows the T_1 - T_2 relaxation correlation map of the pristine uncharged cell. The result shows three peaks. Peaks **I** and **II** with different T_2 lifetimes, but similar T_1 lifetimes of ~ 700 ms are associated with lithium populations in the electrolyte solution in the paper filter. Peak **I**, with a long lifetime T_2 component of 190 ms is associated with mobile electrolyte molecules in the paper and peak **II**, with shorter lifetime T_2 component of 30 ms, is presumed to be associated with regions of space in the separator with restricted mobility [29]. In a control experiment, a cell without electrodes, the T_2 - T_2 correlation experiment confirmed two different Li populations in electrolyte in the Whatman paper filter. T_1 and T_2 components for peaks I and II were expected to be shorter than T_1 and T_2 components of the bulk electrolyte. Li ions in the porous paper filter have restricted motion causing a more efficient relaxation than in the free electrolyte [30]. A minor low-amplitude peak, III, with T_1 and T_2 lifetimes of 680 ms and 5 ms respectively is observed in Fig. 4.6a. This peak is likely to be associated with Li ions in the pore space of the graphite electrode. Porosity of the electrodes plays an important role in the final capacity of the cell. Porosity values for graphite electrodes have been reported from 15% to 55% [31–34]. The porosity of the graphite electrodes [33]. In another control experiment, a pristine uncharged cell was assembled without the NMC electrode. The T_1 - T_2 relaxation experiment confirmed that peak III is associated with lithium ions in the porous graphite. No other Li populations are possible, beyond those in the electrolyte in the uncharged cell.

The Li content in the NMC electrode is 2.7 times higher than the Li content in the electrolyte solution in the cell, allowing for respective volumes. As expected, no signal from the paramagnetic NMC electrode was observed due to the extremely short T_2 relaxation time. Even with a TE of 200 μ s the signal of the NMC has completely decayed before it can be observed.

Fig. 4.6b. shows the T_1 - T_2 relaxation correlation map for the charged cell. The cell potential at the beginning of the T_1 - T_2 measurement was 4.0 V. An overall increase in peak integrals was expected upon charging because unobservable Li ions in the NMC electrode enter the electrolyte while Li from the electrolyte will be intercalated into the graphite



Fig. 4.6. T_1 - T_2 relaxation correlation maps of a graphite/NMC LIB cell measured in the parallel-plate resonator at different state of charge. (a) pristine cell, (b) charged cell, state of charge 4.0 V (c) charged cell, state of charge 3.40 V. (d) control cell graphite/Li metal. Peaks I and II, are Li in the electrolyte. Peak III is hypothesised to be Li ions in the pore space of the graphite electrode. Peak IV is assigned to Li intercalated into graphite. Peak V is Li metal. PI is peak integral.

electrode where it may be detected. The cell was charged with constant current mode until the cell voltage reached 4.2 V. The NMC electrode, with a theoretical capacity of 277

mAh/g, showed at 4.2 V a capacity of approximately 130 mAh/g (manufacturer experimental capacity (2.7 - 4.4 V @ 0.1C): 165 mAh/g). This is equivalent to 45% of the Li ions extracted from the NMC electrode. Approximately 15% of the Li extracted from the NMC electrode is expected to be irreversibly consumed in solid electrolyte interface (SEI) formation [35, 36]. However, the exact amount Li ion consumed in the SEI will depend on several factors such as electrolyte composition, separator thickness, charging rate, etc. Lithium ions consumed on the SEI are unlikely to be observed because the reaction products are solids [37] and due to reduced sensitivity due to \mathbf{B}_1 inhomogeneities produced by the conducting materials near the SEI [1]. The remaining Li ions are hypothesized to be intercalated into the graphite electrode where we anticipated they can be observed. Assuming full RF excitation of the graphite electrode, an increase in the overall peak integrals (PIs) of approximately 100% was expected in Fig. 4.6b when compared with Fig. 4.6a. However, the PI in Fig. 4.6b increased only by 30% compared with PIs in Fig. 4.6a. The peak integral increase in Fig. 4.6b compared to Fig. 4.6a is due to the appearance of new peaks at short T_2 . The lesser than anticipated increase in PI may be due to a less efficient changing process, or it may be due to reduced \mathbf{B}_1 amplitude in the conductive graphite. We also notice that the shortest lifetime T_2 peaks observed are on the order of the echo time and are automatically challenging to quantify.

Four peaks in the T_1 - T_2 correlation map are observed in Fig. 4.6b. Peaks I and II, as in Fig. 4.6a, are associated with electrolyte in the paper filter. PI of peaks I and II did not change significantly between Fig. 4.6b and Fig. 4.6a. This was expected because no significant electrolyte loss was expected during the cell charging. The decrease in T_1 lifetime of peaks I and II in Fig. 4.6b compared to Fig. 4.6a, may be due to leaching of paramagnetic species from the electrodes into solution [38, 39]. Peak III in Fig. 4.6b, as in Fig. 4.6a, may be associated to lithium in the pore space of the graphite electrode. An increase in PI of peak **III** of approximately 40% is observed. This increase in PI was surprising but it is known that complete wetting pores of the electrode generally may be a prolonged process [40, 41].

The new peak, **IV**, in Fig. 4.6b with T_1 and T_2 components of 1600 ms and 0.7 ms respectively appears after the LIB cell was charged. The cell was charged slowly at a c-rate of C/35; therefore, no significant metallic lithium is expected to plate the graphite electrode [42]. T_1 relaxation time values for metallic lithium ranging from 100 ms to 140 ms have been previously reported for frequencies from 3 MHz to 155 MHz [4, 42–44]. A metallic lithium T_2 of 0.87 ms has been reported [42]. The cell was cycled only once, so no dendrites/moss formation is expected [42]. Peak **IV** must therefore be due to lithium intercalated into graphite. The T_1 relaxation time of peak **IV** reinforces the hypothesis that it is lithium intercalated into graphite. The T_1 value of peak **IV** is consistent with studies by Grandinetti *et al.* [42] for the condensed stage 1 of lithium intercalated into graphite, 1.8 s [42]. However, the magnetic field employed is different in the two studies.

Fig. 4.6c shows the T_1 - T_2 relaxation correlation map of the same cell presented in Fig. 4.6b after the cell was kept on the bench for 7 days with the cell potential decreasing to 3.4 V. In this figure four peaks are once more observed. As in Fig. 4.6a-b, peaks I and II are related to the electrolyte in the paper filter. The lifetime coordinates of peaks I and II have changed again but the interpretation of theses peaks as ⁷Li in the electrolyte remains unchanged. The PI of peaks I and II is not significantly different between Fig. 4.6c and Fig. 4.6a. An increase in peak PI of peak III is observed between Fig. 4.6c and Fig. 4.6b, as outlined earlier. A decrease in cell voltage is not surprising with the cell held on the bench for 7 days. Such a decrease in cell voltage is associated with partial discharge of the

cell. We do observe a decrease in the PI of peak **IV** compared to Fig. 4.6b consistent with loss of lithium from the graphite. The PI change was confirmed by the initial amplitudes from bulk CPMG measurements.

Fig. 4.6d illustrates the T_1 - T_2 correlation map for a Li/Graphite (pristine, not lithiated graphite) LIB cell which was undertaken as a control experiment for metallic lithium detection. Two peaks are clearly observed in the figure. One broad peak, **I**, with the T_2 component centred at 95 ms is assigned to the electrolyte in the paper filter as in Fig. 4.6a-c. This peak is elongated in the T_2 direction so the two peaks corresponding to the electrolyte in the paper filter are merged. A second, more localized peak can be observed with a T_2 component of 3 ms which is associated with the Li metal electrode. The Li content in the Li metal electrode is much higher than Li content in the electrolyte, however the PI of peaks **I** and **V** are similar. This is because the RF magnetic field penetration is limited in the Li metal electrode to approximately 25 μ m at 38 MHz. This result is consistent with studies reported in [43, 46] where MR signal of the Li metal is proportional to the area of the electrodes. It is important to highlight that peak **III** is not observed in Fig. 4.6d. Peak

These results suggest that the parallel-plate resonator combined with the cartridge LIB cell may be used to detect and monitor lithium intercalation/de-intercalation into graphite and potentially metallic lithium formation employing T_1 - T_2 relaxation correlation experiments. However, a combined T_1 - T_2 relaxation correlation and spectroscopic experiment is advantageous to assign the peaks.

Although the results presented in this work were obtained with the parallel-probe resonator tuned for ⁷Li 38 MHz, similar RF probes can be built for higher frequency experiments improving measurement sensitivity. The parallel-plate RF probe and cartridge cell are well suited to the study of other battery systems, as is the T_1 - T_2 measurement.

4.5 Conclusion

A Parallel-Plate Resonator was designed and optimized for ⁷Li studies in LIB cells. The probe was combined with a cartridge-like LIB cell which provided a large cell volume, increasing measurement sensitivity and avoiding RF attenuation. 1D ⁷Li profiles of the electrolyte solution shows the probe can be used for both, *in situ* and *ex situ* experiments. A resolution of 35 μ m in the electrolyte was achieved. T_1 - T_2 relaxation correlation MR experiments are reported for the first time for ⁷Li LIB cell studies. The T_1 - T_2 relaxation correlation maps suggest that the parallel-plate probe, combined with the cartridge cell may be used to detect lithium intercalated into graphite. The variety of peaks observed and changes in lifetimes observed with change in state suggest this method may be a very powerful way to probe LIB behaviour.

The parallel-plate RF probe and battery cartridge may be employed for studies of other battery types as may the T_1 - T_2 relaxation correlation measurement.

References

- [1] A. J. Ilott, M. Mohammadi, H. J. Chang, C. P. Grey, A. Jerschow, Real-time 3D imaging of microstructure growth in battery cells using indirect MRI, Proceedings of the National Academy of Sciences 113 (2016) 10779–10784. doi:10.1073/pnas. 1607903113.
- [2] S. Chandrashekar, N. M. Trease, H. J. Chang, L. S. Du, C. P. Grey, A. Jerschow, ⁷Li MRI of Li batteries reveals location of microstructural lithium, Nature Materials 11 (2012) 311–315. doi:10.1038/nmat3246.
- [3] F. Chevallier, F. Poli, B. Montigny, M. Letellier, *In situ* ⁷Li nuclear magnetic resonance observation of the electrochemical intercalation of lithium in graphite: Second cycle analysis, Carbon 61 (2013) 140–153. doi:10.1016/j.carbon.2013.04.
 078.
- [4] M. Letellier, F. Chevallier, F. Béguin, E. Frackowiak, J.-N. Rouzaud, The first *in situ* ⁷Li NMR study of the reversible lithium insertion mechanism in disorganised carbons, Journal of Physics and Chemistry of Solids 65 (2004) 245–251. doi:10.1016/j. jpcs.2003.10.022.
- [5] S. A. Krachkovskiy, J. M. Foster, J. D. Bazak, B. J. Balcom, G. R. Goward, Operando mapping of Li concentration profiles and phase transformations in graphite electrodes by magnetic resonance imaging and nuclear magnetic resonance spectroscopy, Journal of Physical Chemistry C 122 (2018) 21784–21791. doi:10.1021/acs.jpcc. 8b06563.

- [6] M. Letellier, F. Chevallier, M. Morcrette, *In situ* ⁷Li nuclear magnetic resonance observation of the electrochemical intercalation of lithium in graphite; 1st cycle, Carbon 45 (2007) 1025–1034. doi:10.1016/j.carbon.2006.12.018.
- S. P. Rangarajan, Y. Barsukov, P. P. Mukherjee, In operando signature and quantification of lithium plating, Journal of Materials Chemistry A 7 (2019) 20683–20695.
 doi:10.1039/c9ta07314k.
- [8] H. Ge, T. Aoki, N. Ikeda, S. Suga, T. Isobe, Z. Li, Y. Tabuchi, J. Zhang, Investigating lithium plating in lithium-ion batteries at low temperatures using electrochemical model with NMR assisted parameterization, Journal of The Electrochemical Society 164 (2017) A1050–A1061. doi:10.1149/2.0461706jes.
- [9] N. Dupré, J. F. Martin, D. Guyomard, A. Yamada, R. Kanno, Characterization of interphases appearing on LiNi_{0.5}Mn_{0.5}O₂ using ⁷Li MAS NMR, Journal of Power Sources 189 (2009) 557–560. doi:10.1016/j.jpowsour.2008.10.017.
- [10] M. Cuisinier, J. F. Martin, P. Moreau, T. Epicier, R. Kanno, D. Guyomard, N. Dupré, Quantitative MAS NMR characterization of the LiMn_{1/2}Ni_{1/2}O₂ electrode/electrolyte interphase, Solid State Nuclear Magnetic Resonance 42 (2012) 51–61. doi:10. 1016/j.ssnmr.2011.09.001.
- [11] A. I. Freytag, A. D. Pauric, S. A. Krachkovskiy, G. R. Goward, *In situ* magic-angle spinning ⁷Li NMR analysis of a full electrochemical lithium-ion battery using a jelly roll cell design, Journal of the American Chemical Society 141 (2019) 13758–13761. doi:10.1021/jacs.9b06885.
- [12] E. Maiser, Battery packaging technology review, AIP Conference Proceedings 1597 (2014) 204–218. doi:10.1063/1.4878489.

- [13] Z. Zhang, J. Martin, J. Wu, H. Wang, K. Promislow, B. J. Balcom, Magnetic resonance imaging of water content across the Nafion membrane in an operational PEM fuel cell, Journal of Magnetic Resonance 193 (2008) 259–266. doi:10.1016/j. jmr.2008.05.005.
- [14] S. Benders, M. Mohammadi, C. A. Klug, A. Jerschow, Nuclear magnetic resonance spectroscopy of rechargeable pouch cell batteries: beating the skin depth by excitation and detection via the casing, Scientific Reports 10 (2020) 13781–13787. doi:10.1038/s41598-020-70505-0.
- [15] A. R. Aguilera, B. MacMillan, G. R. Goward, B. J. Balcom, Optimization of a parallel-plate RF probe for high resolution thin film imaging, Concepts in Magnetic Resonance Part A 47A (2018) e21465–e21470. doi:10.1002/cmr.a.21465.
- [16] S. A. Krachkovskiy, M. Reza, A. R. Aguilera, I. C. Halalay, B. J. Balcom, G. R. Goward, Real-time quantitative detection of lithium plating by *in situ* NMR using a parallel-plate resonator, Journal of The Electrochemical Society 167 (2020) 130514–130519. doi:10.1149/1945-7111/abb7ea.
- [17] J. Mispelter, M. Lupu, A. Briguet, NMR Probeheads for Biophysical and Biomedical Experiments, 2nd Edition, Imperial College Press, 2006. doi:10.1142/p438.
- [18] O. V. Petrov, G. Ersland, B. J. Balcom, T₂ distribution mapping profiles with phaseencode MRI, Journal of Magnetic Resonance 209 (2011) 39–46. doi:10.1016/j. jmr.2010.12.006.
- [19] Y. Q. Song, L. Venkataramanan, M. D. Hürlimann, M. Flaum, P. Frulla, C. Straley, T₁-T₂ correlation spectra obtained using a fast two-dimensional laplace inversion, Journal of Magnetic Resonance 154 (2002) 261–268. doi:10.1006/jmre.2001.2474.

- [20] A. E. English, K. P. Whittall, M. L. Joy, R. M. Henkelman, Quantitative twodimensional time correlation relaxometry, Magnetic Resonance in Medicine 22 (1991) 425–434. doi:10.1002/mrm.1910220250.
- [21] F. D. Doty, Probe design and construction, eMagRes (2007) 1-12. .doi:10.1002/ 9780470034590.emrstm0414.
- [22] D. I. Hoult, The principle of reciprocity in signal strength calculations- a mathematical guide, Concepts in Magnetic Resonance 12 (2000) 173–187.
- [23] D. I. Hoult, R. E. Richards, The signal-to-noise ratio of the nuclear magnetic resonance experiment, Journal of Magnetic Resonance (1969) 24 (1976) 71–85. doi: 10.1016/0022-2364(76)90233-X.
- [24] H. O. Pierson, Handbook of Carbon, Graphite, Diamonds and Fullerenes: Processing, Properties and Applications (Materials Science and Process Technology), William Andrew Publishing, 1993.
- [25] S. A. Krachkovskiy, J. D. Bazak, P. Werhun, B. J. Balcom, I. C. Halalay, G. R. Goward, Visualization of steady-state ionic concentration profiles formed in electrolytes during Li-Ion battery operation and determination of mass-transport properties by *in situ* magnetic resonance imaging, Journal of the American Chemical Society 138 (2016) 7992–7999. doi:10.1021/jacs.6b04226.
- [26] S. Klamor, K. Zick, T. Oerther, F. M. Schappacher, M. Winter, G. Brunklaus, ⁷Li *in situ* 1D NMR imaging of a lithium ion battery, Physical Chemistry Chemical Physics 17 (2015) 4458–4465. doi:10.1039/c4cp05021e.
- [27] A. R. Aguilera, B. MacMillan, S. Krachkovskiy, F. Alkhayri, C. A. Dyker, G. R. Goward, B. J. Balcom, Parallel-Plate Resonator for MRI studies of lithium ion bat-

teries, ICMRM 2019 15th International Conference on Magnetic Resonance Microscopy, 2019.

- [28] M. J. Dick, D. Veselinovic, D. Green, Reducing Sample Heating During NMR Measurements, Society of Core Analysts Annual Symposium, 2019.
- [29] A. Lepore, S. Baccaro, C. Casieri, A. Cemmi, F. D. Luca, Role of water in the ageing mechanism of paper, Chemical Physics Letters 531 (2012) 206–209. doi:10.1016/ j.cplett.2012.01.083.
- [30] R. J. S. Brown, P. Fantazzini, J. Kärger, R. Kimmich, Chapter 1. NMR under Confinement: Roots in Retrospect, The Royal Society of Chemistry, 2016. doi: 10.1039/9781782623779-00001.
- [31] P. R. Shearing, L. E. Howard, P. S. Jørgensen, N. P. Brandon, S. J. Harris, Characterization of the 3-dimensional microstructure of a graphite negative electrode from a Li-ion battery, Electrochemistry Communications 12 (2010) 374–377. doi: 10.1016/j.elecom.2009.12.038.
- [32] P. Pietsch, D. Westhoff, J. Feinauer, J. Eller, F. Marone, M. Stampanoni, V. Schmidt,
 V. Wood, Quantifying microstructural dynamics and electrochemical activity of graphite and silicon-graphite lithium ion battery anodes, Nature Communications 7 (2016) 12909–12919. doi:10.1038/ncomms12909.
- [33] D. L. Wood, J. Li, C. Daniel, Prospects for reducing the processing cost of lithium ion batteries, Journal of Power Sources 275 (2015) 234–242. doi:10.1016/j. jpowsour.2014.11.019.

- [34] K. E. Thomas-Alyea, C. Jung, R. B. Smith, M. Z. Bazant, *In situ* observation and mathematical modeling of lithium distribution within graphite, Journal of The Electrochemical Society 164 (2017) E3063–E3072. doi:10.1149/2.0061711jes.
- [35] M. R. Palacín, Understanding ageing in Li-ion batteries: A chemical issue, Chemical Society Reviews 47 (2018) 4924–4933. doi:10.1039/c7cs00889a.
- [36] S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, D. L. Wood, The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling, Carbon 105 (2016) 52–76. doi:10.1016/j. carbon.2016.04.008.
- [37] M. Gauthier, T. J. Carney, A. Grimaud, L. Giordano, N. Pour, H.-H. Chang, D. P. Fenning, S. F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp, Y. Shao-Horn, Electrode–electrolyte interface in Li-Ion batteries: Current understanding and new insights, The Journal of Physical Chemistry Letters 6 (2015) 4653–4672. doi: 10.1021/acs.jpclett.5b01727.
- [38] H. Zheng, Q. Sun, G. Liu, X. Song, V. S. Battaglia, Correlation between dissolution behavior and electrochemical cycling performance for LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂-based cells, Journal of Power Sources 207 (2012) 134–140. doi:10.1016/j.jpowsour. 2012.01.122.
- [39] J. A. Gilbert, I. A. Shkrob, D. P. Abraham, Transition metal dissolution, ion migration, electrocatalytic reduction and capacity loss in lithium-ion full cells, Journal of The Electrochemical Society 164 (2017) A389–A399. doi:10.1149/2.1111702jes.

- [40] Y. Sheng, C. R. Fell, Y. K. Son, B. M. Metz, J. Jiang, B. C. Church, Effect of calendering on electrode wettability in lithium-ion batteries, Frontiers in Energy Research 2 (2014) 56. doi:10.3389/fenrg.2014.00056.
- [41] A. Davoodabadi, J. Li, H. Zhou, D. L. Wood, T. J. Singler, C. Jin, Effect of calendering and temperature on electrolyte wetting in lithium-ion battery electrodes, Journal of Energy Storage 26 (2019) 101034–101044. doi:10.1016/j.est.2019.101034.
- [42] J. L. L. Lopez, P. J. Grandinetti, A. C. Co, Enhancing the real-time detection of phase changes in lithium-graphite intercalated compounds through derivative operando (dOp) NMR cyclic voltammetry, Journal of Materials Chemistry A 6 (2017) 231–243. doi:10.1039/c7ta07521a.
- [43] R. Bhattacharyya, B. Key, H. Chen, A. S. Best, A. F. Hollenkamp, C. P. Grey, *In situ* NMR observation of the formation of metallic lithium microstructures in lithium batteries, Nature Materials 9 (2010) 504–510. doi:10.1038/nmat2764.
- [44] D. F. Holcomb, R. E. Norberg, Nuclear spin relaxation in alkali metals, Physical Review 98 (1955) 1074–1091. doi:10.1103/PhysRev.98.1074.
- [45] R. Torgeson, T. Jones, G. Barnes, Steady-state nuclear induction signal shapes in lithium metal, Ames Laboratory Technical Reports. 42, 1960.
- [46] A. J. Ilott, S. Chandrashekar, A. Klöckner, H. J. Chang, N. M. Trease, C. P. Grey, L. Greengard, A. Jerschow, Visualizing skin effects in conductors with MRI: ⁷Li MRI experiments and calculations, Journal of Magnetic Resonance 245 (2014) 143–149. doi:10.1016/j.jmr.2014.06.013.

Chapter 5

The Parallel-Plate Resonator: An RF Probe for MR and MRI Studies Over a Wide Frequency Range

In Chapters 3 and 4, we have shown the potential of the PPR RF probe for high resolution imaging and interrogation of LIBs. However, the frequency range over which the PPR can be successfully tuned and matched for MR studies is still a practical concern. In this Chapter we explore the frequency range over which the PPR can be employed. The importance of the size of the PPR was considered, and different size PPR RF probes were tested. Optimized and non optimized PPR RF probes were also discussed.

This chapter is largely based on the paper "The Parallel-Plate Resonator: An RF Probe for MR and MRI Studies Over a Wide Frequency Range" submitted for publication to the journal *Magnetic Resonance Letters*. The final version of the paper, published in 2023, has minor scientific differences from the work of this chapter. There are more significant formatting and punctuation differences. We follow the notation for variables and equations recommended by this journal. The format of the references in this chapter has been changed to Elsevier's reference style format for the *Journal of Magnetic Resonance*.

Abstract

We explore the use of the Parallel-Plate Resonator for the study of thin cuboid samples over a wide range of frequencies. The Parallel-Plate Resonator functions at frequencies from tens to hundreds of MHz. Seven Parallel-Plate Resonators are presented and discussed in a frequency range from 8 to 500 MHz. Magnetic Resonance experiments were performed on both horizontal and vertical bore magnet systems, with lithium and hydrogen nuclei. Parallel-plate RF probes are easy to build and easy to optimize. Experiments and simulations showed good sensitivity of the probe with a small decrease of sensitivity at higher frequencies.

5.1 Introduction

Radiofrequency (RF) probes play a critical role in all Magnetic Resonance (MR) and Magnetic Resonance Imaging (MRI) experiments. They are responsible for the excitation of the nuclear spins in the sample under study and reception of the resulting MR signal. RF probes are found in a wide variety of shapes and sizes. Selecting the appropriate RF probe design for the MR experiment depends on factors such as static magnetic field orientation, magnet size, the sample under study and the magnetic field strength. No single RF probe geometry can be employed over the range of possible samples and instruments.

In this work we explore the use of the Parallel-Plate Resonator (PPR) RF probe for MR and MRI studies of thin cuboid samples (less than 1 cm thick), over a wide frequency range, from tens to hundreds of MHz. We focus on a thin cuboid sample geometry since this corresponds to the geometry of a wide range of electrochemical cells. We discuss advantages and disadvantages of PPR RF probes, accompanied by characterization at different frequencies. Experimental MR data from six PPRs, at different frequencies is presented. Data from two nuclei, ¹H and ⁷Li, were recorded with different PPRs. ⁷Li studies were performed on fully assembled Lithium-Ion Battery (LIB). Bench testing data from a PPR at 500 MHz is also discussed.

RF probe designs are usually focused on improvement of the RF probe sensitivity [1–3].

Several excellent books have been published covering development and fabrication of RF probes [4, 5]. The static magnetic field orientation is a key factor when choosing a suitable RF probe geometry. An axial (solenoid-like) or transverse (saddle-like) RF probe style is a basic decision. Axial RF probes, producing a magnetic field parallel to their main axis have high sensitivity, but sample accessibility might be a limited in superconducting magnets. These types of RF probes may also create \mathbf{B}_0 inhomogeneities due to the field distortion created by samples axially perpendicular to \mathbf{B}_0 in superconducting magnets [4]. On the other hand, transverse RF probes, which produce a magnetic field perpendicular to their main axis, have good accessibility and are well suited for working with any magnet, but they generally feature a lower sensitivity compared to axial RF probes [4, 5].

The sample under study also imposes restrictions on the RF probe. For samples characterized with a short T_2^* lifetime an RF probe with a short recovery time is necessary [6, 7]. For MR experiments employing spin echo-like sequences [8, 9] the recovery time of the probe is rarely an issue. However, for experiments where the FID must be acquired, such as SPRITE MRI [10] or T_1 - T_2^* relaxation correlation experiments [11], an RF probe with a short recovery time is of great importance. Sample size also plays an important role in the choice of an appropriate RF probe. For relatively large samples volume coils are preferred [5] while for small samples micro coils provide the best sensitivity [12, 13].

Sample conductivity should also be considered in selection of the RF probe. Conductive samples may produce a reduction of the quality factor of the RF probe. Sample conductivity is less of a problem if losses are dominated by the RF probe. In this case, the quality factor is not reduced by the introduction of a lossy sample. The ideal RF probe will not change frequency with sample insertion.

MR experiments are carried out in a wide frequency range from 2 to 900 MHz for

hydrogen [4, 14]. This wide range of working frequencies makes difficult the employment of a single type of RF probe for multiple applications. Designing RF probes that resonate at both high and low frequency is a challenging task. At low frequencies, RF probes are difficult to tune and match because they require large capacitance values that may make it inconvenient to tune the RF probe. At low frequencies, a high inductance RF probe is preferred to reduce the capacitance needed efficiently to tune and match. Special attention must be paid to the coil impedance when employing high inductance RF probes. In practice the impedance should range between 20 to 200 Ω . Outside this impedance range, the performance of the RF will be severely degraded [4]. The most common RF coils used in low-field MR are solenoids or multiturn surface coil RF probes, where the inductive reactance remains manageable.

At higher frequencies, the inductance of some RF probes becomes large, limiting the highest frequencies to which the probe can be tuned. Birdcage probes and solenoids encounter this high frequency limit. At high frequency, the capacitance, inductance, and the dimensions of the RF probe must all be small. If the RF wavelength, λ , becomes comparable to the physical size of the RF probe, RF probe losses increase [4]. The RF probe should be electrically small (conductor length less than $\lambda/10$). However, this will limit the size of the RF probe and sample space. Segmenting the coil conductor is advisable if the RF probe is electrically long (conductor length more than $\lambda/10$). In addition, as the coil impedance increases, the electric field created in the sample increases too, leading to dielectric losses and sample heating [4]. Low impedance RF probes such as the Alderman-Grant and Litz [15] RF probe designs are effective as high frequency probes. However, the complexity of the design is an important factor to consider, as is the size of the RF probe. Attempts to increase the usable frequency range of RF probes have been described [5], such

as the transverse electromagnetic TEM resonator. However, despite improvements the size of RF probes remains limited at high frequencies.

Finding an RF probe geometry that could be used at both at low and high frequency while maintaining \mathbf{B}_1 magnetic field homogeneity and a relatively high sensitivity is a challenge. The probe should have low inductance and a simple design allowing segmentation of the RF probe in case the RF probe becomes electrically long. In addition, it should be easy to insert in a wide variety of magnets.

As outlined in this work the PPR has proven to be an effective RF probe for MR experiments over a relatively wide range of frequencies, and for different applications where thin samples are interrogated. For MR studies of electrochemical devices, the PPR RF probe is a natural choice. It accommodates thin cuboid samples while avoiding RF attenuation due to conductive electrodes. Aguilera *et al.* [16] performed ⁷Li ion batteries studies at 38 MHz with an optimized PPR. At 100 MHz, the ¹H PPR has been employed for studies as varied as measurement of water content in an operational polymer electrolyte membrane PEM fuel cell [17], flow in microchannels [18], and diffusion in thin film liquid crystals [19]. Krachkovskiy *et al.* [20] employed a ⁷Li PPR RF probe at 116 MHz to perform a quantitative evaluation of lithium plating in a Li-ion cell. Sanders *et al.* [21], also at 116 MHz, employed a PPR for the study of transient lithium metal plating on graphite. The PPR has also been employed for 2D imaging of thin films. Meadowcroft *et al.* [22] employed a U-shaped ¹H PPR to image thin histological tissue samples at 127 MHz. Hoang *et al.* [23] built on the work of Meadowcroft et al. [22] and explored different sizes of ¹H PPR sizes to accommodated thicker and wider samples at 301 MHz. Aguilera et al. [24] presented high resolution thin film imaging of flat capillary samples with a nominal resolution of 10 μ m.

The current discussion will focus on lateral size of the PPR as well as the range of

possible resonances frequencies. The separation between the plates is kept small. Three different size PPRs are evaluated with a separation of 0.7 cm between the plates (except the 100 MHz ¹H optimized PPR with 0.35 cm separation between the plates). The separation between plates for most of the PPRs discussed is small due to their employment in the study of electrochemical cells. The parallel-plate geometry is ideal to accommodate cartridge-like electrochemical cells [16, 21].

We discuss the challenges associated with building the PPRs and suggestions are given for further performance enhancement. To aid discussion, the frequency ranges have been divided as follows, the low frequency range is less than 25 MHz, the medium frequency range is from 25 to 250 MHz and the high frequency range is greater than 250 MHz. Experimental MR data from four ¹H PPRs at frequencies 8, 20, 100 and 300 MHz corresponding to magnetic field strengths of 0.1, 0.79, 2.4 and 7 T respectively are presented. In addition, experiments performed with ⁷Li PPRs at two different frequencies (38 and 116 MHz) corresponding to static magnetic field strengths of 2.4 and 7 T are also discussed. Bench testing of a ¹H PPR at 500 MHz is presented.

5.2 Materials and Methods

Three different sizes of MRs were evaluated in the present study: Small, Medium, and Large, as shown in Fig. 5.1. The leads on the Medium and Large PPRs are 1.5 cm long and 1.0 cm wide. On the Small PPR the leads are 1.0 cm long and 0.5 cm wide. All PPRs were cut from single-sided copper clad PCB with a copper layer 25 μ m thick. The separation between the plates was maintained at 0.7 cm. For the optimized PPR, capacitors were attached on the corners, joining the plates, to increase the **B**₁ homogeneity as illustrated in

Fig. 5.2 [24].



Fig. 5.1. Schematic of the PPR with length l, width w and separation between the plates d. Three different PPR sizes, Small (l = 5.0 cm, w = 2.0 cm), Medium (l = 5.0 cm, w = 3.5 cm wide) and Large (l = 25.0 cm, w = 17.5 cm) are presented. The separation between the plates d, was less than 1 cm in all RF probes.

5.2.1 PPR size and Electromagnetic Simulation

All simulations were performed in CST Microwave Studio 2017 (CST of America[®], Framingham, MA). The transient solver with tetrahedral meshing was used for the simulations. The plates were simulated as sheets to reduce model complexity and calculation time. The capacitors were assumed nonideal with equivalent series resistance ESR of 30 m Ω and equivalent series inductance ESL of 0.05 nH. The probe, in simulation, was fed with a Gaussian RF pulse which delivers 0.5 W power to the probe when matched to 50 Ω . The calculation results were scaled for an input power of 115 W. For RF probe homogeneity calculation, a constant volumetric region of interest ROI is usually selected. However, to quantify the \mathbf{B}_1 homogeneity of a range of PPR we took a different approach. Our ROI for homogeneity calculation was an area, the centre area resides in the middle plane between the plates. The area of the ROI we chose to match the area of the plates of the PPR. Deviation of \mathbf{B}_1 magnetic field strength from the field at the centre of the ROI was calculated. Only regions with less than 10% deviation in \mathbf{B}_1 magnetic field strength from the origin were considered homogeneous. The homogeneous region is then compared with the ROI and expressed as fraction of the ROI. The ROI changes for every PPR. But the fractional ROI selected is best choice since we are changing the PPR area with each RF probe. A high fractional area, with a \mathbf{B}_1 magnetic field deviation of less than 10% is desirable.



Fig. 5.2. Medium size PPR with capacitors attached at the corners to improve B_1 homogeneity, reproduced from [16]. The probe was tuned and matched to 38 MHz for ⁷Li battery studies

5.2.2 Bench Measurements

All PPRs constructed were tuned and matched on the bench. An RF network analyser (8714B, Hewlett Packard, Santa Clara, CA) was used to measure the quality factor of the probes based on the reflection mode method [4], $Q = \frac{f_0}{\Delta f}$. f_0 is the resonance frequency and Δf is the bandwidth measured at -3 dB level in the reflection curve. The Q was al-

ways measured with the probe tuned at the resonance frequency f_0 and matched at 50 Ω impedance. Sample-loaded Q_L and unloaded Q_U were measured.

5.2.3 MR Experimental setup

For all PPRs fabricated and tested, FID and CPMG data were acquired. The Large 8 MHz ¹H PPR, the Medium 20 MHz ¹H PPR, the 38 MHz ⁷Li optimized PPR and the 100 MHz ¹H optimized PPR were driven by a 2 kW Tomco RF amplifier (Tomco Technologies, Stepney, Australia). The input power was 115 W for all ¹H experiments. The MR data of these four probes was acquired with a Tecmag (Houston, TX) Redstone console.

The Large 8 MHz ¹H PPR was employed with a Sumitomo (Special Metals Co. LTD, Osaka, Japan) two pole permanent magnet, 30 cm pole gap. Four Neoprene rubber pieces (McMaster-Carr, Robbinsville, NJ) with dimension 13 cm × 13 cm × 0.15 cm, were employed as a sample. 12 echoes were acquired on the CPMG echo train with a TE = 300 μ s and with 16 acquisition points on each echo. 512 scans were averaged with a repetition time of 1.5 s. The dwell time was 4 μ s and the 90-degree pulse was 18 μ s.

The 20 MHz ¹H PPR was employed with a Proteus magnet 25 with a 1.4 cm separation between the two magnet disks. The disk magnets were nickel coated N52 grade NdFeB with, a diameter of 5.0 cm, and a thickness of 1.27 cm. Four Neoprene rubber pieces (McMaster-Carr, Robbinsville, NJ) with dimension 4 cm × 3 cm × 0.15 cm, were employed as a sample. 512 echoes were acquired on the CPMG echo train with a TE = 300 μ s and 16 acquisition points on each echo. The dwell time was 4 μ s and the 90-degree pulse length was 10 μ s. 512 scans were acquired with a repetition time of 1.5 s.

The 38 MHz ⁷Li optimized PPR and the 100 MHz ¹H optimized PPR were employed

in a Nalorac (Martinez, CA) 2.4 T 32 cm i.d. horizontal bore superconducting magnet. The specific details of the experimental setup for the 38 MHz ⁷Li PPR are described in Aguilera *et al.* [16]. A 2D SPRITE image was acquired with the 100 MHz ¹H optimized PPR. The image acquisition time was 7 min for 64 averages and 10 acquisition points. The pulse duration was 2 μ s and dwell time was 1 μ s. The FOV of the image was 5.0 cm × 5.0 cm [24].

The 116 MHz ⁷Li PPR and the 300 MHz ¹H PPR were employed on a Bruker Avance III HD wide-bore instrument at 7 T. The MR data were acquired with Topspin (Bruker, Rheinstetten, Germany). Both PPRs were driven with an input power of 80 W. Both PPR probes were attached to a frame, Fig. 5.3, to mount in a Bruker MicWB40 probe with a Micro 2.5 gradient system. ⁷Li spectra were acquired from a fully assembled lithium cell at maximum charge. The RF pulse was 3 μ s, 9592 averages were performed with an acquisition time of 10.24 ms and a repetition time of 50 ms. For the ¹H spectra a Mn (II) water sample was employed. 4 averages were acquired with acquisition time of 50 ms and repetition time of 0.5 s. The 90-degree pulse duration was 20 μ s. The doped water sample had a $T_1 = 50$ ms and a $T_2 = 2$ ms

The 500 MHz 1H PPR was bench tested only.



Fig. 5.3. A 300 MHz Small ¹H PPR attached to a frame to insert into a Bruker MicWB40 probe head on a 7 T Bruker Avance III HD magnet.

5.3 Results and Discussion

5.3.1 PPR size and geometry

The PPR is a simple and easy to build RF probe. Two identical PCB plates, with a chosen separation, are employed. Depending on the size, frequency and homogeneity requirement, the plates of the PPR are connected through a conductor, a capacitor, or multiple capacitors. Fig. 5.2 shows a Medium size optimized PPR, the plates are connected through five capacitors for homogeneity improvement. The capacitors also act as supports and provide stability for the plates, yielding a more rigid structure and reducing vibration during RF excitation. The PCB plates also contribute to the stability of the design.

The geometry of the PPR is advantageous for MR/MRI studies of thin planar samples like batteries and electrochemical cells. The resonator, as described in Hoang *et al* [23], can be built to closely match the sample and accommodate different lateral sample sizes. The proximity of the conductive elements to the sample increases the sensitivity of the probe, as described by the Principle of Reciprocity [25]. The relatively high sensitivity of the PPR [22] has driven interest in using this type of probe for MR studies where flat planar samples are interrogated [16, 17, 20–24]. The PPR geometry naturally accommodates planar samples, as shown in recent studies of lithium-ion cells [16, 20, 21]. In this case, the geometry avoids RF attenuation during excitation and reception due to the conductive electrodes of the lithium-ion cell.

In the PPR, the currents flow in opposite directions on the top and bottom plates. According to the right-hand rule, the \mathbf{B}_1 magnetic field of both plates will add between the plates. This produces a strong \mathbf{B}_1 magnetic field in the sample area between the plates. Another advantage of the geometry of the PPR is the orientation of the \mathbf{B}_1 magnetic field. The PPR is a transverse RF probe with the \mathbf{B}_1 magnetic field perpendicular to its main axis. This makes the probe suitable for many types of magnets while also providing good sample access.

5.3.2 Simulation results

Fig. 5.4a depicts the fractional area of the ROI with homogeneous \mathbf{B}_1 magnetic field, of a 5.0 cm long PPR as a function of the RF probe width. The RF probe width was varied from 0.5 cm to 5 cm in steps of 0.5 cm. The results showed that the fractional area with homogeneous \mathbf{B}_1 magnetic field depends on the width of the PPR. The fractional area rapidly decreases as the width of the PPR increases. The current on the plates flows along the least resistive path, producing a higher \mathbf{B}_1 magnetic field in the centre of the probe, closer to the leads, and a weaker \mathbf{B}_1 magnetic field far from the probe leads. This result suggests that smaller PPRs are preferred for better homogeneity. However, for a Medium PPR resonator, Aguilera *et al.* [24] showed that the homogeneity can be improved if the plates of the PPR are joined with optimized capacitors as shown in Fig. 5.3. The added capacitors create alternative current paths resulting in more evenly distributed current on the plates and better \mathbf{B}_1 homogeneity between the plates. The approximate capacitance values can be found through simulation using CST microwave studio [24].

Fig.5.4b shows the variation of the \mathbf{B}_1 magnetic field strength of a 5.0 cm long PPR as the width of the plates varies. The \mathbf{B}_1 magnetic field strength is calculated at the centre of the middle plane between the plates. The results showed the \mathbf{B}_1 magnetic field strength increases with a reduction of the PPR width. Smaller RF probes, for a fixed RF power, will result in an increased \mathbf{B}_1 magnetic field strength.

The results shown in Fig. 5.4, suggest that a narrow width PPR will be preferred for higher homogeneity and higher \mathbf{B}_1 magnetic field strength without the need for capacitor optimization. However, this only allows for the study of small samples. For larger samples



Fig. 5.4. Magnetic field simulation for a PPR at 300 MHz for different plate widths. (A) Fractional area of the ROI with homogeneous \mathbf{B}_1 magnetic field in the middle plane between the plates. (B) \mathbf{B}_1 magnetic field strength at the centre of the middle plane. The length of the plates was maintained at 5.0 cm. The separation of the plates was 0.7 cm. The width of the PPR was change from 0.5 to 5.0 cm. Simulations were performed with the high frequency module of CST Studio Suite.

and larger separations between the plates, optimization of the PPR must be considered to increase the homogeneity of the B_1 field in the sample space.

Fig. 5.5a depicts two PPRs of different lateral size, both with a constant separation between the plates of 0.7 cm. The Large PPR with dimensions $25.0 \text{ cm} \times 17.5 \text{ cm}$ has an area 43 times larger than the Small PPR with dimensions $5.0 \text{ cm} \times 2.0 \text{ cm}$. They can both be employed for MR/MRI studies. However, the frequency range at which they can be tuned and matched will depend on the electrical length, the impedance, and the inductance of the probe.

Fig. 5.5b shows the simulated impedance variation with frequency for the Large and Small PPR for a frequency range from 10 MHz to 600 MHz. Ideally, the impedance of the RF probe should range between 20 to 200 Ω . If the impedance is too low losses in the solder joints may dominate the probe losses [4]. If the impedance of the probe is too high, dielectric sample losses will be significant [4].

The results show the impedance of the Small PPR, shown in Fig. 5.5a, steadily increases as frequency increases. Because the impedance of the Small PPR is below 200 Ω , as required, the probe can be tuned to any frequency in the simulated frequency range. However, for better results the Small PPR should be tuned to frequencies below 210 MHz, keeping it electrically small, below the $\lambda/10$ limit. Tuning this PPR at higher frequencies is possible if the electrical length of the probe is reduced. The geometry of the PPR naturally allows segmentation of the RF probe by joining the plates with capacitors. This will produce an evenly distributed capacitance along the conductor, reducing conservative electric fields and therefore losses in the sample [26]. Conductor segmentation also cancels propagation effects and ensures negligible variation of current amplitude along the conductor [27], thereby producing a more homogeneous magnetic field **B**₁. Segmenting the PPR allows the study of larger samples at higher frequencies.

For the Large PPR in Fig. 5.5a, the impedance shows a different behaviour, as shown in Fig. 5.5b. There is high impedance peak at approximately 150 MHz. At this frequency the length of the PPR approaches $\lambda/4$. For better performance, the Large PPR must be tuned below 53 MHz ($\lambda/10$ limit). If the Large PPR must be tuned at a higher frequency where impedance is larger than 200 Ω , distributing the capacitance of the PPR will reduce its impedance [26]. This can be easily done by attaching capacitors between the plates. However, finding the optimized capacitor values to reduce the impedance while maintain the homogeneity of the PPR can be time consuming. Another option is to reduce the physical dimensions of the PPR. The reduction in size reduces losses and extends the upper frequency limit at which the PPR resonates. However, this approach will limit sample size. If the impedance of the PPR is less than 20 Ω at the desired frequency, the size of the PPR should be increased to increase the inductance of the PPR and reduce losses due to solder joints.

For MR studies at low frequency either Small or Large PPRs can be employed. However, the Large PPR is preferable due to the lower capacitance needed for tuning and matching. Large capacitance values will increase the losses of the RF probe. On the other hand, at high frequency the small PPR is preferred due to the lower inductance, allowing for higher frequency MR experiments.

5.3.2.1 Magnetic resonance results and bench test

Table 5.1 shows the PPRs employed for MR experiments and bench testing, at different frequencies and for different nuclei. For all PPRs the quality factor was unaffected by sample insertion. Samples such as, rubber, Lithium-Ion Batteries and doped water samples were tested on different PPRs. The results show that losses are dominated by the RF probe. This is advantageous because it reduces the need for large variable capacitors for tuning and


Fig. 5.5. A) Large size PPR with dimensions $25.0 \text{ cm} \times 17.5 \text{ cm}$ and Small size PPR with dimensions $5.0 \text{ cm} \times 2.0 \text{ cm}$. The separation between the plates in both probes was 0.7 cm. B) Impedance simulation for the Large (dashed line) and Small PPR (solid line).

matching the RF probe. The low inductance of the PPR and the relatively small thickness of the samples led to negligible loading effects. This is reflected in negligible inductive and dielectric sample losses. The large lateral area, relative to the separation between the plates, produces an even distribution of the capacitance of the probe. This reduces the electric field in the sample space, reducing dielectric losses.

Table 5.1: PPRs employed for magnetic resonance and bench testing. Pw90 was determined experimentally for each specific power. Q_U and Q_L were measured based on the reflection method, with a network analyser. The deadtime [7] was theoretically calculated.

| F (MHz) | Size | Nuclei | Power (W) | Pw90 (µs) | Q_U | Q_L | Dead time (μ s) |
|---------|--------|------------------|-----------|-----------|-------|-------|----------------------|
| 8 | Large | $^{1}\mathrm{H}$ | 115 | 18.0 | 116 | 116 | 92 |
| 20 | Medium | $^{1}\mathrm{H}$ | 115 | 10.0 | 80 | 80 | 25 |
| 38 | Medium | ⁷ Li | 115 | 33.0 | 145 | 145 | 24 |
| 100 | Medium | $^{1}\mathrm{H}$ | 115 | 25.0 | 123 | 123 | 8 |
| 116 | Small | ⁷ Li | 80 | 17.0 | 140 | 140 | 8 |
| 300 | Small | $^{1}\mathrm{H}$ | 80 | 32.5 | 83 | 83 | 2 |
| 500 | Small | $^{1}\mathrm{H}$ | - | - | 50 | 50 | 1 |

5.3.2.2 Low frequency PPRs

Two low frequency PPRs are reported in Table 5.1 We have a Large ¹H PPR tuned to 8 MHz and a Medium ¹H PPR tuned to 20 MHz both with the same plate separation. The Large PPR with dimensions 25.0 cm \times 17.5 cm, has a 90-degree pulse duration of 18 μ s and a quality factor of 116. As expected, the Medium 20 MHz has a shorter 90-pulse duration for the same input power. However, due to the increased inductance of the Large 8 MHz PPR the quality factor is significantly larger than the quality factor of the 20 MHz PPR.

Fig. 5.6 depicts a CPMG decay acquired with the Large 8 MHz PPR, shown in Fig. 5.5a. A SNR = 68 was achieved in the measurement using four large $(13 \text{ cm} \times 13 \text{ cm} \times 0.5 \text{ cm} \times 0.$

cm) Neoprene rubber pieces as sample. The PPR was tuned using a matching capacitor of 300 pF and a tuning capacitor of 4560 pF. The great advantage of this PPR is its size which makes it easy to tune at low frequencies. Another advantage is the large sample volume available. The separation between the plates of the PPR is relatively small but it may be increased if thicker samples are interrogated. The homogeneity could be improved using distributed capacitance as shown in Fig. 5.3 for a Medium PPR.

The theoretical deadtime for the Large PPR was estimated as 92 μ s. The deadtime is long because of the low frequency and the large quality factor. However, the theoretical value is longer than that observed experimentally which was 45 μ s.



Fig. 5.6. CPMG decay, for the four large $(13 \text{ cm} \times 13 \text{ cm} \times 0.5 \text{ cm})$ Neoprene rubber pieces, acquired with the Large 8 MHz ¹H PPR. The probe was tuned and matched with fixed ceramic capacitors of 300 pF and 4560 pF respectively. Separation between the plates was 0.7 cm. The SNR for the acquired data was 68

Fig. 5.7a shows the Medium 20 MHz ¹H PPR and a Proteus magnet. This PPR is a

great choice for a Proteus type magnet where the accessible space between the magnets is rectangular. The resonator perfectly matches the space between the two magnets, maximizing the size of the probe and the sample volume. Fig. 5.7b shows a CPMG decay acquired with the 20 MHz PPR, the SNR was 26 for this experiment. The lower quality factor and higher working frequency produce a relatively short deadtime of 25 μ s when compared with the Large PPR. The theoretical deadtime agrees with the measured deadtime of 21 μ s. This smaller PPR has a higher sensitivity than the larger PPR. This results in a shorter 90-degree pulse duration, 10 μ s, for the same input power of 115 W.

For the specific case of the 20 MHz PPR, no ringing was observed due to the proximity of the disk magnets. The conductive plate of the probe act as a shield between the magnet and the sample space, reducing noise pick up due to the currents induced on the magnet.

The Large ¹H 8 MHz PPR and the Medium ¹H 20 MHz PPR, were inserted into similar geometry magnets. The console was the same and the same type of sample was employed in the experiment. This presents a good opportunity to consider the relative sensitivity. Is it better to use the Large PPR with larger sample at 8 MHz or the Medium PPR with smaller sample at 20 MHz?

The SNR [2, 28] of a MR experiment after a 90-degree pulse can be described in a simplified equation as SNR $\propto (B_o)^{\frac{7}{4}} N_s B_1$. In the Large PPR, the number of spins, N_s, is 14 times larger than in the sample of the Medium PPR. The static magnetic field **B**₀ is 2.5 times lower and the **B**₁ magnetic field is 1.8 times weaker. A 1.6-fold improvement in the SNR was expected for the Large PPR with the large sample. However, a 2.6 increase in the SNR was achieved during the experiment. The results suggest that low-field MR experiments, with large samples may be advantageous for some experimental systems.



Fig. 5.7. A) Medium size PPR tuned and matched at 20 MHz for a Proteus Magnet. B) CPMG decay acquired from four small (4 cm \times 3 cm \times 0.5 cm) Neoprene rubber pieces. The probe was tuned and matched with fixed ceramic capacitors of 1440 pF and 130 pF respectively. Separation between the plates was 0.7 cm. The SNR for the acquired data was 26.

5.3.2.3 Medium frequency PPR

For the medium frequency range three PPRs resonator were assembled. A Medium 38 MHz ⁷Li optimized PPR, a Medium 100 MHz ¹H optimized PPR and a Small 116 MHz ⁷Li PPR. The 38 MHz optimized PPR has a similar deadtime to the 20 MHz PPR. However, the quality factor is significantly higher due to the addition of capacitors to improve the B_1 homogeneity. The capacitors attached to the probe corners effectively reduce the length of the PPR, reducing its radiation losses [26]. This optimized PPR was recently employed for ⁷Li studies of lithium-ion batteries [16]. The sensitivity of the probe was compared with a birdcage RF probe with a diameter similar to the width of the optimized PPR. The result showed higher sensitivity for the optimized PPR due to the proximity of the sample to the conductive elements of the probe.

A Medium size optimized PPR was also tested at 100 MHz for hydrogen, as shown in Table 5.1. With a relatively large quality factor and a short dead time the optimized PPR showed good sensitivity. Fig. 5.8 shows a 2D SPRITE image of a homogeneous rubber sample. The homogeneity of the PPR was improved by adding optimized capacitors on the corners of the plates.

A Small PPR was assembled for lithium studies at 116 MHz [21]. This PPR has the second highest quality factor of all the PPRs, although it is not optimized. The increase is due to the reduction of the lateral size of the PPR. However, the theoretical deadtime of 8 μ s, for the Small PPR was similar to the dead time of the Medium ¹H 100 MHz optimized PPR. The 90-degree pulse duration was less than the ¹H 100 MHz optimized PPR even though the input power for the Small PPR was less. Sanders *et al.* [21] compared the sensitivity (Appendix A. Supplementary data) [21] of the PPR with a solenoid RF probe (8 turns, 1 cm diameter) in Lithium-ion batteries studies. It was shown that the PPR was 3 times more sensitive than the solenoid because its sample space was 7 times larger than the

5.3. Results and Discussion



Fig. 5.8. 2D XZ SPRITE image of a homogeneous rubber sample acquired with the 100 MHz ¹H optimized PPR with a FOV of $5.0 \text{ cm} \times 5.0 \text{ cm}$

solenoid.

Fig. 5.9 shows a ⁷Li MR spectrum of a fully charged Lithium-Ion battery, acquired with the 116 MHz ⁷Li PPR. The different stages of lithiated graphite and the quadrupolar satellites are observed in the MR spectrum [20, 21]. The SNR of the spectrum was 980 which is a good indication of the high sensitivity of the PPR. The high sensitivity of the PPR greatly reduce experiment time, permitting the study of larger and more realistic samples. This also allows the implementation of other measurements, such as T_1 - T_2 relaxation correlation experiment [16]. This type of experiments, similar to 2D correlation spectroscopy, could also be also employed for lithium-ion battery characterization and the

study of metallic microstructure formation [29].

The medium frequency range is where most applications for the PPR have been found [16, 20]. In this range of frequencies, it is relatively easy to tune, match and optimize the PPR. However, the PPR could be employed at higher frequencies if the RF probe is segmented.



Fig. 5.9. ⁷Li MR spectra of fully charged lithium-ion cell. The spectrum was acquired with a Small PPR at 116 MHz. The cell was assembled with a LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ cathode, a graphite anode, and a 1.0 M LiPF₆ in 1:1 EC: DEC as the electrolyte. The battery was charged to 4.2 V using a constant current of 1.2 mA (\propto C/20). The SNR of the spectrum was 980 with 9592 averages and acquisition time of 10.24 ms.

5.3.2.4 High frequency PPR

Two Small PPRs were assembled for testing at high frequency. The 300 MHz PPR was employed for MR measurement while the 500 MHz PPR was bench tested. The 300 MHz PPR has a lower quality factor than the small PPR tuned at 116 MHz for lithium studies, as shown in Table 5.1. The increase of frequency increases the losses of the probe, reducing the quality factor. The 300 MHz PPR was segmented to reduce the radiation losses of the probe because the length of the probe was larger than the limit $\lambda/10$. With a low-quality factor and high working frequency the PPR has a short deadtime. Fig. 5.10 depicts the ¹H MR spectra for a Mn (II) doped water sample at 300 MHz. The spectrum was acquired with 4 averages and an acquisition time of 50 ms. The SNR of the spectrum was 21000, showing the high sensitivity of the PPR. This result shows that PPRs are well suited for spectroscopic studies. They have an advantage of a larger sample volume than common RF probes employed at this high frequency.



Fig. 5.10. ¹H MR spectra of Mn (II) doped water sample. The spectrum was acquired with a Small PPR at 300 MHz. The SNR of the spectrum was 21 000 with only four averages and an acquisition time of 50 ms. The observed linewidth for the spectrum was 262 Hz.

The 500 MHz PPR was bench tested. Because the frequency was high, and the length of the PPR is non-negligible fraction of the wavelength, radiation losses are significant. A

quality factor of 50 was achieved with the segmented PPR. A 1 pF capacitor was used to join the plates. This result is of great importance, the PPR can still be tuned and matched at high frequency without a reduction of the sample space. This will allow the employment of the PPR for MR studies at frequencies as high as 500 MHz.

As described in this paper, the PPR RF probe can be employed for studies over a large range of MR/MRI frequencies. They can be employed for both small and large cuboid samples depending on the working frequency. They can be easily segmented to reduce RF probe radiation losses and to achieve higher frequencies. For a Large PPR an optimization approach can be employed to improve the homogeneity of the PPR. The approach taken here was to employ 5 capacitors at the corners of the PPR to improve the homogeneity. However, the number of capacitors is not limited for the optimization. It is important to consider that increasing the number of capacitors will increase the complexity of the probe.

The PPR has shown good results in studies of Lithium-ion batteries because it can accommodate thin cuboid samples and the orientation of the **B**₁ magnetic field reduces the RF attenuation due to the conductive electrodes. However, when performing ¹H and ¹⁹F studies of samples with very short relaxation times, T_2^* and T_2 , attention must be paid to the background signal of the PCB.

5.4 Conclusion

The PPR is simple to build. The PPR has shown good sensitivity at both low and high frequencies. As a transverse RF probe, it can be use in a wide variety of magnets without distorting the \mathbf{B}_0 magnetic field due to sample alignment. Its geometry, naturally reducing its electrical length, combined with its large lateral size, compared to other probes at high frequency, makes the PPR a good candidate for spectroscopy, especially at high fields. At low frequencies, a large PPR is a natural choice for SNR improvement. The \mathbf{B}_1

magnetic field homogeneity of the PPR, at low frequency, can be improved with distributed capacitance on the plates. There is no reduction of the quality factor of the probe after sample insertion. Losses are dominated by the RF probe. These advantages widen the range of applications of the PPR, especially in the field of battery studies where it has already shown great promise.

Despite the success of these studies, there is still room to improve the PPR. For ¹H and ¹⁹F MR/MRI studies the PCB board produces background signal. A PCB board free PPR will be advantageous. The B_1 magnetic field homogeneity could also be improved. Increasing the number of distributed capacitors in the optimization process will lead to an improved homogeneity. However, this could also be a time-consuming process. A trade-off between homogeneity and simplicity of the design is probably necessary.

References

- [1] D. I. Hoult, The NMR receiver: A description and analysis of design, Progress in Nuclear Magnetic Resonance Spectroscopy 12 (1978) 41–77. doi:10.1016/ 0079-6565(78)80002-8.
- [2] D. I. Hoult, R. E. Richards, The signal-to-noise ratio of the nuclear magnetic resonance experiment, Journal of Magnetic Resonance (1969) 24 (1976) 71–85. doi: 10.1016/0022-2364(76)90233-X.
- [3] F. D. Doty, Probe design and construction, eMagRes (2007) 1-12. .doi:10.1002/ 9780470034590.emrstm0414.
- [4] J. Mispelter, M. Lupu, A. Briguet, NMR Probeheads for Biophysical and Biomedical Experiments, 2nd Edition, Imperial College Press, 2006. doi:10.1142/p438.
- [5] J. T. Vaughan, J. R. Griffiths, RF Coils for MRI, 1st Edition, John Wiley and Sons, 2012.
- [6] A. S. Peshkovsky, J. Forguez, L. Cerioni, D. J. Pusiol, RF probe recovery time reduction with a novel active ringing suppression circuit, Journal of Magnetic Resonance 177 (2005) 67–73. doi:10.1016/j.jmr.2005.07.004.
- [7] E. R. Andrew, K. Jurga, NMR probe with short recovery time, Journal of Magnetic Resonance 73 (1969) 268–276. doi:10.1016/0022-2364(87)90198-3.
- [8] E. L. Hahn, Spin echoes, Physical Review 80 (1950) 580–594. doi:10.1103/ PhysRev.80.580.
- B. A. Jung, M. Weigel, Spin echo magnetic resonance imaging, Journal of Magnetic Resonance Imaging 37 (2013) 805–817. doi:10.1002/jmri.24068.

- [10] M. Halse, D. J. Goodyear, B. MacMillan, P. Szomolanyi, D. Matheson, B. J. Balcom, Centric scan SPRITE magnetic resonance imaging, Journal of Magnetic Resonance 165 (2003) 219–229. doi:10.1016/j.jmr.2003.08.004.
- [11] R. Enjilela, J. Guo, B. MacMillan, F. Marica, A. Afrough, B. Balcom, T₁-T₂^{*} relaxation correlation measurements, Journal of Magnetic Resonance 326 (2021) 106961–106968. doi:10.1016/j.jmr.2021.106961.
- [12] A. G. Webb, Nuclear magnetic resonance of mass-limited samples using small RF coils, Analytical and Bioanalytical Chemistry 388 (2007) 525–528. doi:10.1007/s00216-007-1178-2.
- [13] A. G. Webb, Microcoil nuclear magnetic resonance spectroscopy, Journal of Pharmaceutical and Biomedical Analysis 38 (2005) 892–903. doi:10.1016/j.jpba. 2005.01.048.
- [14] R. Fu, W. W. Brey, K. Shetty, P. Gor'kov, S. Saha, J. R. Long, S. C. Grant, E. Y. Chekmenev, J. Hu, Z. Gan, M. Sharma, F. Zhang, T. M. Logan, R. Brüschweller, A. Edison, A. Blue, I. R. Dixon, W. D. Markiewicz, T. A. Cross, Ultra-wide bore 900 MHz high-resolution NMR at the national high magnetic field laboratory, Journal of Magnetic Resonance 177 (2005) 1–8. doi:10.1016/j.jmr.2005.07.013.
- [15] F. D. Doty, G. Entzminger, J. Kulkarni, K. Pamarthy, J. P. Staab, Radio frequency coil technology for small-animal MRI, NMR in Biomedicine 20 (2007) 304–325. doi:10.1002/nbm.1149.
- [16] A. R. Aguilera, B. MacMillan, S. Krachkovskiy, K. J. Sanders, F. Alkhayri, C. A. Dyker, G. R. Goward, B. J. Balcom, A parallel-plate RF probe and battery car-

tridge for ⁷Li ion battery studies, Journal of Magnetic Resonance 325 (2021) 106943–106950. doi:10.1016/j.jmr.2021.106943.

- [17] Z. Zhang, J. Martin, J. Wu, H. Wang, K. Promislow, B. J. Balcom, Magnetic resonance imaging of water content across the Nafion membrane in an operational PEM fuel cell, Journal of Magnetic Resonance 193 (2008) 259–266. doi:10.1016/j.jmr.2008.05.005.
- [18] J. Zhang, B. J. Balcom, Parallel-plate RF resonator imaging of chemical shift resolved capillary flow, Magnetic Resonance Imaging 28 (2010) 826–833. doi:10.1016/j. mri.2010.03.033.
- [19] J. Zhang, R. P. MacGregor, B. J. Balcom, Liquid crystal diffusion in thin films investigated by PFG magnetic resonance and magnetic resonance imaging, Chemical Physics Letters 461 (2008) 106–110. doi:10.1016/j.cplett.2008.06.090.
- [20] S. A. Krachkovskiy, M. Reza, A. R. Aguilera, B. J. Balcom, G. R. Goward, Realtime quantitative detection of lithium plating by *in situ* NMR using a parallel-plate resonator, Journal of The Electrochemical Society 167 (2020) 130514–130519. doi: 10.1149/1945-7111/abb7ea.
- [21] K. J. Sanders, A. R. Aguilera, J. R. Keffer, B. J. Balcom, I. C. Halalay, G. R. Goward, Transient lithium metal plating on graphite: Operando ⁷Li nuclear magnetic resonance investigation of a battery cell using a novel RF probe, Carbon 189 (2022) 377– 385. doi:10.1016/j.carbon.2021.12.082.
- [22] M. D. Meadowcroft, S. Zhang, W. Liu, S. P. Bu, J. R. Connor, C. M. Collins, M. B. Smith, Q. X. Yang, Direct magnetic resonance imaging of histological tissue samples

at 3.0T, Magnetic Resonance in Medicine 57 (2007) 835–841. doi:10.1002/mrm. 21213.

- [23] D. M. Hoang, E. B. Voura, C. Zhang, L. Fakri-Bouchet, Y. Z. Wadghiri, Evaluation of coils for imaging histological slides: Signal-to-noise ratio and filling factor, Magnetic Resonance in Medicine 71 (2014) 1932–1943. doi:10.1002/mrm.24841.
- [24] A. R. Aguilera, B. MacMillan, G. R. Goward, B. J. Balcom, Optimization of a parallel-plate RF probe for high resolution thin film imaging, Concepts in Magnetic Resonance Part A 47A (2018) e21465–e21470. doi:10.1002/cmr.a.21465.
- [25] D. I. Hoult, The principle of reciprocity in signal strength calculations a mathematical guide, Concepts in Magnetic Resonance 12 (2000) 173–187. doi:10.1002/1099-0534(2000)12:4<173::AID-CMR1>3.0.CO;2-Q.
- [26] D. I. Hoult, B. Tomanek, Use of mutually inductive coupling in probe design, Concepts in Magnetic Resonance Part B: Magnetic Resonance Engineering 15 (2002) 262–285. doi:10.1002/cmr.10047.
- [27] M. Decorps, P. Blondet, H. Reutenauer, J. P. Albrand, C. Remy, An inductively coupled, series-tuned NMR probe, Journal of Magnetic Resonance (1969) 65 (1985) 100–109. doi:10.1016/0022-2364(85)90378-6.
- [28] K. R. Minard, R. A. Wind, Solenoidal microcoil design part II: Optimizing winding parameters for maximum signal-to-noise performance, Concepts in Magnetic Resonance 13 (2001) 190–210. doi:10.1002/cmr.1008.
- [29] S. Chandrashekar, N. M. Trease, H. J. Chang, L.-S. Du, C. P. Grey, A. Jerschow, ⁷Li MRI of Li batteries reveals location of microstructural lithium, Nature Materials 11 (2012) 311–315. doi:10.1038/nmat3246.

Chapter 6

Multinuclear MR/MRI Study of Lithium-Ion Cells Using a Variable Field Magnet and a Single RF Probe

In Chapter 4, it was shown that the PPR RF probe can be employed for detection of Li intercalated into graphite. However, in LIB systems there are several other MR accessible nuclei of importance. In this Chapter, the performance of the PPR for different nuclei is evaluated through use of a variable field magnet with a common PPR RF probe.

This chapter is written in paper format but should be considered an exploratory study. We follow the notation for variables and equations recommended by the *Journal of Magnetic Resonance*.

Abstract

An exploratory, multinuclear (⁷Li, ¹⁹F, and ¹H) MR/MRI study was performed on Lithium-Ion cells using a variable field superconducting magnet and a single Parallel-Plate Resonator RF probe tuned at 33.7 MHz. Two cartridge-like graphite/NMC532 Li-ion cells were interrogated: a pristine cell and a charged cell with a voltage of 4.2 V. The magnetic field of the variable field magnet was changed to match the resonance frequency for ⁷Li, ¹⁹F, and ¹H at 33.7 MHz. The results presented show the advantage of multinuclear MR studies using a variable field magnet. The results, also open the door to the development of faster, and simpler methods for detection, quantification, and interpretation of MR/MRI data from Li-Ion Batteries.

6.1 Introduction

Magnetic Resonance (MR) and Magnetic Resonance Imaging (MRI) have proven to be excellent tools to interrogate Lithium-Ion Batteries (LIBs) [1–3]. They have provided information to further increase LIBs performance and safety [4–7]. Due to their ability to provide spatially resolved information about different species [2], MR and MRI have provided fundamental insights on relevant topics such as lithium plating [3, 8–10], lithium intercalation [11, 12], electrolyte degradation [13, 14], and the solid electrolyte interface SEI [15, 16].

The complexity of the materials employed in LIBs and their multiple interactions make it challenging to operationally analyse LIBs by most analytical techniques [17, 18]. Multinuclear MR studies of LIB have proven valuable for characterization and quantification of the different chemical species present in the cell [19–21]. Combined information from different MR active nuclei can provide detailed answers regarding the dynamic properties of the materials and chemical processes in the LIBs, especially during *in operando* studies. However, most multinuclear MR/MRI studies of LIBs employ different magnet systems and/or complex multifrequency RF probes. This leads to an increase of the experiment difficulty and/or precludes a better characterization and quantification of the different species in the LIB.

We present an exploratory multinuclear (⁷Li, ¹⁹F, ¹H) MR/MRI study of Li-ion cells. For the first time, a variable field superconducting magnet with a single RF probe was employed in LIB studies. The results presented here open the door for development of new and faster techniques to study LIBs. MR/MRI can be use for characterization of both liquid and solid components in the cells. They can also be employed to study different MR active nuclei present in LIBs such as, ¹H, ⁶Li, ⁷Li, ¹⁹F and ³¹P [2]. Meyer *et al.* [21] employed a multinuclear (⁷Li, ¹⁹F) MR approach to identify and quantify LiF in the solid electrolyte interface (SEI). The data was collected using two separate magnet systems. A 16.5 T superconducting magnet was employed for ⁷Li studies at a ⁷Li frequency of 272 MHz, and a 14.0 T superconducting magnet was employed for ¹⁹F studies at a ¹⁹F frequency of 565 MHz. Huo *et al.* [19] performed a multinuclear (¹H, ⁷Li, ¹⁹F, ³¹P) study to determine the composition of the Solid electrolyte interface (SEI) in a Li-FeSn₂ negative electrode. Experiments were performed on a wide-bore 2.4 T superconducting magnet and a wide-bore 7.0 T superconducting magnet. Wan *et al.* [20] also employed a multinuclear (⁶Li, ¹⁹F, ¹³C, ¹H) approach to determine the composition of the SEI in Cu|Li cells. MR experiments were performed in a 20 T, 3 channel spectrometer equipped with a 4 mm double resonance pencil type RF probe.

Multinuclear studies of LIB can be complicated and time consuming due to the complexity of the cell materials and the need for different magnets and/or multiple resonance RF probes to interrogate the Li-ion cell. Cell complexity involves small sample volume, nuclei of low sensitivity and RF attenuation due to metallic components of the cell. Using different magnet systems can be troublesome. It will reduce experimental resources in the laboratory, and it will be difficult to quantify and compare the results. Multiple resonance RF probes are expensive and difficult to build [22, 23]. They also have different sensitivity depending on the working frequency.

In this exploratory study, two cartridge-like graphite/NMC532 Li-ion cells were studied *ex situ*. The cells were not attached to the charging system. A pristine cell and a charged cell with a voltage of 4.2 V were studied. Although *in situ* and *in operando* studies can be performed, in this exploratory study only *ex situ* experiments were performed, to reduce experimental time and experiment complexity. The pristine cell and the charged cell were

chosen to represent logical end points of battery operation. After a cell is charged, new Li species are formed, and some electrolyte is expected to be consumed and/or degraded. These changes are expected to be detected with the MR/MRI experiments performed.

The magnetic field of the variable field superconducting magnet was changed to match the resonance frequency of each nucleus to the frequency of the RF probe. Bulk measurements of T_1 , T_2 and T_1 - T_2 were performed on both, pristine and charged Li-ion cell. 2D SPRITE images were acquired for each nucleus in both cells.

6.2 Experiments Details

6.2.1 Cell Assembly and Charging Protocol

Two identical cells were assembled. The electrodes, the separators, and the cartridge parts were dried prior to assembly. They were dried at 80 °C for 36 h. All LIBs cells were assembled inside an argon-filled glovebox (7 ppm oxygen level, 0.5 ppm moisture level, box pressure 6.9 mbar). The separators of both cells were soaked with 1.2 mL of the electrolyte 1.0 M LiPF₆ in EC/DMC=50/50 (v/v). The electrodes and the separators were cut square with an area 9 cm². The cells were assembled with four paper filters as separator. The final separation between the electrodes was approximately 1 mm. One of the cells was charged in constant current mode, with a 2400 Source Meter (Tektronix, Inc., Beaverton, OR) at a low rate of C/35 (500 mA) until the cell voltage reached 4.2 V. The cell was charged over 33 h.

The cells were assembled with a graphite anode and a Lithium Nickel Manganese Cobalt Oxide cathode, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC), both electrodes have a capacity of ~ 2 mAh/cm² (NEI Corporation, Somerset, NJ). The NMC electrode, with active material

loading of 11.83 mg/cm² and a thickness of 70-75 mm, is coated on an aluminium current collector. The graphite electrode, with a porosity of 35% and a thickness of 60-65 mm, is coated on a copper current collector. Whatman glass microfibre filters, Grade GF/C, 250 mm thick (Sigma-Aldrich, Ontario, Canada), were used as separators.

6.2.2 MR Experiments

A variable field magnet with a maximum field of 3 T (MR Solutions, Guildford, Surrey, UK) was employed for all MR/MRI measurements. The magnet was operated at three different magnetic fields, 0.791 T, 0.841 T and 2.035 T, for ¹H, ¹⁹F and ⁷Li studies respectively, which correspond to a frequency of 33.7 MHz. Switching time between fields was less than 45 min. The gradient coils were driven by gradient amplifiers (Performance Controls, Inc., PA, US), providing maximum gradient strengths of 66.4 G/cm, 64.9 G/cm and 87.8 G/cm in the x, y, and z directions.

A homemade PPR tuned and matched at 33.7 MHz was employed for all measurements. The separation between the plates was 0.7 cm. The plates of the PPR are 5 cm long and 3.5 cm width. The PPR was driven by a 2 kW Tomco RF amplifier (Tomco Technologies, Stepney, Australia). The input power for the PPR was set at 58 W. For this input power, the 90° pulse duration for ¹H, ¹⁹F and ⁷Li were, 11 μ s, 12 μ s and 27 μ s respectively. The quality factor Q of the PPR was unchanged at 143 for the unloaded probe and for the probe after cell insertion.

Bulk T_2 measurements were performed in both cells for each nucleus. The echo time, TE, was 400 μ s for ¹H and ¹⁹F experiments and 600 μ s for ⁷Li experiments. The number of echoes acquired was 9375 for ¹H, 17500 for ¹⁹F and 11667 for ⁷Li. In all T_2 measurements

the number of averages was 128.

For T_1 measurements the inversion recovery method was employed with 40 inversion recovery steps. Minimum recovery delay was 0.25 ms in all measurements. The maximum recovery delay was 7966 ms for ¹H, 11380 ms for ¹⁹F and ⁷Li. In all T_1 measurements the number of averages was 128. The measurement time was 44 min for ¹H T_1 measurement and 60 min for ¹⁹F and ⁷Li T_1 measurements.

Bulk T_1 - T_2 measurements were performed with the same parameters used in the T_1 and T_2 measurements. The number of averages was 8 in all T_1 - T_2 measurements. Measurement time for ¹H T_1 - T_2 measurement was 66 min, for ¹⁹F it was 113 min and 102 min for ⁷Li.

2D images were acquired using a Spiral SPRITE sequence. The RF pulse duration was 3 μ s for ¹H, 6 μ s for ¹⁹F and 9 μ s for ⁷Li. For all images a 64 × 64 K-space was acquired with 128 averages. Four interleaves were acquired in each image. The measurement time was 23 min for the 2D ¹H image, and 32 min for ¹⁹F and ⁷Li. The encoding time was 600 μ s for ¹H and ⁷Li images and 400 μ s for ¹⁹F image. Four interleaves were acquired in each acquisition. The field of view was 7 cm in all images.

6.3 **Results and Discussion**

6.3.1 Magnet system and RF probe

The magnetic field of the variable superconductive magnet can be smoothly varied from 0 T to 3 T. This provides new opportunities to characterize LIBs. In our LIB study the magnetic field of the magnet was set at three different fields, 0.79 T, 0.84 T and 2.03 T, for ¹H, ¹⁹F and ⁷Li studies respectively. These correspond to a resonance frequency of 33.7 MHz for each nucleus. Switching between fields for the different studies was a relatively

fast and straightforward process. Switching time between fields was less than 45 min in all cases. Employing a single magnet system and fixed frequency allows for better and more quantitative experiments. The sample remains in the same place when it is interrogated for a different nucleus, avoiding sample perturbation or possible damage. All experiments were performed at the same frequency allowing the use of a single RF probe for all three MR studies.

Metallic components in the LIB may attenuate the RF signal if the proper RF probe is not employed. A Parallel-Plate Resonator (PPR) RF probe was employed in all MR studies. This type of RF probe has proven to be good choice to interrogate LIBs [1, 8, 10]. The PPR was tuned and matched at 33.7 MHz for all three nuclei. The PPR with a B_1 magnetic field parallel to the electrodes of the cell avoids RF attenuation during excitation and reception. Its flat geometry ideally accommodated the cartridge-like cells. Another advantage of the PPR is that it is working in a probe noise-dominated regime. The quality factor of the probe did not change when the LIB was inserted.

The combination of the variable field magnet and a single PPR RF probe greatly reduces the complexity of the MR experiments. This reduces the need for extra magnet systems, multiple RF probes and/or complex multi-resonance RF probes.

6.3.2 Experimental results

Bulk measurements T_1 , T_2 and T_1 - T_2 were performed on both, pristine and charged Liion cells for all three nuclei. Relaxation distributions and relaxation correlation maps are presented to better convey our findings.

Fig. 6.1 shows T_2 relaxation distributions for the three MR nuclei studied in the Li-

ion cell (¹H, ¹⁹F and ⁷Li). The pristine cell T_2 relaxation distribution and charged cell T_2 relaxation distribution line are both presented. Fig. 6.1A illustrates the ¹H T_2 relaxation distribution for both pristine and charged cells. The relaxation distribution of the pristine cell shows three well defined peaks. The peak with the longest T_2 lifetime, 700 ms, is associated with ¹H in the electrolyte solution. The two organic solvents mixed in the electrolyte solution are both rich in ¹H. A strong signal from the electrolyte was expected. The middle peak, in the relaxation distribution of the pristine cell, with a lifetime of 50 ms, is associated with the silicon rubber gasket employed to seal the cell. Control experiments confirmed this. The location and amplitude of this peak should not change with charging. Thus, it could be used as a reference for calibration and quantification purposes. The third peak in the relaxation distribution, with the shortest T_2 lifetime of 2 ms, is associated with ¹H in the copper clad Printed circuit board (PCB) employed to build the PPR. This peak should also not change after the cell is charged. However, for calibration and quantification purposes the peak associated with the rubber gasket is a better choice.

The ¹H T_2 relaxation distribution for the charged cell shown in Fig. 6.1A depicts three different ¹H environments. The peaks associated with the PCB and the rubber gasket did not change as they are not influenced by the charging process of the cell. However, the peak with the longest T_2 lifetime changed after the cell was charged. A wider T_2 relaxation distribution with a shorter T_2 lifetime of 500 ms is observed for the electrolyte. A change in the relaxation distribution for the electrolyte was expected. During the charging process some electrolyte degrades forming new components and the SEI.

Fig. 6.1B illustrates the ¹⁹F T_2 relaxation distribution for both pristine and charged cells. In both cases, two peaks are observed. The peak with the shortest T_2 lifetime of 4 ms is associated with the PCB. This peak remains unchanged for both distributions. The



Fig. 6.1. T_2 distribution for the three different nuclei in the Lithium-ion cells. Distribution for both pristine, uncharged cell (solid line) and charged cell (dashed line) are shown. A) T_2 distribution for ¹H. The amplitude of the electrolyte peak for the charged cell decreases and the T_2 lifetime of the peak shifted down to 500 ms. B) T_2 distribution for ¹⁹F. The amplitude of electrolyte peak decreases for the charged cell but the T_2 lifetime remains unchanged at 1 ms C) T_2 distribution for ⁷Li. The T_2 lifetime of the peak for the charged cell remains unchanged at 500 ms but the amplitude of peak decreases and its spreading significantly increases. The echo time, TE, was 400 μ s for ¹H and ¹⁹F experiments and 600 μ s for ⁷Li experiments.

peak with the longest T_2 lifetime is associated with the electrolyte. Inorganic lithium salt LiPF₆ is dissolved in the organic solvents EC and DMC to form the electrolyte. After the cell is charged the peak becomes wider and its amplitude is reduced. The reduction in the amplitude of the electrolyte peak is due to the formation of the SEI when the cell is charged.

Fig. 6.1C illustrates the ⁷Li T_2 relaxation distribution for both a pristine and a charged cell. A single peak, associated with the lithium in the electrolyte solution, is observed in both distributions. The T_2 lifetime of the peak remains unchanged at 500 ms. However, after the cell is charged, the amplitude of the peak is greatly reduced and the peak is no longer well defined, as in the pristine cell. The relaxation distribution of the charged cell is wider, spreading from 1 ms to 1 s. This may be related to the polarization of the electrolyte solution.

No signal from the NMC paramagnetic cathode nor from the lithium intercalated into the anode is observed. The T_2 lifetime from lithium ions in the cathode and from lithium ions intercalated into the graphite anode are too short to be observed with the TE employed, 600 μ s. With a shorter TE, less than 150 μ s, lithium intercalated into the graphite anode can be observed [1]. Also, no signal from metallic lithium is observed. The cell was charged slowly to avoid lithium plating and dendrite formation. However, if a different charging protocol were employed metallic lithium would be formed plating the anode. A short TE acquisition would allow observation of this plating.

Fig.6.2A shows T_1 relaxation distributions for the three MR active nuclei studied, for both lithium-ion cells. In all cases a single peak, associated with the electrolyte, is observed. T_1 relaxation distributions for ¹H and ¹⁹F remain unchanged after the cells have been charged. However, for the T_1 relaxation distributions for ⁷Li a significant change in amplitude has occurred after the cell was charged. Also, a wider distribution is observed while the T_1 lifetime of the peak remains unchanged at around 1 s. This result suggests that T_1 relaxation lifetimes are less affected by charging of the cell than T_2 lifetimes.

 T_1 - T_2 relaxation correlation techniques are great tools to discriminate different population in complex samples which are not easy to resolve employing simple relaxation



Fig. 6.2. T_1 distribution for the three different nuclei in the Lithium-ion cell. T_1 distribution for both pristine, uncharged cell (solid line) and charged cell (dashed line) are shown. A) T_1 distribution for ¹H, B) T_1 distribution for ¹⁹F and C) T_2 distribution for ⁷Li. The inversion recovery method was employed with 40 inversion recovery steps. No significant changes in the T_1 distribution are observed for ¹H and ¹⁹F after the cell was charged. The T_1 distribution for ⁷Li was wider with a smaller peak amplitude after the cell was charged.

distributions. Fig. 6.3A and Fig. 6.3B show ¹H T_1 - T_2 relaxation correlation maps for the pristine and charged cell respectively. In both correlation maps, three well-defined peaks are observed. The peaks are associated with the PCB, the rubber gasket and the electrolyte as presented in the T_2 relaxation distribution. As expected, the peaks are better resolved along the T_2 axis than along the T_1 axis.

Fig. 6.4A and Fig. 6.4B depict the ¹⁹F T_1 - T_2 relaxation correlation map for the pristine



Fig. 6.3. ¹H T_1 - T_2 relaxation correlation A) pristine, uncharged cell, B) charged cell. The echo time, TE, was 400 μ s for ¹H. Three well-defined peaks are observed on both maps. They are associated with the electrolyte, the rubber gasket, and the RF probe background ranging from the longest to the shortest T_2 lifetime respectively.

and charged cell respectively. A well-defined peak, associated with the electrolyte solution is observed. The peak with a T_1 lifetime of 1 s agrees with the results presented in the T_1 and T_2 relaxation distribution. A reduction in the amplitude of the electrolyte peak is expected. Some fluorine is converted to inorganic compound LiF forming the SEI. The peak observed in the ¹⁹F T_2 relaxation distribution, associated to the PCB is not well-defined in the ¹⁹F T_1 - T_2 relaxation correlation map. This is due the low signal of that peak. Increasing the numbers of averages will help to resolve the peak. However, this peak does not carry any valuable information.

Fig. 6.5A and Fig. 6.5B illustrates the ⁷Li T_1 - T_2 relaxation correlation maps for the pristine and charged cell respectively. Fig. 6.5A shows a well-defined peak with relaxation times $T_1 = 1000$ ms and $T_2 = 500$ ms. The peak is associated with the Li ions in the electrolyte solution. Signal from the Li ions in the NMC cathode electrode was not observed due to the short T_2 relaxation time [24]. The NMC cathode is highly paramagnetic due to the presence of several paramagnetic transition metal species [25]. In Fig. 6.5B no signal from the Li intercalated into graphite was observed due to the long TE employed. However, from previous work [1], the peak associated with lithium intercalated into graphite is expected at T_2 of approximately 1 ms and T_1 of just above 1 s.

Although, no quantification was made of the of the lithium species in each cell, a decrease in the signal intensity of the electrolyte in the charged cell in Fig. 6.5B was expected if compared with the electrolyte signal in Fig. 6.5A. During cell charging some electrolyte is irreversibly consumed in the SEI formation.

Fig. 6.6A and Fig. 6.6B show ¹H ZX 2D SPRITE images for the pristine and charged cells respectively. In both images the signal from the electrolyte and the rubber gasket are observed. No significant difference in the electrolyte image is observed between the pristine



Fig. 6.4. ¹⁹F T_1 - T_2 relaxation correlation A) pristine, uncharged cell, B) charged cell. The echo time, TE, was 400 μ s for ¹⁹F experiments. One well-defined peak is observed on both maps. The peak associated with the electrolyte solution. The peaks elongate along the T_2 axis in the charged cell.



Fig. 6.5. ⁷Li T_1 - T_2 relaxation correlation E) pristine, uncharged cell, F) charged cell. The echo time, TE, was 600 μ s for ⁷Li experiments. A single peak is observed on both maps. The peak associated with the lithium in the electrolyte solution. The peak elongates along the T_2 axis in the charged cell.

and charged cell. This is corroborated through the SNR of the image which was 13 for both cells. The cells were tightly sealed thus no electrolyte evaporation was expected during the experiment duration. However, it was anticipated that some electrolyte will degrade during the charging process. Thus, a lower SNR was expected for the image of the charged cell.

In both images, the signal from the rubber gasket surrounded the electrolyte is reduced at the top and the bottom because there the rubber gasket is outside of the RF probe.

Fig. 6.6C and Fig. 6.6D show the ¹⁹F 2D images for the pristine and charged cell respectively. In both images only the signal from the electrolyte is observed. A reduction in the image intensity is expected during the charging of the cell. During the SEI formation fluorine is irreversibly consumed forming the inorganic compound lithium fluoride (LiF) [16]. However, an increase in the SNR in the image of the charged cell was obtained. The SNR of the pristine cell was 3.7 while the SNR of the charged cell was 4.1. The increase in the electrolyte signal for ¹⁹F may be related to the probe not being perfectly matched and/or mistuned. The artefact signal on the right of the image is due to the background signal of the RF probe. This was confirmed with a control experiment.

Figs. 6.6E and Fig. 6.6F show ⁷Li 2D images for the pristine and charged cell respectively. The SNR of both image is relatively low. The SNR for the pristine cell was 2.4 while the SNR of the charged cell was 2.2. There was an 8% reduction in the SNR of the charged cell when compared to the pristine cell. The reduction of the SNR was expected. During cell charging some lithium-ions are irreversibly consumed in SEI formation. This reduction can be as large as 15% when compared with the pristine cell.

No signal from lithium-ions intercalated into graphite electrode was observed due to the long encoding time employed. Also, no lithium signal from the paramagnetic cathode electrode is observed due to the short lifetime signal. Metallic lithium formation was



Fig. 6.6. ZX 2D SPIRAL SPRITE image for the pristine and charged lithium-ion cells. A) ¹H pristine cell, B) ¹H charged cell, C) ¹⁹F pristine cell, D) ¹⁹F charged cell, E) ⁷Li pristine cell, F) ⁷Li charged cell. The FOV was 7 cm in all images. For all images a 64 \times 64 k-space was acquired with 128 averages. The images can be easily acquired for all three nuclei. The combined information of the images may be useful for quantification of different species in the cells, provided a good SNR is achieved

precluded due to the low-level current employed during charging. Thus, no signal from metallic lithium is observed.

The results presented here can be further improved by increasing the number of averages and reducing the encoding time. The study can be applied to different types of batteries and/or employed in spectroscopy studies.

6.4 Conclusions

A variable field superconducting magnet and a single PPR RF probe were employed for multinuclear MR/MRI study of lithium-ion cells at 33.7 MHz. This reduces experiment time and allows for better quantification of the results because a single RF probe is employed. A pristine and a charged lithium-Ion cell were both studied *ex situ* using bulk relaxation measurements and 2D SPRITE images. T_2 relaxation distribution and T_1 - T_2 relaxation correlation are more suitable for species separations in the cells. The study can be expanded to other types of batteries and other MR-sensitive nuclei. This could also be employed during *in situ* and *in operando* studies to detect and quantify species in transient processes. Metallic lithium could also be studied provided that a different charging protocol is employed producing metallic lithium, and a short TE is employed during signal acquisition to observed it.

References

- [1] A. R. Aguilera, B. MacMillan, S. Krachkovskiy, K. J. Sanders, F. Alkhayri, C. A. Dyker, G. R. Goward, B. J. Balcom, A parallel-plate RF probe and battery cartridge for ⁷Li ion battery studies, Journal of Magnetic Resonance 325 (2021) 106943– 106950. doi:10.1016/j.jmr.2021.106943.
- [2] O. Pecher, J. Carretero-Gonzalez, K. J. Griffith, C. P. Grey, Materials' methods: NMR in battery research, Chemistry of Materials 29 (2017) 213–242. doi:10.1021/acs. chemmater.6b03183.
- [3] S. Chandrashekar, N. M. Trease, H. J. Chang, L.-S. Du, C. P. Grey, A. Jerschow, ⁷Li MRI of Li batteries reveals location of microstructural lithium, Nature Materials 11 (2012) 311–315. doi:10.1038/nmat3246.
- [4] G. Cherkashinin, R. Hausbrand, W. Jaegermann, Performance of Li-Ion batteries: Contribution of electronic factors to the battery voltage, Journal of The Electrochemical Society 166 (2019) A5308–A5313. doi:10.1149/2.0441903jes.
- [5] D. Zhao, S. Li, Regulating the performance of lithium-ion battery focus on the electrode-electrolyte interface, Frontiers in Chemistry 8 (2020) 821-835. doi: 10.3389/fchem.2020.00821.
- [6] X. Wu, K. Song, X. Zhang, N. Hu, L. Li, W. Li, L. Zhang, H. Zhang, Safety issues in lithium ion batteries: Materials and cell design, Frontiers in Energy Research 7 (2019) 65–82. doi:10.3389/fenrg.2019.00065.
- [7] Y. Chen, Y. Kang, Y. Zhao, L. Wang, J. Liu, Y. Li, Z. Liang, X. He, X. Li, N. Tavajohi,B. Li, A review of lithium-ion battery safety concerns: The issues, strategies, and

testing standards, Journal of Energy Chemistry 59 (2021) 83–99. doi:10.1016/j.jechem.2020.10.017.

- [8] S. A. Krachkovskiy, M. Reza, A. R. Aguilera, I. C. Halalay, B. J. Balcom, G. R. Goward, Real-time quantitative detection of lithium plating by *in situ* NMR using a parallel-plate resonator, Journal of The Electrochemical Society 167 (2020) 130514–130519. doi:10.1149/1945-7111/abb7ea.
- [9] R. Bhattacharyya, B. Key, H. Chen, A. S. Best, A. F. Hollenkamp, C. P. Grey, *In situ* NMR observation of the formation of metallic lithium microstructures in lithium batteries, Nature Materials 9 (2010) 504–510. doi:10.1038/nmat2764.
- [10] K. J. Sanders, A. R. Aguilera, J. R. Keffer, B. J. Balcom, I. C. Halalay, G. R. Goward, Transient lithium metal plating on graphite: Operando ⁷Li nuclear magnetic resonance investigation of a battery cell using a novel RF probe, Carbon 189 (2022) 377– 385. doi:10.1016/j.carbon.2021.12.082.
- [11] M. Letellier, F. Chevallier, F. Béguin, *In situ* ⁷Li NMR during lithium electrochemical insertion into graphite and a carbon/carbon composite, Journal of Physics and Chemistry of Solids 67 (2006) 1228–1232. doi:10.1016/j.jpcs.2006.01.088.
- [12] R. E. Gerald, J. Sanchez, C. S. Johnson, R. J. Klingler, J. W. Rathke, *In situ* nuclear magnetic resonance investigations of lithium ions in carbon electrode materials using a novel detector, Journal of Physics Condensed Matter 13 (2001) 8269–8285. doi: 10.1088/0953-8984/13/36/304.
- [13] S. Wiemers-Meyer, M. Winter, S. Nowak, Mechanistic insights into lithium ion battery electrolyte degradation-a quantitative NMR study, Physical Chemistry Chemical Physics 18 (2016) 26595–26601. doi:10.1039/c6cp05276b.

- [14] N. Delpuech, N. Dupré, D. Mazouzi, J. Gaubicher, P. Moreau, J. S. Bridel, D. Guyomard, B. Lestriez, Correlation between irreversible capacity and electrolyte solvents degradation probed by NMR in Si-based negative electrode of Li-ion cell, Electrochemistry Communications 33 (2013) 72–75. doi:10.1016/j.elecom.2013.05.001.
- [15] M. Winter, The solid electrolyte interphase the most important and the least understood solid electrolyte in rechargeable Li batteries, Zeitschrift fur Physikalische Chemie 223 (2009) 1395–1406. doi:10.1524/zpch.2009.6086.
- [16] M. Gauthier, T. J. Carney, A. Grimaud, L. Giordano, N. Pour, H.-H. Chang, D. P. Fenning, S. F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp, Y. Shao-Horn, Electrode–electrolyte interface in Li-Ion batteries: Current understanding and new insights, The Journal of Physical Chemistry Letters 6 (2015) 4653–4672. doi: 10.1021/acs.jpclett.5b01727.
- [17] S. Zugmann, M. Fleischmann, M. Amereller, R. M. Gschwind, H. D. Wiemhöfer, H. J. Gores, Measurement of transference numbers for lithium ion electrolytes via four different methods, a comparative study, Electrochimica Acta 56 (2011) 3926–3933. doi:10.1016/j.electacta.2011.02.025.
- [18] L. F. Li, H. S. Lee, H. Li, X. Q. Yang, K. W. Nam, W. S. Yoon, J. McBreen, X. J. Huang, New electrolytes for lithium ion batteries using LiF salt and boron based anion receptors, Journal of Power Sources 184 (2008) 517–521. doi:10.1016/j.jpowsour.2008.03.016.
- [19] H. Huo, M. Chamas, P. E. Lippens, M. Ménétrier, Multinuclear NMR study of the solid electrolyte interface on the Li-FeSn₂ negative electrodes for Li-Ion batteries, Journal of Physical Chemistry C 116 (2012) 2390–2398. doi:10.1021/jp210017b.
- [20] C. Wan, S. Xu, M. Y. Hu, R. Cao, J. Qian, Z. Qin, J. Liu, K. T. Mueller, J.-G. Zhang, J. Z. Hu, Multinuclear NMR study of the solid electrolyte interface formed in lithium metal batteries, ACS Applied Materials and Interfaces 9 (2017) 14741–14748. doi: 10.1021/acsami.6b15383.
- [21] B. M. Meyer, N. Leifer, S. Sakamoto, S. G. Greenbaum, C. P. Grey, High field multinuclear NMR investigation of the SEI layer in lithium rechargeable batteries, Electrochemical and Solid-State Letters 8 (2005) A145–A149. doi:10.1149/1.1854117.
- [22] S. Kan, M. Fan, J. Courtieu, A single-coil triple resonance probe for nmr experiments, Review of Scientific Instruments 51 (1980) 887–890[•] doi:10.1063/1.1136352.
- [23] J. Mispelter, M. Lupu, A. Briguet, NMR Probeheads for Biophysical and Biomedical Experiments, 2nd Edition, Imperial College Press, 2006. doi:10.1142/p438.
- [24] K. Märker, C. Xu, C. P. Grey, Operando NMR of NMC811/graphite lithium-ion batteries: Structure, dynamics, and lithium metal deposition, Journal of the American Chemical Society 142 (2020) 17447–17456. doi:10.1021/jacs.0c06727.
- [25] C. P. Grey, N. Dupré, NMR studies of cathode materials for lithium-ion rechargeable batteries, Chemical Reviews 104 (2004) 4493–4512. doi:10.1021/cr020734p.

Chapter 7

Conclusions and Future Work

In this thesis we proposed the Parallel-Plate Resonator (PPR) for MR and MRI studies of LIBs. The performance of the PPR was evaluated and optimized through simulation and validated experimentally. This final chapter briefly summarizes the main contributions of this thesis and point the direction to further improve the results presented here.

7.1 Conclusions

In Chapter 3 a PPR RF probe was designed and optimized for thin film imaging. The B_1 inhomogeneity of the PPR was reduced using capacitors in the corner of the RF probe. Electromagnetic simulation was employed to find the optimum capacitance values to maximize B_1 homogeneity and B_1 magnetic field. A nominal resolution of <10 μ m was achieved in an imaging experiment with the PPR prototype constructed.

The geometry of the PPR naturally accommodates flat samples. With homogeneous B_1 magnetic field strength and B_1 parallel to the plates of the RF probe, the PPR design was naturally well suited for MR and MRI in LIBs. In Chapter 4, a PPR prototype was employed for ⁷Li studies in LIB cells. A cartridge-like cell was designed to work along with the PPR. T_1 - T_2 relaxation correlation MR experiments were reported for the first time for ⁷Li studies in LIB. Lithium intercalated into graphite was observed using T_1 - T_2 relaxation correlation, suggesting the RF probe combined with the cartridge-like cell are

sensitive to probe LIB behaviour. The RF probe was employed for both, *in situ* and *ex situ* experiments.

The PPR was simple to build and showed good sensitivity for LIB studies at 38 MHz. In Chapter 5 the PPR was tested over a wide range of frequencies and sizes. The results have shown that the PPR RF probe have good sensitivity at both low and high frequencies. As a transverse RF probe, it was employed in a wide variety of magnets without distorting the \mathbf{B}_0 magnetic field due to sample alignment. Its geometry naturally allows to reduce its electrical length, combined with its large lateral size, compared to other probes at high frequency, makes the PPR a good candidate for spectroscopy, especially at high fields. At low frequencies, a large PPR is a natural choice for SNR improvement. The \mathbf{B}_1 magnetic field homogeneity of the PPR, at low frequency, can be improved with distributed capacitance on the plates. There is no reduction of the quality factor of the probe after sample insertion. Losses are dominated by the RF probe. These advantages widen the range of applications of the PPR in the field of battery studies where it has already shown great promise.

Chapter 6 presented a preliminary multinuclear study of LIBs. A single PPR RF probe was combined with a variable field superconducting magnet. This reduces experiment time and allows for better quantification of the results because a single RF probe is employed. A pristine and a charged lithium-Ion cell were both studied *ex situ* using bulk relaxation measurements and 2D SPRITE image. T_2 relaxation distribution and T_1 - T_2 relaxation correlation are more suitable for species separations in the cells.

7.2 Future Work

Despite the success of the studies presented in this thesis, there is still room to improve the PPR RF probe and to widen its applications.

RF probe improvements

For ¹H and ¹⁹F MR/MRI studies the PCB produces background signal. A PPR free of background signal would be advantageous for better quantification of the results. One possible solution to eliminate the background signal is to employ a thicker copper sheet for the plates of the PPR. Thicker plates act as supports for the RF probe and also help to reduce the probe losses.

Other ways to improve the PPR include maximizing the homogeneity of the \mathbf{B}_1 magnetic field. Increasing the number of distributed capacitors in the optimization process could lead to an improved homogeneity. However, this could also be a time-consuming process. A trade-off between homogeneity and simplicity of the design is probably necessary.

The samples interrogated in this thesis were thin cuboid-like samples. However, employing the PPR with larger samples has merit. Thus, designing and optimizing PPR with larger separation between the plates for the study of thicker samples will be advantageous.

Other Applications

The PPR RF probe can be readily employed for MR studies of other types of batteries, and other MR active nuclei, such as sodium based rechargeable batteries [1] and redox flow batteries [2]. Redox flow batteries are promising for large scale energy storage. It is relatively inexpensive and can be scaled up simply by increasing the size of the reservoirs of reactive electrolytes. Sodium rechargeable batteries are analogous to the LIB. However, sodium is more abundant and cheaper than lithium.

The PPR should be employed during *in situ* and *in operando* studies to detect and quantify species in transient processes. This could be done during LIB formation or during battery continuous operation [3]. This is important in order to assess the life cycle of the LIB, mitigate degradation during continuous operation and increase its safety.

Metallic lithium could also be studied provided that a different charging protocol is employed during the battery study to produce metallic lithium. Metallic lithium is the most important factor that limits how fast the LIB can be charged. Reducing metallic lithium formation during fast charging will reduce changing time, which is one of the inconveniences of electric vehicles.

References

- J. M. Bray, C. L. Doswell, G. E. Pavlovskaya, L. Chen, B. Kishore, H. Au, H. Alptekin, E. Kendrick, M. M. Titirici, T. Meersmann, M. M. Britton, Operando visualisation of battery chemistry in a sodium-ion battery by ²³Na magnetic resonance imaging, Nature Communications 11 (2020) 2083–2092. doi:10.1038/s41467-020-15938-x.
- [2] E. W. Zhao, T. Liu, E. Jónsson, J. Lee, I. Temprano, R. B. Jethwa, A. Wang, H. Smith, J. Carretero-González, Q. Song, C. P. Grey, *In situ* NMR metrology reveals reaction mechanisms in redox flow batteries, Nature 579 (2020) 224–228. doi: 10.1038/s41586-020-2081-7.
- [3] K. Märker, C. Xu, C. P. Grey, Operando NMR of NMC811/graphite lithium-ion batteries: Structure, dynamics, and lithium metal deposition, Journal of the American Chemical Society 142 (2020) 17447–17456. doi:10.1021/jacs.0c06727.

APPENDIX A

RF Penetration Into Graphite: Simulation Results

Graphite is the most widely use anode material for LIBs. It has been widely study by MR to understand the intercalation process of the Li ions. However, due to the anisotropy of the graphite and its high conductivity RF penetration is always a concern. The graphite has a conductivity of 3.3×10^2 S/m perpendicular to the basal plane and a conductivity of 2×10^5 S/m parallel to the basal plane. The ZY plane is the basal plane in Fig A.1

Full RF penetration into the graphite electrode is important for the detection and quantification of Li ions intercalated into graphite. In this Appendix, a simple electromagnetic simulation have been performed to examine RF penetration of the graphite.

Fig. A.1 shows a Medium size PPR with a sandwiched graphite electrode. The \mathbf{B}_1 magnetic field of the PPR is perpendicular to the basal plane of the graphite electrode. So, \mathbf{B}_1 is directed perpendicular to the basal plane, the lower conductivity direction. The simulations were performed at 38 MHz using the High Frequency Module in CST Microwave Studio.

Fig. A.2 (top) illustrates the \mathbf{B}_1 magnetic field distribution in a 1 mm thick graphite sample. The PPR RF probe was hide to better observe \mathbf{B}_1 magnetic field distribution. It can be seen in this Fig, that the \mathbf{B}_1 magnetic field is heavily reduced in face of the graphite perpendicular to \mathbf{B}_1 . This is due to the eddy currents opposing the generating \mathbf{B}_1 magnetic field. The RF cannot fully penetrate the graphite sample. This result agreed with the results presented by Ilott *et al.* [1] and Vashaee *et al.* [2]. This result is complementary to the one presented on Fig. A.2 (bottom) which presents the magnetic field distribution of the three components of \mathbf{B}_1 magnetic field through the centre of the graphite. It can be observed that all components of \mathbf{B}_1 are reduced to zero at the centre of the graphite electrode. This confirms that for a thick graphite electrode full RF penetration is not achieved.



Fig. A.1. Geometry model of the PPR and a graphite electrode. The graphite electrode has a lateral size of 30×30 mm. Three different thicknesses were evaluated, 5 mm, 1 mm and 0.2 mm. The red chamfered disk is the excitation port

Fig. A.3 (top) presents the \mathbf{B}_1 magnetic field distribution for a thinner graphite sample, 0.2 mm thick. The \mathbf{B}_1 magnetic field is homogeneously distributed in all the faces of the graphite electrodes. This is an indication that \mathbf{B}_1 magnetic field fully penetrates the graphite sample. This results can be confirmed in the Fig. A.3 (bottom). The magnetic field distribution of all \mathbf{B}_1 magnetic field components are relatively constant in the centre of the graphite. This is very important for the detection and quantification of lithium intercalated into graphite. If the RF excitation completely penetrates the graphite thickness of 0.2 mm in this simulation is thicker than the commercial graphite electrodes. The normal thickness for a graphite electrode is 65-125 μ m (0.065-0.125 mm). Thus, for thinner electrodes full RF penetration is always achieved.



Fig. A.2. (top) \mathbf{B}_1 magnetic field distribution in a graphite electrode with a lateral size of 30 × 30 mm and a thickness of 1 mm. The colour bar represents the \mathbf{B}_1 magnetic field strength in units of $\frac{V \cdot s}{m^2}$ (1 $\frac{V \cdot s}{m^2} = 1$ $T = 10^4$ G). (bottom) \mathbf{B}_1 magnetic field distribution in different directions through the centre of the graphite. The thickness of the graphite has been scaled for better display.



Fig. A.3. (top) \mathbf{B}_1 magnetic field distribution in a graphite electrode with a lateral size of 30×30 mm and a thickness of 0.2 mm. The colour bar represents the \mathbf{B}_1 magnetic field strength in units of $\frac{V \cdot s}{m^2}$ (1 $\frac{V \cdot s}{m^2} = 1$ $T = 10^4$ G). (bottom) \mathbf{B}_1 magnetic field distribution in different directions through the centre of the graphite. The thickness of the graphite has been scaled for better display

References

- [1] Andrew J. Ilott, S. Chandrashekar, Andreas Klöckner, Hee Jung Chang, Nicole M. Trease, Clare P. Grey, Leslie Greengard, and Alexej Jerschow. Visualizing skin effects in conductors with MRI: ⁷Li MRI experiments and calculations. *Journal of Magnetic Resonance*, 245:143–149, 2014.
- [2] S. Vashaee, F. Goora, M. M. Britton, B. Newling, and B. J. Balcom. Mapping B₁induced eddy current effects near metallic structures in MR images: A comparison of simulation and experiment. *Journal of Magnetic Resonance*, 250:17–24, 2015.

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- K.J. Sanders, A.R. Aguilera, J. Keffer, B.J. Balcom, G.R. Goward. Transient lithium metal plating on graphite: Operando ⁷Li nuclear magnetic resonance investigation of a battery cell using a novel RF probe. *Carbon* (2022), 189, 377-385.
- S. Ahmadi, A.R. Aguilera, B. MacMillan, I. Mastikhin. Studies of periodic seawater spray icing with unilateral NMR. *Journal of Magnetic Resonance* (2022), 334, 107109-107119
- A.R. Aguilera, B. MacMillan, S.A. Krachkovskiy, K.J. Sanders, F. Alkhayri, C.A. Dyker, G.R. Goward, B.J. Balcom, A Parallel-Plate RF probe and battery cartridge for ⁷Li ion battery studies, *Journal of Magnetic Resonance* (2021), 325, 106943-106950.

- S.A. Krachkovskiy, M. Reza, A.R. Aguilera, I.C. Halalay, B.J. Balcom, and .R. Goward. Real-Time Quantitative Detection of Lithium Plating by In Situ NMR Using a Parallel-Plate Resonator. *J. Electrochem. Soc.* (2020),167, 130514.
- A.R. Aguilera, B. MacMillan, G.R. Goward, and B.J. Balcom. Optimization of a Parallel-Plate RF probe for high resolution thin film imaging. *Concepts Magn. Reson. Part A* (2018), 21465-21473.
- Guevara, M.A.L., Torres, Y.M., Naranjo, J.C.G., A.R. Aguilera, Beyrio, L.C.S., Felue, M.A.M., Brada, T.S. and Philippé, J. Water Efflux in Red Blood Cells of Sickle Cell Patients under Spontaneous Deoxygenation. *Journal of Biosciences and Medicines* (2016), 4, 152-161
- 8. B.T.R. Ferro, **A.R. Aguilera**, R.R.F. Prieto, Automated detection of the onset and systolic peak in the pulse wave using Hilbert transform. *Biomedical Signal Processing and Control* (2015), 20, 78-84
- H.M.C. Ciria, L.E.B. Cabrales, A.R. Aguilera, J.J.G. Nava, J.A.G. Joa, *et al.* Influence of electrode array parameters used in electrotherapy on tumor growth kinetics: A mathematical simulation. *Math. Comput. Simul.* (2012), 82, 1396–1406
- D.A. Brooks, A.R. Aguilera, and R.A. Miller. ImageROC: software para la evaluación diagnóstica de la calidad de imágenes médicas. *Imagen Diagnostica* (2012), 3(1),6-10
- R.P. Jiménez, A.E.B. Pupo, J.M.B. Cabrales, J.A.G. Joa, L.E.B. Cabrales, J.J.G. Nava, A.R. Aguilera, et al. 3D Stationary electric current density in a spherical

tumor treated with low direct current: An analytical solution. *Bioelectromagnetics* (2011) 32, 120-130.

- L.E.B. Cabrales, J.J.G. Nava, A.R. Aguilera, *et al.* Modified Gompertz equation for electrotherapy murine tumor growth kinetics: predictions and new hypotheses. *BMC Cancer* (2010), 10, 589-602
- A.R. Aguilera, L.E.B. Cabrales, H.M.C. Ciria, Y.S. Pérez, *et al.* Electric current density distribution in planar solid tumor and its surrounding healthy tissue generated by an electrode elliptic array used in electrotherapy. *Math. Comput. Simul.* (2010), 80, 1886–1902
- A.R. Aguilera, L.E.B. Cabrales, H.M.C. Ciria, Y.S.Pérez, E.R. Oria, S.A. Brooks and T.R. González. Distributions of the potential and electric field of an electrode elliptic array used in tumor electrotherapy: Analytical and numerical solutions. *Math. Comput. Simul.* (2009), 79, 2091–2105
- L.E.B. Cabrales, A.R. Aguilera, R.P. Jiménez, *et al.*, Mathematical modeling of tumor growth in mice following low-level direct electric current. *Math. Comput. Simul.* (2008), 78, 112–120

Conference Presentations:

• A.R. Aguilera, B. MacMillan, S.A. Krachkovskiy, K.J. Sanders, F. Alkhayri, C.A. Dyker, G.R. Goward, B.J. Balcom, A Parallel-Plate RF Probe and Battery Cartridge

for ⁷Li ion Battery Studies, 22nd International Society of Magnetic Resonance Conference, August 22-27, 2021, Osaka, Japan (ONLINE) (*POSTER*)

- A.R. Aguilera, B. MacMillan, S.A. Krachkovskiy, F. Alkhayri, C.A. Dyker, G.R. Goward, B.J. Balcom, Parallel-Plate MR Micro Coil for Studies of Materials., 102nd Canadian Chemistry Conference and Exhibition, June 03-07, 2019, Québec City, Canada. (*POSTER*)
- A.R. Aguilera, B. MacMillan, S.A. Krachkovskiy, G.R. Goward and B.J. Balcom, Parallel-Plate Resonator for MRI studies of lithium-ion batteries., 15th International Conference on Magnetic Resonance Microscopy (ICMRM), August 18-22, 2019, Paris, France. (*POSTER*)
- A.R. Aguilera, B. MacMillan and B.J. Balcom, Optimization of a Parallel-Plate Resonator for High Resolution Thin Film Imaging in Lithium-Ion Batteries, 14th International Conference on Magnetic Resonance Microscopy (ICMRM), August 13-17, 2017, Halifax, Nova Scotia, Canada. (*POSTER*)