

FELLOWSHIP FINAL REPORT

Understanding sodium battery materials using high-field solid-state nuclear magnetic resonance spectroscopy

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ABSTRACT

Two novel solid-state sodium battery electrolyte materials (a polymerised ionic liquid block co-polymer and a zwitterionic plastic crystal) have been characterised by high-field NMR spectroscopy. The results allow the identification of the Na⁺ solvation environment, which will determine the ion transport mechanism. Additionally, solid-electrolyte interphase products formed in sodium metal batteries containing two different ionic liquid electrolytes have been studied by the same experimental method and a breakdown product of the ionic liquid anion has been tentatively identified. These results demonstrate the power of NMR to provide new insights into sodium battery materials.

1- Introduction

Batteries and related energy storage devices will be crucial technologies to enable society to transition away from fossil fuels and towards renewable, but intermittent, sources of energy such as wind and solar. Lithium ion batteries have become commercially successful and power everything from portable electronic devices to electric cars. However, lithium as a resource is finite, is only produced in a small number of locations, and is becoming increasingly expensive. Thus, attention has turned towards sodium as a potential alternative, as this element is ubiquitous and can be obtained relatively cheaply and easily (e.g., it can be harvested from sea water).

Sodium shares many characteristics with lithium in terms of its properties and electrochemical behaviour, but it also has some crucial differences including its larger ionic

radius. This means that it cannot simply be substituted for lithium in existing battery components such as electrode and electrolyte materials. Rather, entirely new materials need to be developed and tailored specifically for sodium batteries. To achieve this, a detailed understanding of the molecular-level structure and dynamics of the material and its interactions with the Na⁺ cation are needed [1,2].

In this project, a number of different materials relevant to sodium batteries have been studied using high-field solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. This experimental characterisation technique can provide detailed information on the local sodium environment via the ²³Na isotope, and its proximities with other species (e.g., via ¹⁹F nuclei on surrounding anionic groups). Strong magnetic fields like the 850 MHz instrument at the CEMHTI laboratory

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that was used in this work are particularly advantageous for studying ^{23}Na as they minimize peak broadening due to the quadrupolar interaction and thereby improve spectral resolution and sensitivity. Combining this approach with fast MAS allows the acquisition of two-dimensional correlation spectra which can provide direct evidence of ion interactions.

This work consists of two parts. First, a series of novel solid-state sodium electrolyte materials were studied to understand the solvation environment of the sodium cations and their interactions with the various anionic species present in the materials. This is important to understand as it will determine the ion transport mechanism within the material as well as the desolvation process that will occur at the electrode surface when the material is used in a battery. Two classes of novel solid-state electrolytes developed at Deakin University were selected for study, a polymerized ionic liquid block co-polymer [3] and a zwitterionic plastic crystal [4].

In the second part of this project, ^{23}Na and ^{19}F solid-state MAS NMR have been used to study the solid-electrolyte interphase (SEI) products formed inside a symmetric sodium metal cell containing two distinct ionic liquid electrolytes after 20 charge-discharge cycles [5]. Such SEI products form at the electrode surface due to breakdown of the electrolyte species and are crucial to the stable operation of the device as this layer passivates the reactive sodium metal surface while allowing sodium cations to diffuse through it [6].

The results obtained provide new insights in both cases. We show that the ^{19}F - ^{23}Na HETCOR NMR experiment is a powerful tool for identifying Na^+ -anion interactions in these electrolyte materials, and we also identify previously undiscovered breakdown products of the ionic liquid electrolyte anions in the symmetric sodium metal cells.

2- Experimental details

The block co-polymer and zwitterionic plastic crystal samples were prepared at Deakin University, Australia, following methods previously reported [3,4]. Two symmetric Na|Na coin cells were also prepared at Deakin as described in previous work [5], with ionic liquid electrolytes consisting either of $[\text{P}_{1114}][\text{FSI}]$ + 42 mol% NaFSI (maximum solubility) or $[\text{C}_3\text{mpyr}][\text{FSI}]$ + 50 mol% NaFSI. These were cycled 20 times at 50 °C with an applied current density of 1.0 mAcm $^{-2}$ (2 h per cycle). After cycling the sodium metal electrodes were removed from the cells inside an argon glove box, dried by patting gently with a tissue, and then mixed with BN powder before packing for NMR.

Samples were packed into 1.3 mm o.d. zirconia MAS NMR rotors inside an argon glove box. ^1H , ^{11}B , ^{13}C , ^{19}F and ^{23}Na MAS NMR experiments were carried out at 19.9 T (850 MHz ^1H frequency) using a Bruker four-channel 1.3 mm HXY MAS NMR probe. Additional experimental details are provided in section 3.

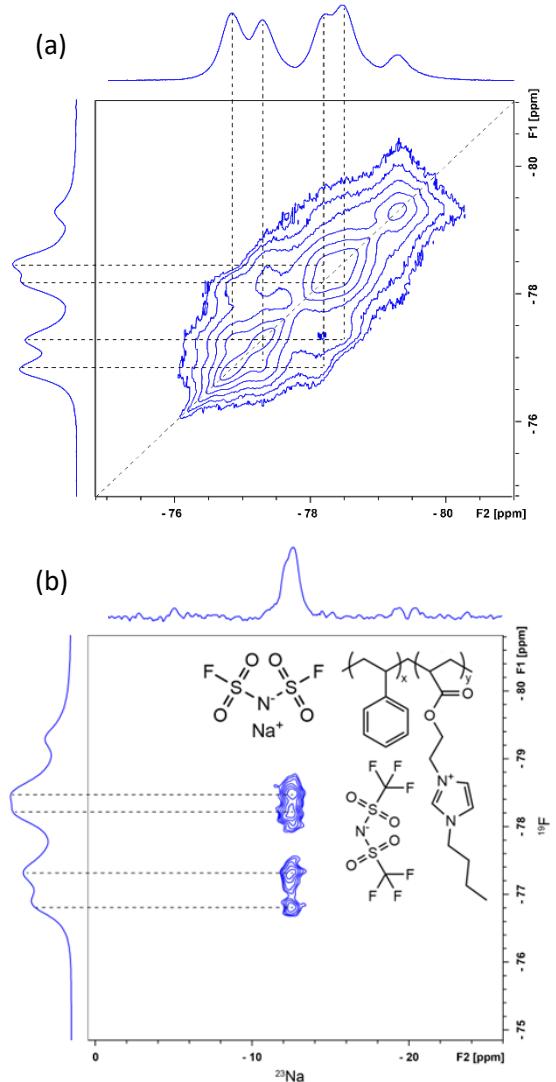
3- Results and discussion

3.1 Sodium-anion interactions in a novel polymer electrolyte

Figure 1(a) shows a ^{19}F EXSY NMR spectrum obtained from the polymerised ionic liquid block co-polymer sample with an exchange time of 5 ms. The spectrum shows five distinct ^{19}F NMR signals in both the horizontal and vertical dimensions, all arising from the CF_3 group of the TFSI (tetra fluoro sulfonyl imide) anion. The off-diagonal peaks show magnetisation exchange between these nuclei, which only occurs over relatively short distances. This therefore indicates that the four most prominent of these peaks arise from CF_3 groups in close proximity to one another, while the fifth peak (at -79.3 ppm) is more distant.

The ^{19}F - ^{23}Na HETCOR spectrum in Figure 1(b) shows that the same group of four CF_3 groups are also proximate to a sodium cation, while the fifth is not. It can therefore be concluded that the four most prominent ^{19}F NMR signals from

the TFSI arise from anions directly coordinated to sodium cations in a $\text{Na}(\text{TFSI})_2$ cluster. Moreover, these TFSI anions can be identified as being in the *cis* conformation due to their shifts matching closely with a previous study of the pure NaTFSI salt [7]. The fifth TFSI signal is therefore proposed to arise from TFSI anions not coordinated to Na^+ but instead interacting

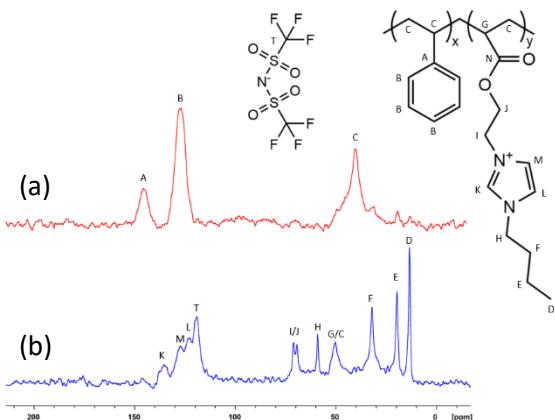


with the imidazolium cationic group on the side

Figure 1 – (a) ^{19}F EXSY spectrum and (b) ^{19}F - ^{23}Na HETCOR NMR spectrum obtained from the polymerised ionic liquid block-copolymer. The molecular structures of the polymer and anions are shown inset in (b).

chain of the ionic component of the polymer, and likely in the *trans* conformation.

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It should be noted that a similar ^{19}F - ^{23}Na HETCOR experiment carried out with the ^{19}F NMR frequency centred on the ^{19}F signal from the smaller FSI (fluoro sulfonyl imide) anion showed no evidence of Na^+ -FSI coordination (i.e., no cross peaks observed). Thus it can be concluded that the Na^+ cations are preferentially solvated by the larger TFSI anions over the FSI anions, and while our results do not rule out the existence of short-lived Na^+ -FSI interactions, the solvation of the sodium by the TFSI is more stable and dominant in this material.

Figure 2 – ^{13}C MAS NMR spectra obtained from the block co-polymer electrolyte via (a) ^1H - ^{13}C cross polarisation and (b) direct ^{13}C excitation, with peaks assigned to the molecular structure shown inset.

^{13}C MAS NMR experiments were also carried out on this polymer electrolyte using two distinct approaches. The first involves cross polarisation (CP) of magnetisation from the ^1H nuclei to ^{13}C . The resulting spectrum, shown in Figure 2(a), shows only the ^{13}C signals from immobile regions of the polymer (i.e., the styrene block) as dynamics in mobile regions prevent the CP mechanism. In contrast, a direct excitation ^{13}C NMR spectrum, shown in Figure 2(b), shows only the ^{13}C signals from mobile groups (i.e., the ionic component of the polymer and the TFSI anion) due to the rigid part having much longer ^{13}C T_1 relaxation times. Thus, these experiments allow the different regions of the block co-polymer to be distinguished on the basis of differences in local molecular dynamics, and confirm that the ionic component

shows a higher mobility than the styrene component.

In addition to the above experiments, ^{19}F and ^{23}Na MAS NMR spectra were also obtained from a second sample of block co-polymer of the same composition but with some ionic liquid $[\text{C}_3\text{mpyr}][\text{FSI}]$ incorporated during synthesis. In all cases, the NMR peak widths were found to be narrower after incorporation of the ionic liquid, indicating an enhancement of ion dynamics in the electrolyte and correlating with an observed increase in ionic conductivity (results not shown).

3.2 Sodium-anion interactions in a novel zwitterionic electrolyte

The novel zwitterionic plastic crystal mixed with 20 mol% sodium TFSI salt (structures shown in Figure 3) was studied using a similar suite of experiments as the block co-polymer. The ^{19}F - ^{23}Na HETCOR spectrum from this sample (Figure 3) showed a strong cross peak between the ^{23}Na signal and the ^{19}F peaks arising from the BF_3 anionic group of the zwitterion at around -145 ppm. In contrast no visible signal was observed at the position of the ^{19}F signal of the TFSI anions (red circle in Figure 3). Thus, while the Na^+ cations showed preferential coordination to the TFSI anions in the block co-polymer sample, in this electrolyte they clearly interact more strongly with the anionic group of the zwitterion, despite the nearby positive charge of this molecule. This is attributed to the more localised negative charge on the BF_3 group compared to the TFSI, the latter of which is designed to be more charge diffuse.

Interestingly, multiple ^{19}F NMR peaks were observed in the BF_3 region of the zwitterionic plastic crystal sample. The most prominent peak could be deconvoluted into three peaks of equal intensity, suggesting that the three fluorines of the BF_3 group are made chemically distinct by the interaction with the Na^+ cations. However, the presence of a number of additional peaks in this nominally quite simple material, including one peak with a noticeably longer T_1 relaxation time, cannot easily be explained, and so further

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work must be carried out to eliminate the possibility of impurities or decomposition of the zwitterion before these peaks may be identified.

Additional NMR experiments were carried out on this sample (not shown), including a ^1H - ^{19}F HETCOR experiment that showed strong interactions between the TFSI anions and the zwitterion itself, and ^{11}B MAS NMR experiments that appeared to show a single ^{11}B peak (potentially consisting of overlapped quadrupolar line shapes).

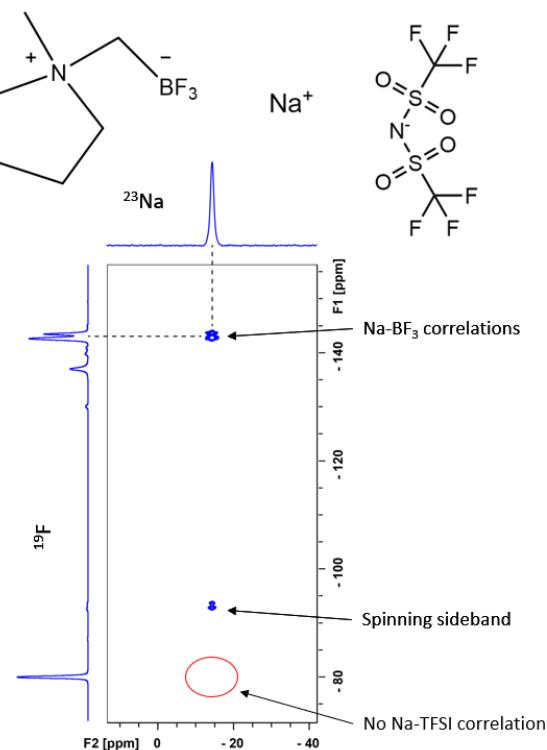


Figure 3 – ^{19}F - ^{23}Na HETCOR NMR spectrum obtained from the zwitterionic plastic crystal containing 20 mol% sodium salt. The molecular structures of the zwitterion and sodium salt are shown above. The signal labelled as spinning sideband is an artifact of the MAS.

3.3 SEI products formed in sodium metal symmetric cells with ionic liquid electrolytes

Figure 4(a) shows ^{19}F solid-state MAS NMR spectra obtained from the SEI products that formed inside the symmetric sodium metal cells after 20 cycles. The red spectrum shows the SEI products formed from the cell containing the $[\text{C}_3\text{mpyr}][\text{FSI}]$ ionic liquid electrolyte with 50 mol% NaFSI salt, while the blue spectrum is from the cell with the $[\text{P}_{111i4}][\text{FSI}]$ electrolyte with 42 mol% NaFSI. For both samples, three groups of peaks are observed. The peak at 52 ppm is from residual FSI anions remaining on the surface of the metal electrodes. A peak at -227 ppm corresponds to NaF, which was also observed by ^{23}Na NMR (see below).

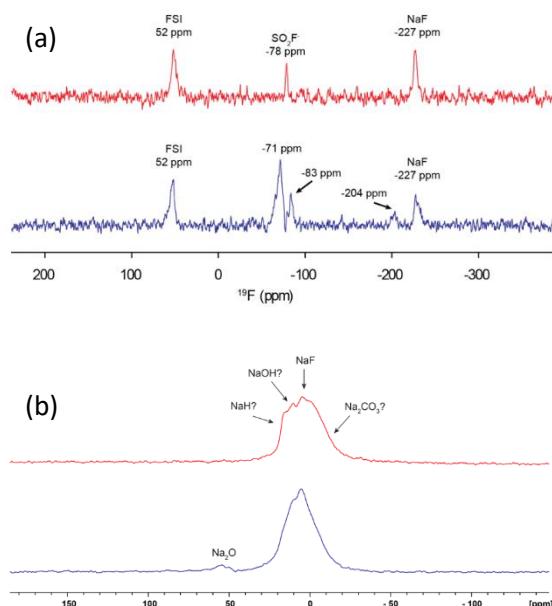


Figure 4 – (a) ^{19}F and (b) ^{23}Na MAS NMR spectra obtained from the SEI products extracted from symmetric sodium metal cells containing ionic liquid electrolytes $[\text{C}_3\text{mpyr}][\text{FSI}] + 50 \text{ mol\% NaFSI}$ (spectra in red) and $[\text{P}_{111i4}][\text{FSI}] + 42 \text{ mol\% NaFSI}$ (spectra in blue) after 20 cycles.

The ^{19}F peaks observed between -71 and -83 ppm are tentatively attributed to the fluorosulfite (SO_2F) anion, which has a reported chemical shift of -78 ppm [8]. This anion might

be expected to form from the breakdown of the FSI, and the variation in chemical shifts may be due to its association with different cations. This potentially provides new mechanistic insights into the breakdown of the ionic liquid electrolyte and formation of the SEI products, though this peak assignment still needs to be verified. Additionally, a lower intensity peak is observed at -204 ppm in the $[\text{P}_{111i4}][\text{FSI}]$ system. This shift is consistent with a fluorinated alkyl group such as CH_2F , potentially indicating some fluorination of the cation during the SEI formation process, though more work is needed to confirm this.

Figure 4(b) shows the ^{23}Na MAS NMR spectra obtained from the two different SEI systems. Despite the very high magnetic field used, the spectra show overlapping peaks attributed to various sodium containing products, which differ in their relative amounts between the two different ionic liquid electrolytes. An additional peak at around 55 ppm is due to sodium oxide (Na_2O) which was observed to grow over time and is attributed to some oxidation of the sodium metal inside the NMR rotor. The remaining peaks in this spectrum were unaffected by this process.

Finally, a preliminary ^{23}Na MQMAS spectrum (not shown) was run on one of the SEI systems to test the feasibility of using this two-dimensional method to improve the spectral resolution and better enable the identification of the different sodium containing phases. The fast T_1 relaxation times of the sodium signals in these samples allowed a very short recycle delay (0.1 s) to be used, and an initial spectrum was obtained in 24 h, albeit with a relatively low signal-to-noise ratio. This experiment will be further optimised and run again in the future, and should enable a more reliable peak fitting of the spectra in Figure 4(b).

4- Conclusions

A suite of high-field solid-state MAS NMR experiments have been carried out on two novel solid-state sodium electrolyte materials as well as SEI products extracted from cycled sodium metal batteries containing ionic liquid

electrolytes. Selected NMR spectra highlighting the most significant observations have been presented and discussed herein.

^{19}F - ^{23}Na HETCOR experiments enabled the interactions of the Na^+ cations with the different fluorinated anions to be identified. In the block co-polymer system the sodium is preferentially solvated by two TFSI anions with relatively little interaction with the FSI. In the zwitterionic plastic crystal material the sodium interacts primarily with the BF_3 group of the zwitterion rather than with the TFSI. Solid-state NMR experiments also allow other interactions and dynamics to be probed.

The initial breakdown mechanism of FSI anions in ionic liquid electrolytes within sodium metal batteries is hinted at via the tentative observation of the SO_2F anion by ^{19}F MAS NMR. ^{23}Na MAS NMR of the resulting SEI products shows a number of different sodium containing products including NaF . Additional experiments to enable the identification of the other products are underway.

5- Perspectives of future collaborations with the host laboratory

This Le Studium Fellowship has supported a long-term collaboration between A/Prof O'Dell and Prof Deschamps that was established in 2015. It enabled A/Prof O'Dell to work directly with Dani Kourati, a cotutelle PhD student between Deakin University and Université d'Orléans and co-supervised by A/Prof O'Dell, Prof Forsyth, Dr Salager and Prof Deschamps. Dani's project will extend the preliminary work described herein, and he will spend 12 months working at Deakin as part of his PhD studies, before returning to the CEMHTI lab. Another cotutelle student will also begin at CEMHTI in 2023, funded by RMIT/AUFRANDE and with the same group of supervisors. Thus, this productive collaboration between Deakin and Orléans/CEMHTI-CNRS will continue well into the future and A/Prof O'Dell hopes to visit CEMHTI again in 2024.

6- Articles published in the framework of the fellowship

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Several journal articles are anticipated to arise from the preliminary work carried out during this 3 month Fellowship, and will be prepared and submitted for publication by the authors over the next 12-24 months.

7- Acknowledgements

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