Electrochemical characterization of hexamethylguanidinium bis(fluorosulfonyl)imide [HMG][FSI] based electrolyte and its application in sodium metal batteries

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Abstract
With the increasing energy demand for both electronic portable devices and energy storage for fluctuating renewable energy sources, there is a strong need for alternatives beyond lithium batteries. Sodium batteries have been attracting great attention recently due to the abundance and low supply cost of the raw materials. However, they require highly conductive, safe and electrochemically stable electrolytes in order to enable their practical realization. In this work we present the promising physicochemical properties of the electrolyte based on hexamethylguanidinium bis(fluorosulfonyl)imide [FSI] at a sodium concentration of 25 mol% NaFSI. The liquid-state electrolyte supports stable Na plating and stripping at 1 h polarization times at 0.5 mA cm⁻² current density in a Na symmetrical coin cell at 50 °C, maintaining a low polarization potential of ≈45 mV throughout 160 cycles. Moreover, this electrolyte is characterized by relatively high Na-ion transference number of 0.36 ± 0.03 at 50 °C. A long cycle life of 300 cycles with 285 mAh g⁻¹ is achieved in a half cell set up with hard carbon. The solid-electrolyte interphase layer on the anode, which contributes to this high capacity, is investigated by x-ray photoelectron spectroscopy and solid-state nuclear magnetic resonance spectroscopy. The long-term cycling performance of Na|NaFePO₄ cell is also demonstrated with a high specific capacity of 106 mAh g⁻¹ and 80% capacity retention after 110 cycles.

1. Introduction

The continuously increasing penetration of fluctuating renewable energy sources, along with forecasted growth of the electric vehicle market, are the main drivers for increasing battery demand. Lithium-ion batteries (LIBs) are presently the most commonly used and advanced power sources for a wide range of applications, e.g. consumer electronics, automotive, energy storage system and industrial markets. However, due to the increasing raw material cost, non-uniform distribution in the Earth’s crust and significant environmental impacts associated with the production of LIBs, other chemistries should be considered for post LIBs. Among many possible alternatives to lithium-ion chemistries (e.g. sodium, magnesium, potassium, zinc), sodium-ion batteries (NIBs) have attracted the greatest attention in the last decade. Sodium is the sixth most abundant element on earth, has a very wide geographic distribution and low supply cost (Na₂CO₃ $593.99 AUD/tonne vs Li₂CO₃ $97 642.94 AUD/tonne) [1, 2]. Moreover, NIBs have the same...
fundamental working principles, material components, manufacturing protocols and cell engineering considerations as LIBs. These similarities make NIBs a ‘drop-in’ technology for LIBs, enabling them to be produced on the existing LIB manufacturing lines with minimum modification, meaning that potential cell manufactures will suffer from a minimal cost penalty to change to new chemistry. Additionally, NIBs can be stored and transported at 0 V which results in reduced shipping cost and safety risks compared to LIBs, alleviating their worldwide commercialization. Despite their very close proximity in the periodic table, lithium and sodium have some differences such as the greater atomic weight (23 g mol⁻¹) and larger ionic radius of Na (1.02 Å) vs Li (6.9 g mol⁻¹, 0.76 Å) as well as different electrochemical characteristics. Thus, LIB strategies around materials and cell parameters do not completely carry over to NIB devices. In theory, the maximum specific energy density is expected to be lower for NIBs in comparison to LIBs, due to the difference in mass and ionic radii. However, NIBs can potentially replace some of the LIB applications, such as off-grid energy storage and load leveling, where the volume and weight are less important.

Na batteries, like other batteries, contain three main components: the positive electrode (cathode), negative electrode (anode) and electrolyte, all of which require further research. Electrolytes play a critical role in the overall lifetime, rate capability and battery safety, electrically separating electrodes and at the same time ensuring good ion transfer between them during battery operation. Ideally, the electrolyte should have low volatility and flammability, be thermally stable over a wide range of temperatures, cost-efficient and non-toxic. Moreover, the electrolyte should be characterized by chemical stability against the electrodes. Commercial electrolytes for LIBs or NIBs are mainly based on the traditional organic carbonates which, despite their low ionic conductivities, have some drawbacks such as volatility and flammability causing safety issues and poor long term cyclability. Although 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) is a standard electrolyte used for LIBs, forming a well characterized solid-electrolyte interphase (SEI) at the anode, an effective and optimized electrolyte for NIBs is still lacking. This calls for the urgent development of high-performance electrolytes for NIBs to speed up adoption of this technology.

The flammability and volatility of traditional organic carbonates are posing important safety issues. Thus, other systems such as ionic liquids (ILs), water in salt electrolytes (WiSEs) and solid-state electrolytes (SSes), including organic ionic plastic crystals (OIPCs), polymers and gels are being investigated. Most of WiSEs are characterized by narrow electrochemical stability window due to water decomposition, which strictly limits the selection of potential electrode materials for aqueous NIBs. On the other hand, the main drawback of SSes is their low ionic conductivities and poor mechanical properties (many of them are brittle). Recently, ILs and OIPCs have been attracting increasing interest for use in sodium secondary batteries due to their exceptional properties, such as negligible volatility, non-flammability, high thermal stability and wide electrochemical stability window [3–7]. OIPCs can be defined as disordered solid state analogues of ILs, where ILs are water free salts characterized by melting point lower than decomposition temperature [8]. They are considered to be a promising electrolyte family whose adoption could overcome safety issues of conventional organic solvent-based electrolytes. Nonetheless, reports on such electrolytes for sodium secondary batteries are at present still limited.

Most studies focus on pyrrolidinium, imidazolium and phosphonium based ILs, predominantly coupled with the bis(fluorosulfonyl)imide [FSI] and/or the TFSI anion. For example, N-propyl-N-methylpyrrolidinium ([C₃mpyr][FSI]) with a NaFSI showed excellent electrochemical properties (i.e. rate capability and cycling stability) when paired with various electrodes such as hard carbon (HC) [9, 10], CuP₂/C [11], and Na₂Ti₃O₇/C [12]. Both theoretical and experimental studies of super concentrated NaFSI in [C₃mpyr][FSI] for NIBs were conducted by Chen et al. who investigated changes in the electrolyte material’s microstructure and ion dynamics as a function of Na salt concentration [13, 14].

Carbonaceous anode materials are characterized by relatively high capacity, abundance and non-toxicity. Among them, HC electrodes have frequently been demonstrated to exhibit high reversible capacity [9, 15], reaching up to 300 mAh g⁻¹ if the organic liquid electrolyte is optimized [16]. Moreover, many previous reports, including the work of Sun et al. [15], demonstrated a more stable SEI for ILs compared to organic electrolytes, resulting in better battery performance when using IL based electrolytes [17–19]. Unfortunately, a large reversible capacity loss is often observed for HC when used as an anode material for NIBs, which results in a severe decrease in the cell energy density [20, 21].

In regards to cathodes, most studies of pyrrolidinium based ILs use NaCrO₂ cathodes, which are less desirable for practical applications due to their toxicity drawbacks and environmental issues [10, 22–24]. Cathodes composed of the layered transition metal oxides (P₂- and O₃-Na₂/3[Fe₂/3Mn₁/3]O₂) have been cycled in a sodium metal battery consisting of 2.3 M NaFSI in trimethyl isobutyl phosphonium FSI ([P₁₁₄₃FSI][NaFSI]) and these cells were shown to outperform a 0.5 M NaPF₆ in EC/DMC (1:1) electrolyte in terms of capacity retention, cycle stability and safety [25]. In subsequent studies, in order to understand
the relationship between the physico-chemical properties and electrochemical performance in long term cycling with NaFePO₄ (NFP) cathodes in Na[NFP] cells, [P₁₁₄₄][FSI] and two other ILs ([P₁₁₄₄][FSI] and [N₂(2020)I₂][FSI]) were studied [26]. The [P₁₁₄₄][FSI] based electrolyte demonstrated the best electrochemical performance and most stable SEI layer among the studied electrolytes. This work showed the importance of SEI characterization for the future electrolyte development.

Only very few studies which investigated the applicability or performance capabilities of OIPCs for sodium secondary batteries are available in the literature. Among them, phosphonium based OIPCs (i.e. methyl tri-isobutyl phosphonium [P₁₄₄₄₄], triisobutylmethyl phosphonium [P₁₄₄₄₄₄], trimethyl isobutyl phosphonium [P₁₁₄₄]⁺) mixed with sodium salt have been reported to exhibit a stable and reversible sodium stripping and plating in a symmetrical cell [27–30]. More recently, the use of the first sodium metal batteries with an OIPC based solid electrolyte (90 mol% NaFSI + 10 mol% [P₁₄₄₄₄][FSI]) utilizing sodium vanadium phosphate–carbon composite Na₂V₂(PO₄)₃ (NVP) as anode and a sodium iron pyrophosphate NFP cathode carbon-coated cathode was reported by Makhloughiazad et al. Full cell with OIPC based electrolyte showed a stable cycling performance and high coulombic efficiency at 60 °C [31].

In this study, we combine the merits of Na metal paired with an HC electrode and an NFP electrode using a novel, promising OIPC electrolyte based on hexamethylguanidinium [HMG][FSI]. The detailed investigations of the thermal phase behavior coupled with conductivity studies identified unusual conductivity behavior of the neat [HMG][FSI], confirmed by two methods (Electrochemical Impedance Spectroscopy (EIS) and Broadband Dielectric Spectroscopy (BSD)), where ions appear to be more mobile during the heating cycle than cooling shows novelty of this OIPC. This behavior was assigned to the large number of grain boundaries and defects at low temperatures, in phase III [32]. [HMG][FSI] was also previously mixed with NaFSI and the whole composition range of OIPC with NaFSI (0–100 mol% NaFSI in [HMG][FSI]) was studied and the phase diagram constructed. Interestingly, it was found that the [FSI]⁻ in NaFSI, [HMG][FSI] mixtures, is significantly more mobile than [HMG]⁺ which is opposed the behavior of most other IL and OIPC systems, where cations and anions were diffusing at least within the same order of magnitude [33]. Based on this previous work on NaFSI/[HMG][FSI] mixtures, the eutectic composition (25 mol% NaFSI in [HMG][FSI], Tₑᵤₑᵗᵢ𝐜ₑ = 44 °C) was chosen for this study. This eutectic composition, whose complex microstructure can be compared to a two phase composite, presented the highest ionic conductivity (5.9 × 10⁻³ S cm⁻¹ at 40 °C) of all compositions [33]. Here we examine the 25 mol% NaFSI in [HMG][FSI] as a potential electrolyte for sodium secondary batteries. The electrolyte was tested in different cell configurations: Na|Na symmetrical cells, Na|HC, and Na|NFP cells. Moreover, considering the importance of the SEI layer on the battery performance, the SEI layer on the HC electrode was studied by detailed x-ray photoelectron spectroscopy (XPS) and solid-state nuclear magnetic resonance (ssNMR).

2. Method

2.1. Materials preparation
Neat OIPC HMG (((CH₃)₂N)₃)C][FSI], was synthesized following our previously reported procedure [34, 35]. NaFSI (>99.9%, Coors tek US) was purchased commercially and used as received. 25 mol% NaFSI in [HMG][FSI] was prepared in an argon-filled glovebox by mixing appropriate amounts of [HMG][FSI] and NaFSI. Prepared samples varied between 1 and 4 g. The binary mixture was dissolved in dry acetonitrile (>99.9%, Merck Milipore Australia), which was removed by high-vacuum drying for 24 h at room temperature followed by 24 h at 50 °C on a Schlenk line [32]. HC was purchased from Kuraray company (Kuranode, SSA = 4 m² g⁻¹). The triphylite-NFP, analogous to triphylite -LiFePO₄ (LFP), was synthesized from abundant and cost-efficient reactants through a two-step reaction. Firstly, commercial C/LFP was oxidized using aqueous Na₂S₂O₃ as the oxidizing agent [36]. Then, the obtained C/FePO₄ was chemically sodiated using aqueous Na₂S₂O₃ at 60 °C [37].

2.2. Electrochemistry
Sodium symmetrical coin cells (CR2032 type) were prepared in order to perform rate capability and long-term cycling studies at 25 mol% NaFSI in [HMG][FSI]. The whole procedure, as explained in detail below, was performed under an Argon atmosphere in a glovebox. Na metal (sigma) which was stored in paraffin oil (Merc Milipore), was cleaned with a brush and hexane and rolled into thin sheets, after which sodium metal electrodes, 10 mm diameter discs, were cut from the film. The Solupor® polyethylene (19 mm diameter) was used as separator between the sodium discs with 150 mg of electrolyte in the cell. Coin cells were assembled on a hot plate using Na electrodes, wetted separator (150 mg of electrolyte was melted at 50 °C), 0.5 mm spacer and 1.4 mm spring to ensure a uniform contact between electrodes and the electrolyte
in the CR2032 coin cell. All the cell components were assembled together and crimped in a manual cell press. After preparation, cells were stored outside the glovebox, in an oven at 50 °C for 24 h before being tested.

Half cells were prepared following the same above described procedure except the HC anode or NFP cathode foil replaced one of the Na disks. Electrodes were prepared by mixing active material (Kuranode HC, Kuraray Company and/or lab made NFP) with binder carboxymethyl cellulose, CMC (Sigma-Aldrich) for HC and polyvinyliden fluoride PVdf (Kureha Chemicals, Japan) for NFP with carbon black (Sigma-Aldrich) in mass ratio 8:1:1 respectively. Firstly, the pre-weighted amount of active material was ground with the conductive carbon in agate mortar. Then the binder solutions were prepared: CMC dissolved in small amount of water and PVDF in NMP (N-2-methyl-pyrrolidinone). Solutions in small beakers were stirred for 30 min after which the ground mixtures were added, NFP mixture to PVDF solution and HC mixture to PVDF solution. slurries were stirred for 24 h and then coated on Al current collectors and dried in a vacuum oven firstly at 80 °C for 24 h, then 100 °C under vacuum for 24 h. The CR2032 half-cells were assembled by placing NFP or HC electrode (8 mm diameter) as working electrode, and Na metal as a counter and reference (10 mm diameter). The Solupor® polyethylene (19 mm in diameter) was used as separator between the electrodes with 150 mg of electrolyte in the coin cell. The half-cells were rested for 48 h at 50 °C oven prior to the electrochemical test to ensure proper wetting of separator and electrodes.

Electrochemical measurements for symmetric cells were performed on a Multi Potentiostat VMP3/Z (Bio-Logic) at 50 °C. C-rate capability and long term cycling was also performed for both cells, i.e. Na|HC and Na|NFP. Applied current densities were calculated based on electrode mass loadings. C-rate capability was studied by applying the following C-rates for five charge/discharge cycles: C/20, C/10, C/5, C/2, 1 C and 2 C (assuming maximum capacity of 300 mAh g\(^{-1}\) for HC and 145 mAh g\(^{-1}\) for NFP). Long term galvanostatic cycling was performed at 0.1 C for five initial cycles, followed by 0.2 C.

Sodium transfer numbers (\(t_{Na^+}\)), which quantify the fraction of the current carried by Na\(^{+}\), were determined by d.c. polarization method combined with a.c. impedance method introduced by Evans \textit{et al} [38]. Measurements were performed using Na|Na symmetrical cells. Electrochemical cells were stored for 24 h at 50 °C after which the measurement took place in the same oven, at 50 °C. Measurements were performed on Biologic VMP3/Z potentiostat driven by EC-lab software. Polarization with a small potential difference of 10 mV was applied to each sample until the resulting current became stable. Galvano electrical impedance spectroscopy was acquired before and after polarization with the input a.c. signal of 10 mV from 7 MHz to 10 MHz.

Sodium cation transfer number determined by potentiostatic polarization was calculated from the following Evans \textit{et al} [38]:

\[
t_{+} = \frac{I_{s} (\Delta V - R_{0}I_{0})}{I_{0} (\Delta V - R_{s}I_{s})}
\]

where:
- \(\Delta V\) [V] – the applied potential
- \(R_{0}\) [Ω] – initial passive layer resistance
- \(R_{s}\) [Ω] – steady-state passive layer resistance
- \(I_{0}\) [A] – initial current
- \(I_{s}\) [A] – steady-state current.

2.3. Characterization

2.3.1. X-ray photoelectron spectroscopy (XPS)

The Nexsa Surface Analysis System (Thermo Scientific) equipped with a hemispherical analyzer was used for all XPS characterisations. The incident radiation was monochromatic Al K\(\alpha\) x-rays (1486.6 eV) at 72 W (6 mA and 12 kV) with a spot size of 400 \(\mu\)m \(\times\) 250 \(\mu\)m for all surface scans and depth profiles. Survey scans collected between –10 eV–1350 eV were recorded at an analyser pass energy of 150 eV, a step size of 1.0 eV and a dwell time of 10 ms. High-resolution scans for C 1 s, F 1 s, N 1 s, Na 1 s, O 1 s and S 2p were obtained with a pass energy of 50 eV, a step size of 0.1 eV and dwell time of 50 ms. Depth profiles were collected using the MAGCIS™ Dual Beam Ion Source in Monatomic Mode with an ion gun energy of 1000 eV (high current). The base pressure in the analysis chamber was less than 5.0 \(\times\) 10\(^{-9}\) mbar. A low-energy dual-beam (ion and electron) flood gun was used to compensate for surface charging. All data were collected using the Avantage software (v5.9922) and processed using the CasaXPS software. The energy calibration was referenced to the low binding energy component of the C 1 s peak at 284.8 eV.
2.3.2. Solid state nuclear magnetic resonance (SSNMR)
Static solid-state $^1$H, $^{23}$Na and $^{19}$F NMR spectra were collected on a Bruker Avance III wide-bore solid-state spectrometer (500 MHz $^1$H frequency) with a 1.3 mm magic angle spinning (MAS) probe and a sample spinning speed of 40 kHz. Pristine and cycled electrodes were washed with (DMC, $\geq 99\%$; Sigma-Aldrich) after which the HC material was scratched from the current collector surface using a spatula in an argon filled glove box. Samples were mixed with boron nitride powder and packed into 1.3 mm zirconia MAS NMR rotors under an argon atmosphere in a glove box. The obtained data was recorded and analysed in Topspin software.

3. Results and discussion

3.1. Electrochemical behaviour
The sodium plating and stripping behaviour for the [HMG][FSI] electrolyte with 25 mol% NaFSI was assessed at a copper working electrode, which was reported previously to facilitate deposition/dissolution of sodium metal [29, 39]. Figure 1 shows the cyclic voltammetry (CV) of 25 mol% NaFSI in [HMG][FSI] performed using a three electrode system (working electrode—Cu, counter—Pt and reference—Na) at 50 °C at a scan rate of 10 mV s$^{-1}$. 6 cycles were performed, starting at 0.5 V until—0.5 V. The electrolyte shows stable and reversible cycling behaviour, with obvious Na plating and stripping peaks without any side reactions, which shows the electrolyte supports Na electrochemistry and has the potential to be used in a Na electrochemical device. The reduction current densities at the cut-off ($-0.5$ V) are decreasing slightly upon successive cycles and the oxidation peak is increasing after the second cycle, which leads to the increasing sodium redox coulombic efficiency. This may indicate the formation of a stable and effective SEI after the second cycle.

3.2. Rate capability and long term cycling symmetrical Na|Na cells
In order to know at which current density this electrolyte is able to transfer charge, the rate capability of 25 mol% NaFSI in [HMG][FSI] was studied at 50 °C (figure 2). Various current densities from 0.1 up to 0.5 mA cm$^{-2}$ were applied for 5 cycles at each current. The stripping and plating of Na occurs with good stability and low polarisation potential even at 0.5 mA cm$^{-2}$ with an overpotential of only 45 mV. When the current density reverted back to 0.1 mA cm$^{-2}$, the overpotential was even lower (8 mV) than initial cycling (10 mV). This trend, where overpotential is lower after applying high current density, was also observed for other OIPC and IL systems [27, 40]. In the previous reports, lower overpotential was assigned to the size decrease of the grains at the interface and increase in the grain boundaries which led to the favourable modification of the electrode surface and more conductive SEI layer formation [41].

Moreover, a change in peak shape can be observed with increasing current densities; the potential profiles when cycling at low current densities shows very symmetric and smooth peaks, whereas increasing current densities (from 0.4 mA cm$^{-2}$) shows an upturn in the voltage profile consistent with mass transfer limitations at the electrode interface. This trend was also previously observed by Iermakova et al who performed a comparative study of Li and Na anodes in carbonate electrolytes. They reported different shapes for symmetrical cell cycling voltage profiles—a flat and stable potential for Li, whereas a significant decay was observed for Na|Na cells [42].

The long-term cycling stability of 25 mol% NaFSI in [HMG][FSI] was also investigated at high current density at 0.5 mA cm$^{-2}$ with 1 h polarization steps in a Na symmetrical coin cell at 50 °C. As can be seen from figure 3, the electrolyte shows outstanding stability over 160 plating/stripping cycles (320 h), without short circuit while maintaining a low polarization potential of $\approx$45 mV throughout the cycling period, indicative of efficient and stable Na$^+$ transport within the electrolyte and SEI layer. The recorded overpotential is significantly lower than what was obtained for other previously published IL/NaFSI systems, such as dry/wet 42 mol% NaFSI in [P11144][FSI] (131 mV 81 mV$^{-1}$) or 50 mol% NaFSI in C3mpyrFSI IL (139 mV 83 mV$^{-1}$) when cycled at 1 mA cm$^{-2}$ at 50 °C [43].

The overpotential for 25 mol% NaFSI in [HMG][FSI] is higher and the voltage profile is asymmetric during the first 6 cycles (figure S1) likely because the morphology of the two Na electrodes (initially stripped or plated) is different at the outset, and when the SEI layer is formed it makes the electrodes more uniform after a few cycles of plating and stripping. Similar behaviour was observed previously for Li symmetrical cells with ILs and OIPCs [41, 44, 45]. Interestingly, this was not the case for the 90 mol% [P11144][FSI]/NaFSI system when cycled in Na symmetrical cells at 0.05 mA cm$^{-2}$ and 0.1 mA cm$^{-2}$ at 50 °C [27]. This difference might be due to lower current densities/step durations, which are not sufficient for this “preconditioning” process. When a longer polarization time of 1 h with a 1.0 mA cm$^{-2}$ current density was applied for the
Figure 1. Cyclic voltammogram of 25 mol% NaFSI in [HMG][FSI] using a Cu working electrode, Pt counter electrode and Na reference electrode at 50 °C with a scan rate of 10 mV s⁻¹.

Figure 2. Symmetric cell cycling of 25 mol% NaFSI in [HMG][FSI] with increasing applied current density from 0.1 to 0.5 mA cm⁻² at 50 °C with Solupor separator with 1 h polarization time, 5 cycles at each current density.

42 mol% NaFSI in [P₃₁₁₁₄][FSI] and 50 mol% NaFSI in C₃mpyrFSI, a decrease in initial overpotential was also observed [43].

As can be seen from figure 3, the shape of the features changes during cycling. After the SEI layer is created and the overpotential remains constant, voltage spikes, often termed “peaking” shapes, are observed (figure 3(b)). “Peaking” behaviour is usually associated with varying surface kinetics, i.e. formation of mossy dendrites and pits during cell cycling which are correlated to transformation between kinetically fast and slow interfacial reactions at the electrode/electrolyte interface [46]. These peak shapes were also previously observed for 50 mol% NaFSI/C₃mpyrFSI when cycled in a symmetrical cell at a high current density of 1.0 mAh cm⁻² with 1 h polarization time [47]. After about 40 cycles (80 h), the peak features change, with voltage peaking behaviour being reduced and arch shapes followed by a plateau can be observed (figure c). The shift from peaking shapes to an arching voltage profile was studied in detail by Chen et al who found that this transition in voltage shape is driven by mass transport [48]. Initial peaking behaviour is limited by the kinetics of the reactions, caused by evolving morphology. The voltage profile changes when a concentration gradient is created and the reactions become limited by mass transport, resulting in arch profiles [48]. Interestingly, after about 110 cycles (220 h) the voltage profiles become more plateau-like (figure 3(d)). This transition in voltage shape is in contrast to the one previously reported for Li|Li cells utilising 1 M LiPF₆ in 1:1 (volume ratio) ethyl methyl carbonate (EC/EMC), where the arching feature became more profound with the successive cycles [48].

In order to evaluate the interfacial stability of Na in the 25 mol% NaFSI/[HMG][FSI] electrolyte, EIS spectra were recorded in these symmetrical cells after every 20 cycles. The evolution of the EIS impedance is presented in figure S2. The equivalent circuit used to obtain the interfacial resistance is presented in figure S3. The interfacial resistance decreases from 570 Ohm to 35 Ohm after 20 cycles, which could be attributed...
Figure 3. Na|Na symmetric cell cycling performance of 25 mol% NaFSI in [HMG][FSI] (solupor separator) at 0.5 mA cm$^{-2}$ at 50 °C for 60 plating/stripping cycles (320 h) (a), highlighting 15–30th hour (b), 110–120th hour (c), and 220–230th hour (d) of cycling. Bulk and interfacial resistance of a Na symmetrical cell with 25 mol% NaFSI in [HMG][FSI] electrolyte as a function of cycling. (e) The charge–discharge interval was 1 h, rested for 24 h at 50 °C before testing.

Figure 3(e) shows the values of interfacial resistance ($R_{\text{int}}$) and bulk resistance ($R_b$) as a function of cycling. It shows that $R_{\text{int}}$ decreases over 200 cycles, due to the formation of a conductive SEI layer, and then slightly increases above 200 cycles. This might be because the surface of the electrode passivates further, and to the formation and growth of a conductive SEI layer on the Na foil; this also confirms the excellent stability of the electrolyte with long term cycling. This interfacial resistance is lower compared to cells with phosphonium based ILs, i.e. P$_{1444}$FSI/NaFSI (∼75 Ohm after 10 cycles and 35 Ohm after 100 cycles) [43].
the electrode/electrolyte interface rearranges slightly. Figure 3(e) shows that bulk resistance has increased after 100 cycles from 4 Ohm to 7 Ohm, which is attributed to the occurrence of concentration gradients within the electrolyte during Na stripping/plating that may lead to crystallization of the high melting NaFSI salt rich phase at the electrode as the interfacial Na$^+$ ion concentration moves either higher or lower than the eutectic composition. Our previous work reported lower ionic conductivities for concentrations higher than 25 mol% NaFSI, and also higher melting temperatures for compositions either side of the eutectic [33]. This could also possibly explain why the highest possible current density in this electrolyte is 0.5 mA cm$^{-2}$; when 25 mol% NaFSI [HMG][FSI] was tested with higher current densities, i.e. 1 mA cm$^{-2}$, the cell failed after only a few cycles. At higher current densities a larger concentration gradient is created more rapidly, and if the rate of dissolution is higher than the rate of diffusion then the concentration gradient at the interface will increase, resulting in concentration polarization and possible solidification of the electrolyte at the electrode leading to a rapid decrease in ionic conductivity. In a symmetrical cell this can happen on both sides of the cell, as both higher and lower NaFSI concentrations (than 25 mol% NaFSI) are characterized by higher melting points, as mentioned above [33]. Moreover, these two-step changes in bulk and interfacial resistance after 100 and 220 cycles are in agreement with the voltage profiles where a change in voltage curve shapes was observed.

3.3. Transference number

The transference number of the electrolyte was measured and calculated according to the Bruce–Vincent method [38]. Figure 4 shows the current profile as a function of time and the impedance of the Na|25 mol% NaFSI in [HMG][FSI] |Na cell before and after polarization under 10 mV applied voltage. The transference number of this electrolyte is very promising, achieving 0.36 ± 0.03 at 50 $^\circ$C. This value is higher than for the 50 mol% [C$_3$mpyr][FSI] + NaFSI electrolyte (0.3). This high transference number of Na$^+$ may give us a possible explanation for the stable cycling at 0.5 mA cm$^{-2}$. Based on our diffusion coefficient measurements of this electrolyte, the [HMG]$^{+}$ has a lower diffusion coefficient compared to the [FSI]$^{+}$ [32]. The high Na$^{+}$
transference number supports our hypothesis that Na ions move along with [FSI]− leading to an overall high Na+ transference number observed in this electrolyte. Ion decoupling was reported in our previous studies for various compositions (5 mol%, 25 mol%, 45 mol% and 55 mol% NaFSI in [HMG][FSI]), i.e. diffusion rates for [FSI]− were found to be few orders of magnitude higher than diffusivity of [HMG]+ [33]. Interestingly, this was not observed for LiFSI/LiTFSI mixed with [HMG][FSI] systems [34]. This ion decoupling and high ionic conductivity together with a high tNa+ makes this system desirable for Na battery applications.

3.4. Na metal|hard carbon cell

25 mol% NaFSI in [HMG][FSI] was then tested in a half cell (Na|HC) at 50 °C. CV at 0.1 mV s−1 scan rate was performed in order to elucidate the sodium intercalation behaviour with this electrolyte. Figure 5(a) shows the peak currents increased gradually with cycling, which may be attributed to the high electrolyte viscosity and the time dependent electrode wetting process. During the first sodiation cycle, two small reduction peaks were observed, suggesting decomposition of only small amount of the electrolyte. By the 5th cycle, the sodiation/desodiation peak has a high current value, and the polarization is small, indicating good Na+ reaction kinetics. Moreover, the peak around 0.4 V observed during the first cathodic scan was not seen during the following cycles, indicating electrolyte decomposition and formation of a stable SEI layer [21]. At lower potentials, a main reversible peak around 0.05 V was observed and maintained for all performed scans, confirming the reversibility of Na intercalation. During the anodic scan a reversible peak around 0.25 V, corresponding to Na de-intercalation from HC, was observed.

Rate capacity studies were performed for the Na|HC half-cell by applying different C rates from C/20 to 2 C for 5 cycles (figures 5(b) and (c)). These values are comparable with the ones previously reported for the traditional carbonate-based electrolytes used for NIBs. Capacities of 1 M NaFSI EC/DMC in half cell Na|mesoporous carbon at low C rates were almost identical, with except to the high C rate (2 C), when capacity for [HMG][FSI] electrolyte dropped bellowed 100 mAh g−1 (~150 mAh g−1 for carbonate based electrolyte). After that, the half-cell was cycled at C/5 for 50 cycles. Initially at 0.05 C rate, the observed discharge capacity is 341 mAh g−1 and subsequently decreases with C rate resulting in 295, 292, 233, 150 and 63 mAh g−1 for 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C, respectively (figure 5(c)). The rate capability curve (figure 5(b)) indicates that 25 mol% NaFSI is not suitable for high current densities as the capacity drops significantly with increasing C rate. This may also be related to the above discussion of concentration gradients at the electrode interface for the Na symmetric cell measurements. A similar phenomenon was previously reported for a [P1i4i4i4][FSI]:NaFSI system where a concentration gradient was observed during cell cycling [30]. One way to overcome this would be to operate the cell at elevated temperatures to enhance mass diffusion and avoid phase precipitation, and this is currently under investigation as part of our future work. On the other hand, at the lower rates, ions have more time for diffusion and insertion into the electrode, generating more capacity. Subsequently, after performing the rate capability studies, the cell continued to be run at 0.2 C to understand the recoverability of the discharge capacity. 25 mol% NaFSI in [HMG][FSI] HC|Na half-cell showed recoverable, stable and reproducible capacity of 293–302 mAh g−1 (the capacity increased during cycling) for 100 cycles. Cycling data of HC|Na cells for 300 cycles in 25 mol% NaFSI are shown in figure 5(d). Galvanostatic measurements were performed at 0.2 C with five pre-conditioning cycles at 0.1 C. This testing protocol is consistent with our previous reports on ILs where few pre-conditioning cycles were applied for ILs and was chosen for the purpose of drawing comparison [15, 49]. Comparison of electrochemical performance of [HMG][FSI] based electrolyte with other ILs/OIPCs based system is summarized in table S1.

Figure 5(d) shows charge/discharge voltage profiles for the 1st, 5th, 10th, 50th, 100th and 200th cycle. During the first cycle an initial capacity of 327 mAh g−1 with a corresponding initial coulombic efficiency (ICE) 86.6% was recorded and this increased with cycling. Irreversible capacity loss during the first cycle is attributed to the decomposition of the electrolyte on the surface of the negative electrode and subsequent formation of the SEI [50]. Although the capacity of the initial cycle is lower than the one reported for carbonate based electrolyte (1250 mAh g−1 achieved in 1 M NaFSI EC/DMC), the ICE is significantly higher (86.6% for [HMG][FSI] electrolyte vs 40.7% for EC/DMC electrolyte).

Interestingly, the initial capacity loss observed during the first cycle is not significant, suggesting formation of a very stable SEI layer formed on the HC electrode [21]. In order to investigate this hypothesis further, XPS and NMR studies were performed and will be presented in the sections below. Furthermore, during the 10th cycle a promising high discharge capacity of 271.2 mAh g−1 at a 0.2 C was obtained. Interestingly, the capacity increased during successive cycles and reached 285 mAh g−1 after 280 cycles. Increasing capacity during cycling can possibly be explained by simultaneous electrode wetting and creation of a low resistive, stable SEI layer during successive cycles, which was observed in decreasing the interfacial
resistance in symmetrical cell cycling after successive cycling in figure 3(e) and will be discussed in more detail in the following section of SEI characterization by XPS technique. Furthermore, reported capacity values are higher than the ones reported for carbonate based electrolytes, where after 20 cycles, capacity dropped under 200 mAh g\(^{-1}\).

Two regions are observed in the charge–discharge profiles (figure 5(d)): two plateaus and a sloping region. This plateau is reproducible during increasing cycles and the specific capacity remains consistent. Sloping and plateau profiles were previously reported in multiple publications and were assigned to the
complex structural nature of HCs that results in a multi-step storage mechanism during charging-discharging. To-date, various sodium insertion-de-insertion to HC mechanistic models have been reported, including intercalation of $\text{Na}^{+}$ ions into graphene sheets (the sloping region) and $\text{Na}^{+}$ ion adsorption on the reactive surface and defects sites (the low potential plateau) [51–54].

3.5. Characterization of the SEI on hard carbon

Interfacial characteristics of the HC in 25 mol% NaFSI [HMG][FSI] were evaluated by XPS on two samples: pristine HC (in contact with electrolyte for 24 h at 50 °C) and HC after cycling (HC|Na was cycled for 5 cycles before the XPS experiment). The etching depth profiles for C, N, Na and F elements for HC after cycling are presented in figures 6(a)–(c) respectively. XPS spectra for pristine HC is presented in figure SI. The C 1 s spectra of HC after cycling indicates initially four peaks corresponding to, C–N/C–O (286.5 eV), O–C=O (289.6 eV) C=N (288.2 eV) and C–F$_2$ (291.8 eV). Some of species which were observed at 0 s, and gradually decreased after 1230 s etching, indicating that they are at the outer layer of the SEI (C–F$_2$, O–C=O, C=N and C–N/C–O). The signal is assigned to C–F$_2$ peak on the SEI outer layer and disappeared during etching. This suggests some degradation product on the outermost surface of the anode, although the precise chemical mechanism is not clear. Interestingly, in figure 6(a), C–C (284.8 eV) peak appears after 30 s and is dominant at 1230 s, demonstrating that the etching of the SEI is reaching to the bulk HC (figure S4(a)), and the SEI thickness can be roughly calculated.

Furthermore, the N 1 s spectra (figure 6(b)) reveals the presence of two peaks, $\text{N}^{+}$ which comes from residual [HMG]$^{+}$ on the surface and NS=O which is a product of [FSI]$^-$ decomposition [15, 55]. More $\text{N}^{+}$ could be observed in the outer SEI layer due to the direct contact with the electrolyte, whereas a higher amount of NS=O is observed after etching, suggesting that the NS=O species existing in the inner layer of

![Figure 6. XPS spectra of HC electrode after five charge/discharge cycles in HC|Na half cell with 25 mol% NaFSI in [HMG][FSI], C 1 s (a), N 1 s (b), Na 1 s (c) and F 1 s (d) as a function of etching times (0, 30 and 1230 s).](image-url)
the SEI. Moreover, Na$_2$O/NaF, products of electrolyte decomposition and reduction of [FSI]$^-$, are present in the SEI layer (figure 6(c)) with the peak intensity remaining constant during etching, indicating stable inorganic product throughout the SEI layer. As seen from previous reports, uniform inorganic dominant SEI layer has a positive impact on Na$^+$ diffusion kinetics and enables reversible redox reactions [15, 56, 57]. On the other hand, organic dominant SEI species usually decrease the ionic conductivity and are responsible for sluggish Na$^+$ kinetics [58]. The presence of NaF can be also be confirmed from F 1 s spectra (figure 6(d)), and its unchanged intensity during etching indicated the electrolyte residues.

To further understand the SEI characteristics on the HC anode, SSNMR spectroscopy was performed. $^{23}$Na and $^{19}$FMASNMR was employed in order to investigate the SEI composition. Two samples were measured as for the XPS experiment, pristine HC (soaked in the electrolyte) and HC after five charge/discharge cycles.

Figure 7(a) shows a comparison of $^{23}$Na NMR spectra of the 25 mol% NaFSI in [HMG][FSI] (in red) and HC from the half cell (with 25 mol% NaFSI electrolyte) before (in green) and after cycling (in blue). The pristine electrode spectrum (in green) shows a singular peak at −11.8 ppm, which is attributed to electrolyte residuals (consistent with the $^{23}$Na spectra recorded for the neat electrolyte). After 5 cycles, two peaks at −11.8 ppm and 7.5 ppm were observed. The new peak recorded at 7.5 ppm can be assigned to NaF, according to the literature [15]. NaF is usually formed during decomposition of the electrolyte and SEI formation. This also confirms the XPS studies, where NaF was detected in the SEI layer. Moreover, broadening of the $^{23}$Na peak at −11.8 ppm after cell cycling may be due to confinement of the residual electrolyte within the SEI pores (caused by magnetic susceptibility effects).

The $^{19}$F MAS NMR spectra were also recorded for the neat electrolyte (in red), pristine HC (in green) and HC after cycling (in blue, figure 7(b)) to further investigate SEI formation. Multiple peaks were recorded during the MAS NMR experiment, with the main peak corresponding to S–F (54.9 ppm) from the residual electrolyte and symmetrical side bands of this resonance from sample spinning. For the HC electrode which was cycled 5 times, a new peak appears at −224.6 ppm which can be assigned to NaF from the electrolyte decomposition during SEI formation. Moreover, peak broadening was also observed for the $^{19}$F spectrum of the cycled sample, further confirming that this trend is related to magnetic susceptibility effects as mentioned above (poor magnetic field homogeneity in the SEI).

3.6. Na metal/NFP cell

The 25 mol% NaFSI in [HMG][FSI] electrolyte was also tested against a NFP cathode. Figure 8(a) shows CV curves of a NFP/Na half cell at 50 °C. A scan rate of 0.1 mV s$^{-1}$ was used in the voltage range of 1.5–4 V for 5 cycles. During the oxidation scan two peaks were recorded, one around 3.1 V and second around 3.2 V. During the reduction process the main reduction peak was observed around 2.4 V, and a minor reduction peak was recorded at higher potential (around 2.6–2.7 V). Overall, good ion transport and kinetics were identified from these CV experiments suggesting this electrolyte is compatible with NFP cathodes.

The cycling performance of NFP/Na half cells with 25 mol% NaFSI in [HMG][FSI] was tested in a voltage range 1.5–4 V at 0.2 C (with five preconditioning cycles at 0.1 C) at 50 °C. Figures 8(b) and (c) display the cycling performance and respective galvanostatic charge–discharge cycles. The voltage-capacity profiles show asymmetrical behavior with two plateaus during charge at 2.9 and 3.1 V and a single plateau during discharging at 2.8 V vs Na$^+$/Na. The two steps observed during charging are in agreement with the
two oxidation peaks recorded during CV. The two plateaus upon Na extraction are attributed to the intermediate phase reported previously (Na$_{2/3}$FePO$_4$), whose transformation occurs in a two-step process [59, 60]. On the other hand, Na insertion which appears as single plateau is due to coexistence of the three phases FePO$_4$, Na$_{0.7}$FePO$_4$ and NFP [59, 61]. At 0.1 C, the half cell delivered an initial discharge capacity of 131 mAh g$^{-1}$, and decreased to 115 mAh g$^{-1}$ in the 10th cycle. These values are similar to the capacity reported for 50 mol% NaFSI in [C$_3$mpyr][FSI] (117 mAh g$^{-1}$ at 0.2 C, table S1) [47].

Building up on the promising electrochemical behavior of 25 mol% NaFSI [HMG][FSI], NFP|HC full cell NIB was fabricated. Full cell was prepared by pairing NFP electrode with presodiated HC. Prior to this setup, multiple variations of various mass loading electrodes were tested but unfortunately cells were failing after first charge–discharge cycle. HC was presodiated in order to avoid the irreversible capacity loss which could be a reason of cell failure [21, 62–64]. The operating voltage range was set up between 1 V and 4 V (vs. Na/Na$^+$. Charge–discharge behavior at 0.1 C (with respect to the cathode mass) of the NFP|HC full cell with 25 mol% NaFSI in [HMG][FSI] electrolyte cycled at 50 $^\circ$C is shown on figure S5. The voltage vs capacity plot on figure S5(a) shows that first charge is greater the discharge capacity, due to SEI formation on HC electrode. Moreover, as can be seen from figures S4(a) and (b), specific capacity is decreasing with subsequent cycles. The battery showed initial capacity of 62 mAh g$^{-1}$ which decreased to 43 mAh g$^{-1}$ after 50 cycles.

Similar trends were observed previously for 1 M NaFSI in C$_3$mpyrFSI in full cell composed of sodium vanadium phosphate–carbon composite (NVP@C) cathode and HC anode. Manohar et al reported capacity decrease from around 90 mAh g$^{-1}$–70 mAh g$^{-1}$ (after 100 cycles) [65]. Despite quite low capacity, these results underline the good compatibility between OIPC based electrolyte and HC anode, NFP cathode. Unfortunately, up to now there is not many reported studies on full NIBs utilizing OIPCs and more work needs to be done in order to better understand the sodium intercalation and deintercalation mechanism into electrodes and further optimize the electrolyte and electrode design.
4. Conclusions

This work has demonstrated favorable electrochemical performance of 25 mol% NaFSI in [HMG][FSI] electrolyte for sodium secondary batteries. Stable sodium cycling in a symmetrical coin cell with very low overpotential of ≈45 mV at 0.5 mA cm\(^{-2}\) current density with 1 h charging and 160 cycles was demonstrated. Efficient Na\(^+\) transport in this electrolyte was indicated by the high transference number for Na\(^+\) of 0.36. Moreover, the [HMG][FSI] based electrolyte was investigated against HC anode and NFP cathode materials for the first time. This electrolyte exhibits promising performance when studied with individual electrodes (HC and NFP) i.e. outstanding ICE of 86% and 285 mAh g\(^{-1}\) capacity (300 cycles) in Na|HC half cell and 105 mAh g\(^{-1}\) capacity after 100 cycles in Na|NFP cell.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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