



Protic and Aprotic Ionic Liquids in Combination with Hard Carbon for Lithium-Ion and Sodium-Ion Batteries

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In this work we report the use of the aprotic ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI) and the protic ionic liquid 1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr_{H4}TFSI) in combination with olive pits derived hard carbon electrodes in view of the realization of advanced Li-ion and Na-ion batteries. We show that in the case of Li-based systems both classes of ionic liquids can be successfully utilized at room-temperature to build high performance and stable hard carbon-based systems. In the case of Na-ion chemistry, Pyr₁₄TFSI appears very promising while the use of Pyr_{H4}TFSI is not applicable due to the lack of electrochemical stability below 1 V vs. Na/Na⁺.

Carbonaceous materials are widely used as negative electrodes in Li- and Na-ion batteries (LIBs and NIBs). Graphite has been and still is the most commonly used material in commercial LIBs owing to its low operational potential, low-cost and good cycle life.^[1] On the contrary, its use in NIBs was almost abandoned until the recent discovery of diglyme-based electrolytes that also enables the use of graphite in sodium technology.^[2,3] The short interlayer distance of graphite, however, limits both Li⁺ and Na⁺ electrochemical insertion and consequently the capacity of the material. Thus, to enhance the electrochemical behaviour of batteries, in the last decades alternatives to graphite have been widely explored.^[4] Among them, non-graphitizable hard carbons (HCs) have attracted much attention.^[5] Their disordered microstructure allows Li⁺ and Na⁺ binding onto the edges and surface of randomly oriented graphitic layers,^[6] and as a result, larger capacity values can be obtained.^[7,8]

In order to improve the safety of LIBs and NIBs, which is limited by the use of highly flammable and volatile organic solvents, different electrolytes have been investigated. Among the various types of possible electrolytes, ionic liquids (ILs) have been one of the most studied alternatives.^[9,10] ILs can be divided into two main groups, aprotic ionic liquids (AILs) and protic ionic liquids (PILs).^[11] The main difference between them is that PILs have an available proton on the cation. Up to now, the studies with negative electrode materials for both LIBs and NIBs have been focused on the use of AILs owing to their wider electrochemical stability window (ESW) compared to PILs. However, recent works suggest that PIL-based batteries can perform better than their AIL-based counterparts at high rates. Moreover, taking into account the fact that PILs are a more affordable option, then, the use of these electrolytes becomes even a more attractive alternative in the search for next generation batteries.^[12–15] Regarding NIBs, Fukunaga et al. studied the electrochemical performance of a HC in N-methyl-N-propylpyrrolidiniumbis(fluorosulfonyl)amide [C₃C₁pyrr][FSA], reporting a reversible capacity of 260 mAh g^{−1} at 0.05 A g^{−1} and 90 °C.^[16] Using the same IL, Ding et al. reported the behaviour of a HC at different temperature ranges and showed that this anodic material could deliver 230 mAh g^{−1} at 90 °C and 25 mAh g^{−1} at 25 °C.^[17] Wang et al. reported the performance of a (HC:Na_{0.44}MnO₂) NIB containing N-propyl-N-methylpyrrolidinium (PMP)-FSI with 1 M NaFSI at room temperature (RT). Surprisingly, the performance of this full cell in the IL-based electrolyte was even better than that observed in a conventional organic electrolyte. This improvement was ascribed to the low charge transfer resistance (R_{ct}) values of the interface between the electrode materials and the IL.^[18] A recent study shows that a NIB containing HC:(Na₃V₂(PO₄)₃/C) as electrodes and working in 1 M NaFSI dissolved in N-propyl-N-methylpyrrolidinium bis(fluoromethanesulfonyl)imide (C₃mpyrFSI) can show a RT energy density of 368 Wh kg^{−1}.^[19] In the case of LIBs, the best performance of a HC was reported by Zheng et al. who investigated the behaviour of this material in 1 M LiTFSI trimethyl-n-hexylammonium (TMHA) -bis(trifluoromethanesulfone)imide (TFSI) at different temperatures, reporting a capacity value as high as 675 mAh g^{−1} at 80 °C.^[20] As evidenced by this short literature overview, most of the studies dedicated to HCs in ILs have been carried out at high temperature. Furthermore, to the best of our knowledge, the behaviour of a HC in PILs has never been investigated. Against this background, in this study we report for the first time the performance of a HC in AILs and PILs at RT for both Na- and Li-ion technologies.

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For the investigations reported two ILs have been considered, the AIL 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI) and the PIL 1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr_{H4}TFSI) (Figure 1). As salts, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) have been used.

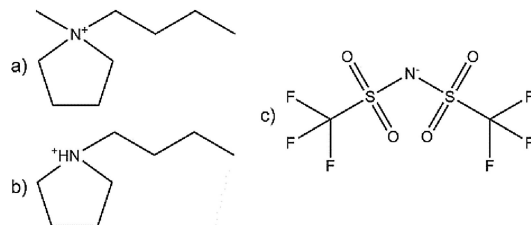


Figure 1. a) 1-butyl-1-methylpyrrolidinium (Pyr₁₄⁺) cation, b) 1-butylpyrrolidinium cation (Pyr_{H4}⁺) and c) bis(trifluoromethanesulfonyl)imide (TFSI⁻) anion.

Figure 2 shows a comparison of the cyclic voltammograms (CVs) recorded using HC electrodes at RT and 0.1 mV s⁻¹ between 0.002 and 2 V vs. Li/Li⁺ and Na/Na⁺ in 0.5 M LiTFSI-

Pyr₁₄TFSI (AIL-Li), 0.5 M LiTFSI-Pyr_{H4}TFSI (PIL-Li), 0.5 M NaTFSI-Pyr₁₄TFSI (AIL-Na) and 0.3 M NaTFSI-Pyr_{H4}TFSI (PIL-Na) electrolytes. According to previous studies, vinyl ethylene carbonate (VEC) decomposes within the ESW of the prepared PIL, and thus, it can avoid the exfoliation of a graphite electrode and ultimately improve the electrochemical performance. Also, due to the limited cathodic stability of the Pyr_{H4}⁺ cation (Table 1),

Table 1. Conductivity and viscosity at 30 °C of the used electrolytes.

Electrolyte	Conductivity [mS cm ⁻¹]	Viscosity [mPa s]	ESW [V vs. Ag]	Ref.
0.5 M LiTFSI-Pyr ₁₄ TFSI	1.9	136.7	−3 to 3 V	[19]
0.5 M LiTFSI-Pyr _{H4} TFSI	2.0	99.7	−1 to 3 V	[19]
0.5 M NaTFSI-Pyr ₁₄ TFSI	1.7	111	−3.3 to 2.5 V	[21]
0.3 M NaTFSI-Pyr _{H4} TFSI	2.8	70	−1 to 2.5 V	[23]

the presence of a film-forming additive is always necessary when working with this PIL.^[21] In order to test the effect of using this additive with HC electrodes, AIL-Li-VEC and PIL-Li-VEC electrolyte formulations were also studied. Figure 2a and 2b show the behaviour of the HC in AIL-Li and AIL-Li-VEC,

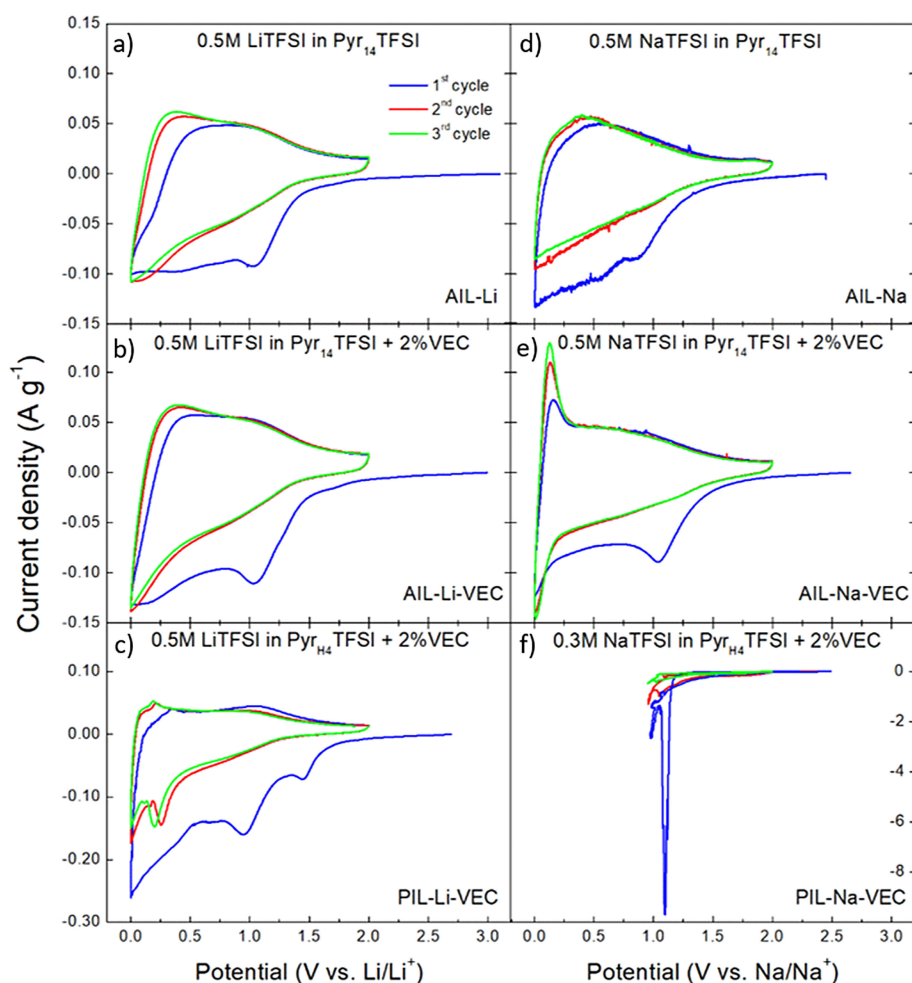


Figure 2. CVs recorded at 0.1 mV s⁻¹ from 0.002 V to 2 V vs. Li/Li⁺ or Na/Na⁺ for HC-based electrodes in a) AIL-Li, b) AIL-Li-VEC, c) PIL-Li-VEC, d) AIL-Na, e) AIL-Na-VEC and f) PIL-Na-VEC.

respectively. As shown, the CVs obtained in both electrolytes exhibit a peak at ~ 1 V vs. Li/Li^+ , which can be ascribed to the solid electrolyte interphase (SEI) formation. These results show that in HC, contrary to graphite, the use of an additive is not always required when working in $\text{Pyr}_{14}\text{TFSI}$.^[22] Nevertheless, its use promotes a more stable and suitable SEI, which is reflected in the sharper cathodic peak observed below 1 V (Figure 2b), indicative of an improved Li^+ insertion in the microstructure of the HC.^[23] Moreover, by using the additive, the first cycle coulombic efficiency (CE) calculated from the CVs rises from 48% to 54% in the case of the AIL-Li. In the following cycles the CE is stabilized at 96% independent of the addition of VEC. In the case of the HC cycled in PIL-Li-VEC (Figure 2c), the decomposition of VEC occurs at ~ 1.5 V, whereas the SEI formation and reversible Li^+ insertion/de-insertion peaks are observed at about 1 V and below 0.5 V, respectively. The first cycle CE of the HC in this electrolyte is as low as 34%, while in the following cycles it is stabilized at 88%. Formerly, Menne et al. reported the use of $\text{LiTFSI-Pyr}_{\text{H4}}\text{TFSI}$ in combination with graphite and soft carbon-based electrodes. Now, these results show for the first time, that it is possible to use PIL-based electrolytes also in combination with HC electrodes. Figure 2d and 2e show the CVs of the HC in AIL-Na and AIL-Na-VEC electrolytes, respectively. Similar to the results obtained in Li-ion, a more pronounced and better resolved peak at ~ 1 V vs. Na/Na^+ reveals an improved SEI formation owing to the use of a film-forming additive. This allows to better identify the typical HC profile indicative of a Na^+ insertion mechanism.^[24,25] Furthermore, the use of the additive shows a major enhancement in the first cycle CE going from 44% to 58%. In the following cycles, the CE stabilizes at 90% and 99% for AIL-Na and AIL-Na-VEC, respectively. As in the Li-based PIL, the limited cathodic stability of the Pyr_{H4}^+ cation in the Na-based PIL (Table 1) makes again necessary the use of a film-forming additive for the SEI formation. Contrary to Li-based systems, after testing different additives and maintaining always the water content of the electrolyte below 30 ppm, PIL-Na-VEC electrolyte appears to be unstable below ~ 1.2 V vs. Na/Na^+ , hindering its use with the studied carbonaceous material in Na-based electrolytes (Figure 2f).

Figure 3 shows Galvanostatic (GA) charge/discharge measurements performed just after the CVs in a potential window of 0.002–2 V vs. Li/Li^+ . Figure 3a shows the charge/discharge profile of the HC in AIL-Li, AIL-Li-VEC and PIL-Li-VEC electrolytes at C/5. As shown in Figure 3a, all charge/discharge profiles are in good agreement with the absence of sharp peaks observed in the CVs, and they are all displaying a sloppy region from 1 V to 0.002 V, which can be assigned to the Li^+ insertion through the HC layers.^[8] Figure 3b compares the specific capacities delivered by the HC at different C-rates in the investigated Li-based electrolytes. As shown, the HC electrode in combination with AIL-Li-VEC delivers a specific capacity of 242 mAh g^{-1} at C/5 and 102 mAh g^{-1} at 1C, while the system working in AIL-Li delivers 224 mAh g^{-1} at C/5 and 88 mAh g^{-1} at 1C. Taking into account these results, it appears that at low rates SEI features play an important role on the Li^+ de-insertion mechanism, while increasing the C-rate, the

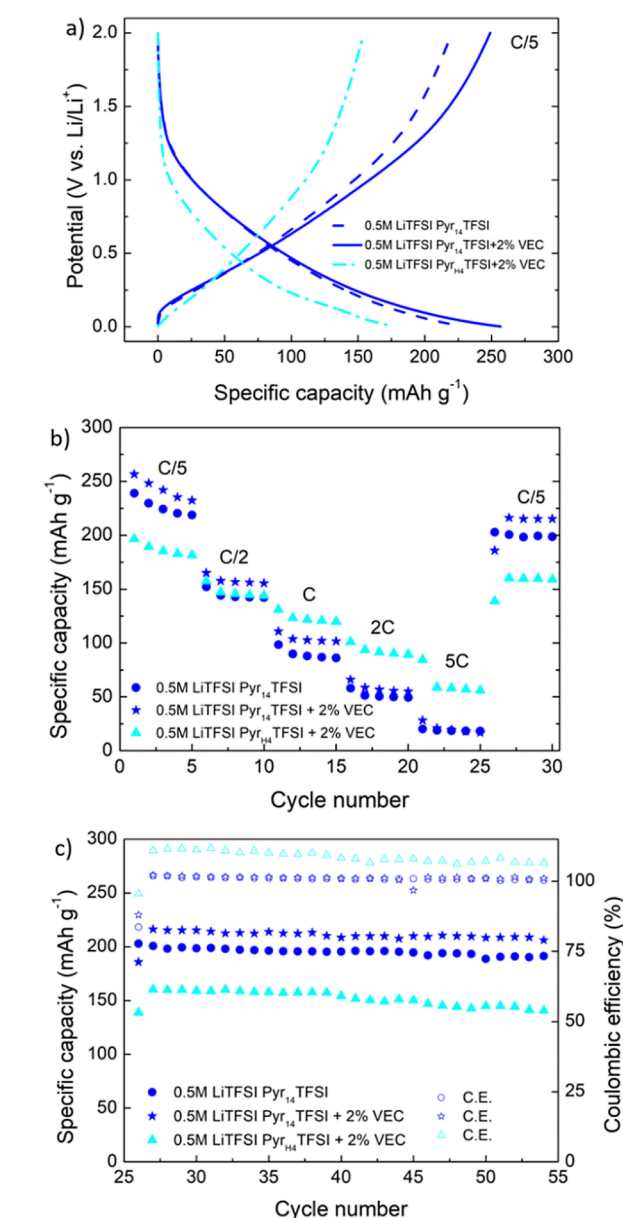


Figure 3. GA charge/discharge characterization of the HC electrodes between 0.002 V to 2 V vs. Li/Li^+ in the investigated electrolyte: a) Charge/discharge profiles of the HC, b) Rate capability and c) Stability at C/5.

difference in capacity due to the VEC addition is attenuated. The use of PIL-Li-VEC leads to a different behaviour. As shown, at C/5 the HC electrode displays a specific capacity of 185 mAh g^{-1} which is lower than those observed in AIL-based electrolytes (with and without VEC). At high rates, however, the use of the PIL appears to be more advantageous as indicated by the fact that the HC electrode displays a capacity of 122 mAh g^{-1} at 1C and 58 mAh g^{-1} at 5C. These higher values show that the unique lithium environment of PIL-based electrolytes^[12,26] and their higher ionic conductivity (Table 1) have a positive effect on carbonaceous negative electrodes. After the C-rate tests, the electrodes were cycled at C/5 to measure the stability of the investigated systems. As shown in Figure 3c, after 30 cycles both the capacity retention and the

CE of the HC in AIL-based electrolytes is almost 100%. After the same number of cycles, the HC electrodes cycled in PIL-Li electrolyte retains around 90% of the initial capacity. In the latter system, some degradation processes were presumably taking place during cycling as evidenced by the CE values exceeding 100%. Nevertheless, considering that better CE values could be obtained through the electrolyte formulation optimization, the main conclusion drawn from these results is that PIL-based electrolytes can be successfully utilized in combination with a variety of carbonaceous negative electrodes for LIBs.

Figure 4a compares the GA charge/discharge profiles of HC electrodes in AIL-Na-based electrolytes. These profiles were

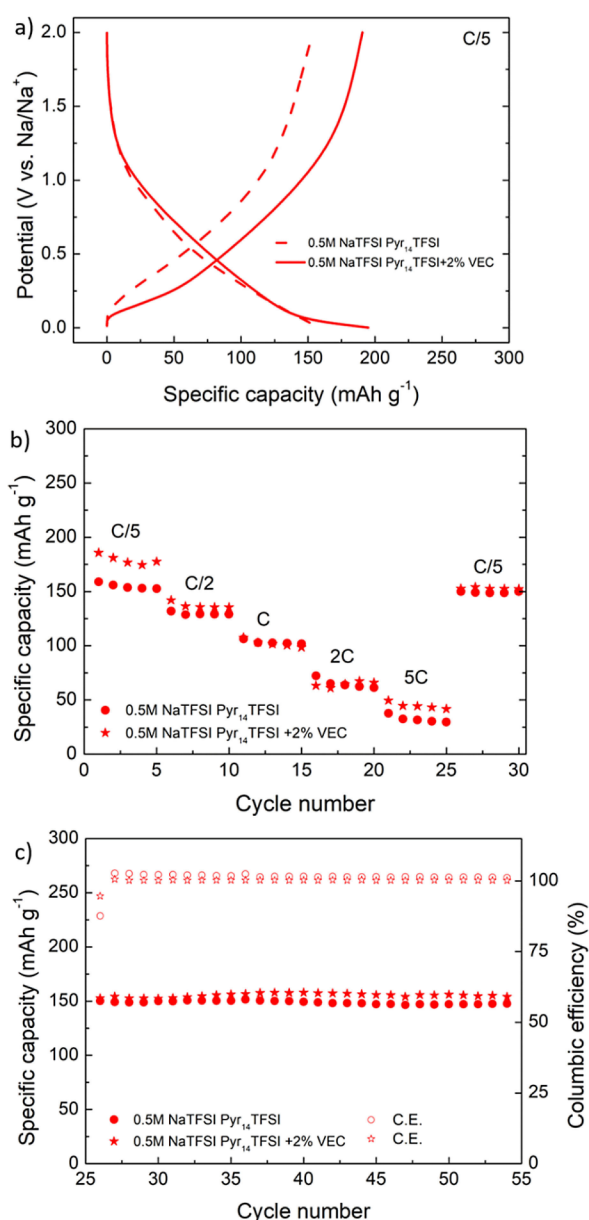


Figure 4. GA charge/discharge characterization of the HC in Na-ion between 0.002 V to 2 V vs. Na/Na⁺ in the investigated electrolyte: a) Charge/discharge profiles of the HC, b) Rate capability and c) Stability at C/5.

obtained at C/5 and in the potential window comprise between 0.002 and 2 V vs. Na/Na⁺. As shown in the figure, the sloppy region observed from ca. 1 V to 0.2 V vs. Na/Na⁺, followed by a low potential plateau is in good agreement with the CV profiles (Figure 2d and 2e). As already discussed in the literature, the sloppy region can be ascribed to the interlayer insertion of Na⁺, while the plateau could be related to the Na⁺ insertion into the micropores.^[24,25] Figure 4a and 4b show that when VEC is added the initial capacity is slightly higher probably due to the decomposition of the additive. Then, in both AIL-Na and AIL-Na-VEC electrolytes, there is an initial capacity drop during the first 5 cycles at C/5 (stabilizing/conditioning stage) while the capacity seems to recover after the rate capability testing. Already at the 30th cycle at C/5 the capacity is not dependent on the presence of VEC. As shown in Figure 4b the HC electrodes cycled in AIL-Na-VEC deliver 178 mAh g⁻¹ at C/5 while in AIL-Na the capacity is 154 mAh g⁻¹. At an increased discharge rate of 2C both systems deliver a capacity of 64 mAh g⁻¹, whereas at 5C capacity values differ slightly, 44 and 32 mAh g⁻¹ for AIL-Na-VEC and AIL-Na systems, respectively. As shown in Figure 4c, the use of both electrolytes allows a very stable performance. In fact, after 30 cycles at C/5 HC electrodes are able to keep all their initial capacity and during cycling the CE is always close to 100%. Therefore, based on the high and stable specific capacity values achieved by HC electrodes, these results indicate that IL-based electrolytes can also be used in NIBs even at RT.^[16,17,20]

In summary, in this study we investigate the use of AIL and PIL based electrolytes at RT in view of the realization of Li and Na-based batteries. We show that Pyr₁₄TFSI can be successfully utilized, with or without additive, when a HC is used as negative electrode. In combination with LiTFSI, the HC displays a RT capacity of ca. 200 mAh g⁻¹ at C/5 and a good cycling stability when using this AIL. We also show, for the first time that PIL-based electrolytes such as Pyr_{H4}TFSI could be effectively used in LIBs built with HC electrodes. Particularly interesting appears to be the use of this PIL for high rate applications. Finally, we show that Pyr₁₄TFSI is also a very promising candidate for the realization of Na-ion based systems. As a matter of fact, the use of this AIL in combination with NaTFSI guarantees high RT capacity and a good cycling stability. However, Pyr_{H4}TFSI cannot be used with HC electrodes in Na-ion batteries, most probably because the additive is not able to hinder the decomposition of Pyr_{H4}⁺ which is not stable below ~1.2 V vs. Na/Na⁺. Even so, to better understand the performance of HC electrodes in AILs and particularly in PIL both in Li- and Na-ion chemistries, further studies are necessary to determine, for instance, SEI formation in the different electrode-electrolyte combinations.

Experimental Section

1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI) has been purchased from Iolitec (99% purity), while 1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr_{H4}TFSI) has been synthesized as previously reported.^[27] Both lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) salts have been purchased from

Solvionic (99.5% purity). The electrolytes used in this work were: 0.5 M LiTFSI-Pyr₁₄TFSI, 0.5 M LiTFSI-Pyr₁₄TFSI, 0.5 M NaTFSI-Pyr₁₄TFSI and 0.3 M NaTFSI-Pyr₁₄TFSI. This last concentration has been selected based on the maximum solubility of NaTFSI in Pyr₁₄TFSI. All of them were also characterized using 2 wt.% of vinyl ethylene carbonate as additive and denoted with VEC. The water content of the ILs was measured using a Karl-Fisher coulometer, and was found to be lower than 30 ppm for all electrolytes.

The synthesis, physicochemical characterization and electrode preparation of the studied HC was reported elsewhere.^[28]

All the electrochemical measurements were carried out in a three-electrode Swagelok®-type cell, using one Li or Na metal disc as counter electrode and another Li or Na metal disc as reference electrode in the case of Pyr₁₄TFSI-based electrolytes. In order to avoid the reaction between the alkali metals and the protons from Pyr₁₄TFSI, in Pyr₁₄TFSI-based electrolytes an oversized LiFePO₄ or Na[Fe_{0.5}Mn_{0.5}]O₂ was used as counter electrode and Ag wire as pseudo-reference. In this latter case, for the sake of comparison, the voltage values reported in the figures are referring to Li/Li⁺ or Na/Na⁺ scales. A glass fibre membrane (Whatman GFB) drenched with 150 µl of electrolyte was used as the separator. All the cells were assembled inside a glove box under argon atmosphere. Cyclic voltammetry (CV) and galvanostatic (GA) charge/discharge measurements were recorded in a multichannel potentiostat (Biologic VMP3).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: aprotic ionic liquids • protic ionic liquids • carbon • lithium-ion batteries • sodium-ion batteries

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