



Short communication

Carbonaceous anodes for lithium-ion batteries in combination with protic ionic liquids-based electrolytes



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HIGHLIGHTS

- Protic ionic liquids (PILs) are promising electrolyte for lithium-ion batteries.
- Protic ionic liquids display all favorable properties of ionic liquids.
- PILs-based electrolyte can be used in combination with carbonaceous anodes for LIB.

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ABSTRACT

Protic ionic liquids (PILs) have been recently proposed as a new class of electrolytes for lithium-ion batteries (LIBs). So far, PILs-based electrolytes have been used in combination with several battery materials, but never with carbonaceous anodes. Since graphite is the state-of-the-art anode in LIBs, the use of PILs-based electrolyte in combination with this material appears of particular importance. In this work we showed, for the first time, that PILs-based electrolytes can be successfully used also in combination with graphite. Even if the lithium intercalation and deintercalation process of these electrode materials occur outside the ESW of PILs, the addition of film-forming additive makes possible the formation of a stable SEI and, consequently, the use of PILs-based electrolytes. The results of this study indicate that the performance of graphite electrode in PILs-based electrolytes is comparable, and even slightly higher, than that observed in AIL-based electrolytes.

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1. Introduction

Ionic liquids (ILs) display negligible vapor pressure, high chemical and thermal stabilities, high ionic conductivity and large electrochemical stability [1–3]. Thanks to this unique combination of properties ILs are presently regarded as one of the most interesting alternative electrolytes for advanced electrochemical storage devices, including lithium-ion batteries (LIBs). In the last years many types of ILs have been proposed as electrolytes for LIBs and used in combination with several cathodic and anodic materials [4–9]. The results of these studies indicate that the use of ILs might have a positive impact on the safety of LIBs [10]. Nevertheless, they also indicated that further improvements are still necessary for ILs-based LIBs in order to match the performance of the systems containing conventional organic solvents [11,12]. Additionally, also the price of ILs has been indicated as an important obstacle for the introduction of these electrolytes on LIBs.

Graphite is currently the anode of choice in commercial LIBs and its use in combination with electrolytes containing aprotic ionic liquids (AILs) has been widely investigated [13,14]. AILs display rather large cathodic stabilities, which might exceed the lithium plating/stripping potential [14–16]. It has been shown that when these ILs, e.g. *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethane sulfonyl)imide (PYR₁₄TFSI), are used in combination with graphite their cation might co-intercalate into the graphite layers, leading to the exfoliation of the graphite itself [17,18]. Therefore, like in conventional electrolytes, the presence of SEI forming components, e.g. VC, EC or the anion of the ILs itself [19–21], appears necessary for a successful use of ILs in combination with graphite electrodes.

Recently, we proposed the use of protic ionic liquids (PILs) as electrolytes for LIBs. We showed that PILs-based electrolytes display good affinity for battery materials and, when dry electrolytes are used, battery materials can be safely used in these protic electrolytes [22,23]. Moreover, we also showed that PILs-based LIBs containing lithium iron phosphate (LFP) as cathode and lithium titanate (LTO) as anode display, at room temperature, promising performance also at high current densities [23]. Taking into account

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these results, PILs can be therefore regarded as an interesting class of ILs-based electrolytes for LIBs. Additionally, since they are typically cheaper than AILs, their use could be helpful to overcome the cost limitation related to the use of the ILs-based electrolytes. However, in order to be fully competitive with aprotic ILs and conventional electrolytes, the use of PILs should be also extended to systems containing graphite. As a matter of fact, if PILs-based electrolytes could not be used in combination with the state-of-the-art anode, their introduction would be much less appealing.

In this manuscript we report for the first time about the use of PIL-based electrolytes in combination with graphite and soft carbon-based electrodes. The PIL used for this investigation was the *N*-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR_{H4}TFSI). For comparison, also an electrolyte containing the aprotic ionic liquid (AIL) PYR₁₄TFSI was considered. For the preparation of both, protic and aprotic electrolytes, LiTFSI (0.5 M) and vinyl ethylene carbonate (VEC) were used as lithium salt and film-forming additive, respectively. Initially, the conductivity, viscosity, electrochemical stability (ESW) and thermal stability of the two electrolytes were considered. Afterward, their use in combination with graphite and soft carbon-based electrodes was investigated using cyclic voltammetry (CVs) and constant current cycling (CC).

2. Experimental

1-Butylpyrrolidine (Aldrich >98%) was distilled directly before use. HCl (37%) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), *N*-methylpyrrolidine (>97%) 1-iodobutane (>99%), ethyl acetate (ACS grade, >99.5%), vinyl ethylene carbonate were used as received. *N*-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR_{H4}TFSI) was synthesized following a procedure similar to that described elsewhere [24]. PYR₁₄TFSI was synthesized following the procedure described in Ref. [25]. At the end of the synthesis the obtained ILs were dried under vacuum at 60 °C. The water content of the ILs was measured using coulometric Karl–Fisher titration, and was found to be lower than 10 ppm for both ILs. The conductivity and the viscosity of the three investigated electrolytes were evaluated at 20 °C as indicated in Ref. [11].

Electrochemical stability windows of all electrolytes at RT and 60 °C were evaluated in a three-electrode, Swagelok-cell by linear sweep voltammetry (LSV) at 1 mV s⁻¹. The working electrode was a platinum microelectrode (embedded in PEEK; active area = 0.79 mm²). An activated carbon pellet was used as counter and Ag-wire as reference electrode. The measurements were performed at 20 °C using a Solartron model 1287A potentiostat controlled by Corrware[®] software. Separate LSV tests were carried out on each sample to determine the cathodic and anodic electrochemical stability limits. The measurements were performed by scanning the cell potential from the open circuit potential (OCP) toward more negative (cathodic limit) or positive (anodic limit) potentials. Clean electrodes and fresh samples were used for each test.

Graphite (SFG6, TIMCAL, Switzerland, specific nitrogen BET surface area: 17 m² g⁻¹ [26]), soft carbon (Petrol coke, TIMCAL, Switzerland, specific nitrogen BET surface area: 17 m² g⁻¹ [27]) and carbon-coated LiFePO₄ (Südchemie, Germany) as active materials, sodium carboxymethyl cellulose (Walocel CRT 2000, Dow Wolff Cellulosics) and polyvinylidene fluoride (PVdF, Kynar 761) as binders and carbon black (Super C65, TIMCAL) as conductive agent were used as delivered. For preparation of the used anodes, PVdF was dissolved in NMP to obtain a 1.5 wt.% solution and equilibrated for 1 h at room temperature with a magnetic stirrer. The active material (graphite or soft carbon) and conductive agent (Super C65) were added. The anode coating was applied with a doctor blade to a copper foil (dendritic, SCHLENK, Germany). The obtained

electrodes were dried at 100 °C under vacuum. The mass loading of the electrodes was 2 mg. The area was 1.13 cm².

All the electrochemical tests were carried out in three-electrode Swagelok[®] cells. The cells were assembled in a dry box (MBraun) with oxygen and water contents lower than 1 ppm. As separator, a stack of three non-woven fleeces (FS2226, Freudenberg, Germany) drenched with 80 mm³ of electrolyte was used. As counter electrode an oversized LFP electrodes (ca. 11 mg cm⁻²) were used.

The electrochemical measurements were carried out using a MACCOR Series 4000 battery tester. Constant current cycling (CC) was carried out at 30 °C using different current densities. Current density corresponding to 1C, was used for the CC investigations. The C-rate was calculated on the base of the theoretical capacity of graphite (372 mA g⁻¹).

3. Results and discussion

Fig. 1 shows the thermal stability of the two investigated (neat) ILs as obtained by thermogravimetric analysis. As shown, PYR₁₄TFSI is thermally stable up to almost 400 °C, while the PYR_{H4}TFSI up to 300 °C. Most likely, the thermal stability of PYR_{H4}TFSI is lower than that of PYR₁₄TFSI because of the more reactive protic character of the PILs. Nevertheless, these results clearly indicated that the thermal stability of PILs, as for AILs, is significantly higher than that of conventional organic electrolytes [10–12].

Table 1 compares the conductivity and the viscosity of the PIL-based electrolyte 0.5 M LiTFSI in PYR_{H4}TFSI with those of the AIL-based electrolyte 0.5 M LiTFSI in PYR₁₄TFSI. As shown, the conductivities of both electrolytes are almost identical (ca. 2 mS cm⁻¹). On the other hand, the viscosities of the two electrolytes are rather different, and the AIL-based electrolyte is more viscous than the PIL-based electrolyte (ca. 30%). This difference might be originated by the lower sterical hindrance cation PYR_{H4}⁺ compared to that of PYR₁₄⁺ [28].

Fig. 2 compares the overall ESW of the two electrolytes. As shown, both of them display nearly the same anodic stability, which is above 5.5 V vs. Li/Li⁺. These values are comparable with those reported in literature for other TFSI-based electrolytes [29]. On the other hand, the cathodic stability of the two electrolytes is significantly different. Whilst the stability of 0.5 M LiTFSI in PYR₁₄TFSI is exceeding the lithium plating/stripping potential (0 V vs. Li/Li⁺), 0.5 M LiTFSI in PYR_{H4}TFSI is electrochemically stable only

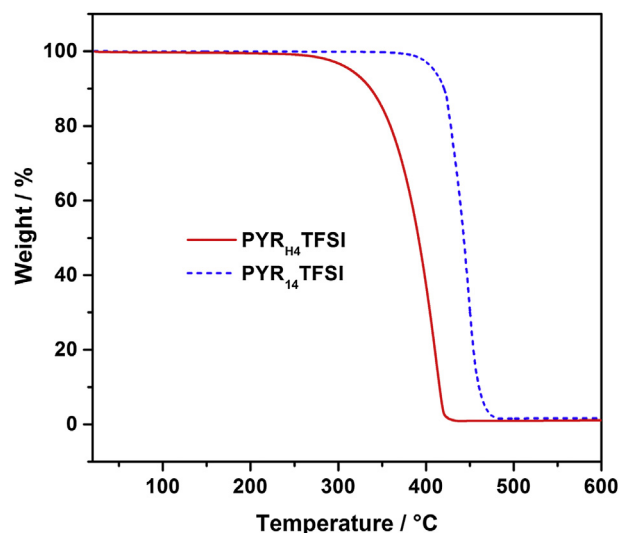


Fig. 1. Thermogravimetric analysis of PYR_{H4}TFSI and PYR₁₄TFSI in the temperature range from RT to 600 °C.

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