

Aprotic and protic ionic liquids in lithium ion batteries: a comparative study

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Ionic liquids (ILs) are room-temperature molten salts. Due to their interesting properties, like non-flammability, negligible vapour pressure and high chemical and thermal stability, they are considered as a promising class of material to replace conventional electrolytes in several electrochemical storage devices [1]. Especially, aprotic ILs based on the anion bis(trifluoromethanesulfonyl)imide (TFSI) have been widely studied because of their high thermal and also electrochemical stability [2]. Likewise, due to the high viscosity of pure ILs, which displays a disadvantage towards commonly used electrolytes in lithium-ion batteries (LIBs), also mixtures of these TFSI based IL with organic solvents have been investigated in terms of performance, safety and corrosion protection of the aluminum current collector [3-5].

A subset of ILs are protic ionic liquids (PILs) which are formed by the transfer of a proton between a Brønsted acid and a base. They display interesting properties due to their “free” available proton (e.g. hydrogen bond). Pure PILs or mixtures of PIL with acetonitrile or water have been proposed as electrolyte for supercapacitors. Moreover, the proton conductivity of PIL-based polymers were also investigated in view of the use of this IL in fuel-cells [6]. Only few works considered the use of PILs as electrolyte solvent for lithium ion batteries. Nevertheless, as PILs are cheaper than aprotic IL, easy to synthesize and environmentally friendly their use in lithium-ion batteries could be of interest [7].

Recently, we showed that a LIBs consisting of a lithium iron phosphate (LFP) cathode and a lithium titanate (LTO) anode can be cycled in the PIL-based electrolyte 1M LiTFSI in triethylammonium bis(tetrafluoromethylsulfonyl)amide (Et₃NHTFSI). As shown in Fig. 1A, the LFP electrode of the LIB displayed a stable capacity of 58.9 mAh g⁻¹ about 300 cycles at 1C. This value of capacity is clearly lower than those observed in conventional electrolytes. Nevertheless, it is important to note that this value is comparable with those obtained with aprotic IL-based electrolytes. The voltage profiles of both electrodes, anode and cathode, are presented in Fig. 1B. It can be seen, that the typical plateaus were obtained for each material. Even though, the voltage excursion of the LTO anode is limited due to a cathode limited cell [8].

Driven by these interesting results we decide to investigate more in details the differences, advantages and disadvantages of AILs and PILs as an electrolyte solvent in LIBs. In this work we compare a selection of protic and aprotic ionic liquids concerning their physicochemical properties and their electrochemical limitations for the use in LIBs. The thermal properties of these electrolytes, as well as their conductivity and electrochemical stability windows were investigated. Moreover, a detailed comparison of the electrochemical performance of LIBs containing aprotic and protic ILs was carried out.

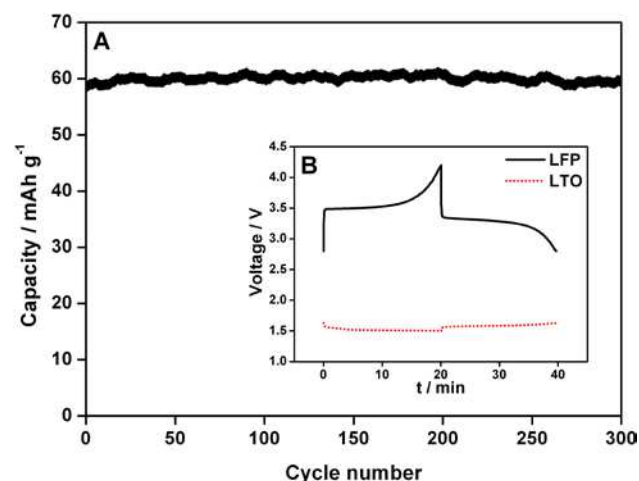


Fig. 1. Discharge capacity as a function of cycle number obtained for 1M LiTFSI in Et₃NHTFSI at room temperature and 1C in a LIB (A) and voltage profiles of the used LIB (B). Capacities are calculated for the cathode.

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