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Use of natural binders and ionic liquid electrolytes for greener and safer lithium-ion batteries

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ABSTRACT

This manuscript reports on the development of a safe and green lithium-ion battery containing sodium salt of CarboxyMethylCellulose (CMC) as binder, lithium titanate ($Li_4Ti_5O_{12}$) as anodic active material, lithium iron phosphate ($LiFePO_4$) as cathodic active material and an electrolytic solution based on the ionic liquid N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide ($PYR_{14}FSI$). The battery showed, at room temperature, a very stable specific capacity of 140 mAh g^{-1} constant for more than 150 cycles. This indicated that the introduction of low cost and environmentally benign binders, like CMC, and non-flammable electrolytes, such as $PYR_{14}FSI$, represents a viable strategy for the development of new, greener and safer lithium-ion batteries.

1. Introduction

Lithium ion batteries dominate the consumer portable electronic and telecommunications market and they are also indicated as the most promising option for the next generation of hybrid and electric vehicles (HV, EV). The wide deployment of lithium ion batteries in the automotive industry would have tremendous consequences on the battery-market and it would further strengthen the central role of these systems in the field of the energy storage. For that, considerable efforts are now focused on the development and realization of lithium ion batteries able to fulfil the requirement necessary for the application in HV and EV.

When the present lithium ion technology is considered, the safety of batteries appears to be one of the main drawbacks holding the introduction of this technology in HV and EV. The commercial systems nowadays available use electrolytes commonly based on organic carbonates (e.g. propylene carbonate, PC, ethylene carbonate, EC) but since these electrolytes are flammable their use poses a serious safety risk and strongly reduces the battery operative temperature range [1,2]. For these reasons, the replacement of non-flammable, non-volatile ionic liquids (ILs) (see Fig. 1) for the organic carbonates appears very promising.

ILs are generally comprise a bulky, asymmetrical organic cation and a weakly coordinating inorganic/organic anion. They represent today a very interesting new class of room temperature ionic fluids. The main advantages of ILs toward organic solvents are, in addition to the previously mentioned non-flammability and negligible vapor pressure, the high chemical and thermal stability and, in some cases, hydrophobicity. For that, ILs have attracted a large attention for use as "green" solvents and recently have been intensively investigated as electrolytes (or electrolyte components) for various electrochemical devices. In the last few years a large number of ILs have been proposed and tested in combination with several anodic and cathodic materials for lithium and lithium-ion batteries [3–12]. The results of these studies have shown that ILs can be successfully used as electrolytes in lithium ion batteries at the place of the conventional organic carbonates. Between the ILs recently proposed and investigated, the N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide ($PYR_{14}FSI$) appears as one of the most interesting. $PYR_{14}FSI$ displays high conductivity (>4 mS cm^{-1} at 20 °C) and an electrochemical stability window wider than 5.5 V [13]. In addition, because of the presence of the anion FSI^- it also displays SEI film forming abilities [14]. For these reasons, we considered this ionic liquid as the most attractive candidate for lithium ion battery electrolytes.

Another important aspect concerning safety and environmental impact of the present battery technology is related with the

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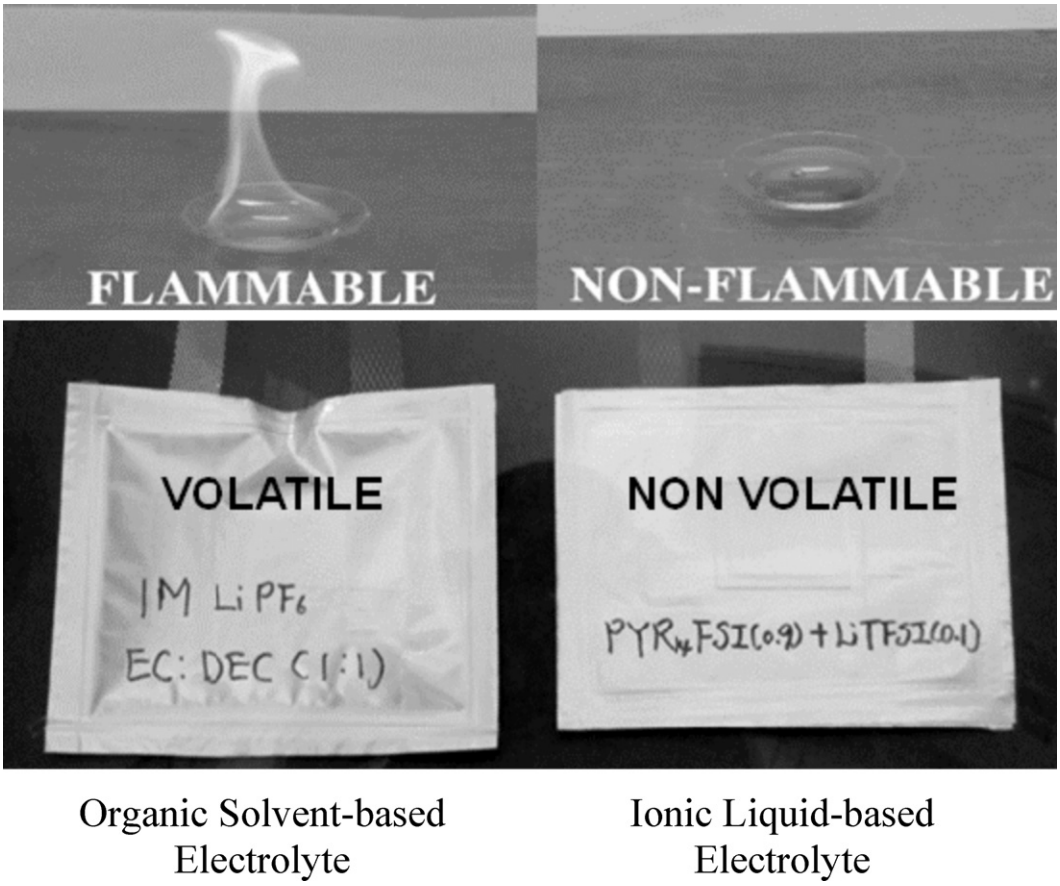

Fig. 1. Flammability and volatility tests performed on organic solvent- and ionic liquid-based electrolytes. The upper images show the results of the flammability tests performed by exposing the two electrolytes to a LPG flame for 2 s. The lower images show the effect of vacuum on two identical pouch cells based on the different electrolytes placed under vacuum in the same vacuum chamber.

electrode manufacturing. In fact, present electrode manufacturing frequently involves the use of polyvinyliden-di-fluoride (PVdF) binder that requires the use of volatile organic compounds for the processing such as N-methyl-pyrrolidone (also named as NMP). These solvents are not only expensive, but also environmentally harmful and toxic thus introducing safety concerns in the manufacturing process. In addition, PVdF is a relatively costly polymer (industrial cost in the multiton scale is around 15–18 EUR kg^{-1}) and not easily disposable at the end of the battery life. For these reasons, the substitution of PVdF with a cheaper and more environmental-friendly binder would be very welcome.

In the last few years, alternative binders have been introduced for the manufacturing of anodes for lithium ion-batteries [15–27]. Between them, one of the most interesting is certainly the sodium salt of CarboxyMethylCellulose (CMC). CMC is produced by the insertion of carboxymethyl groups in natural cellulose. The presence of these groups makes the CMC water-soluble. This is certainly the greatest advantage of CMC since it allows the processing in aqueous slurries rather than in polluting, health and environment unfriendly, volatile organic compound-based slurries. The second great advantage of CMC resides in the easy disposability at the end of the battery life. Once the electrode is extracted, the active electrode material can be easily recovered by pyrolysis of the binder. Last but not least, the material cost. CMC industrial price is about 1–2 EUR kg^{-1}, i.e., about one order of magnitude lower than PVdF.

Recent works showed that CMC can be used as a replacement for PVdF in lithium iron phosphate ($LiFePO_4$) based electrodes [28–32]. The excellent results of these studies indicated that the introduction of CMC as binder is a viable and extremely promising solution toward the environment-friendly preparation of cathode electrodes based on $LiFePO_4$ as the active material. If the use of non-volatile ionic liquid-based electrolytes is also contemplated in the battery system, than the possibility to develop safer and greener lithium ion batteries is fully open, where not only the safety of the systems, but also the safety of the overall batteries preparation process is enhanced.

This manuscript is focused on the study of the performance of a lithium ion battery containing CMC as binder both for cathode and anode, using an electrolytic solution based on ionic liquids. The considered battery contains $Li_4Ti_5O_{12}$ and $LiFePO_4$ at the anode and cathode, respectively, which are also considered to be safe and environment-friendly materials. The electrolytic solution is based on the ionic liquid $PYR_{14}FSI$. The results of the electrochemical tests carried out at 20 °C and 40 °C on this safe and green battery are reported in this paper.

2. Experimental

2.1. Synthesis of $PYR_{14}FSI$

The $PYR_{14}FSI$ room temperature ionic liquid was synthesized and dried as reported in [11].

2.2. TGA

Thermo gravimetric measurements were carried out using a Q 5000 IR TGA instrument (TA Instruments). High-temperature platinum pans loaded with 10–20 mg samples were used for the tests.