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Development of ionic liquid-based lithium battery prototypes

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ABSTRACT

The lab-scale manufacturing of Li/$LiFePO_4$ and $Li_4Ti_5O_{12}$/$LiFePO_4$ stacked battery prototypes and their performance characterization are described here. The prototypes were realized in the frame of an European Project devoted to the development of greener and safer lithium batteries, based on ionic liquid electrolytes, for integration with photovoltaic panels. *N*-Butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR_{14}TFSI) and *N*-butyl-*N*-methylpyrrolidinium bis(fluoromethanesulfonyl)imide (PYR_{14}FSI), selected as the ionic liquids (ILs), were used to formulate the poly(ethylene oxide)-$LiN(SO_2CF_3)_2$-PYR_{14}TFSI (PEO-LiTFSI-PYR_{14}TFSI) polymer electrolyte and the LiTFSI-PYR_{14}FSI liquid electrolyte, which were employed to produce lithium metal and lithium-ion prototypes, respectively. The composite electrodes for the lithium metal and lithium-ion prototypes were prepared through, respectively, a solvent-free and a water-based procedure route. The performance of the lithium battery prototypes was evaluated in terms of specific capacity, energy, cycle life and coulombic efficiency at different current densities. The results have indicated high reproducibility and the feasibility of scaling-up solvent-free, lithium batteries based on ionic liquids for low and mid rate applications such as renewable energy storage.

1. Introduction

Ionic liquids (ILs), organic/inorganic salts generally molten at room temperature, represent a very interesting new class of room temperature fluids since their non-flammability, negligible vapor pressure in conjunction with remarkable ionic conductivity, high thermal, chemical and electrochemical stability, high heat capacity and, in some cases, hydrophobicity [1]. Because of these unique properties ILs are excellent candidates as electrolytes and/or electrolyte components to replace volatile and hazardous organic solvents (alkyl carbonates) in lithium batteries.

Ionic liquids based on saturated, cyclic, quaternary ammonium cations as *N*-alkyl-*N*-methyl-pyrrolidinium (PYR_{1A} where the subscripts indicates the number of carbons in the alkyl side chains, alkyl = n-propyl, n-butyl), and bis(trifluoromethanesulfonyl)imide (TFSI) or bis(fluoromethanesulfonyl)imide (FSI) as the anion have been successfully proposed for use in lithium batteries since their sub-ambient melting temperature, high room temperature conductivity, suitable electrochemical stability [2–5]. The last characteristic originates from the absence of acidic protons and double bounds that would strongly deplete the electrochemical stability and compatibility with the lithium metal anode [2,6,7]. Therefore, LiX-PYR_{1A}X (X = FSI or TFSI, A = propyl, n-butyl) mixtures have been extensively investigated, showing very good cycling reversibility into lithium [8] and graphite [9–12] anodes, and $LiCoO_2$ cathodes [13]. Particularly, PYR_{14}FSI-LiTFSI mixtures have been recently employed as electrolytes in $Li_4Ti_5O_{12}$/$LiFePO_4$ lithium-ion cells, which have displayed very good cycling performance [14,15].

Moreover, it was successfully demonstrated [16–19] that the incorporation of PYR_{1A}TFSI ionic liquids (mainly PYR_{14}TFSI) into solid polymer electrolytes (SPEs) largely enhances the room temperature ionic conductivity (above $10^{-4}\,S\,cm^{-1}$ at 20 °C) while maintaining wide electrochemical stability and good compatibility towards the lithium metal anode even after prolonged storage times. The addition of ionic liquids allowed reducing the operative temperature of lithium metal polymer batteries (LMPBs) without depleting their performance [20–22]. Recently, it was shown that UV cross-linking allows incorporating higher ionic liquid amounts into the polymer electrolyte, thus further enhancing the ionic conductivity (e.g., $3.7 \times 10^{-4}\,S\,cm^{-1}$ at 20 °C) without depleting its electrochemical and mechanical properties [23].

In this scenario, we decided to investigate the scale-up of lithium cells based on two different chemistries: (i) Li/$LiFePO_4$ (*high energy*)

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lithium metal polymer cells using an UV cross-linked PEO-LiTFSI-PYR_{14}TFSI membrane as the electrolyte and, (ii) $Li_4Ti_5O_{12}/LiFePO_4$ (*room temperature*) lithium-ion cells using a PYR_{14}FSI-LiTFSI electrolyte mixture. The objective was to realize greener and safer lithium cell prototypes having a capacity up to 1 A h for low-mid rate applications such as renewable energy storage. The use of non-flammable, non-volatile, ionic liquid-based (polymer or not) electrolytes is, in fact, expected to largely improve the safety of lithium battery systems. For the Li-ion prototype, the safety level results further enhanced by the use of lithium titanate (instead lithium metal) as anode active material. $Li_4Ti_5O_{12}/LiFePO_4$ cells are considered among the safest, if not the safest, lithium-ion battery chemistry. In addition, it should be pointed that the composite electrodes were made using the fluorine-free, water-soluble, natural binder carboxymethylcellulose sodium salt (CMC) instead of the more expensive and less environmentally friend polyvinyliden-di-fluoride (PVdF). Thus, the lithium-ion electrode manufacturing involved the use of water as the only solvent [14,15] in the place of the hazardous, toxic and much more expensive N-methyl-pyrrolidone (NMP). The use of CMC allows not only low cost and environmentally friend manufacturing processes but also easier recycle of the battery components. The dissolution in water of the binder allows, for example, a full recovery of the metallic current collectors [14,15].

In the present paper we report the characteristics and the cycling performance of rechargeable, $Li/LiFePO_4$ (LMPB) and $Li_4Ti_5O_{12}/LiFePO_4$ (LIB) stacked battery prototypes.

2. Experimental

2.1. Synthesis of ionic liquid materials

The *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, PYR_{14}TFSI, and *N*-butyl-*N*-methylpyrrolidinium bis(fluoromethanesulfonyl)imide, PYR_{14}FSI, ionic liquids were synthesized through a procedure route developed at ENEA [24,25]. The chemicals *N*-methylpyrrolidine (ACROS, 98 wt%) and 1-bromobutane (Aldrich, 99 wt%) were previously purified through activated carbon (Aldrich, Darco-G60) and alumina (Aldrich, acidic, Brockmann I) before the synthesis process. The LiTFSI (3 M, 99.9 wt%) and KFSI salts (99.9 wt%, Dai-ichi Kogyo, Seiyaku Co., Ltd, Japan), activated carbon, alumina and ethyl acetate (Aldrich, >99.5 wt%) were used as received. The synthesized ionic liquids exhibited water content below 2 ppm and other impurities below 100 ppm as determined by Karl-Fischer, ICP-OES and ion chromatography techniques.

2.2. Preparation of cross-linked PEO electrolytes and lithium metal cell cathodes

A solvent-free, hot-pressing process developed at ENEA [23] was followed to prepare the cross-linked PEO-LiTFSI-PYR_{14}TFSI ternary solid polymer electrolytes and the $LiFePO_4$ composite cathodes. The process was performed in a very low relative humidity dry room (R.H. < 0.1% at 20 °C). For the SPE samples, LiTFSI (3 M, 99.9 wt%) and PYR_{14}TFSI were dried under vacuum at 120 °C for at least 18 h before use while poly(ethylene oxide) (PEO, Dow Chemical, WSR 301, $M_W = 4,000,000$) was dried at 50 °C for 48 h. Benzophenone (Bp, Aldrich) was used (as received) as the initiator for the cross-linking process. The Bp/PEO weight ratio was kept equal to 0.05 [23] while the $(PYR_{14})^+/Li^+$ mole ratio was fixed equal to 2 [23]. Firstly, Bp was dissolved in PYR_{14}TFSI by heating under vacuum. PEO and LiTFSI (EO/Li mole ratio = 10) [19] were mixed in a mortar and, then, added to the Bp/PYR_{14}TFSI solution. After complete blending, the PEO-LiTFSI-PYR_{14}TFSI-Bp mixture was annealed under vacuum at 100 °C for several hours to obtain a homogeneous, plastic-like material. The latter was sandwiched between two Mylar foils and, then, hot-pressed at 70 °C and 180 kg cm^{-2} for 7–8 min to obtain thin tapes of about 0.1 mm thickness. Finally, the polymer electrolyte tapes (9.0 cm × 6.0 cm) were cross-linked by UV irradiation (UV Karl-Suss MA 45 photo-irradiator equipped with a 350 W Hg lamp) for 8 min (4 min for each side). The final weight composition of the cross-linked electrolytic tapes was 35.0 wt% PEO, 10.0 wt% LiTFSI and 55.0 wt% PYR_{14}TFSI.

Cross-linked, composite, cathode tapes were prepared by intimately mixing carbon-coated $LiFePO_4$ (43% in weight, Süd Chemie, average particle size: 0.3 μm, carbon content: 2.3 wt%) and carbon (KJB, Akzo Nobel, 7 wt%) which were previously dried in a vacuum oven at 120 °C for at least 24 h. PEO, LiTFSI and PYR_{14}TFSI were dried as well as for the SPE tapes. Then, PEO (17.5 wt%), LiTFSI (5.0 wt%) and PYR_{14}TFSI (27.5 wt%) and Bp (Bp/PEO weight ratio = 0.05) were separately mixed to obtain a paste-like mixture, which was added to the previous $LiFePO_4$/C blend. The final cathodic mixture was firstly vacuum annealed at 100 °C overnight and, then, cold-calendared to form about 0.05 mm thick cathode films. Finally, the cathode tapes (8.0 cm × 5.0 cm) were UV photo-irradiated for 8 min (4 min on each side) by using a Karl-Suss MA 45 equipment. The active material mass loading approaches 4.5 mg cm^{-2}, corresponding to 0.75 mA h cm^{-2} (e.g., considering the $LiFePO_4$ theoretical capacity equal to 170 mA h g^{-1}). The composite cathodes as well as the cross-linked electrolytes exhibited a water content below 20 ppm.

2.3. Preparation of lithium-ion cell electrodes

Carbon-coated $LiFePO_4$ (average particle size: 0.3 μm, carbon content: 2.3 wt%) and uncoated $Li_4Ti_5O_{12}$ (average particle size: 2 μm), both provided by Süd Chemie, were used as received. Sodium-carboxymethylcellulose (CMC, Dow Wolff Cellulosics, Walocel CRT 2000 PPA 12) with a degree of substitution of 1.2 was used as the binder whereas Super-P carbon (TIMCAL, average particle size: 30 nm) was used as the electronic conducting agent. $LiFePO_4$ and $Li_4Ti_5O_{12}$ electrodes were prepared following a common recipe [14,15]. CMC was firstly dissolved in deionized water by magnetic stirring at room temperature. The required amount of Super-P was then added to the aqueous solution containing CMC and the resulting mixture was ball milled in a zirconia jar loaded with 5 mm zirconia balls. The mixing was performed for more than 1 h with a planetary ball miller (Fritsch, Pulverisette 4; rotation speed: 800 rpm). The selected amount of active material was then added to the mixture and the resulting slurry was homogenized by ball milling at room temperature for one additional hour. During the preparation of the lithium titanate anodes, 0.025 g of formic acid per gram of active material was introduced to neutralize (pH = 7) the slurry, which had a very basic character, in order to prevent corrosion phenomena at aluminium current collectors. The so-formed slurries were cast onto both the faces of Al foils (30.0 cm × 15.0 cm, 20 μm thick, purity >99.9%) by using a laboratory scale blade coater to obtain double-side coated electrodes. A pre-drying in an atmospheric oven with stagnant air at 80–100 °C for 1 h was applied after coating each side of the current collector. Double-side coated electrodes having an overall electrochemically active area of 80 cm^2 (8.0 cm × 5.0 cm each face) were cut and, finally, dried at 180 °C under vacuum for 24 h. The dry material composition of the cathode was 88 wt% $LiFePO_4$, 8 wt% Super-P and 4 wt% CMC whereas that of the anodes was 87 wt% $Li_4Ti_5O_{12}$, 8 wt% Super-P and 5 wt% CMC. The dry thickness of the cathode and anode materials was about 40 μm on each side of the current collector corresponding to an average active material mass loading ranging from about 5.0 mg cm^{-2} to 5.5 mg cm^{-2}, i.e., corresponding to a capacity of 0.85–0.95 mA h cm^{-2} by considering the