



Short communication

Characteristics of an ionic liquid electrolyte for sodium-ion batteries

Ivana Hasa^a, Stefano Passerini^{b, c}, Jusef Hassoun^{a, d, *}^a Department of Chemistry, "Sapienza" University of Rome, Piazzale Aldo Moro, 5, 00185 Rome, Italy^b Helmholtz Institute Ulm, Helmholtzstraße 11, 89081 Ulm, Germany^c Karlsruhe Institute of Technology (KIT), PO Box 3640, 76021 Karlsruhe, Germany^d University of Ferrara, Department of Chemical and Pharmaceutical Sciences, Via Fossato di Mortara 17, 44121 Ferrara, Italy

HIGHLIGHTS

- Pyr₁₄TFSI-NaTFSI IL-electrolyte is characterized for sodium-ion battery.
- The IL-electrolyte has high sodium conductivity and thermal stability.
- The suitability of the IL-electrolyte is verified in sodium half cells.
- The cells employ P2-Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O₂ cathode and nanostructured Sb–C anode.
- A full sodium-ion cell combining the two electrodes is studied.

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ABSTRACT

We study the liquid mixture of sodium bis(trifluoromethanesulfonyl)imide in N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI-NaTFSI) for application in sodium-ion batteries. The ionic liquid-based electrolyte is characterized in terms of electrochemical and thermal properties. Ionic conductivity and electrochemical stability windows are evaluated through electrochemical impedance spectroscopy (EIS) measurements and voltammetry tests, respectively. The thermal stability is evaluated by differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA). Moreover, the suitability of the IL-electrolyte is preliminary verified in half and in full-cells at room temperature, using P2-Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O₂ layered oxide cathode and nanostructured Sb–C composite anode. The cell shows promising characteristics with a working voltage of about 2.7 V and a delivered capacity of about 100 mAh g⁻¹. Despite requiring further optimization in terms of cycle life and energy density, the data here reported suggest the suitability of the ionic liquid electrolyte for application in sodium-ion battery.

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1. Introduction

The rapid growth of the electricity grids, the urgent need for energy as well as the global warming are presently triggering increasing interest on renewable and environmental-friendly energy systems, such as solar and wind. However, these intermittently operating systems require decentralized supports for energy storage to ensure the grid stability [1]. Batteries represent the most promising electrochemical energy storage systems. In particular, lithium-ion batteries (LIBs) are considered the power sources of

choice due to their high energy density, efficiency and long life [2,3]. The great success of lithium-ion batteries, particularly in portable electronics, has led to a large-scale diffusion of these energy storage systems and they are now considered, also, as the best choice for powering hybrid and electric vehicles [4]. However, the already implemented automotive application and the expected grids employment will result in a continuous growing demand of this promising battery technology, leading to increasing lithium price [5], in particular considering the limited geographical resources of lithium brines and issues related to its future availability [6]. These issues triggered rising interest on alternative chemistries for energy storage application, such as sodium and, in general, alkali metals-based batteries. The recent rapid growth of the research focused on sodium-ion batteries, initially based on low-cost and abundance of raw materials, is suggesting this rechargeable system as the most

* Corresponding author. University of Ferrara, Department of Chemical and Pharmaceutical Sciences, Via Fossato di Mortara 17, 44121 Ferrara, Italy.

E-mail address: jusef.hassoun@unife.it (J. Hassoun).

promising for the development of the new-sustainable-energy storage market [7–10]. Indeed, sodium-ion batteries are presently considered suitable choice in order to meet the large-scale requirements for energy storage, in particular from renewable energy plants requiring low operative costs. Several efforts have been devoted to develop electrode materials and electrolyte solutions for Na batteries [11,12]. Among the cathodes, sodium transition metal layered oxides, studied since 1970s–1980s [13] in parallel with lithium, recently attracted renewed interest as reversible insertion cathode materials. These electrodes show several advantages, including simple synthesis, suitable potentials for Na-ion intercalation within the layers and satisfactory capacity values [14]. However, oxides such Na_xCoO_2 [15], Na_xCrO_2 [16], Na_xFeO_2 [17] and Na_xMnO_2 [18], have revealed poor capacity and cycling stability. The partial introduction of electrochemically active and/or inactive transition metals is revealing as a possible strategy to enhance the electrochemical performance of Na-ion layered cathodes [14,19]. In addition, high performance anodes, in replacement of sodium metal, may represent a key factor in determining the diffusion of safe Na-ion batteries. Sodium alloying materials, such as Sn, Sb and Pb, conversion oxides and Na-insertion materials, such as amorphous carbons and poly-anionic compounds, are the most promising candidates as Na-ion anodes [20–23]. Furthermore, suitable electrolytes, characterized by the formation of a stable solid electrolyte interphase (SEI) film as well as by high safety content are required to fully develop such an attractive system [24]. The employment of common organic liquid electrolytes may be potentially hazardous due to their high flammability and volatility. Instead, room temperature ionic liquids (RTILs) represent an intriguing class of electrolytes in view of their intrinsic safety properties. RTILs are characterized by high ionic conductivity and satisfactory electrochemical stability window. Furthermore, the excellent thermal stability, the non-flammability and non-volatility, make them appealing for alternative Na-ion batteries [25]. Several IL-based mixtures have been investigated as electrolytes media for application in sodium-ion batteries, revealing interesting electrochemical properties. However, large part of the reported studies focused on the use of ionic liquid based electrolyte in sodium half-cells employing metallic sodium as anode and various cathode materials, including NaFePO_4 [26,27], NaCrO_2 [28], $\text{Na}_{0.44}\text{MnO}_2$ [29] and $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ [30]. C. Ding et al. [31] recently reported a study on full-cell employing hard carbon as anode and NaCrO_2 as cathode operating at 90 °C exhibiting a Coulombic efficiency higher than 99%. However, to the best of our knowledge, investigations on the use of room temperature ILs-based electrolytes employed in full sodium-ion cell using an alternative anode material to have been not yet reported. Accordingly, we report in this paper an electrolyte formed by mixing two salts, one bearing the sodium cation (NaTFSI) and the other being an ionic liquid ($\text{Pyr}_{14}\text{TFSI}$), as safe medium suitable for sodium-ion battery in terms of conductivity, sodium transport properties, electrochemical and thermal stability. The solution is characterized, with promising results, in sodium half-cells using P2-type $\text{Na}_{0.6}\text{Ni}_{0.22}\text{Fe}_{0.11}\text{Mn}_{0.66}\text{O}_2$ transition metal layered oxide and nanostructured Sb–C Na-alloying electrode, as well as in full Na-ion cell coupling the two electrodes at room temperature.

2. Experimental

2.1. Material synthesis and characterization

P2-type layered $\text{Na}_{0.6}\text{Ni}_{0.22}\text{Fe}_{0.11}\text{Mn}_{0.66}\text{O}_2$ was obtained following a wet chemistry route described in detail in our previous works [32,33]. Briefly, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in water in stoichiometric proportions. In a second

step, the solid-state reaction between the nickel-iron-manganese hydroxide precursor and NaOH, as sodium source, was conducted at 900 °C. Finally the material was subjected to water rinsing process. The nanostructured Sb–C composite material synthesis consisted in the infiltration of an organometallic antimony precursor, triphenylantimony (III) (Aldrich, 99%), in an organic resorcinol (benzene-1,3-diol)–formaldehyde (methanol) gel. The gel was washed with tert-butanol and immersed in a solution of triphenylantimony(III) (Aldrich, 99%), toluene (Aldrich, puriss.) and tert-butanol, in a mass ratio of 1:1:4. The recovered gel was annealed at 700 °C under argon flux for three hours [21,34]. The ionic liquid, i.e., N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($\text{Pyr}_{14}\text{TFSI}$) (99.9%) and the corresponding sodium salt (NaTFSI) (99.9%) were purchased from Solvionic. The water content of the room temperature ionic liquid was determined by Karl-Fisher titration and found to be <10 ppm. NaTFSI was vacuum dried overnight at 120 °C and then dissolved in $\text{Pyr}_{14}\text{TFSI}$ obtaining a 0.2 m (NaTFSI: $\text{Pyr}_{14}\text{TFSI}$ = 0.085:1 mol ratio) electrolyte solution. Differential scanning calorimetry (DSC) measurements were performed on the pure $\text{Pyr}_{14}\text{TFSI}$ ionic liquid and on the 0.2 m NaTFSI added electrolyte, using a DSC 821 (Mettler-Toledo). Samples were previously sealed in Al crucible under inert atmosphere in an argon-filled glove box. Measurements were performed initially heating the sample up to 80 °C at 5 °C min^{-1} to get a fully melt sample. Following, cold annealing cycles between –150 °C and –25 °C (2 cycles) and –15 °C (1 cycle) were performed with isothermal steps of twenty minutes at the high temperature value. Finally the samples undergone two heating cycles from –150 °C to 80 °C. The procedure allows the samples to fully crystallize obtaining more reproducible thermal behavior.

Thermogravimetric analysis (TGA) was carried out under N_2 flux (60 ml min^{-1}) from room temperature to 600 °C at 10 °C min^{-1} scan rate.

2.2. Electrochemical characterization

The $\text{Na}_{0.6}\text{Ni}_{0.22}\text{Fe}_{0.11}\text{Mn}_{0.66}\text{O}_2$ and Sb–C electrodes were prepared by dispersing the active material (80% w/w), carbon black super P (Imerys, 10% w/w) and polyvinylidene fluoride (PVdF 6020, Solvay, 10% w/w) in N-methyl-2-pyrrolidone (NMP, Aldrich). The resulting slurries were cast on aluminum and copper foils, respectively, by doctor-blade technique. After drying at 70 °C to remove the NMP, punching of 10 cm-diameter disks and drying at 110 °C under vacuum for 3 h, the electrodes were stored in an argon-filled glove box with a H_2O and O_2 content lower than 1 ppm. The electrochemical tests were run on Swagelok-type cells, assembled in argon-filled glove box. Sodium metal was cut from sodium pieces (Alfa Aesar), roll pressed, punched on the current collector and used for the counter and reference electrodes. Sodium half-cells were assembled by using 0.2 m NaTFSI- $\text{Pyr}_{14}\text{TFSI}$ electrolyte impregnated in a glass fiber (Whatman) separator. The electrochemical stability windows of the electrolyte was evaluated by cyclic voltammetry (CV) for the cathodic scan and by linear sweep voltammetry (LSV) for the anodic scan, employing a three electrode cell using sodium as counter and reference electrode and Super-P (Imerys) cast on Cu (cathodic scan) or on Al (anodic scan) as working electrode. Tests were performed at room temperature at 0.1 mV s^{-1} scan rate using a VSP multipotentiostat Biologic Science Instrument.

Ionic conductivity was determined from room temperature to 90 °C by electrochemical impedance spectroscopy (EIS) measurements, using a Bistat Biologic Science Instrument. A 5 mV amplitude signal was applied to a two blocking stainless steel electrode cell within the 200 kHz to 100 MHz frequency range. The Nyquist plots, not reported in here, consisted of an inclined line, which high

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