

Electrolyte based on 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulphonyl)imide for Li-ion batteries



Agnieszka Swiderska-Mocek*

Faculty of Chemical Technology, Poznań University of Technology, PL-60 965 Poznań, Poland

ARTICLE INFO

Article history:

Received 10 January 2014

Received in revised form 3 March 2014

Accepted 28 March 2014

Available online 6 April 2014

Keywords:

Ionic liquid

1-ethyl-3-vinylimidazolium

bis(trifluoromethanesulphonyl)imide

Lithium-ion battery

Graphite anode

LiFePO₄ cathode

ABSTRACT

In this study, a new electrolyte for Li-ion batteries in the form of lithium salt solution in ionic liquid (IL) based on imidazolium cation with vinyl group is reported. This electrolyte was obtained by dissolution of solid lithium bis(trifluoromethanesulphonyl)imide (LiNTf₂) in 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulphonyl)imide (EVImNTf₂). 1 M LiNTf₂ in the EVImNTf₂ electrolyte has good cathodic stability (the presence of the vinyl group) and flash point above 220 °C, which makes it practically non-flammable. The olivine-type lithium iron phosphate (LiFePO₄, LFP) cathode and the graphite-lithium anode working together with the electrolyte were tested with the use of cyclic voltammetry (CV), galvanostatic charge/discharge cycles and electrochemical impedance spectroscopy (EIS). The surface morphology of electrodes was studied using scanning electron microscopy (SEM). Charge/discharge tests of LiFePO₄/1 M LiNTf₂ in the EVImNTf₂/Li cell at different C rates exhibited a good specific capacity of 115 mAh g⁻¹ and 110 mAh g⁻¹ at 0.5 C and 1.0 C, respectively. The graphite anode showed good cyclability (307 mAh g⁻¹ after 40 cycles) and coulombic efficiency (94%). The efficiency of the full LFP|electrolyte|G cell charging/discharging under study was high (ca. 125 mAh g⁻¹ after 30 cycles).

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The fundamental advantage of Li-ion batteries is their exceptionally high energy density (up to 180 Wh kg⁻¹), resulting from a high working voltage (typically 3.6–3.8 V) and a long cycle life. Lithium ion batteries are not only to be used in electronic devices (mobile phones, digital cameras and notebook computers), but also applied in vehicles [1–3]. In these batteries the electrolyte reacts with electrodes by the formation of a passivation layer. This layer is usually called the solid electrolyte interphase (SEI) and protects them against further corrosion [1,2]. The protective layer formed in such systems is responsible for the chemical stability of the anode and the cathode [4–8]. Li-ion battery anodes are generally prepared of graphite with a theoretical capacity of 372 mAh g⁻¹. For the negative electrode material graphite is preferred, due to its stable cycling properties and its improved safety compared to the lithium anode. The fact that graphite electrodes can function is due to the use of electrolytes containing ethylene carbonate (EC). Electrolytes based on EC, commonly used as a SEI-forming component, have certain limitations, such as poor

low temperature behaviour. On the other hand, use of propylene carbonate (PC), which is potentially a good alternative, always results in exfoliation of graphite, electrolyte decomposition and liberation of organic gas in the battery [9]. However, linear and cyclic carbonates are flammable because they have low boiling points (below 150 °C) and low flashing points (below 30 °C). These solvents are disadvantageous from the point of view of safety. Ionic liquids (ILs) have been attracting interest for lithium and lithium-ion batteries, as they show considerable thermal stability, a wide liquid-phase range, broad electrochemical stability and they exhibit high conductivity [10–12]. They show a much reduced flammability and a nearly non-existent vapour pressure even at elevated temperatures [13–21]. Among ILs, those based on 1-ethyl-3-methylimidazolium [EtMeIm⁺], N-alkyl-N-methylpyrrolidinium [RMePyr⁺] and N-alkyl-N-methylpiperidinium, [RMePip⁺] cations and the bis(trifluoromethanesulphonyl)imide anion, [NTf₂⁻] seem to be promising solvents for lithium salts in Li-ion batteries. It is observed that these electrolytes were compatible with the graphite, LaSi₂/Si and TiO₂ nanotube anodes [14,16,17,19,21–23] and LiCoO₂, LiFePO₄, Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ and LiNi_{0.5}Mn_{1.5}O₄ cathodes [15,16,20,24–26]. Recently, ionic liquids based on imidazolium and piperidinium cations with vinyl or allyl groups and [NTf₂⁻] anion are of great interest as co-solvents for the Li-ion battery (LiNi_{0.5}Mn_{1.5}O₄ and LiFePO₄ [27,28]).

* Corresponding author.

E-mail address: agnieszka.swiderska-mocek@put.poznan.pl

Olivine-type lithium iron phosphate LiFePO_4 (LFP) is one of the most promising cathode materials for use in the new-generation Li-ion batteries. LiFePO_4 is very attractive due to its high theoretical capacity (170 mAhg^{-1}), thermal stability and long cycling life [29–31]. In addition, LFP is low-cost and exhibits high intrinsic safety (the strength of the P–O covalent bond rule out any risk of oxygen release) [2]. A major disadvantage of LiFePO_4 is its low electronic conductivity ($\sim 10^{-9} \text{ Scm}^{-1}$) which controls the transfer of Li^+ ions upon lithium insertion/deinsertion [32,33]. To increase the conductivity of the LiFePO_4 particles, cover them with thin layers of carbon or add conductive metallic phases [34,35].

Lithium, lithiated graphite and most cathode materials are usually unstable in contact with ionic liquid-based electrolytes. Hence, solvent-free ILs may be used as electrolytes provided that they contain additives, as electrolyte additives participate in the formation of SEI films [8]. Molecular additives, such as vinylene carbonate (VC) [14,16,17,19,21,34,36,37], chloride EC (Cl-EC) [34,38], vinyl ethylene carbonate (VEC) [39], fluoro ethylene carbonate (FEC) [34,36], vinyl acetate (VA) [35,40], tris(pentafluorophenyl) borane [41] and ethylene sulphite (ES) [14,34,35,40] have been used in ILs as SEI-forming agents and exhibited good performance. The most popular ionic liquids, based on the 1-ethyl-1-methylimidazolium cation (EMIm^+) and bis(trifluoromethanesulphonyl)imide anion (NTf_2^-), do not efficiently show the negative limit of the electrolyte cathodic decomposition and the reduction of EMI cations prevents lithium ion insertion into graphite layers to form LiC_6 compounds. However, the graphite anode may be reversibly intercalated from the ionic liquid at the presence of the polymerizable monomer additive such as vinylene carbonate (VC) [14,16]. Vinyl- and oxy-group additives such as VC give the best results in the formation of a protective layer on graphite. The main function of the vinyl-group is electrochemical polymerization on the graphite surface during SEI film formation.

The general aim of the present work was to study a new ionic liquid- 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulphonyl)imide (EVImNTf₂) based electrolyte working together with graphite and LFP electrodes. This electrolyte, was obtained by dissolution of solid lithium bis(trifluoromethanesulphonyl)imide (LiNTf_2) in liquid EVImNTf₂.

2. Experimental

2.1. Materials

Graphite SL-20 (G, BET surface area $6.0 \text{ m}^2 \text{ g}^{-1}$, Superior Graphite, USA), lithium iron phosphate (LiFePO_4 , carbon coated, battery grade, BET surface area $15.4 \text{ m}^2 \text{ g}^{-1}$, Aldrich), carbon black (CB, Alfa Aesar), poly(vinylidene fluoride) (PVdF, Fluka), lithium bis(trifluoromethanesulphonyl)imide (LiNTf_2 , Fluka) and 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulphonyl)imide (EVImNTf₂, Iolitec) were used as received.

Liquid electrolyte (1 M LiNTf_2 in EVImNTf₂) was obtained by dissolution of solid LiNTf_2 salt in liquid EVImNTf₂ at room temperature in a dry argon atmosphere in a glove box. Fig. 1 shows the chemical structure of EVImNTf₂. The water content in electrolytes, analyzed with a standard Karl–Fisher titrant (Aldrich), was below 50 ppm.

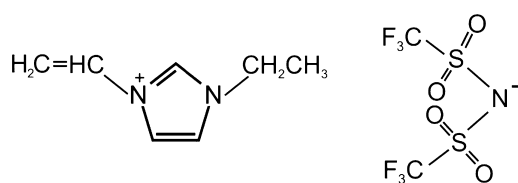


Fig. 1. Chemical structure of EVImNTf₂.

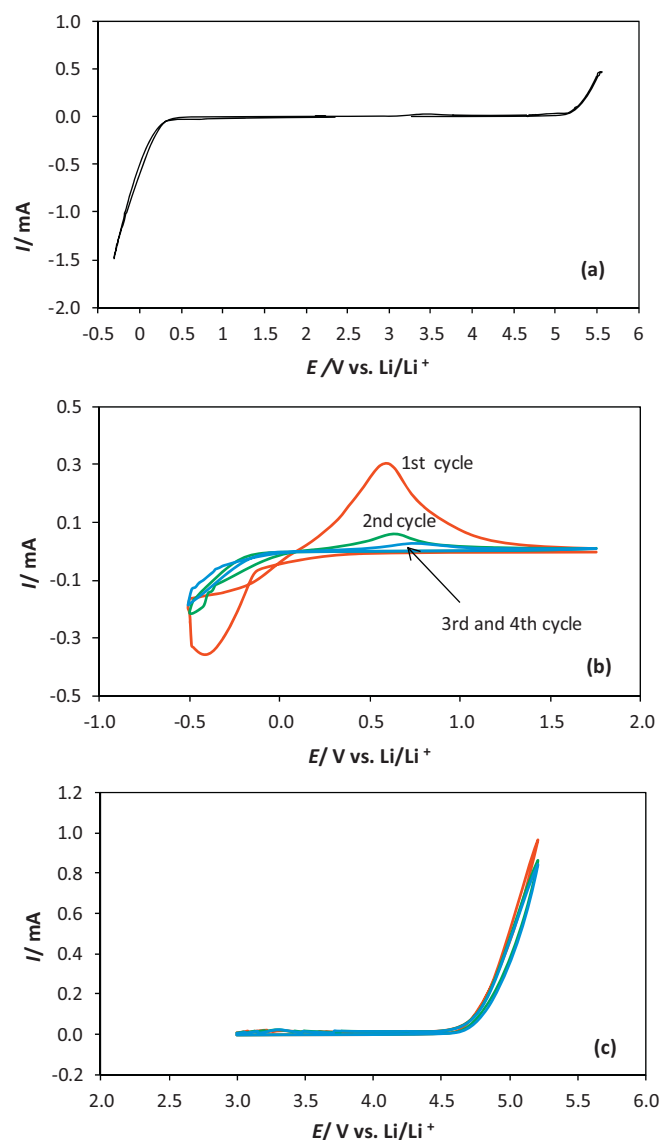


Fig. 2. Cyclic voltammetry of EVImNTf₂ (a) and 1 M LiNTf_2 in EVImNTf₂ (b), (c). Scan rate: 10 mV s^{-1} .

Electrodes were prepared using a casting technique from a slurry of the graphite (G) or LiFePO_4 , carbon black (CB) and PVdF in *N*-methyl-2-pyrrolidone (NMP, Fluka). The ratio of components(G):(CB):(PVdF) and (LFP):(CB):(PVdF) was 85:5:10 (by weight). The layer of the graphite electrode on a copper foil (Hohsen, Japan, area 0.875 cm^2) and the olivine electrode on a golden current collector (area 0.875 cm^2) were formed by vacuum evaporation of the solvent (NMP) at 120°C . The negative electrode typically contained $4.0 \text{ mg} - 4.3 \text{ mg cm}^{-2}$ of graphite. The average mass coating of the LFP was ca. 2.5 mg cm^{-2} . The complete cell weight of the olivine electrode was ca. 9 mg cm^{-2} . A round-shaped lithium electrode was cut off from the metallic-lithium foil (Aldrich, 0.75 mm thick) and was used as the counter and reference electrode.

2.2. Measurements

Cyclic voltammetry as well as electrochemical impedance spectroscopy (EIS) were performed with the use of the G750 Potentiostat/Galvanostat Measurements System (Gamry, USA). The ionic conductivity of electrolytes was measured in a two

Download English Version:

<https://daneshyari.com/en/article/185805>

Download Persian Version:

<https://daneshyari.com/article/185805>

[Daneshyari.com](https://daneshyari.com)