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Ternary polymer electrolytes with 1-methylimidazole based ionic liquids and aprotic solvents

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Abstract

New polymer gel electrolytes containing ionic liquids were developed for modern chemical power sources—supercapacitors and lithium-ion batteries. Ternary systems polymer–ionic liquid–aprotic solvent as well as materials containing also lithium salts ($LiClO_4$ or $LiPF_6$) were prepared by direct, thermally initiated polymerisation. Poly(2-ethoxyethyl methacrylate) PEOEMA was combined with various ionic liquids based on 1-methylimidazole. Only 1-butyl-3-methylimidazolium hexafluorophosphate $BMIPF_6$ formed a homogenous and slightly translucent polymer electrolyte, where aprotic solvents—propylene carbonate and ethylene carbonates were used as plasticisers. Materials were studied using the electrochemical and thermogravimetric methods and exhibit high ionic conductivity up to 0.94 mS cm^{-1} at 25 °C together with high electrochemical stability: the accessible potential window on the glassy carbon was found ca. 4.3 V. Prepared non-volatile materials are long-term and thermally stable up to 150 °C.

Keywords: Polymer gel electrolyte; Ionic liquids; Glassy carbon; Lithium-ion batteries; 2-Ethoxyethyl methacrylate

1. Introduction

Recent technology of modern chemical power sources deals with several limiting factors of further development. Commercialised lithium-ion batteries and supercapacitors usually contain liquid organic compounds and their mixtures, which serve as a solvent for electrolytes (e.g. lithium or alkylammonium salts) [1–3]. This situation brings threat of possible leakage or evaporation of the solvent, what leads not only to decrease of the battery capacity, but is also environmentally hazardous. Commonly used organic solvents like aliphatic carbonates, acetonitrile, tetrahydrofuran or various fluorinated compounds are volatile and flammable. Therefore a new kind of non-flammable and environmentally friendly solvents is required for large size lithium-ion batteries and supercapacitors possibly used in electric or hybrid vehicles.

At the present time, many solid and gel polymer electrolytes are being developed with the aim to substitute the liquid electrolytes in chemical power sources. First attempts were done by M.B. Armand in late 1970s, when the first generation of polymer electrolytes based on poly(ethylene oxide) containing lithium perchlorate was introduced [4,5]. Various polymers, organic solvents and salts were later combined and studied [6–10]. Used materials have to fulfil several requirements: reasonable ionic conductivity, high chemical and electrochemical stability, especially towards oxidation and hydrolysis and have to be available with low content of impurities and water. Aliphatic carbonates (e.g. propylene, ethylene or dimethyl carbonate) are recently used as solvents immobilised in acrylate-based polymers or copolymers due to their sufficient electrochemical stability and low toxicity, when poly(methyl methacrylate) is widely used in the dental praxis. These materials were studied for the first time by Iijima et al. [11], than by Bohnke et al. [12] and also in our laboratory [13–15].

Room temperature ionic liquids (RTILs, ILs), also called room temperature molten salts (RTMS) are promising organic compounds to be used in modern chemical power sources

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[16–18]. They attracted the attention of many researchers due to their excellent properties: high ion content and high conductivity, liquidity in wide temperature range, high thermal stability (up to 400 °C) and low toxicity. Especially for lithium-ion batteries their non-volatility and non-flammability is highly appreciated. However the ionic liquids are known since 1914 (cit. [19]), recently the interest for them increased in 1992, when new compounds with hydrolytically stable ions were introduced by Wilkes and Zaworotko [20]. Generally the ionic liquids can be used in organic synthesis as recyclable "green solvents" [21,22] and they can also serve as conductors in electrochromic devices [23]. Nowadays several ionic liquids were introduced for liquid electrolytes based on aliphatic tetraalkylammonium [24] or aromatic pyrrolidinium and isoquinolinium cations [25]. To improve the electrochemical stability, the organic cation is combined with bulky anion such as tetrafluoroborate, bis((trifluoromethyl)sulfonyl)imide or hexafluorophosphate [26]. Also novel, "inversed" ionic liquids with lithium cation and borate-based anions were also reported [27].

Our recent research is based on previously reported gel electrolytes based on poly(ethyl methacrylate) PEMA and poly(2-ethoxyethyl methacrylate) PEOEMA polymers prepared by UV initiated polymerisation. Reasonably high ionic conductivity, up to 0.23 mS cm^{-1}, was reached in the case of lithium perchlorate solution embedded in the cross-linked PEMA or PEOEMA polymer matrix [28,29]. Both systems exhibited wide potential window (over 4.2 V), and the cross-linkage of the polymer network in the PEMA–PC–$LiClO_4$ system showed positive effect on the ionic conductivity [28].

This paper introduces new conducting polymer electrolytes with embedded ionic liquids. Our work was aimed at development of highly conductive solid electrolyte with suitable properties for lithium-ion batteries and supercapacitors. New, defined way of preparation together with excellent chemical and electrochemical long-term stability of used compounds offers combination of acrylate-based polymer electrolytes with ionic liquids based on 1-methylimidazole. Ternary systems polymer-IL-aprotic solvent (propylene carbonate or mixture of propylene carbonate–ethylene carbonate 50:50, mol%) and quaternary systems polymer–IL–aprotic solvent–lithium salt ($LiPF_6$ or $LiClO_4$) were prepared and studied. Materials were investigated from the electrochemical point of view as well as they were characterised by using thermogravimetric analysis. Composition of all samples was optimised to obtain samples with sufficient mechanical and electrochemical properties. Ternary systems polymer–IL–aprotic solvent can be combined with high-surface carbon materials and used in supercapacitors. Systems polymer–IL–aprotic solvent–lithium salt systems are developed for lithium-ion batteries, when good ionic conductivity and high content of lithium salt is utilized and further improvement of conductivity is reached by employing fourth phase, aprotic organic solvent with high boiling point and wide accessible potential window (PC or PC–EC).

Various hydrophilic as well as hydrophobic ionic liquids were synthesized by Bonhôte et al. [30] and combined with polymers by Fuller et al. [31] and Lewandowski and Swiderska [32]. Materials based on poly(acrylonitrile), poly(ethylene oxide), poly(vinylalcohol) or poly(vinylidene fluoride)–hexafluoropropylene copolymer were prepared by the casting technique, when particular polymers swollen in an organic solvent were mixed with an ionic liquid with consequent evaporation of the solvent. Our method of preparation is based on mixing of the ionic liquid with monomer and the cross-linking agent and subsequent direct polymerisation and formation of cross-linked methacrylate polymer. This method is combining advantages of the exactly defined and uniform composition on contrary to materials prepared by the casting technique. Thermally initiated polymerisation is carried out by using 2,2′-azobis(isobutyronitrile) initiator that is active already at temperature 65 °C and finally produces aprotic compound and nitrogen on contrary to previously used dibenzoylperoxide.

The compatibility of highly polar ionic liquid with generally low polar monomer or polymer is the crucial problem in the sample preparation. Methyl methacrylate and styrene were found to be non-compatible with 1-ethyl-3-methylimidazolium tetrafluoroborate or 1-butylpyridinium tetrafluoroborate due to the phase-to-phase separation [33]. Noda and Watanabe succeed in forming polymer electrolyte with an ionic liquid when using hydrophilic 2-hydroxyethyl methacrylate [33], however this monomer can not be used in aprotic systems for lithium-ion batteries or supercapacitors due to limited electrochemical stability caused by presence of free hydroxyl groups. Morita used more polar aprotic poly(ethylene glycol)-methacrylate)matrix [34]. Solution of this compatibility problem is in using low-volatile aprotic solvent in combination with a hydrophobic, low polar ionic liquid such as 1-butyl-3-methylimidazolium hexafluorophosphate.

2. Experimental

2.1. Materials

Butylbromide (Sigma–Aldrich) was distilled prior to the ionic liquid synthesis. 1-Methylimidazole (Sigma–Aldrich) was used as received. Monomer, 2-ethoxyethyl methacrylate (EOEMA) was obtained from Sigma–Aldrich and purified by distillation under the reduced pressure. Cross-linking agent, ethylene dimethacrylate (EDMA; Sigma–Aldrich) was used as received. The polymerisation initiator, 2,2′-azobis(isobutyronitrile) (AIBN) was purchased from Fluka and recrystallised from chloroform. All monomers and the initiator were stored at 4 °C before use.

Propylene carbonate (Sigma–Aldrich, >99.7%, water content <0.005%) and ethylene carbonate (Sigma–Aldrich) were stored under molecular sieves (3A pellets, Sigma–Aldrich). Acetonitrile (Merck), chloroform (Lachema, Czech Republic) and hexane (Lachema, Czech Republic) were used as received.

Lithium perchlorate (Merck) was dehydrated in vacuum at 110 °C for 48 h and than stored in a desiccator. Ammonium tetrafluoroborate (Sigma–Aldrich), lithium hexafluorophosphate and potassium hexafluorophosphate (both Merck) were used as received. $LiPF_6$ was stored under nitrogen.