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Lithium electrolytes based on modified imidazolium ionic liquids

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ABSTRACT

In this study, new electrolytes for Li-ion batteries in the form of lithium salt solutions in room temperature imidazolium ionic liquids (RTIL) are reported. The ionic liquids applied, for higher reduction potential stability, were substituted at position C2 with oligoethylene groups of various length ($[\text{Im } n\text{EO}]^+\text{X}^-$; where: $n = 0, 3, 7, 20$ and $\text{X} = \text{Cl}, \text{BF}_4, \text{N}(\text{CF}_3\text{SO}_2)_2$). It was found that they are good solvents for lithium salts ($\text{LiBF}_4, \text{LiN}(\text{CF}_3\text{SO}_2)_2, [[\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{O}]_3\text{BC}_4\text{H}_9]\text{Li}$) forming liquid solutions of low glass transition temperature (T_g in the -70 to -40 °C range). Ionic conductivity depends on the length of oxyethylene substituent in $\text{Im } n\text{EO}$ and on the concentration of the salt applied, for 10 mol%, σ_{RT} is of the order of 10^{-4} S cm^{-1} . On the basis of polarization measurements by the variable-current method, the proportion of lithium cations in electric charge transfer (t_{Li}) has been determined. The values obtained (typical for ionic liquids) are low and depend on n and lithium salt concentration but do not exceed a dozen or so percent.

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1. Introduction

Reversible lithium-ion batteries are currently produced on a large scale mainly for powering portable electronic devices, but simultaneously intensive research is carried out on the development of large, high power-source systems for other applications. Lithium-ion and especially lithium batteries, due to high energy density, less self-discharge, and a negligible memory effect are considered promising devices for accumulating energy obtained from renewable sources, load-leveling and also powering hybrid electric vehicles (HEVs), plug-in HEVs and batteries for electric vehicles (EVs) [1–5]. From among the requirements put before batteries, their reliability, especially regarding safety issues is a very

important problem which must be solved to develop large, high power and high voltage lithium batteries [6–8]. The application of ionic liquids instead of volatile and flammable solvents for the lithium salt in the electrolyte allows to solve the problem of battery safety and widens the temperature range of its operation toward high temperatures [9–19]. There has been a lot of research concerning ionic liquids involving imidazolium cation as solvent of lithium salts in electrolytes. In some of them is pointed out the problem of electrochemical stability limited by the susceptibility of the imidazolium cation to the reduction potential, especially due to the presence of an acidic C2 proton [20–23]. The properties of the imidazolium cation can be changed by introducing various types of substituents, such as: aliphatic chains or ether

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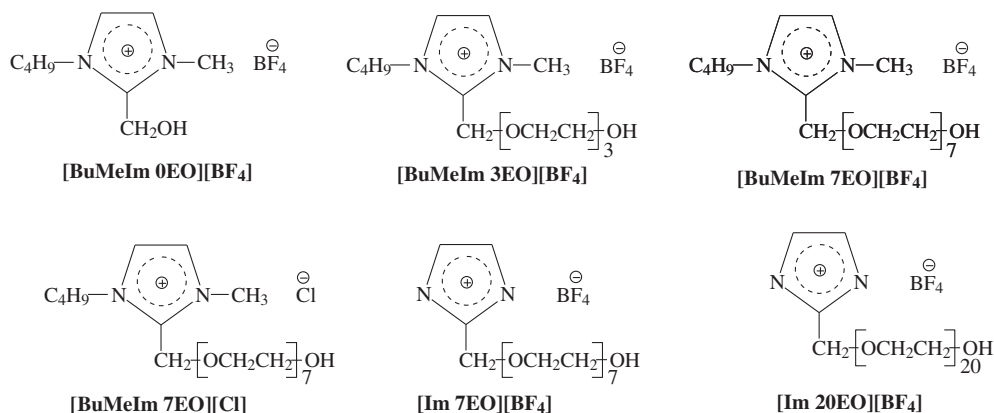
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chains, which can modify the physicochemical properties of the ionic liquids, such as viscosity, melting point, glass transition temperature, surface tension and Lewis acid–base interactions of cation and anion [24,25]. The effects of ethylene oxide (EO) units substituted to nitrogen in imidazolium or pyrrolidinium ring on the thermal and physical properties were investigated earlier [25–28]. It was shown that ether groups were effective in lowering the crystallinity of imidazolium ionic liquid and also in improving the ionic conductivity.

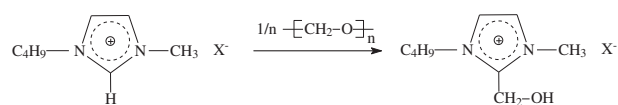
Another problem which limits the electrochemical properties of ionic liquid based electrolytes is the low share of lithium cations in the electric charge transport. Lithium transference numbers in typical liquid systems consisting of LiPF_6 in PC solutions determined by electrochemical polarization or NMR measurements are within the limits 0.3–0.5 [29], whereas in ionic liquids, due to their ionic structure, these transference numbers are much lower and generally do not exceed the value of 0.1 [30,31]. Studies aiming to an increase in t_+ by increasing the salt concentration without causing the crystallization effect for N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl) imide/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) system allowed to reach the value of 0.13 [32]. Apparent transference number of N-butyl-N-methyl-pyrrolidinium cation is significantly higher, it is equal about 0.5.

In this research study, in order to limit the cation mobility, we assumed another strategy consisting in applying ionic liquids with larger organic cation. An increase in the cation mass was achieved by introducing oligooxyethylene groups into the imidazolium ring, and, moreover, the introduction of a substituent at position C2 in the imidazolium ring should favorably affect the electrochemical stability by preventing reactions involving the acidic hydrogen atom present at that position in non-modified salts. Oligooxyethylene groups of various length introduced into the imidazolium ring as described earlier [33] were the substituents used. In Scheme 1 are presented the ionic liquids applied.

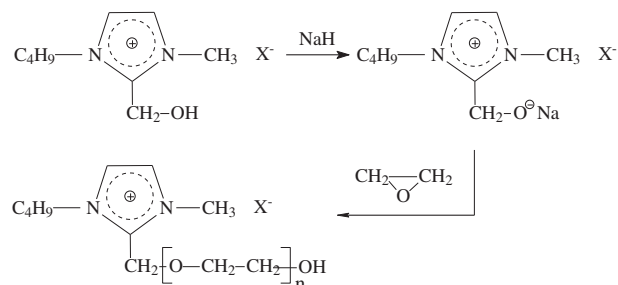
This paper reports on the characterization of a new class of imidazolium-based ionic liquid electrolytes with various anions in the form of solutions with lithium salts. Ionic conductivity, electrochemical stability and for selected electrolytes the lithium cation transference numbers have been determined for the thus obtained systems.



Scheme 1 – Structures of the imidazolium ionic liquids studied.



Scheme 2 – Reaction of 1-butyl-3-methylimidazolium ionic liquids with paraformaldehyde.



Scheme 3 – Synthesis of 1-butyl-2-oligooxyethylene-3-methylimidazolium salts.

2. Experimental

2.1. Synthesis of imidazolium ionic liquids with short polyoxyethylene chains (*Im* nEOs)

Im nEOs were obtained according to the method earlier described, where in the first step a hydroxymethyl group was introduced at position 2 of the imidazolium ring in the reaction of corresponding 1-butyl-3-methylimidazolium ionic liquids with paraformaldehyde, as presented in Scheme 2 [33].

Then, the hydroxyl group is converting into an alkoxide group to initiate anionic polymerization of ethylene oxide (EO) as shown in Scheme 3.

2.2. Experimental techniques

The electrolytes were prepared by dissolving selected lithium salts: LiBF_4 or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Aldrich, anhydrous 99.9%); salts were heated before use for 48 h at 120 °C) in appropriate ionic

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