

Synthesis and properties of new carboxyborate lithium salts as electrolytes for lithium-ion batteries



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ABSTRACT

Bis(carboxytrifluoroborate lithium) salts $[R(\text{CH}_2\text{COOBF}_3\text{Li})_2]$ with oxyethylene groups R of oligomeric molar masses $[R = \text{O}(\text{CH}_2\text{CH}_2\text{O})_n]$, where $n = 3$ or 11, BCB3 and BCB11, respectively] were synthesized via reaction of carboxylates salts with boron fluoride. The new salts were characterized by spectroscopic analysis. The physical properties of the salts were determined by oxyethylene chain length. For $n = 3$ the salt was crystalline with $m_p = 197^\circ\text{C}$ and for $n = 11$ it showed properties of an ionic liquid at ambient temperature. Their thermal stability was at least 250°C . The values of lithium-ion transference numbers (T_+) of the solutions in polar aprotic solvents, determined by a well established steady-state technique, were in the range of 0.2–0.6. Electrochemical impedance spectroscopy analysis of solid polymer electrolytes (SPEs) based on PEO and studied salts with different concentration (from 24 to 94 wt %) was carried out. The ionic conductivity of SPEs was in the order of 10^{-8} – $10^{-7} \text{ S cm}^{-1}$ at room temperature and $10^{-4} \text{ S cm}^{-1}$ at 80°C . A distinguishing feature of SPEs with the studied new salts is the high immobilization of anions, which causes almost a monoconducting character of charge transport. Lithium transference numbers (T_+) exceed 0.9.

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1. Introduction

Lithium-ion batteries (LIBs) are, nowadays, the most widely used power sources for electronic devices for which requirements are continuously increasing in terms of their energy and power density, reliability and cyclability [1,2]. Commercial LIBs as electrolyte employ liquid solutions of LiPF_6 in aliphatic carbonates. These solutions are either introduced into porous separator or they are part of a polymer gel [3,4]. LiPF_6 is characterized by relatively high ionic conductivity and is not corrosive against current collectors, but it is known to be thermally and hydrolytically unstable. Its decomposition results in the formation of HF, which can then act destructively on the chemical components of the cell [5–8].

Recently, several new lithium salts have been proposed that could replace LiPF_6 . These include a whole class of imide salts [9], orthoborate [10], salts containing a superweak aluminate anion [11], phosphorus salts (including LiPF_6 derivatives) [12,13] or chelate-type salts [14] and, recently proposed, imidazolide salts

[15–18]. However, none of these solutions can yet be found commercially. Therefore, studies on new salts are being conducted, in which attention is focused on developing systems with both high diffusion coefficients and high cation transference numbers [19].

The presence of the low-molecular organic solvents in electrolytes causes a serious problem connected with battery operation safety, since they are volatile and flammable. When the temperature inside a device increases, its unsealing can take place. In emergency situations, the solvent vapors may ignite and such cases have already taken place. Due to the required high capacity of the cell, short charging times and large energy densities, there arises an issue associated with efficient removal of considerable amount of generated heat [20]. Therefore, one of the major problems to be solved is the elimination of flammable organic solvents.

Moreover, liquid electrolytes have one more limitation, namely they are characterized by low share of lithium cations in the transport of electric charge. Lithium transference numbers in typical liquid systems consisting of LiPF_6 in PC solutions, as determined by electrochemical polarization or NMR measurements, are between 0.3–0.5 [21]. Mobility of anions causes severe concentration gradients of the conducting salts during current flow and limits the cell current.

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In contrast to the liquid electrolytes, solid electrolytes (SEs) do not create risk of ignition or leak and are considered a safe alternative to currently used electrolytes. SEs can be divided into two major groups: inorganic solids – either crystalline, glass or glass-ceramic materials and organic solid polymers [22,23]. Inorganic materials offer high mobility and selective transport of lithium cations within their structure, however the major drawback of many inorganic SEs is their low thermodynamic stability and mechanical properties connected with rigidity and fragility [24]. Organic SEs – polymer electrolytes (SPEs) are flexible and can compensate volume changes of electrodes during charging and discharging by elastic and plastic deformation. SPEs combine solid-state properties with the ease of processing plastic materials. On the other hand, the polymer electrolytes (PEs) exhibit too low ionic conductivity for battery operation at room temperature. One of the approaches to increasing ionic conductivity of PEs relies on the addition of low-molecular plasticizer. In order to avoid evaporation of introduced plasticizers, non-volatile ionic liquids (ILs) can be employed for this purpose [25–29]. However, despite that many of ILs show excellent ionic conductivity, both of their ions migrate at the potential gradient. Cations of IL compete with lithium cations in ionic charge transport and cause a drastic decrease in lithium transference number values ($T_+ < 0.1$) [30,31]. Therefore, many ILs are not suitable for application in lithium-ion batteries. This work is dedicated to the obtaining of salts of the properties of ILs, which are characterized by selective charge transfer with lithium cations. One method of obtaining low-melting lithium salts is to introduce organic oligomeric chains into the structure of anions. Due to their flexible segmental motion the crystallization is inhibited. Salts have been reported with polyether chains bonded to carboxylic [32], sulfonate [33–35], sulfonamide [36–39] or sulfonimide moieties [40]. Carboxylic acids with oligo-ethylene chains are commercially available. It is easy to obtain salts from them with a simple method, such as reaction with butyllithium. However, the bulk ionic conductivity of carboxylate salts is very low because of poor dissociation of the carboxylates. Our previous works show that the effect of increasing the degree of dissociation can be achieved by complexing anions of the salt with BF_3 [41]. The mechanism of the reactions of BF_3 with carboxylic salts depends on the structure of the anions [42]. The goal of this study is to investigate the structure and properties of products of reactions of lithium carboxylate salts containing oligo-ethylene chains with boron fluoride. Because ionic conductivity is a function of mobility of ions and the number of carrier ions, we selected dicarboxylic salts. We prepared salts of different molecular weights to demonstrate the impact of anion's structure on its mobility and salt's ability to crystallize.

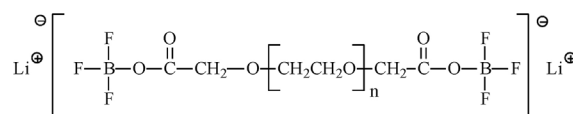
2. Experimental

2.1. Reagents

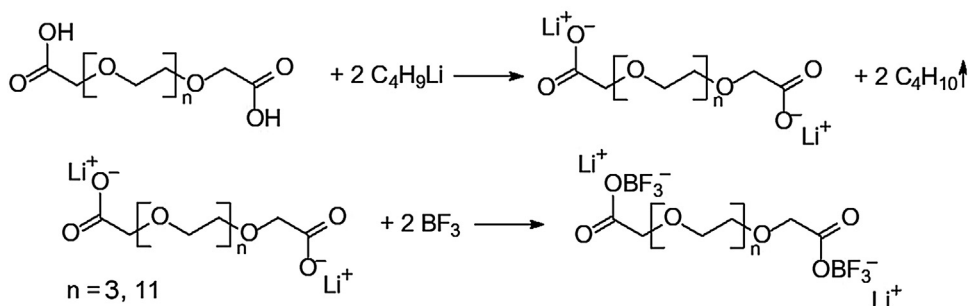
Prior to use, hexane (anhydrous, 95%, Sigma-Aldrich), tetrahydrofuran (anhydrous, $\geq 99.9\%$, Sigma-Aldrich), acetonitrile (anhydrous, 99.8%, Sigma-Aldrich) and PC (anhydrous, 99.7%, Sigma Aldrich) were dried according to standard methods and stored over molecular sieves in argon atmosphere. Boron fluoride in the form of a diethyl ether complex (Aldrich), n-butyllithium solution (2.5 M in hexanes, Aldrich) and poly(ethylene glycol) bis(carboxymethyl) ethers of various molecular weights ($M_w = 250$ and 600 g mol^{-1} , Aldrich) were used as received. Poly(ethylene oxide) (PEO) ($M_w = 5 \times 10^6 \text{ g mol}^{-1}$, Aldrich) was dried under vacuum for 48 h at 50°C and stored in argon atmosphere.

2.2. Synthesis and characterization of bis(carboxytrifluoroborate lithium) salts $[\text{R}(\text{CH}_2\text{COOBF}_3\text{Li})_2]$ with $\text{R} = \text{O}(\text{CH}_2\text{CH}_2\text{O})_n$

Bis(carboxytrifluoroborate lithium) salts $[\text{R}(\text{COOBF}_3\text{Li})_2]$ with $\text{R} = \text{O}(\text{CH}_2\text{CH}_2\text{O})_n$ where $n = 3$ or 11 [BCB3 and BCB11] with the following structure:



were obtained in a two-step reaction. The first step involved the reaction between poly(ethylene glycol) bis(carboxymethyl) ethers and n-butyllithium. Then, the formed carboxylate lithium salt was reacted with boron fluoride etherate. The course of these reactions is presented in Scheme 1. Both reactions were carried out in dry THF, in the presence of an equimolar amount of substrates. In the first reaction step, n-butyllithium was added dropwise to the flask, which required cooling of the system. The second step of the reaction was conducted at room temperature. All operations were carried out under argon atmosphere or on a vacuum line. After the reaction, the solvents formed a separate liquid layer, which was isolated using a syringe and the salts were washed with hexane. The residues of solvents were removed by distillation under reduced pressure. BCB3 was recrystallized from a mixture of acetonitrile and THF, prior to further studies. Depending on the molecular weight of the anion, the obtained salts have different physical properties. The salt with a molecular weight of 400 g mol^{-1} (BCB3) is a crystalline solid, whereas with a molecular weight of 750 g mol^{-1} (BCB11) has the properties of ionic liquid. The structure of the products was determined by ^1H , ^{11}B and ^{19}F NMR spectroscopy.



Scheme 1. Synthesis of bis(carboxytrifluoroborate lithium) salts in the reaction of poly(ethylene glycol) bis(carboxymethyl) ethers with n-butyllithium and boron fluoride etherate.

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