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A novel gel electrolyte with lithium difluoro(oxalato)borate salt and Sb_2O_3 nanoparticles for lithium ion batteries

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Abstract

A new type of lithium difluoro(oxalate)borate salt was synthesized by solid state reaction method and has been incorporated into polyvinyledenefluoride−hexafluoropropylene (PVdF−HFP) skeleton. Ethylene carbonate (EC) and diethyl carbonate (DEC) mixture was used as plasticizing agent. Sb_2O_3 nanoparticle was used as the filler in the polymer host to prepare the nanocomposite polymer electrolytes (NCPE) for lithium ion batteries by solution casting technique. All the membranes were subjected to a.c. impedance, mechanical stability and morphological analysis. Among them 5 wt% Sb_2O_3 having NCPE exhibited enhanced conductivity of 0.298 mS cm^{-1} at ambient temperature and Young's modulus increased from 1.32 to 2.31 MPa after the addition of Sb_2O_3. The conductivity enhancement is explained in terms of Vogel−Tamman−Fulcher (VTF) theory.

Keywords: Young's modulus; LiDFOB; Nanoparticle; Polymer electrolytes

1. Introduction

There has been an increasing interest to synthesize the novel salt for lithium ion power packs in recent years [1]. Other commercially available lithium salts failed to replace $LiPF_6$ which has been used as electrolyte salt in the conventional rechargeable batteries [2,3]. The commonly used $LiPF_6$ is prone to spontaneous decomposition to LiF and PF_5. In aprotic solvents, $LiPF_6$ tends to generate PF_5 according to the following equilibrium:

$$LiPF_6 \leftrightarrow LiF + PF_5$$

PF_5, being a strong Lewis acid reacts with organic solvents thereby shifting the equilibrium forward. Furthermore, the labile P−F bonds are highly susceptible to hydrolysis by even trace amounts of moisture in the electrolyte [4].

$$LiPF_6 + H_2O \rightarrow POF_3 + LiF + 2HF$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF$$

Thus, HF is invariably present in all $LiPF_6$-based electrolytes. The presence of HF in the electrolyte induces dissolution of the transition metal cations in the cathode materials, which can cause structural changes that lead to capacity fade [5]. Any LiF layer formed on the electrode surfaces also hinders insertion and reinsertion of Li^+ ions. In order to improve the stability of $LiPF_6$ one or more fluorine atoms are to be successfully removed and replaced with perfluorinated alkyl groups which stabilize the P−F bond, rendering it stable against hydrolysis ($LiPF_3(CF_3CF_2)_3$). It fulfils the basic criteria for electrolyte salt, but at the same time it cannot be commercialized due to its high cost [6,7]. Recently, lithium bis(oxalato)borate (LiBOB) was introduced as an alternative to $LiPF_6$. It exhibits the unique properties like solid electrolyte interface (SEI), passivation of current collectors and overcharge tolerance which has not been observed in other salt system studied. The drawbacks are the highly resistive SEI which

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consequently reduces the power capability of the cell and poor solubility in linear carbonates attributes to the low conductivity [8–11]. To overcome the above drawbacks, in the present paper we have synthesized a novel lithium salt and it has been incorporated into polyvinyledenefluoride–hexafluoropropylene (PVdF–HFP) host matrix for the application of using as electrolyte for lithium ion batteries.

2. Materials and methods

2.1. Materials

Polyvinylidenefluoride–hexafluoropropylene (PVdF–HFP) was obtained form Solvay Solexis. Ethylene carbonate (EC), antimony oxide (Sb_2O_3) nanoparticles (90–210 nm) and boron trifluoride diethyletherate ($BF_3O(CH_2CH_3)_2$) were purchased from Aldrich, USA. Tetrahydrofuron (THF), lithium oxalate ($Li_2C_2O_4$) and the plasticizer diethyl carbonate (DEC) were procured from E. Merck India, and used without further purification. Appropriate amounts of materials are blended together (given in Table 1) using tehrahydrofuran as solvent; this solution is stirred until the solution becomes homogeneous, and then the solution is casted on the glass plates. It is allowed to evaporate at room temperature, after complete evaporation of the solvent, electrolyte membranes are kept in a vacuum for about 10 h and membranes were subjected to various characterizations.

2.2. Synthesis of LiDFOB

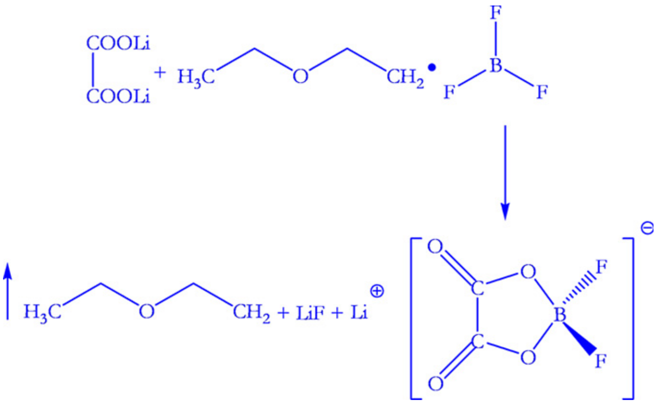
Lithium difluoro(oxalato)borate (LiDFOB) was synthesized by solid state reaction method (Scheme 1). The starting materials are boron trifluoride diethyletherate and lithium oxalate in a 1:1 molar ratio and purified through extraction and recrystallization using dimethyl carbonate (DMC) solvent. One of the unique properties of this method is no separate solvent is needed for synthesis [11,12].

2.3. Instrumentation

Ionic conductivities of LiDFOB based membranes were measured by a.c. impedance spectroscopy in the 5 MHz–1 Hz frequency range by using Solartron 1260 Impedance/Gain Phase analyzer coupled with a Solartron Electrochemical interface with two stainless steel blocking electrodes (SS/CPE/SS). Morphological analyses were carried out by using JEOL (Japan) Scanning Electron Microscope JSM-5610LV; one side of the samples has been gold sputtered prior to SEM analysis.

Table 1
Composition of polymer electrolytes

Sample	Polymer PVdF–HFP	Plasticizer (1:1 wt/wt)		LiDFOB	Sb_2O_3
		EC	DEC		
S1	30	32.50	32.50	5.0	0.00
S2	30	31.25	31.25	5.0	2.50
S3	30	30.00	30.00	5.0	5.00
S4	30	28.75	28.75	5.0	7.50
S5	30	27.50	27.50	5.0	10.0



Scheme 1. Synthesis of LiDFOB.

Instron Corporation series IX automated mate has been used to measure the mechanical stability of the polymer electrolytes.

3. Results and discussion

3.1. Properties of LiDFOB

The chemical structure of LiDFOB possesses the combined advantages of LiBOB and $LiBF_4$ [11–15]. The ability to provide a high cycling efficiency for metallic lithium plating and stripping on the surface of Cu (a current collector material of the graphite anode) and it showed good passivation towards Al (a current collector for cathode materials) at high current rates. Compared with LiBOB, LiDFOB has higher solubility in linear carbonates and it has unique capability in forming and stabilizing SEI, which can effectively protect the negative electrode from being attacked by other cell components. This is done by forming a robust SEI on the electrode surface like LiBOB does. With LiDFOB, graphite can be cycled reversibly in high PC-containing solutions, and the resulting Li-ion cell shows significantly improved low temperature performance. Unlike LiBOB which is extremely sensitive to impurities such as the trace amount of unreacted reactants, LiDFOB is less sensitive to the impurities. It has been experienced that a mild vent with temperature beyond 100 °C did not catch fire or sparks whereas $LiPF_6$-based electrolyte did not cause a violent explosion even with the maximum temperature reaching 400 °C. This type of overcharge tolerance may be attributed to the oxalate molecular moieties of LiBOB, which are preferably oxidized and produce CO_2 by the oxygen released by the cathode. Similar type of behavior is expected for LiDFOB, because which also have oxalate molecular moieties leads to safety protection under abuse conditions. Compared with $LiBF_4$, LiDFOB has higher ionic conductivity and results in the formation of more stable SEI while still providing good low temperature performance as well at elevated temperatures [11–15].

3.2. Ionic conductivity studies

Electrochemical impedance spectroscopy is a powerful technique to characterize electrical properties of interfaces