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Improved performance of polyvinylidenefluoride–hexafluoropropylene based nanocomposite polymer membranes containing lithium bis(oxalato)borate by phase inversion for lithium batteries

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ABSTRACT

Nanocomposite polymer electrolyte membranes were prepared by phase inversion technique in polyvinylidenefluoride–hexafluoropropylene (PVdF–HFP) matrix. These membranes were gelled with 0.5 M LiBOB in EC:DEC (1:1 v/v). These gel polymer membranes (GPMs) were incorporated with nanoparticles of $AlO(OH)_n$ and prepared composite polymer membranes (CPMs) also. The a.c. impedance analysis shows that $AlO(OH)_n$ filled membrane exhibits conductivity of 1.82×10^{-3} S cm^{-1} at ambient temperature. The Li/CPM/$LiFePO_4$ cell delivered a specific discharge capacity of 158 and 147 mAh g^{-1} at first and at 20th cycle respectively discharged at C/20 rate. The cell experiences a capacity fade of 0.1 mAh g^{-1} cycle^{-1} over the investigated 20 cycles. The studies vindicate that $AlO(OH)_n$ filled PVdF–HFP polymer membranes could be the potential material to use as separator cum electrolyte in lithium batteries in conjunction with $LiFePO_4$ as a counterpart.

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1. Introduction

Of late, an increasing interest is being devoted towards the development of polymer electrolyte membranes for lithium rechargeable batteries with improved ionic conductivity, mechanical, electrochemical and thermal stabilities. Porosity is also one of the basic requisites envisaged for polymer electrolyte membranes to allow the Li^+ ions to transit between the anode and cathode during charging and discharging. Tarascon et al. [1] pioneered the preparation of porous membranes by a two-step process with/without SiO_2 fillers by varying hexafluoropropylene (HFP) units in polyvinylidenefluoride (PVdF) in the first step and in the second step extraction of di-butyl phthalate (DBP) was found to be very difficult and enhances production cost.

The phase inversion technique [2] has been adopted for preparing polymer membranes without sacrificing the basic requisites with optimized solvent/non-solvent ratio and effectively controlling the pore size distributions. Recent investigations identify that the addition of nano-sized ceramic oxides substantially increases the conductivity [2–6], Li^+ transference number, mechanical, thermal and electrochemical stabilities. In this line numerous investigations were reported [2,7–9] based on SiO_2, TiO_2, Al_2O_3, etc. as fillers, which guarantee superior properties to the polymer membranes as their surface exists either as acidic or basic or a mixture of these two. These surfaces effectively interact with the polymer chains and preventing their reorganization resulting in the formation of more amorphous domain in the host [2–9].

Yu et al. [10] investigated the LiBOB based polymer electrolytes for lithium batteries with various cathode materials for the first time and discharge capacities of 132.6, 113.6 and 160 mAh g^{-1} were obtained for $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials respectively. Dahn and co-workers [11] have reported the severe interaction of lithium bis(oxalato)borate (LiBOB) based electrolytes with these cathode materials except $LiFePO_4$ by accelerating rate calorimetric studies however, a thorough electrochemical cycling study using $LiFePO_4$ as a cathode material has not been extensively studied. In this context, the present investigation is envisaged to explore the possibility of using polyvinylidenefluoride–hexafluoropropylene (PVdF–HFP) based polymeric membranes with and without $AlO(OH)_n$ nanoparticles gelled with LiBOB in ethylene carbonate (EC)/diethyl carbonate (DEC) in conjunction with $LiFePO_4$ as cathode material.

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2. Materials and methods

2.1. Chemicals

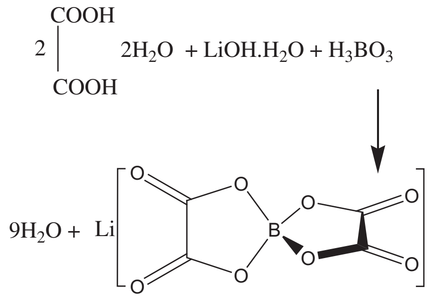
Very high molecular weight PVdF–HFP with 12 mol% of HFP (Solvay Solexis, Italy, Mw 5.34×10^5), lithium hydroxide monohydrate (Aldrich, USA); $AlO(OH)_n$ (Candia, Taiwan with the size of 14 nm); $LiFePO_4$ (Hydro Quebec, Canada), ethylene carbonate, diethyl carbonate, acetone, ethanol and *n*-butanol (E. Merck, India) were used as received.

2.2. Synthesis of LiBOB

LiBOB was synthesized by solid-state method [10,12] according to the reaction shown in Scheme 1. Oxalic acid dihydrate, lithium hydroxide, and boric acid were dissolved in triple distilled water in molar ratio of 2:1:1 using a blender for 1 min. The solution was annealed in an oven at 240 °C for 5 h to prepare LiBOB. The product was purified by dissolving in the boiling tetrahydrofuran/diethyl ether (1:1 molar ratio) and re-crystallizing at −25 °C. Subsequently, the sample was dried in vacuum at about 60 °C for 48 h [13–16].

2.3. Instrumentation

In the typical phase inversion technique, the polymer PVdF–HFP, is dissolved in a mixture of acetone (solvent) and ethanol (non-solvent) (5:1 volume ratio) with the proportion of the non-solvent low enough to allow dissociation and high enough to allow phase separation during evaporation. The non-solvent is to be fixed in such a way that it will have better porosity during the solvent evaporation process. The prepared solution is formed into thin films on a glass substrate, and the solvent is allowed to evaporate. The prepared films are kept under vacuum for 12 h at 100 °C to remove the traces of non-solvents. A similar procedure has been adopted for the composite membrane preparation and $AlO(OH)_n$ nanoparticles were introduced once the polymer dissolution occurs with the optimized concentration of 10 wt% [13]. Morphological features of the polymer membranes were examined using a Hitachi Model S-3000H scanning electron microscope (SEM). Ionic conductivities of the membranes were measured by a.c. impedance spectroscopy in the frequency range between 5 MHz and 1 Hz in a Solartron 1260 Impedance/Gain Phase Analyzer coupled with a Solartron Electrochemical Interface using a stainless steel blocking electrode impedance cell of 1 cm^2 area. Differential scanning calorimetric studies of the polymer membranes were recorded using a Perkin–Elmer Pyris 6 instrument under nitrogen atmosphere between 50 °C and 250 °C at a heating rate of 10 °C/min. Instron Corporation series IX automated mate has been used to measure the mechanical strength of the polymer membranes. The surface area and pore size of the membranes were determined by a continuous flow nitrogen gas adsorption/desorption BET apparatus (Gemini, Micromeritics, USA).



Scheme 1. Schematic representation of the synthesis of LiBOB.

2.4. Coin cell assembly

Coin cells of 2016 configuration were assembled using lithium metal as a anode, $LiFePO_4$ as a cathode and composite polymer membranes as separator cum electrolyte soaked in 0.5 M LiBOB in EC:DEC (1:1 v/v) for an hour. The $LiFePO_4$ cathodes were prepared by a slurry coating process over the aluminium foil using doctor blade comprising of $LiFePO_4$ (60%), carbon black (30%) and PVdF binder (10%). The *N*-methyl pyrrolidone (NMP) was used as slurrying agent. The coated aluminium foil was dried in an oven at 110 °C for 2 h and pressed and 18 mm diameter blanks were punched out from the coated area and used as cathode. Coin cells were assembled inside an argon filled glove box (M Braun, Germany) and subjected to electrochemical cycling studies. Cycling behaviour of Li/$LiFePO_4$ cells with polymer electrolyte membranes was performed galvanostatically in a computerized battery cycling unit at C/20 rate for the first cycle and the rest at C/10 rate between the potential windows 2.5–4.5 V.

3. Results and discussion

3.1. Thermal studies

Thermal stability is also vital to guarantee acceptable performance at elevated temperatures in addition to high ionic conductivity, high lithium ion transport number and good mechanical strength of the polymer membranes. Fig. 1 depicts the DSC traces of the bare, gel and composite PVdF–HFP membranes. In the case of bare PVdF–HFP membranes, endotherm observed at 137.03 °C is owed to the melting of dominant a crystalline phase of the polymer. Except bare membrane, rest of the two-gelled membranes exhibited the endotherm at around ∼80–100 °C are ascribed to the removal of moisture during the loading of the sample. This is expected only, because lithium ion solvated EC:DEC solution having the tendency of absorbing moisture quickly in the atmosphere. For gel membranes (GPMs), this endotherm shifts towards the lower temperature (102.30 °C) and present as two stage events. In addition to that, gelling agents greatly reduce the melting temperature

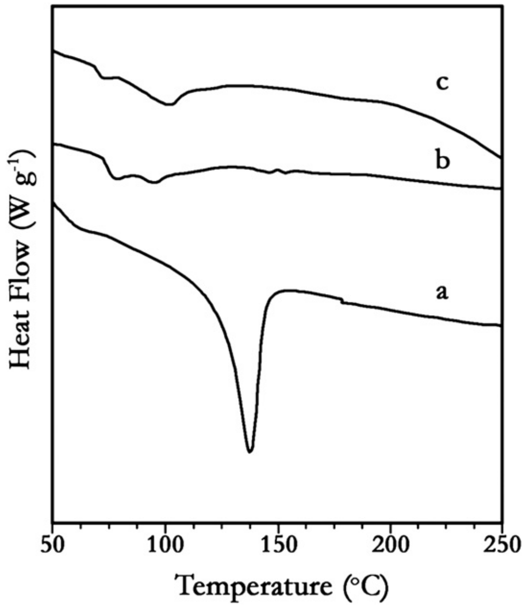


Fig. 1. Differential scanning calorimetric traces of (a) bare (b) gel and (c) composite PVdF–HFP membranes.

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