



## Enhanced ionic conductivity in borate ester plasticized Polyacrylonitrile electrolytes for lithium battery application



Mehmet Kaynak<sup>a</sup>, Abdulmalik Yusuf<sup>b</sup>, Hamide Aydın<sup>b</sup>, Mehmet Uğur Taşkıran<sup>c</sup>, Ayhan Bozkurt<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, Fatih University, Büyükcçekmece-İstanbul 34500 Turkey

<sup>b</sup> BioNanoTechnology R&D Center, Fatih University, Büyükcçekmece-İstanbul 34500 Turkey

<sup>c</sup> Kaleseramik Çanakkale Kalebodur Seramik San. A. Ş., Çan-Çanakkale 17400, Turkey

### ARTICLE INFO

#### Article history:

Received 4 November 2014

Received in revised form 23 February 2015

Accepted 25 February 2015

Available online 26 February 2015

#### Keywords:

Poly (acrylonitrile)

Poly (ethylene glycol) borate ester

Polymer electrolytes

Li-ion conductivity

### ABSTRACT

The effect of low molecular weight borate ester on the ionic conductivity of polyacrylonitrile (PAN) was systematically investigated by means of measuring conductivity using the impedance technique. Gel polymer electrolyte (SPE) films consisting of PAN as host polymer, LiCF<sub>3</sub>SO<sub>3</sub> and LiBF<sub>4</sub> as ionic salts, and poly (ethylene glycol) borate ester (PEGB), ethylene carbonate/propylene carbonate (EC/PC) as plasticizers were prepared by physical blending method. All measurements were performed on electrolyte samples with various contents. Fourier transform infrared spectroscopy (FT-IR) gave evidence of the interactions among PAN, plasticizers and lithium salt. The surface morphology of the electrolytes was investigated by scanning electron microscopy (SEM). Thermal properties of these materials were searched with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Conductivity studies of these blend polymer electrolytes were carried out in the temperature range 20–100 °C. The maximum ionic conductivity values of  $1.8 \times 10^{-3}$  and  $1.4 \times 10^{-4}$  S cm<sup>-1</sup> were measured for the film containing 4PAN-10EC/PC-4LiBF<sub>4</sub> and 4PAN-10PEGB-4LiCF<sub>3</sub>SO<sub>3</sub>, respectively, at room temperature. These films have a good conductivity, better dimensional stability and wide electrochemical stability window. These unique properties make the composite gel membranes suitable for application as electrolyte in rechargeable Li-ion batteries.

© 2015 Elsevier Ltd. All rights reserved.

### 1. Introduction

Lithium ion batteries have acquired great importance in the last several decades as the energy storage of portables devices, such as cell phones and laptop computers [1]. However most lithium ion batteries containing liquid electrolytes have potential safety problems, due to the presence of large amount of organic solvents. In order to solve the safety problems, polymer electrolytes have attracted attention [1,2]. Solid polymer electrolytes as well as gel polymer electrolytes have been reported by many groups [3–5]. Solid polymer electrolytes have advantages like high specific energy, high energy density, leak proof, high ionic conductivity, wide electrochemical stability windows, light, solvent free and easy processability [6].

PAN is one of the popular polymers used as gel-type polymer electrolyte for lithium batteries, which generally exhibit about

$10^{-3}$  S/cm of the ionic conductivities [7,8]. PAN-based electrolytes have shown interesting characteristics like high ionic conductivities, thermal stability, good morphology for electrolyte uptake and compatibility with lithium electrodes [9,10]. However its practical application in gel-type polymers is limited by some factors like the poor dimensional stability, the possible hazard due to high amount organic solvent incorporated, and a progressive evaporation of the liquid solvent that may induce a progressive decrease in the ionic conductivity. To minimize these disadvantages, the preparation and properties of the PAN-based solid polymer electrolytes have been reported [7,11,12].

Several methods have been carried out in order to improve the ionic conductivity of the polymer electrolytes as well as their mechanical properties. They consist of synthesizing new polymers, blending two polymers, cross linking two polymers, addition of inorganic inert fillers and addition of salts [6,13]. Another approach to improve the ionic conductivity of a polymer electrolyte is to add small amounts of low molecular weight nonprotic organic solvents such as ethylene carbonate, propylene carbonate, dialkyl carbonate, or their mixtures, which serve as plasticizers. Such solvents

\* Corresponding author: Tel.: +90 212 8663300.

E-mail address: [bozkurt@fatih.edu.tr](mailto:bozkurt@fatih.edu.tr) (A. Bozkurt).

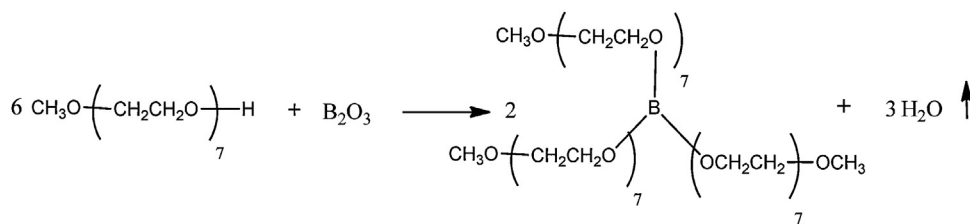


Fig. 1. Synthesis scheme of PEGB.

with high dielectric constants enhance the dissociation and also the solubility of the salt and hence increase the ionic conductivity. However, they impart problems in the applications as they are volatile and flammable [14].

The interest in using of borate esters as additives have increased as they can lead to higher conductivities by trapping the anions due to their Lewis acidic nature, in spite of a very low solvent dielectric constant. They are non-volatile and also have high flash points [15–17]. Many borate esters have been recently synthesized and studied both as additives [18–20] and as solvents [21–25] in salt-in-polymer electrolytes. It is therefore of interest to analyze their influence on conduction of PAN-based electrolytes.

In this work, polymer electrolyte systems of PAN, LiX (X = LiCF<sub>3</sub>SO<sub>3</sub> and LiBF<sub>4</sub>), EC/PC and PEG borate ester, were prepared. Various additives were used in order to obtain the best compromise between high conductivity, homogeneity and dimensional stability. The polymer electrolytes were characterized via FT-IR, SEM, TGA, DSC and CV. Li-ion conducting properties of the materials were investigated by dielectric-impedance analyzer and the results are discussed and compared with previously reported systems.

## 2. Experimental

### 2.1. Materials

PAN (average  $M_w$  = 150,000) and Lithium tetrafluoroborate (LiBF<sub>4</sub>, 98%) were purchased from Sigma-Aldrich Chemical Company. PEGME (average  $M_w$  = 350), Boron oxide (B<sub>2</sub>O<sub>3</sub>, 99%), Ethylene Carbonate (EC, 99%), Propylene Carbonate (PC, 99%) and Lithium trifluoromethane sulfonate (LiCF<sub>3</sub>SO<sub>3</sub>, 97%) were purchased from Alfa Aesar Chemical Company. Lithium tetrafluoroborate and Lithium trifluoromethane sulfonate were stored in the glove box.

### 2.2. Polymer electrolytes synthesis

The PEG borate esters (PEGB) were synthesized, as shown in Fig. 1, by the reaction of methoxy poly(ethylene glycol) (CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>7</sub>H) (PEGME) and boric acid anhydride (B<sub>2</sub>O<sub>3</sub>) [26]. The mixture was dissolved in toluene under N<sub>2</sub> atmosphere and refluxed at 110 °C to eliminate the generated water. After the completion of the reaction, toluene was evaporated under vacuum condition, and finally, clear liquid was obtained. The obtained PEGB was preserved in glove box.

Selected amounts of PAN (4 g), plasticizers (10 g PEGB or 10 g EC/PC (1/1) or 5 g PEGME and 5 g EC/PC (1/1)) and LiX (4 g, X = LiCF<sub>3</sub>SO<sub>3</sub> and LiBF<sub>4</sub>) were taken and dissolved in dimethyl formamide (DMF). Then this solution was stirred continuously for several hours until a homogeneous suspension was obtained. The obtained mixture was cast onto teflon plate. DMF was allowed to evaporate slowly at room temperature and then at 60 °C for the removal of the residual DMF content if any. The obtained film was visually examined for its dryness and free standing nature. The film

was then dried under vacuum at 60 °C for 72 h, followed by storing the film in a glove box.

Solid polymer electrolytes were produced and abbreviated by the amount of used polymer, plasticizers and lithium salt Fig. 2. The thickness of the film was controlled less than 120 μm. All these films can be easily prepared into thin films with good mechanical strength and elasticity.

### 2.3. Characterizations

Prior to FT-IR spectra measurements, samples were dried under vacuum and stored in a glove box. The IR spectra (4000–400 cm<sup>-1</sup>, resolution 4 cm<sup>-1</sup>) were recorded with a Bruker Alpha- P in ATR system.

Thermal stabilities of the polymer electrolytes were examined by thermogravimetry analysis (TGA) with a PerkinElmer Pyris 1. The samples (~8 mg) were heated from room temperature to 750 °C under N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup>.

The thermal behavior of the obtained polymer electrolyte samples was investigated by DSC using a Perkin Elmer Pyris 1 instrument. The samples were first cooled from room temperature to -25 °C, kept isothermally for 10 min, and then heated up to 150 °C. After the samples were cooled to -25 °C, and then finally heated to 180 °C. All thermograms were recorded at a rate of 10 °C min<sup>-1</sup> under nitrogen flow. All DSC experiments were done in duplicate and the thermograms shown refer to the final heating.

The morphologies of NCFE films were observed by scanning electron microscopy (SEM, Philips XL30S-FEG). All of the samples were sputtered with gold for 150 s before SEM measurements.

The alternating current (AC) conductivities of the copolymer samples were measured using a Novocontrol dielectric-impedance analyzer in the frequency range from 0.1 Hz to 3 MHz as a function of temperature. The samples with a diameter of 10 mm and a thickness of approximately 0.4 mm were sandwiched between

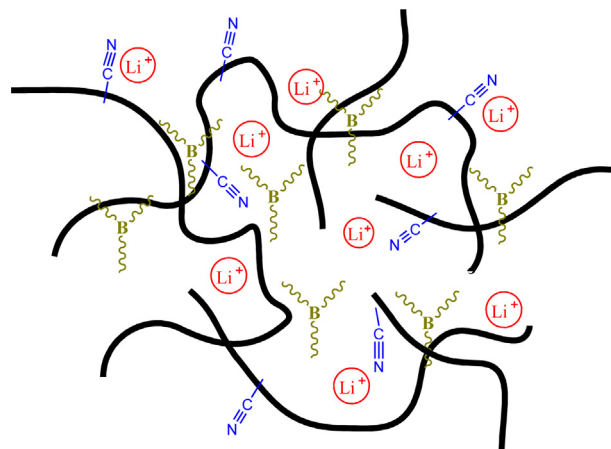


Fig. 2. Illustration of proposed structure of PAN-PEGB based polymer electrolytes.

Download English Version:

<https://daneshyari.com/en/article/184281>

Download Persian Version:

<https://daneshyari.com/article/184281>

[Daneshyari.com](https://daneshyari.com)