Journal of Power Sources 228 (2013) 294–299

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Cycling profile of innovative nanochitin-incorporated poly (ethylene oxide) based electrolytes for lithium batteries

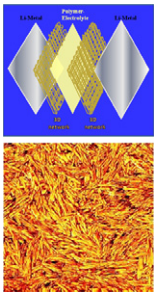
N. Angulakhsmi [a], S. Thomas [b], Jijeesh R. Nair [c], R. Bongiovanni [c], C. Gerbaldi [c], A. Manuel Stephan [a,*]

[a] EPS Division, Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi 630006, India
[b] Mahatma Gandhi University, Kottayam 686560, India
[c] Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

HIGHLIGHTS

- Nanocomposite polymer electrolytes have been identified as separators for safe batteries.
- Nanochitin has been incorporated in poly (ethylene oxide) matrix for the first time.
- A high discharge capacity of 150 mA h g^{-1} at C/5-rate has been achieved even at 70 °C.
- The overall performance of Li/NCPE/$LiFePO_4$ cell is better than the earlier reports.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 September 2012
Received in revised form
6 November 2012
Accepted 8 November 2012
Available online 24 November 2012

Keywords:
Nanocomposite polymer electrolytes
Chitin
Ionic conductivity
Compatibility
Discharge capacity

ABSTRACT

Nanochitin has been incorporated in a poly (ethylene oxide) (PEO)-$LiPF_6$ matrix for the first time. The incorporation of chitin whiskers significantly improves the ionic conductivity, thermal stability, mechanical integrity along with the interfacial properties. The prepared membrane is also tested in a $LiFePO_4$/C—Li cell and the galvanostatic cycling behaviour is analysed at 70 °C showing an improved specific capacity and outstanding cycling stability. The obtained results and the use of such environment friendly component would make these hybrid organic, nanochitin-based composite polymer electrolyte systems a strong contender in the field of flexible and green lithium-based power sources.

1. Introduction

The effect of global warming, fluctuation of oil prices, dwindling resources of fossil fuels and revolution in the portable electronic devices have forced researchers to find alternative energy storage systems. Lithium-ion batteries, supercapacitors and fuel cells are considered strongly as major contenders for power source applications. Rechargeable lithium-ion batteries are extensively used in consumer electronic products including laptop computers, cellular phones, cameras, camcorders and medical devices [1–4]. The state-of-the-art lithium ion batteries employ many variations in cell components and chemistries. Most of them use a graphitic carbon anode (negative electrode), a liquid electrolyte comprised of lithium salts dissolved in organic solvents, a microporous polymer separator and lithium intercalated transition-metal oxide cathode (positive electrode). The solid polymer electrolyte has several

* Corresponding author. Tel.: +91 4565 241 426; fax: +91 4565 227 779.
E-mail addresses: amstephan@cecri.res.in, arulmanuel@gmail.com (A.M. Stephan).

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http://dx.doi.org/10.1016/j.jpowsour.2012.11.007

advantages over its liquid counterpart such high energy density, no-leakage of electrolyte and flexible geometry [5]. The prerequisites of solid polymer electrolytes for lithium battery applications are (i) high ionic conductivity, (ii) good transference number,(iii) better interfacial property, (iv) good mechanical integrity and (v) appreciable thermal stability.

Poly (ethylene oxide) as a host has been most extensively studied for battery applications. PEO chains adopt a helical conformation with all the C–O bonds in trans and the C–C bonds in either gauche or gauche minus configuration [5]. In this geometry, cations can be located in each turn of the helix and are coordinated by three ether oxygens. However, the basic structure of the host is retained for all sizes of anions. PEO is a good polymer electrolyte but suffer from poor mechanical strength and limited thermal resistance: these properties are required for safety and performance reasons, in addition to high ionic conductivity and a wide electrochemical stability window.

The introduction of reinforcing particles has been first proposed by Weston and Steele [6] and in the recent years nanosized fillers have been preferred [7–10]. Alternatively, fibres, nanofibres and whiskers have been employed, preferably of natural origin e.g. cellulose microfibrils [10] and cellulose whiskers [11–13]. In the present study, chitin was employed as novel inert filler in solid polymer electrolytes. Chitin is a long complex polysaccharide made up of repeating units of the disaccharide acetyl glucosamine. Chitin, poly (β-(1-4)-*N*-acetyl-D-glucosamine), is the most abundant biopolymer after cellulose [11]. Chitin occurs as ordered crystalline microfibrils and is useful in applications that require reinforcement and strength. Chitin is available in two allomorphs, namely, α and β forms, which can be differentiated by infrared, solid-state nuclear magnetic resonance (NMR), and X-ray diffraction (XRD) spectroscopy [12]. Chitin has low toxicity, biodegradability and antibacterial properties. It also possesses gel-forming properties and finds many applications. Chitin is used as an additive to thicken and stabilize foods and pharmaceuticals, acts as a binder in dyes, fabrics and adhesives. Industrial separation membranes and ionic exchange resins can be made from chitin, finally it has been used as a biosensor [11–13]. To the best of our knowledge; chitin has never before been investigated as filler in nanocomposite polymer electrolytes for battery applications.

Recent studies indicate that membranes prepared by conventional solvent casting method lead to poor interfacial properties at the lithium/polymer electrolyte interface. Impurities, mostly the traces of solvent, are trapped in the high surface area, nanosized inert fillers in solvent-cast electrolytes, even after prolonged drying [14]. Hence, in the present study the hot press technique was employed for the preparation of nanocomposite polymer electrolytes.

2. Experimental procedure

In order to remove the proteins, the chitin precursor was boiled and stirred with 5% aqueous solution of KOH. It was then washed with distilled water and dried and this procedure was repeated three times. The bleaching solution was prepared by dissolving 17 g of NaCl in 1 l of water with 0.3 M sodium acetate as buffer and the sample was bleached at 80 °C for 6 h. The bleaching solution was changed every 2 h. For further removal of residual proteins the chitin suspension was bleached in 5% KOH for 72 h, centrifuged at 3000 rpm for 20 min and hydrolysed with 3 N HCl under continuous stirring for 1.5 h. The suspension was dialysed in a dialyses bag for 24 h until its pH reached the value of 6 and further the pH of the suspension was adjusted to 3.5 with HCl. The dispersed viscous suspensions were treated ultrasonically and filtered to remove residual aggregates. The resulting nanochitin was refrigerated with sodium – azoture as a protectant against microorganisms. The prepared nanochitin particle size was found to be between 400 and 500 nm of length and diameter of 1 nm and its atomic force microscopy (AFM) picture is displayed in Fig. 1.

PEO (M_w = 200,000, Sigma–Aldrich) and $LiPF_6$ (Sigma–Aldrich) were dried under vacuum for 2 days at 50 and 60 °C, respectively. Polymeric membranes were prepared as follows. The composition of PEO, chitin and $LiPF_6$ are shown in Table 1 and are denoted as samples S1–S5. In order to get a homogeneous polymeric membrane, appropriate amounts of PEO, $LiPF_6$ and chitin were dissolved in acetonitrile, stirred for 6 h and casting the solute in Teflon sheet. The resulting mass was hot-pressed into films as described elsewhere [14].

The films had an average thickness of 30–50 μm. This procedure yielded homogeneous and mechanically strong membranes, which were dried under vacuum at 50 °C for 24 h for further characterization. The ionic conductivity of the membranes sandwiched between two stainless steel blocking electrodes (area 1 cm^2 diameter) was measured using an electrochemical impedance analyser (IM6-Bio Analytical Systems) in the 50 mHz to 100 kHz frequency range at various temperatures (0, 15, 30, 40, 50, 60 and 70 °C). The bulk resistance of the polymer electrolyte was found from the impedance spectrum. Thus, the ionic conductivity was calculated based on the equation [15]:

$$\sigma = (l/A) \times (1/R_b)\left(\mathrm{S\ cm^{-1}}\right)$$

where σ is the ionic conductivity, R_b the bulk resistance; l and A are the thickness of the membrane and area of the specimen, respectively. Symmetric non-blocking cells of the type Li/NCPE/Li were assembled for compatibility studies and were investigated by studying the time dependence of the impedance of the systems under open circuit condition at 70 °C.

The mechanical strength of the nanocomposite polymer electrolytes (NCPE)'s was determined using a tensile machine (Tinius Olsen) with a constant cross-head speed of 10 mm min^{-1}. The sample was prepared exactly by following the instructions given

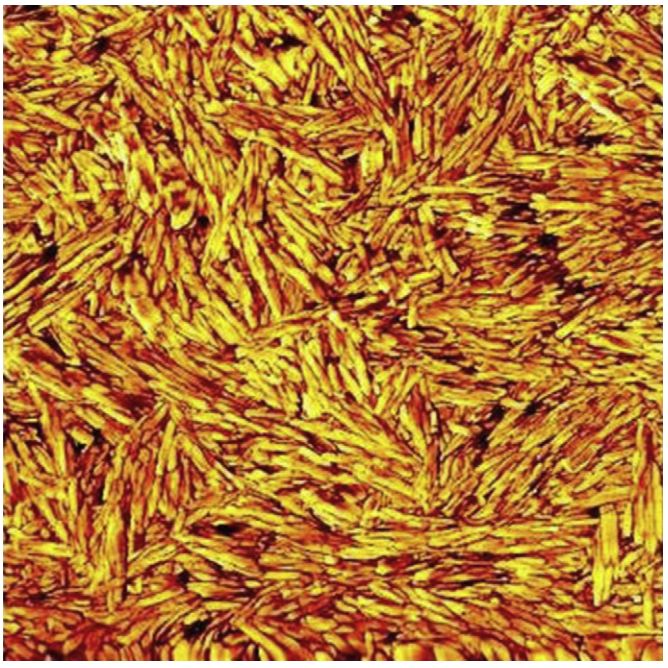

Fig. 1. AFM image of chitin.