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Ternary polymer electrolyte with enhanced ionic conductivity and thermo-mechanical properties for lithium-ion batteries

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ABSTRACT

Cellulose is the main building block of plant's cell wall that provides structural stability. This idea inspired us to use modified cellulose (Networked cellulose) to provide thermal and mechanical stability to a polymer electrolyte system. The system composed of polyethylene glycol (PEG) (or tetraethylene glycol dimethyl ether (TEGDME)), polyethylene oxide (PEO), networked cellulose (NC) and LiClO_4 as a salt. The PEG (or TEGDME) was used as a high mobility phase for lithium ions, PEO acted as a binder and NC provided structural support for the quasi-solid polymer electrolytes. A high conductivity of the order of $10^{-4} \text{ S cm}^{-1}$ was obtained at room temperature. Dynamic mechanical analysis of PEG (or TEGDME):PEO:NC (70:20:10 wt%) showed an improvement of storage modulus as compared to the pristine PEO in the 60–120 °C temperature range. Differential scanning calorimetry (DSC)/Thermal gravimetry analysis (TGA) revealed that the developed ternary polymer electrolyte is thermally stable in the lithium-ion battery operational temperature range. Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

In today's world, there is a high demand for electrical energy storage devices for stationary and mobile applications such as uninterrupted power supply, voltage regulations, electric vehicles (EVs) and hybrid electric vehicles (HEVs). Lithium-ion battery (LIB) technology has high energy density among other commercial secondary storage batteries with no memory effect and low self-discharge rate. The LIB has mainly three components namely, anode, cathode and electrolyte. The electrolyte separates the anode and the cathode to avoid short circuiting and to provide a conduction path for ions (Li^+ ion in the case of LIBs) transportation during charge–discharge processes. Safety and performance of the LIBs

depend significantly on the type of electrolyte used. Conventional electrolytes are prepared by using organic solvents such as ethylene carbonate (EC), propylene carbonate (PC) etc. These solvents are highly flammable in nature and responsible for safety concerns in LIBs [1–4]. Based on the temperature sensitivity of these electrolytes, temperature monitoring and control during charge and discharge processes of the LIBs is typically needed. This raises LIBs manufacturing cost.

Solid polymer electrolytes have potential to overcome the safety concerns of the use of organic electrolytes and other drawbacks such as leakage, reactivity with the electrodes and poor electrochemical stability [5,6]. Polyethylene oxide/lithium salt complexes are extensively studied polymer electrolytes for LIBs [4,7–14]. PEO can effectively solvate and

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conduct Li ions. However, the conductivity of PEO electrolytes containing lithium perchlorate (LiClO_4) and lithium triflate (LiCF_3SO_3) [7,8,10,15,16], are in the range of 10^{-6} to 10^{-8} S cm^{-1} at room temperature and 10^{-3} to 10^{-4} S cm^{-1} at 100 °C. The low ionic conductivity is due to a semi-crystalline phase of PEO, above 60–65 °C the semi-crystalline phase melts and shows a 2–3 order of magnitude increase in conductivity. However, in the high conduction region, PEO/Li–salts complexes lose its mechanical strength [17,18]. Other methods such as addition of low molecular weight and high dielectric constant plasticizers and inert fillers of micro/nanometer size particle in polymer electrolytes have been reported to improve the room temperature conductivity [18–21]. The addition of plasticizers can improve the conductivity, but it deteriorates the mechanical properties of polymer electrolytes.

Cellulose is an abundant, biodegradable and low cost material. The cellulosic cell wall in plants provides structural integrity by encapsulating the cell components inside; this property has been explored to develop mechanically improved polymer electrolytes. Cellulosic constituents are gaining increasing importance due to their high strength and stiffness and high potential as a reinforcing agent [17,22–26]. Cellulose has been used to prepare the separators for lithium-ion batteries and its nano-whiskers as reinforcement for polymer electrolytes [27–29]. In order to maintain structural stability of the polymer electrolyte and high conductivity in the battery operational temperature range, generally 25–60 °C, the authors have previously developed electrolytes based on PEG/NC [30] and PEO/NC [31]. The NC based electrolyte has proved NC capability in providing thermal and mechanical stability for the PEG and PEO without significantly affecting their ionic conductivity. For further improvement and development of NC based polymer electrolyte, a ternary polymer system is proposed.

In this work, quasi-solid polymer electrolyte with appropriate composition of PEG (or TEGDME), PEO and NC has been developed and studied in terms of its mechanical stability and ionic conductivity. The addition of 10–20 wt% of NC provides a sufficient structural support to PEO which helps to hold the 60–70 wt% liquid content (PEG or TEGDME) in the polymer matrix. Addition of NC assists to improve conductivity and mechanical integrity of the polymer electrolyte. Thermo-mechanical, structural and electrochemical properties have been investigated to determine the applicability of the developed material as an electrolyte for LIBs. In addition, Li-ion cells were devised using the developed electrolytes and their charge–discharge performance was tested.

2. Experimental

2.1. Materials

Microcrystalline Cellulose (MCC) ($M_w = 350,000$) was provided by FMC Biopolymer (Philadelphia, PA). Sulfuric acid (99.9%), Polyethylene glycol ($M_w = 200$), Tetraethylene glycol dimethyl ether (TEGDME), Polyethylene Oxide ($M_w = 100,000$), Ethanol and Lithium perchlorate (LiClO_4) were purchased from Aldrich (St. Louis, MO).

2.2. Preparation of NC suspension

Acid Hydrolysis of MCC was performed using a Varian® dissolution system following a procedure reported before_ENREF_26 [26]. The dissolution system bath was adjusted to 5 °C temperature using ice cubes. Sulfuric acid of 70% (w/w) concentration was added to a vessel and then cooled to reach 5 °C. Subsequently, 10 g MCC was added to 100 ml sulfuric acid and the resulting solution was mixed for 30 min at 5 °C at 250 rpm (rotations per minute) to form a viscous and transparent liquid of cellulose completely dissolved in sulfuric acid. Ethanol, which is kept at 5 °C, is added to the dissolved cellulose solution to regenerate the cellulose. The mixture is further mixed for 10 min to allow for complete regeneration of cellulose. The resulting material is centrifuged at 4700 rpm and 4 °C temperature and the acidic top layer is decanted. The centrifugation process is repeated three times to remove sulfuric acid. The centrifugation process resulted in separating the precipitated material from the spent liquor. The precipitate was collected again and dialyzed (against running tap water) for 3 days until the pH of the suspension reached 6–7. The NC suspension was completely homogenized using a mechanical homogenizer (IKA-T25 ULTRA-TURRAX) and heated at 50 °C for 5 h at an agitation of 250 rpm to yield a thick suspension with a concentration of 4.5 % (w/w) in water.

2.3. Fabrication of polymer electrolytes

An appropriate amount of PEG (or TEGDME), PEO solution (in water) and NC suspension were mixed at room temperature and LiClO_4 (EO/Li = 12; mole ratio) was dissolved in the mixture. The mole ratio of LiClO_4 is fixed for all the samples. The different compositions of PEG, PEO and NC (including LiClO_4 salt) were solution casted in Teflon boats to obtain polymeric electrolyte films. They were left to dry in the ambient conditions for 2–3 days and were kept in a vacuum of 100 kPa for 24 h at 80 °C in order to remove all the moisture content and directly transferred to an Argon filled glove box (MBraun, Germany) having moisture and oxygen contents <0.1 ppm.

2.4. Characterization

2.4.1. Dynamic Mechanical Analysis

PerkinElmer DMA 8000 was used to investigate the variation of storage modulus, from 25 °C until the rupture, in tension deformation mode at the frequency of 0.5 Hz and heating rate 2 °C min^{-1} . Rectangular samples of dimensions 10 mm × 3.3 mm were used with thicknesses ranging ~150–200 μm .

2.4.2. Thermal analysis

Thermal stability of the polymer electrolyte was characterized by DSC (PerkinElmer DSC 4000) and Dynamic mechanical analysis (DMA; PerkinElmer DMA 8000) analysis. The samples were sealed in the aluminum pans using crimp machine. DSC was performed at heating rate of 10 °C min^{-1} over temperature range of 25–150 °C under nitrogen atmosphere.

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