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A dense cellulose-based membrane as a renewable host for gel polymer electrolyte of lithium ion batteries

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ABSTRACT

A dense instead of porous gel polymer electrolyte for lithium ion batteries is reported for the first time. Its host is a renewable and environment friendly polymer, hydroxyethyl cellulose (HEC). The preparation of HEC membrane is very simple. The membrane is stable up to 280 °C, much higher than the melting points of those commercial separators based on polyolefin. The evaporation temperature of the organic electrolyte in the prepared gel polymer electrolytes is up to 75 °C. In addition, the gel polymer electrolyte shows good electrochemical performance including high ionic conductivity at room temperature, and a high lithium ion transference number. When tested as separator and electrolyte, a LiFePO₄ positive electrode displays satisfactory electrochemical properties including high discharge capacity and stable cycling. These results indicate a very promising direction for a low cost and renewable gel polymer electrolyte for lithium ion batteries.

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1. Introduction

Nowadays, lithium ion batteries (LIBs), which have become one of the most important energy storage technologies, play a crucial role in the modern world and have become an indispensable part of our daily life. They were invented in the early 1990s, and now are widely used to power many portable devices such as cellular phones, laptops and digital cameras [1–5]. Accordingly, some remaining challenges for the future widespread development of LIBs are the reduction of costs, the use of environment friendly materials and safety enhancements [6].

A lithium-ion cell is comprised of four components, i.e. a positive electrode, a negative electrode, a separator membrane and an electrolyte (solution). The separator in battery plays an important role in electrically insulating positive and negative electrode to prevent electrical short-circuits and at the same time allow rapid transfer of ionic charge carriers [7–9]. So far, the separators used in commercial lithium ion batteries are nearly exclusively micro-porous polymer membranes. Although commercial separators have shown satisfactory performance, they are still associated with the risk of accidents because of the wide use of flammable organic liquid electrolyte solutions in the conventional lithium ion batteries [10–13], and are also expensive because of the delicate manufacturing technologies

[14]. In addition, they are porous and micro-short-circuits from the electrode particles are very difficult to prevent.

Gel polymer electrolytes (GPEs) have recently received much attention again, owing to their high ionic conductivity at ambient temperature and reduction of risk of leakage of electrolyte solution [15–17]. Nevertheless, the well-studied polymer hosts are based on poly(vinylidene difluoride) (PVDF) and its copolymers, and modified polyethylene and polypropylene, which are not friendly to the environment [15–19]. GPEs based on copolymers of PMMA, PAN and PEO have already been described. Although they have displayed good performance, their preparations are not easy and their costs are high [20,21]. With exhausted fossil oil and severe environmental pollution, it is obligatory for scientists to find out a sustainable way. An alternative way to solve this problem is to move from fossil-based resources to biomass-based ones. It is well-known that cellulose is one of the most abundant, renewable resources on the earth and possesses outstanding properties such as biocompatibility, desired chemical stability and environmental benignancy since it is easily available from plants [22–28].

So far most separators and membranes for the gel polymer electrolytes are porous [2,7–9,15–19,27], which cannot prevent micro-short-circuits due to the peeling off of electrochemically active materials from the current collector [29]. This is the main reason why lithium ion batteries could not ensure 100% reliability or safety. In addition, their preparation processes are complicated, and the qualified yields are not high, leading to high cost of the separators and gel polymer electrolytes [2]. For example, the former Bellcore Corp. invented a phase inversion method to prepare gel

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polymer electrolytes. However, its scaling-up for mass-production failed due to complexity [2]. As a result, these two issues are needed to be solved prior to their commercialization in electric vehicles.

Hydroxyethyl cellulose (HEC) is a water-soluble polymer and nonionic in nature. This polymer has excellent properties such as thickening, binding, emulsifying, suspending, dispersing and stabilizing [6]. It is renewable, cheap and biocompatible. Herein, we used it as a host for a gel polymer electrolyte in lithium-ion batteries. Our results demonstrate that this kind of cellulose-based gel polymer electrolyte is dense (non-porous), which can avoid the micro-short-circuit problem that all the other reported separators or gel polymer electrolytes could not solve. It also displays good electrochemical performance including ionic conductivity and cycling stability for the positive electrode. These interesting results provide a new direction for the development of gel polymer electrolytes.

2. Experimental

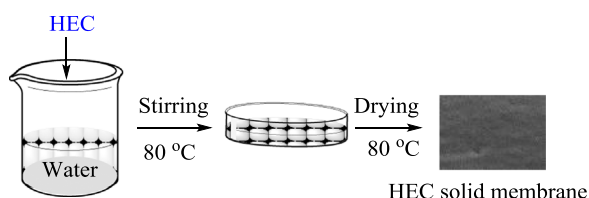
2.1. Preparation of the gel membrane of HEC

Preparation of the gel membrane of HEC is very simple as shown in Scheme 1. In brief, hydroxyethyl cellulose (HEC) (Aladdin, CAS 9004-62-0, 200 mg) was dissolved in 40 mL distilled water under constant stirring at 80 °C for 3 h. Then the solution was cast onto a flat glass plate at 80 °C to remove the solvent and to get membranes. It was punched into circular pieces ($d = 19$ mm). After drying under vacuum at 80 °C for 24 h, the pieces were soaked in an organic electrolyte, 1 mol L⁻¹ LiPF₆ solution in EC/DMC/EMC (ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate, 1/1/1 for w/w/w, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.), over 12 h in a glove box to obtain the gel polymer electrolytes for further measurement.

2.2. Characterization and electrochemical evaluation

Unless stated otherwise, the following measurements were performed at room temperature. Fourier transformation infrared spectroscopy (FT-IR) was employed to measure infrared spectra (IR) of the membranes from HEC. Prior to the IR measurements, the membrane samples were dried at 80 °C under vacuum for 12 h again and then stored in a glove box for 2 h. The IR spectra (4000–400 cm⁻¹, resolution 2 cm⁻¹) were recorded with a Bruker Vector-22 spectrometer. The surface morphology of the prepared membranes was examined by scanning electron microscopy (SEM, Philip XL30). The membranes were dipped into liquid nitrogen and broken into two parts, then the SEM micrograph of the cross-section was taken. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the membranes were carried out on a Perkin-Elmer TGA7/DSC7. Stress-strain tests were conducted using a Sansi YG832 tensile testing machine with a cross-head speed of 1 mm min⁻¹.

The amount of liquid electrolyte uptake (η) was calculated using

$$\eta = (W_t - W_0) / W_0 \times 100\% \quad (1)$$


Scheme 1. Schematic illustration of the preparation of HEC-based membrane as a host for gel polymer electrolyte.

where W_0 and W_t are the weights of the membranes before and after absorption of the organic electrolyte, respectively. The weight was determined in a glove box.

The porosity of the membrane was determined by using *n*-butanol uptake tests and the porosity was calculated using

$$\text{Porosity} = (W_w - W_d) / \rho_b V \times 100\% \quad (2)$$

with W_w and W_d are the weights of wet and dry membranes, respectively, ρ_b is the density of *n*-butanol, and V is the geometric volume of the membrane.

The ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) on an electrochemical workstation CHI660C (Chenhua) in the frequency range 10 Hz–100 kHz between 25 and 75 °C. The samples were measured in blocking-type cells ($A = 2.54$ cm²) where the GPE membranes were sandwiched between two stainless steel electrodes.

The lithium ion transference number of the membrane was obtained by the electrochemical workstation measuring in non-blocking-type cells where the GPE membranes were sandwiched between two lithium metal electrodes. The electrochemical stability window of the membrane was determined by linear sweep voltammetry performed on a working electrode of stainless-steel and a counter-electrode of lithium metal between 0 and 6 V (vs. Li⁺/Li) at a scan rate of 1 mV s⁻¹.

A 2025-type coin cell was assembled by sandwiching a GPE membrane between a LiFePO₄ positive electrolyte (LiFePO₄/acetylene black/PVDF, 80/10/10 w/w/w) and a lithium foil, which was used as counter- and reference electrode. The GPE was used as the separator and electrolyte. All cells were assembled in an Ar-filled glove box. The cyclic voltammograms (CVs) of the cells were measured at the scan rate of 0.1 mV s⁻¹. Cycling tests were carried out on a Land battery tester (CT2001A) at the current density of 0.2 C between 2.5 and 4.2 V.

The Nyquist plots were obtained with an electrochemical workstation CHI660C (Chenhua) in the frequency range 0.01 Hz–100 kHz using the gel HEC membrane saturated with the liquid electrolyte as the separator and electrolyte for the symmetric Li//Li cell.

3. Results and discussion

Some characteristics of the prepared HEC membranes are shown in Fig. 1. In the IR spectra of the prepared HEC membrane (Fig. 1a) there is a broad band at 3422 cm⁻¹, which is assigned to the OH-stretching vibration. The band at 2878 cm⁻¹ is due to the C–H stretching vibration, and the absorption band at 1647 cm⁻¹ is assigned to C–C ring stretching. The absorption band at 1430 cm⁻¹ is caused by the symmetric CH₂ bending vibration, that at 1355 cm⁻¹ by the CH, the absorption band at 1066 cm⁻¹ by the C–O vibration [6].

The smooth surface and a cross-section of the prepared HEC membrane are shown in Fig. 1b and c. No obvious porous structure can be seen at the surface or the cross section. The porosity of HEC membrane is 0.063%, practically it means 0% taking into account measurement errors. This dense structure is completely different from the former membranes for gel polymer electrolytes, which are porous. This implies that this dense structure is advantageous to prevent the micro-short-circuits of lithium ion batteries caused by e.g. peeling-off of electrochemically active particles from the electrode pellets. Its thickness is 34 μm, which can be easily adjusted by the concentration or the amount of the aqueous solution of HEC. From the stress-strain curves of the prepared HEC membrane (Fig. 1d), it can be seen that the tensile strength of HEC membrane is 10.2 MPa. This value is enough for use in lithium ion batteries.

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