Natural macromolecule based carboxymethyl cellulose as a gel polymer electrolyte with adjustable porosity for lithium ion batteries

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HIGHLIGHTS

- A porous membrane of carboxyl methyl cellulose is prepared by a simple non-solvent evaporation method.
- The porous membrane is used as a host of a gel polymer electrolyte for lithium ion batteries.
- The lithium ion transference in the gel membrane at room temperature is as high as 0.46.
- The prepared gel membrane exhibits very good electrochemical performance.
- This porous polymer membrane shows great attraction to the lithium ion batteries.

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ABSTRACT

A porous membrane of carboxymethyl cellulose (CMC) from natural macromolecule as a host of a gel polymer electrolyte for lithium ion batteries is reported. It is prepared, for the first time, by a simple non-solvent evaporation method and its porous structure is fine-adjusted by varying the composition ratio of the solvent and non-solvent mixture. The electrolyte uptake of the porous membrane based on CMC is 75.9%. The ionic conductivity of the as-prepared gel membrane saturated with 1 mol L^{-1} $LiPF_6$ electrolyte at room temperature can be up to 0.48 mS cm^{-1}. Moreover, the lithium ion transference in the gel membrane at room temperature is as high as 0.46, much higher than 0.27 for the commercial separator Celgard 2730. When evaluated by using $LiFePO_4$ cathode, the prepared gel membrane exhibits very good electrochemical performance including higher reversible capacity, better rate capability and good cycling behaviour. The obtained results suggest that this porous polymer membrane shows great attraction to the lithium ion batteries requiring high safety, low cost and environmental friendliness.

1. Introduction

The rapidly growing demands for powering portable electronic devices, wearable electronic device, electric vehicles (EVs) and green energy storage (biomass, solar radiation, wind, waves, etc.) in smart grids are driving the development of rechargeable lithium ion batteries (LIBs) of higher energy and power density, longer cycle life, more reliability and lower cost [1–5]. However, catastrophic thermal failures of LIBs generally related to organic liquid electrolytes and polyolefin microporous separators must be confronted [6–8]. Gel polymer electrolytes (GPEs), which are formed by attracting a large amount of liquid electrolytes in polymer matrices and have characteristics of both the solid and the liquid electrolytes, have got increasing attentions for their good ionic conductivity (above 10^{-4} S cm^{-1} at room temperature), wide electrochemical window, good thermal stability and good compatibility with both electrodes (anode and cathode) during cycling [9–11]. Polymers such as poly(vinylidene fluoride) (PVDF) and its copolymer poly(vinylidene fluoride co-hexafluoropropylene) (P(VDF-co-HFP)), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO) have been widely studied in the GPEs [12–20]. However, the sources of polymer matrices as the GPEs are mainly dependent on

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the ever-decreasing fossil oil, and most of them are not biodegradable, leading to severe environmental pollution. Renewable and biocompatible natural macromolecule materials are highly motivated as alternative hosts of GPEs.

Cellulose, the earth-abundance of the biopolymer material, with outstanding properties such as biocompatibility and biodegradability, desired chemical stability, environmental benignancy, good mechanical strength and superior thermostability (decomposition temperature is up to 250 °C), has drawn considerable attentions as a promising sustainable building block source for advanced materials in various application fields such as displays, information storage, flexible electronics and energy storage [21–25]. With exhausted fossil oil and severe environmental pollution, a number of cellulose-based materials have been developed for potential applications in LIBs such as binder, separator, electrolyte and electrolyte additive to substitute the petrochemical products and other electrochromic devices [26–37]. Carboxymethyl cellulose (CMC) is a linear polymeric derivative of cellulose, consisting of β-linked glucopyranose residues with partial hydroxyl groups substituted with carboxymethyl ($-CH_2COO-$) groups. It can dissolve in water to form viscous solution and is widely used as a binder or thickener in pharmaceuticals, foods and ceramics [38–40].

In this study, we reported for the first time a CMC-based porous membrane that was prepared by a simple non-solvent evaporation method, which is called since the formation of pores is mainly from the evaporation of the non-solvent instead of the solvent (water). The unusual porous structure is fine-adjusted by varying the composition ratio of the solvent mixture (N, N-dimethylformide (DMF)-water) in the CMC suspension, wherein DMF is introduced as a pore-forming agent (nonsolvent) while water promotes dense packing of CMC. The porous membrane displays high ionic conductivity, high Li^+ transference number, high thermostability and good mechanical property. Its electrochemical performance as a host of gel polymer electrolyte for lithium ion batteries was evaluated by using $LiFePO_4$ cathode. Primary results are much better than those based on a commercial separator. The porous membrane is easily prepared, economic and environmentally friendly, and provides great promise for practical application.

2. Experimental

CMC (100 mg, Aladdin, MW: 700,000, DS = 0.9) was dissolved in 40 mL distilled water. To obtain suitable porosity, variable amount of N, N-dimethylformamide (DMF) was added into the CMC solution under vigorous stirring at 70 °C and a clear solution was prepared after further stirring for 4 h, and then the solution was cast on a glass plate. After the water was evaporated at 80 °C, a thin CMC membrane with a thickness of about 20 μm was obtained. The codes for the porous polymer membranes are presented as CMC-0, CMC-1, CMC-2, CMC-3 and CMC-4 which refer to the samples prepared with 0, 2.0, 2.5, 3.0 and 3.5 mL DMF, respectively. The membrane was punched into circular pieces (d = 19 mm), and dried under vacuum at 80 °C for 24 h. The pieces were soaked in an organic electrolyte (1 mol L^{-1} LiPF$_6$ solution in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC), 1/1/1, w/w/w, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd) over 2 h in a glove box (water content: <1 ppm) to get the gel membranes or GPEs for further measurement. For comparison, a commercial separator, Celgard 2730, was used as a control as our former work reported [10,12].

Except stated, the following measurements were performed at room temperature. The diffuse reflectance infrared spectrometry (DRIFT) method was employed to measure infrared spectra (IR) of the samples. Before IR measurements, the samples were dried at 80 °C under vacuum for 24 h again and then stored in a dry box for

2 h. The IR spectra (4000–400 cm^{-1}, resolution 2 cm^{-1}) were recorded with a BRUKER VECTOR-22 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the membranes were carried out by utilizing a Perkin–Elmer TGA7/DSC7. The surface morphology of the prepared membranes was examined by scan electron microscope (SEM, Philip XL30). The membranes were dipped into liquid nitrogen and broken into two parts, and then the SEM micrographs of the cross-sections were taken. All of the samples were sputtered with gold prior to the SEM measurement. The thickness of the membranes was measured with a micrometer (SM & CTW, Shanghai). Stress-strain tests of the membranes with the width of 4 mm were conducted by using a Sansi YG832 tensile testing machine with a crosshead speed of 1 mm min^{-1}. To measure the porosity, the prepared polymer membranes with different ratios of DMF were immersed into n-butanol for 4 h. The porosity (P) was obtained according to the Equation (1) [41,42]:

$$P = (m - m_0)/\rho V \tag{1}$$

where m_0 and m are the weights of the membranes before and after absorption of n-butanol, respectively, ρ is the density of n-butanol and V represents the volume of the polymer membrane which can be got by the thickness and diameter of the samples. The calculation of the uptake amount of liquid electrolyte, η, is estimated according to the Equation (2):

$$\eta = (W_t - W_o)/W_o \times 100\% \tag{2}$$

where W_o and W_t are the weights of the membranes before and after absorbing the organic electrolyte, respectively. The chronoamperometry profile was obtained by the electrochemical working station CHI660C measuring in blocking-type cells where the gelled PE membranes were sandwiched between two lithium metal electrodes. The step potential was 10 mV. The lithium ion transference number was calculated according to the following equation [43,44]:

$$t_{Li+} = I_s/I_o \tag{3}$$

where I_s and I_o represent the currents at the steady state and initial state, respectively.

The ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) in the temperature range of 25 °C–75 °C by using an electrochemical working station CHI660C (Chenhua) in the frequency range of 10 Hz–100 kHz. The GPEs were sandwiched between two stainless steel electrodes of 2.54 cm^2 in area to measure their ionic conductivities. The electrochemical window of the polymer electrolytes was determined from the linear sweep voltammogram which was carried out by the electrochemical working station using a two-electrode cell. Stainless steel was used as the working electrode and lithium foil as the counter and reference electrode. The measurement was done between 0 and 6 V (vs. Li$^+$/Li) at the scan rate of 2 mV s^{-1}.

Electrochemical performance of the GPE was evaluated by coin-type cells, where lithium foil was used as the counter and reference electrode, and the mixture of LiFePO$_4$ (E60, China), acetylene black and PVDF in the weight ratio of 8:1:1 as the working electrode. The cyclic voltammograms (CVs) of the LiFePO$_4$ cathodes were measured at the scan rate of 0.1 mV s^{-1}. The charge–discharge and cycling behavior of the LiFePO$_4$ cathodes were carried out by a Land battery tester at the current density of 0.2 C (34 mA g^{-1}) between 2.5 and 4.2 V. The rate behavior of the cell was tested under the current density of 0.1 C, 0.2 C, 0.5 C, 1 C and then returned to 0.2 C at each rate for five cycles between 2.5 and 4.2 V.