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Research Paper

Gel polymer electrolyte based on polyethylene glycol composite lignocellulose matrix with higher comprehensive performances

Amin Song[a], Yun Huang[a,*], Bo Liu[a], Haijun Cao[b], Xuepeng Zhong[a], Yuanhua Lin[a], Mingshan Wang[a], Xing Li[a], Weihong Zhong[c,*]

[a] School of Materials Science and Engineering, Southwest Petroleum University, Chengdu, 610500, China
[b] Institute of Blood Transfusion, Chinese Academy of Medical Sciences, Chengdu, 610052, China
[c] School of Mechanical and Materials Engineering, Washington State University, Pullman, 99164, USA

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ABSTRACT

A novel gel polymer electrolyte (GPE) based on polyethylene glycol (PEG) composite lignocellulose (LC) with compact structure for application in lithium ion batteries (LIBs) is prepared. The GPE membrane dramatically enhances mechanical properties, and displays as high as 3–4 times than that of pure LC when adopting 30% PEG-1000. Meanwhile, the increased liquid electrolyte uptake is obtained (267%), and caused high ionic conductivity (3.22 mS cm^{-1}) at room temperature. Moreover, the lithium ion transference number is as high as 0.81, much higher than most of reported separators, and shows good thermal and electrochemical stability. The rate and cycling performances further confirm that the GPE a very promising candidate for LIBs.

1. Introduction

In recent years, efficient electrical environment-friendly energy storage systems become more and more important for the global environment pollution and the depletion of fossil fuels. Lithium ion batteries (LIBs) have captured the portable electronics market owning to its high voltage and high energy density [1–5]. The key favorable points include higher specific capacities and output voltages, longer cycle life. However, the safety issue, which is aroused from the incorporation of liquid electrolyte [6–10], becomes crucial for the application of high power rechargeable LIBs. In order to overcome the safety problems and keep the high performances of LIBs, as the substitutes for liquid electrolyte, polymer electrolyte (PE) [11–14] and gel polymer electrolyte (GPE) [15–17] have been widely researched. Especially, GPEs, are formed by attracting a large amount of liquid electrolyte in polymer matrix and presented one homogeneous gel phase. This kind of electrolyte, which not only can tightly lock the liquid electrolyte inside polymer matrix and solve the safety problem but also possess high enough electrochemical properties as liquid electrolyte does, has been paid much attention [18–20]. At present, the well-studied polymer matrixes include polyethylene oxide (PEO) [21–23], polyacrylonitrile (PAN) [24,25], polymethyl methacrylate (PMMA) [26–28] and polyvinylidene fluoride (PVDF) [29,30]. However, these polymers are mainly deriving from the petroleum industry and nondegradable. Finally, these polymers will cause serious environmental problem of so-called white pollution when LIBs are total loss and discarded. Therefore, renewable and biocompatible natural polymers are ideal materials for GPEs used in LIBs. Natural polymers have been studied include chitosan [31], cellulose [32–38], natural rubber [39,40] and soy protein isolate [41,42]. However, the natural polymers based GPE indeed do not show satisfactory electrochemical properties: low ionic conductivity, low lithium ion transference number and battery capacity. Therefore, exploring new natural polymer matrix for GPE is the most important and efficient method to endow LIBs with zero environment impact and high comprehensive performances.

Lignocellulose (LC) is one kind of biomass, is most of the major components of plants and includes cellulose, hemicellulose and lignin [43]. As shown in Fig. 1, it has a large specific surface area, excellent wetting and flexibility properties. The proportion of three components of cellulose, hemicelluloses and lignin are various in different plants. In wood, the content is 40–50% of cellulose, 10–30% of hemicellulose and 20–30% of lignin. Cellulose is the most abundant in nature, a beta (1–4)-linked chain of glucose molecules, constitutes the skeleton structure of cell wall and exists in highly ordered crystalline microfibrils. Hemicellulose is a kind of

* Corresponding authors.
E-mail addresses: huangyun982@163.com (Y. Huang), katie_zhong@wsu.edu (W. Zhong).

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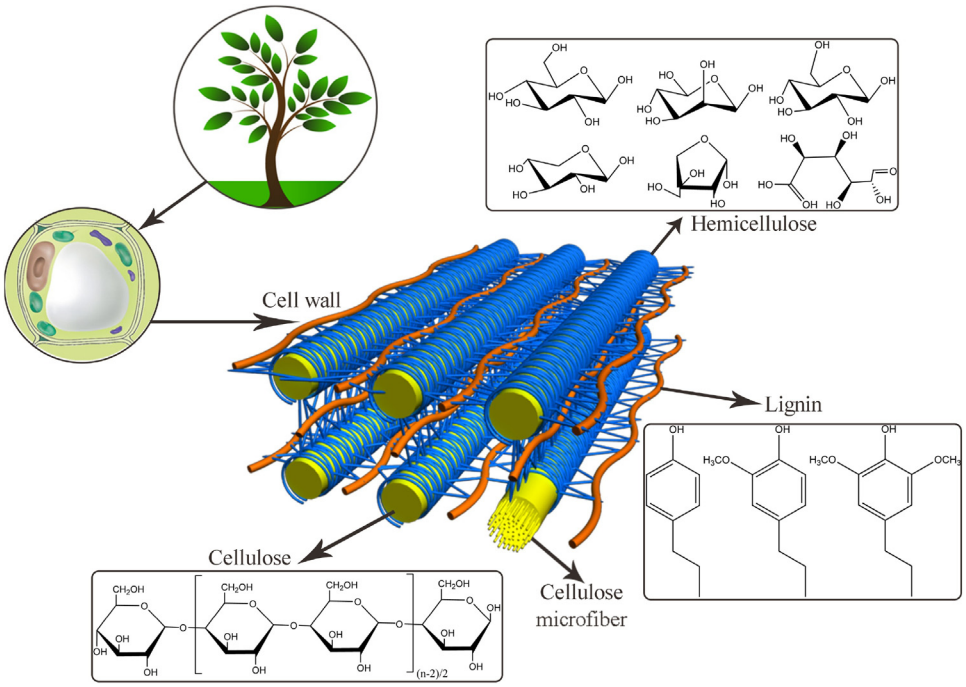

Fig. 1. Composition and chemical structure of LC.

copolymer composed of different sugars, including pentose (xylose and Arabia sugar), hexose (glucose, mannose and galactose) and uronic acid and so on. In the internal structure of biomass, hemicelluloses adhere to the surface of microfibrils, interweave with each other and form dense amorphous network structure. Lignin is composed of three major phenolic components, namely *p*-coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S). Lignin exists in woody tissue, which is formed an intertexture network to harden the cell wall. In the plant cell wall, the hemicelluloses and cellulose microfibrils hold together by hydrogen bond and Van der Waals forces, and then form a chemical bond with lignin, which is named lignin carbohydrate complex (LCC). Obviously, it must be very difficult and take much cost in the process of separation of three components in LC, which undoubtedly results in high cost of prepared GPEs based on each component of cellulose, hemicelluloses or lignin. Therefore, if LC can be directly used as the matrix of GPE, the cost will be significantly reduced.

Polyethylene glycol (PEG) is a linear chain structure of repeated oxyethylene group [44], the average molecular weight of about 200–8000. Both ends of molecular chain contain hydroxyl group, structure as shown in Fig. 2. PEG is biocompatible polymer and one kind of flexible matrix [45], and what is more the chemical properties vary according to the relative molecular weight (MW), such as viscosity, moisture absorption and microstructure.

In this work, firstly preparing LC membrane through a simple solution casting; then various MW and mass ratios of PEG are incorporated to prepare the composite membranes; lastly immersing the obtained composited membranes into liquid electrolyte to swell and form gel. The prepared GPE are environmental friendly and its comprehensive performances have been investigated to determine whether it is one novel kind of electrolyte candidate for LIBs.

2. Experimental

2.1. Materials

Lignocellulose (LC, Industrial grade) supplied by Shanghai Yingjia Company was washed with DI water before use. PEG (molecule weight from 600 to 2000 g mol^{-1}, Kelong Chemical, AR), lithium iron phosphate (LFP, Deyang Weixun Company, Battery grade) and carbon black (Indigo Power Sources, Battery grade) were used as received. LA-132 aqueous binder (Indigo Power Sources, Battery grade) was dissolved into DI water and stirred to form 2.5 wt.% emulsion. Liquid electrolyte (1.0 mol L^{-1} lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate/dimethyl carbonate/diethyl carbonate) was purchased from ShenZhen KeJing Star Technology Co., Ltd. Lithium sheet, aluminum foil and the battery case were obtained from Shenzhen Poxon Company.

2.2. Preparation of gel polymer electrolyte (GPE)

2.2.1. Preparation of PEG composited LC membranes

Firstly, the pure LC membrane was prepared in the following process. LC (900 mg) and DI water (40 ml) were introduced into one beaker; the mixture was sonicated for about 30 minutes and then stirred at 30 °C for 2 hours; the obtained uniform suspension was brought into a glass dish, and then dried at 60 °C overnight to

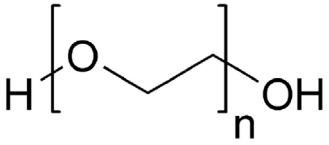

Fig. 2. Structure of PEG.