Journal of Power Sources 307 (2016) 624–633

Contents lists available at ScienceDirect

Journal of Power Sources

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

A green and environment-friendly gel polymer electrolyte with higher performances based on the natural matrix of lignin

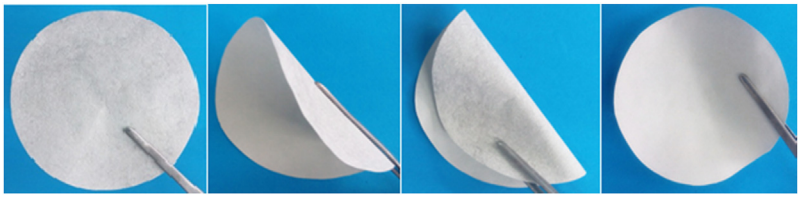
Sheng-Dong Gong [a], Yun Huang [a, *], Hai-Jun Cao [b, **], Yuan-Hua Lin [a], Yang Li [a], Shui-Hua Tang [a], Ming-Shan Wang [a], Xing Li [a]

[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

HIGHLIGHTS

- One kind of natural polymer lignin is firstly explored for gel polymer electrolyte.
- The obtained GPE presents the outstanding comprehensive performances.
- The super simple film formation technology demonstrates the potential application.
- It is a realistic milestone for lithium ion battery with zero environmental impact.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 December 2015
Received in revised form
8 January 2016
Accepted 9 January 2016
Available online xxx

Keywords:
Gel polymer electrolyte
Lignin
Lithium ion battery
Membrane

ABSTRACT

In order to explore one truly green and environment-friendly gel polymer electrolyte (GPE), the natural biopolymer of lignin is firstly all over the world used as matrix to prepare GPE. The electrolyte membrane based on lignin can be easily fabricated just with lignin, liquid electrolyte and distilled water. Through comprehensive investigation of obtained GPE, it is found that the liquid electrolyte uptake reaches up to 230 wt.%; before 100 °C, GPE does not lose any weight and is thermal stable; at room temperature the ion conductivity is 3.73 mS cm^{-1}; the amazing property of lithium ion transference number is high up to 0.85; GPE expresses complete electrochemical stability before 7.5 V and favorable compatibility with lithium anode; the outstanding cell performance of C-rate and cycle capacity. All these remarkably excellent performances endow lignin with application potential in GPE used in lithium ion batteries (LIBs) with higher performances.

1. Introduction

The recent concern about clean energy storage systems are growing to meet the increasing demands for use of the intermittent renewable energy sources from such as wind, solar and waves. Rechargeable lithium ion battery (LIB) has been regarded as one important next-generation power storage device because of its higher output voltage, greater specific capacity and longer cycle life than others [1–5]. Usually, LIB is comprised of four components such as positive electrode, negative electrode, separator membrane and liquid electrolyte. However, the usage of isolated liquid electrolyte in LIBs causes some serious problems including leakage, flame and blast [6]. Subsequently, the substituted electrolytes such

* Corresponding author.
** Corresponding author.
E-mail addresses: huangyun982@163.com (Y. Huang), chj007@163.com (H.-J. Cao).

http://dx.doi.org/10.1016/j.jpowsour.2016.01.030
0378-7753/

as polymer electrolyte (PE) [7–11] and gel polymer electrolyte (GPE) [12–14] were created. Especially, GPEs together combine polymer separator and liquid electrolyte to form one kind of homogeneous gel phase, and exhibit gel solid state and higher ionic conduction in the level of 10^{-3} S cm^{-1} [15]. So GPEs in batteries play an important role in electrically insulating positive and negative electrode to prevent electrical short-circuits and meanwhile allowing rapid transfer of ionic charge carriers [16–18]. So far, in GPEs, a variety of polymers, such as polyethylene oxide (PEO) [19–21], polyacrylonitrile (PAN) [22–24], polymethyl methacrylate (PMMA) [25–28], polyvinylidene fluoride (PVDF) [29–32], polyvinyl pyrrolidone (PVP) [33–35] and polyvinyl acetate (PVA) [36–38] have been used as the main polymer matrix. Although GPEs based on these polymer matrixes have shown satisfactory performances, there is still an associated risk of impact on environment. The massive use of GPE polymer matrixes captured 30–40 wt.% in LIBs, when these polymer matrixes have to be abandoned into the nature environment after LIBs are completely invalidated, will result in serious “pollution” because they can't be easily degraded in nature conditions. Especially, at present, in market the most LIB products are used with liquid electrolyte and Polypropylene (PP) or polyethylene (PE) separator which belongs to more difficultly degraded polymer and results in the so called “white pollution” in environment. At this problem point, LIBs are not totally pure green energy storage device.

Lignin, one of the main constituent of lignocellulose biomass, is the second abundant biopolymer on the earth [39]. Lignin is a tridimensional polymer consisting of 9-carbon phenol propane units, non-uniformly linked together by different types of bonds (alkyl–aryl, alkyl–alkyl and aryl–aryl ether bonds) [40]. As a natural biopolymer, lignin is more interesting than synthetic polymers for applications in different fields due to its higher biodegradability and biocompatibility [41]. In addition, the lignin polymer as one kind of by-product in the paper pulp manufacturing and biomass conversion processes for biofuel production is a readily available, cheap and an underutilized biopolymer nowadays [42]. Every year about 50 million tons of lignin is generated all over the world, but only less than 10% is utilized [43]. So it is very necessary to carry out extensive research worldwide to find the sustainable use of lignin.

Accordingly, the ultimate challenge remained for the future truly green and environment-friendly LIBs are to achieve the balance between reduction of costs, excellent performances and the use of environment friendly materials. For GPEs in LIBs, the bran-new substituted polymer matrix is one wonderful and meaningful research direction. Obviously, the exploration of appropriate matrix is fairy difficult, so in the last ten years the related literature is rarely appeared. To the best of our knowledge, despite there are some literature on application of lignin, the association of lignin with GPEs has not been absolutely studied.

From a conceptual point of view, the exploration of newly green and environmental friendly matrix of lignin for GPEs in LIBs seems a very realistic milestone for the development of battery with zero environmental impact. So the objectives of this present research include:

i. To explore pure natural biopolymer of lignin as the matrix of the fabricated GPEs with low cost, easy preparation, zero environment impact and comparative performances;
ii. To expand bran-new application of lignin in energy storage devices field.

2. Experimental

2.1. Materials

Gran lignin fiber (FH-1000) was supplied by Shang Hai Yingjia Industrial Development Co., Ltd., liquid electrolyte with EC/DMC/EMC (ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate, 1/1/1, w/w/w, LBC305-01) was bought from CAPCHEM.

2.2. Fabrication of GPE membrane based on matrix of lignin

The GPE membrane based on lignin was prepared as follows: Firstly 850 mg lignin was put into 40 ml distilled water in a glass cup at 35 °C under constant stirring, and after 3 h, the uniform suspension was obtained; secondly, the suspension was poured into a flat glass plate and the plate was heated on a heating platform to remove water at 60 °C; thirdly, after heated for 6 h, one kind of opaque and dry membrane was produced; fourthly, the membrane was punched into round pieces with diameter 19 mm, and then these pieces were dried in vacuum drying oven at 70 °C for 6 h; finally, the dried pieces were transformed into a glove box and immersed into liquid electrolyte for enough time to obtain the GPE for further using.

2.3. Characterization and performance evaluation

The surface morphology of the lignin membrane was examined by using a ZEISS Ultra 55 Scanning Electron Microscope (SEM, CarlZelss, Germany) with an acceleration voltage of 5 kV. Prior to the test, the piece with the size of 5 × 5 × 3 mm^3 was sputter-coated with gold. The mechanical tensile property of membrane was characterized by SANS CMT6104 Electromechanical Universal testing machine with a cross-head speed of 1 mm min^{-1}. The size of sample was 50 mm × 10 mm × 500 μm. The thermal property of pure lignin membrane and GPEs were estimated by Thermogravimetric Analyzer (METTLER TOLEDO TGA/SDTA851^e) and Differential Scanning Calorimetry (METTLER TOLEDO DSC823).

The lignin piece was immersed into organic liquid electrolyte solution to obtain the liquid electrolyte uptake (η) calculated by using the equation (1):

$$\eta = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

where W_1 and W_2 are the weight of piece before and after soaked in organic electrolyte, respectively.

The ionic conductivity of the GPE was determined by preparing cell in which the GPE sandwiched between two stainless steel discs electrodes (Φ = 19 mm), which is measured by electrochemical impedance spectra (EIS) on the electrochemical working station CHI-660D (Chenhua, China) over the frequency from 0.1 Hz to 10^5 Hz and the amplitude of the alternative signal 10 mV in the temperature range 25°C–60 °C.

According to the Evans and Abraham method [44], the lithium ion transference number (t_{Li}^+) was obtained using a symmetric cell of Li/GPE/Li by the Direct Current (DC) polarization combined with EIS method and it can be calculated according to equation (2):

$$t_{Li}^+ = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_s I_s)} \quad (2)$$

where I_0 and I_s are the initial and steady-state DC current, respectively; R_0 and R_s are the initial and steady-state interfacial resistances, respectively; ΔV is the applied potential.

The electrochemical stability of GPE was estimated by cyclic