



# Novel cellulose/polyurethane composite gel polymer electrolyte for high performance lithium batteries



Kailiang Liu<sup>a</sup>, Meng Liu<sup>b</sup>, Junmei Cheng<sup>a</sup>, Shanmu Dong<sup>b</sup>, Chengdong Wang<sup>b</sup>, Qingfu Wang<sup>b</sup>, Xinhong Zhou<sup>a</sup>, Hongguang Sun<sup>a,\*</sup>, Xiao Chen<sup>b,\*</sup>, Guanglei Cui<sup>b,\*</sup>

<sup>a</sup> School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China

<sup>b</sup> Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, PR China

## ARTICLE INFO

### Article history:

Received 4 July 2016

Received in revised form 31 July 2016

Accepted 17 August 2016

Available online 17 August 2016

### Keywords:

Cellulose  
Polyurethane  
Polymer electrolyte  
lithium batteries

## ABSTRACT

The increasing interest in gel polymer electrolyte for the lithium battery is attributed to its excellent plasticity, enhanced safety and significantly improved electrochemical stability. Herein, on account of the two-phase structure of thermoplastic polyurethane (TPU) consisting of soft and hard segments, the cellulose/TPU with ether bond composite gel polymer electrolyte (CGPE) was fabricated and investigated for applications in lithium batteries. This study demonstrated that the CGPE possessed preminent comprehensive properties such as sufficient ionic conductivity ( $4.8 \times 10^{-4} \text{ S cm}^{-1}$ ) at 80 °C, high lithium ion transport number ( $t_{\text{Li}} = 0.68$ ) and improved electrochemical stability. Moreover, the assembled LiFePO<sub>4</sub>/Li battery using CGPE exhibited outstanding rate capacity and remarkable cycle performance at the elevated temperature of 80 °C. Notably, the discharge capacity was still 128.2 mAh g<sup>-1</sup> after 200 cycles, 95% of the capacity retention at a charge/discharge rate of 2C. These findings suggest that CGPE is a very prospective polymer electrolyte for high-performance lithium batteries.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Recently, high performance portable power sources and electric vehicles are attracting more and more attentions [1]. The rechargeable lithium battery (LIB) has been identified as an appealing power source in many fields because of its high energy density and excellent cycling performance [2–5]. Polymer electrolytes are promising candidate with better safety characteristics to replace traditional liquid electrolytes for large capacity batteries [6]. Currently, these gel polymer electrolytes (GPEs) with high ionic conductivity are generally plasticized by liquid electrolyte into polymer matrix such as poly(ethylene oxide) PEO [7,8], poly(acrylonitrile) PAN [9,10], poly(methyl methacrylate) PMMA [11,12] and poly(vinylidene fluoride) PVDF [13]. However, these GPEs usually suffer from several critical shortcomings, such as low mechanical properties, poor thermal stability and high cost [14,15]. Thus, a lot of efforts have been made to improve their performance in the past few decades, i.e., composite polymer electrolytes, graft polymers and cross-linked polymer electrolytes [16–19].

Thermoplastic polyurethane (TPU) with ether bond is considered as a remarkable host polymer for GPEs due to its high flexibility and spatial stability [20,21]. TPU possesses two-phase microstructure, i.e. the soft segments and the hard segments. The soft phases composed of polyhydric alcohols with ether bond are capable of solvation with alkali metal salts, which are favorable for depressing combination of the cations and anions, and result in promoting transportation of ions [22]. The hard segments mainly refer to isocyanate (MDI) that interact with neighboring ones through  $\pi$ – $\pi$  interactions as well as hydrogen bondings between the urethane groups [23]. The hard segments also generate physical cross-link points to keep good strength and film-forming property [22,24]. Hence, previous fruitful efforts have been attempted to prepare composite polymer electrolytes by tailoring TPU with other polymers, such as TPU/polyacrylonitrile (PAN) (TPU–PAN) [25] and TPU/linear poly(ethylene oxide) (PEO) (TPU–PEO) [26]. Zhou et al. [24] reported a novel porous GPE based on TPU/PVDF by electrostatic spinning, which showed high ionic conductivity, electrochemical stability and good rate capacity. Nevertheless, prolonged cycling stability is still an apparent challenge, which is critical factor for practical application in lithium battery. Consequently, it is essential to seek out a novel material to be compatible with TPU to fabricate composite polymer electrolyte that have remarkable electrochemical stability. From a

\* Corresponding authors.

E-mail addresses: [hgsun816@qust.edu.cn](mailto:hgsun816@qust.edu.cn) (H. Sun), [chenxiao@qibebt.ac.cn](mailto:chenxiao@qibebt.ac.cn) (X. Chen), [cui@qibebt.ac.cn](mailto:cui@qibebt.ac.cn) (G. Cui).

practical point of view, cellulose is a promising alternative due to its merits which have high dielectric constant, good chemical and thermal stability. Many previous works [27–31] have reported a cellulose supported polymer electrolyte, which shows good electrochemical stability and excellent cycle performance. Hence, we aim to prepare TPU/cellulose composite polymer electrolyte for lithium batteries relying on its attractive performance.

In this study, we establish an efficient electrolyte system (CGPE) to play the synergetic effect of the component, including TPU containing ether bond, cellulose, tetraethylene glycol dimethyl ether (TEGDME), which has good solvating capability for salts [32], and lithium salt-bis(trifluoromethanesulfonyl)imide (LiTFSI)-with high electrochemical stability and ionic conductivity [33]. It has been demonstrated that the as-prepared composite polymer electrolyte membrane showed wide electrochemical window, high lithium ion transference number, prominent cycle performance and good rate capability.

## 2. Experiment

### 2.1. Materials

Polyether-based thermoplastic polyurethane (TPU, Yantai Miracl Chem. Co, M90,  $M_w = 160000$ ) was dried at 80 °C for 24 h. N,N-dimethylformamide (DMF, 99.8%, Aladdin), tetraethylene glycol dimethyl ether (TEGDME, 99%, Aladdin), lithium salts bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma–Aldrich Co. LLC.),  $\text{LiFePO}_4$  (Tianjin STL Energy Technology Co., Ltd).

### 2.2. Preparation of cellulose/TPU composite polymer electrolyte

The composite polymer electrolytes were prepared by a solvent-casting method. A certain amount of LiTFSI was added into TEGDME and stirred constantly to form a 1 mol/L solution. 1.2 g TPU was dissolved in 5 ml DMF. Then, 2.8 ml LiTFSI/TEGDME solution was added into TPU/DMF mixtures to afford a homogeneous solution.

The mixture was cast onto a polytetrafluorethylene plate and then covered a cellulose film. The CGPEs were obtained after drying at 60 °C for 6 h to remove DMF but retain TEGDME. The TPU composite polymer electrolyte without cellulose (GPE) was also prepared by the similar procedure for a reference.

### 2.3. Physicochemical and electrochemical measurements

Scanning electron microscope (SEM, HITACH S-4800) was used to examine the morphology of electrolytes' membranes with operating voltage of 3.0KV.

Their thermal behavior was analyzed on a differential scanning calorimeter (DSC204C, Netzsch) at a scan rate of 10 °C/min. FTIR spectra of the gel polymer electrolyte was obtained from ATR-FTIR (Nicolet 6700) in the range of 700–4000  $\text{cm}^{-1}$  by using a Thermo Scientific DXRXI system.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE III 600 spectrometer using THF-D8 as solvent. The electrochemical stability of the gel polymer electrolyte was measured through linear sweep voltammetry at a scan rate of 1 mV/s.

Ionic conductivity was evaluated by an AC impedance analysis over a frequency range from 0.01 Hz to 1 MHz using the Autolab PGSTAT 302N system. The ionic conductivity was calculated from Eq. (1):

$$\sigma = L/R_b S \quad (1)$$

where  $R_b$ ,  $L$ , and  $S$  present bulk resistance, thickness and area of the membrane, respectively.

The Li ion transference numbers ( $t_+$ ) was achieved according to the method described by Evans et al. [34]. The gel polymer electrolyte membranes were sandwiched between two lithium metal electrodes with the frequency ranged from 1 Hz to 1 MHz, and the applied voltage for DC polarization test set as 10 mV.  $t_+$  was calculated from Eq. (2):

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

Where  $I_0$  and  $I_s$  are the initial and steady-state current, respectively;  $\Delta V$  presents the applied voltage;  $R_0^{el}$  is the initial resistance, and  $R_s^{el}$  is steady-state resistance.

### 2.4. Fabrication and testing of Li/LiFePO<sub>4</sub> cell

A coin cell (CR 2032) was assembled by sandwiching the CGPE or GPE membrane between a  $\text{LiFePO}_4$  cathode and a lithium anode. The  $\text{LiFePO}_4$  electrode was prepared by a doctor-blading and the mass ratio of  $\text{LiFePO}_4$ /carbon black/PVDF was 8/1/1 (w/w/w). All cells were fabricated in a glove box. The charge-discharge capacity of cell was examined using a LAND battery testing system at elevated temperature and 25 °C in the voltage range from 2.5 V to 4 V.

## 3. Result and discussion

### 3.1. Structure and thermal analysis

Fig. 1a and b presented the typical SEM images of the CGPE and GPE. From these SEM images, it could be found that the surface of CGPE was more smooth and homogenous than GPE due to the effect of cellulose. As revealed by the SEM image from Fig. S1, cellulose membrane possessed large-sized pores which extended free volume endowing polymer chains more flexible and irregular [35]. These irregular polymer chains would result in lower crystallinity, glass-transition temperature ( $T_g$ ) and better transparency [36]. Therefore, the CGPE exhibited more transparent morphology than GPE from the optical photograph as shown in Fig. S2.

The glass-transition temperature ( $T_g$ ) is one of significant thermal property, which is shown in Fig. 1c. As for TPU, the  $T_g$  in the region of  $-34.8$  °C was associated with the transition of the soft segment from the glassy state to the rubbery state. In a sharp contrast,  $T_g$  of GPE was  $-63.8$  °C. It is deduced that chain segments of polymer move more facile and freely owing to reduced crystallinity by adding plasticizer. It is noted that  $T_g$  of CGPE ( $-65.8$  °C) was slightly lower than GPE, which was ascribed to a decreased crystallinity of CGPE through introducing cellulose. According to the free volume theory [35,37], the CGPE has more free volumes than GPE due to the synergetic effect of cellulose, which possesses irregular holes making polymer chains tangled and folded more easily. Consequently, the lower crystallinity and glass-transition temperature would favorably enhance ionic conductivity and improve rate capability.

The FT-IR spectra of TPU, GPE and CGPE were shown in Fig. 1d. The characteristic peaks of TPU could be clearly assigned, i.e., 3326  $\text{cm}^{-1}$  (stretching vibration of NH), 1730  $\text{cm}^{-1}$  (stretching vibration of C=O) and 1108  $\text{cm}^{-1}$  (stretching bond of C—O—C). The peaks at 3326 and 1730  $\text{cm}^{-1}$  represented the typical structure of  $-\text{NH}-\text{C}=\text{O}$  in TPU. It was also proved by the spectra of  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR (Fig. S3b and S3c). The cellulose possessed several typical FT-IR absorbance peaks, which were 3441  $\text{cm}^{-1}$  (stretching bond of O—H), 2900  $\text{cm}^{-1}$  (stretching vibration of C—H), 1156  $\text{cm}^{-1}$ , 1060  $\text{cm}^{-1}$ , 895  $\text{cm}^{-1}$  (stretching vibration of C—O—C). Obviously,

Download English Version:

<https://daneshyari.com/en/article/6473136>

Download Persian Version:

<https://daneshyari.com/article/6473136>

[Daneshyari.com](https://daneshyari.com)