



# A sandwich structure polymer/polymer-ceramics/polymer gel electrolytes for the safe, stable cycling of lithium metal batteries



Hao Li<sup>a</sup>, Mengjie Li<sup>a</sup>, Sajid Hussain Siyal<sup>a</sup>, Ming Zhu<sup>a</sup>, Jin-Le Lan<sup>a,\*</sup>, Gang Sui<sup>a</sup>, Yunhua Yu<sup>a,\*</sup>, Weihong Zhong<sup>a,b</sup>, Xiaoping Yang<sup>a</sup>

<sup>a</sup> State Key Laboratory of Organic-Inorganic Composites, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

<sup>b</sup> School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA

## ARTICLE INFO

### Keywords:

Sandwich structure electrolytes  
LLTO  
PEO  
Lithium metal batteries  
Lithium dendrite free

## ABSTRACT

The highest specific capacity (3860 mAh g<sup>-1</sup>) and minimum negative electrochemical potential make lithium metal as a perfect candidate for next-generation high energy battery. However, the safety issue caused by the lithium dendrite growth hinders the practical use of lithium metal battery. Herein, a polymer/polymer-ceramic/polymer sandwich structure electrolytes (SWEs) are proposed to address this problem by combing the advantage of inorganic and gel-type polymer electrolytes. The flexible SWEs show a high ionic conductivity ( $\sim 3.01 \times 10^{-3}$  S/cm) at room temperature, high lithium transference number ( $t_{Li^+} = 0.74$ ), and stable electrochemical windows up to 5.0 V. Furthermore, the SWEs can effectively prevent lithium dendrites in a symmetric Li/SWEs/Li test during charge and discharge with a current density of 1 mA/cm<sup>2</sup> for 240 h at room temperature. Meanwhile, the lithium metal battery assembled using LiCoO<sub>2</sub>/SWEs/Li exhibits the high cycling capacity of  $\sim 110$  mAh g<sup>-1</sup> at 2 C over 100 cycles and fascinating rate performance (144 mAh g<sup>-1</sup>@ 1 C and 98 mAh g<sup>-1</sup>@ 5 C) at room temperature. Our work provides a new design paradigm to exploit the advanced electrolyte for lithium metal battery and flexible devices.

## 1. Introduction

Recently, lithium ion batteries (LIBs) with flexibility and high safety are progressively required and essential for the applications in wearable electronic devices [1,2]. The advanced electrolytes are believed to be the key to achieve high safety and flexibility. Especially, the solid polymer electrolytes (SPEs) has drawn the “biggest concern” due to the attractive advantages such as flexibility, high safety and easy processing in recent years [3,4]. However, there are some serious issues that restrict the further development of SPEs in LIBs, especially the low ionic conductivity at room temperature and narrow electrochemical stable windows [5]. In order to address these issues, several strategies including co-polymerization, adding plasticizers and composing of organic-inorganic electrolytes were proposed [6].

A variety of polymers such as polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polyvinylidene fluoride (PVDF), and polyethylene oxide (PEO) have been investigated and used in SPEs [7–21]. Among those SPEs, PEO is the earliest and the most studied owing to flexibility, good mechanical properties and high lithium salt solubility characteristics [22,23]. However, the low ionic conductivities ( $10^{-6}$ – $10^{-8}$  S/cm) of PEO-based electrolytes at room temperature

limit their use as commercial electrolytes [22]. To overcome this problem, introducing ceramic fillers into PEO polymer is extensively adopted, which can reduce the crystallization of the polymer to increase ionic conductivity and help to improve the electrochemical stability. As studied in previous work, there are two kinds of the ceramic fillers: (i) the inactive ceramic fillers (e.g., Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) and (ii) the active ones (e.g. Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub> (LLZTO), Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub> (LLTO), Li<sub>1+x</sub>Ti<sub>2-x</sub>Al<sub>x</sub>(PO<sub>4</sub>)<sub>3</sub>), which are widely used to improve the properties of PEO-based electrolytes [11,12,23–37]. Among them, LLZTO and LLTO have recently been widely investigated as promising fillers [28–39]. LLZTO has the excellent chemical stability in contact with lithium metal, so it has been adopted in lithium metal batteries and solid-state LIBs [14]. Recently, C-W. Nan group found that LLZTO/PVDF composite could be a promising electrolyte for all solid-state lithium metal batteries [38]. Q. Zhang et al. also confirmed that LLZTO could prohibit the lithium dendrites and extend the electrochemically stable window [39]. Nevertheless, the LLZTO filled polymer electrolytes exhibited inferior ionic conductivities ( $5 \times 10^{-4}$  S/cm in LLZTO/PVDF and  $1.12 \times 10^{-5}$  S/cm in LLZTO/PEO) [38,39] due to the intrinsic low ionic conductivity of LLZTO ( $\sim 10^{-4}$  S/cm). It is no doubt that the new-type electrolytes with high ionic conductivity and good

\* Corresponding authors.

E-mail addresses: [lanjl@mail.buct.edu.cn](mailto:lanjl@mail.buct.edu.cn) (J.-L. Lan), [yuyh@mail.buct.edu.cn](mailto:yuyh@mail.buct.edu.cn) (Y. Yu).

interface stability with lithium metal should be designed to meet the requirement of solid-state lithium metal batteries.

LLTO has some advantage over LLZO/LLZTO: (1) much higher ionic conductivity ( $\sim 10^{-3}$  S/cm); (2) simple and convenient preparation process; (3) no rare element other than Lithium. (3) cost efficient and earth-abundant raw materials for mass production. Therefore LLTO holds great promise for commercial-used solid-state LIBs or lithium metal batteries [28]. Although, a remarkable work was done by Liu et al. [28], which showed that the addition of LLTO nanofibers is beneficial to the promotion of ionic conductivity in PAN polymer electrolytes. Unfortunately, LLTO has a disadvantage of chemical instability with lithium metal, which hinders the use for solid-state lithium metal battery. Therefore, LLTO has been used in few works on lithium metal batteries and solid-state lithium ionic batteries by the surface coating or other protection methods [40–45]. Recently, a sandwich architecture of polymer/ceramic/polymer electrolyte was proposed by J. B. Goodenough group, which may be an interesting and effective way used for reference to solve the problems of LLTO against lithium metal by introduction of the polymer skin layers [46]. Beyond that, the sandwich architecture combines the advantage of polymer and ceramic electrolytes, which shows high performance for lithium metal batteries.

Inspired by this sandwich structure, we proposed a modified sandwich structure composed of PVDF/LLTO-PEO/PVDF to achieve the high ionic conductivity and high electrochemical stability as a polymer-based composite electrolyte against lithium metal anode (Fig. 1a). In this sandwich structure, the PVDF skin layer can not only prevent the reaction between LLTO and lithium metal, but also suppress the lithium dendrite growth, which is also reported by some previous works [37,54]. The LLTO-PEO interlayer (Interlayer) can reduce the bulk resistance and improve the electrochemical stability of the electrolyte. Furthermore, considering the high ionic conductivity and high safety of gel polymer electrolytes (GPEs), GPEs are introduced in the sandwich structure to improve the overall performance of lithium metal battery. As we know, the GPEs is a kind of polymer electrolytes which have

higher ionic conductivity ( $\sim 10^{-3}$  S/cm) than the SPEs and high safety due to avoid the leakage of liquid electrolyte. More recently, the scientists reported that the GPEs possessed a high electrochemical stability to lithium metal and could strongly resistant the growth of lithium dendrites [47,48], which open a new opportunity for the research of solid-state lithium ion batteries. Our newly-designed sandwich-structured electrolyte shows a superior Li-ion conductivity of  $\sim 3.01 \times 10^{-3}$  S/cm at room temperature, high lithium ion transference number ( $t_{\text{Li}^+} = 0.74$ ), low interfacial resistance and wide electrochemical window ( $\sim 5.0$  V), and effectively prevent lithium dendrites in lithium metal battery. The  $\text{LiCoO}_2/\text{SWEs}/\text{Li}$  full cell was assembled and exhibited fascinating rate, capacity retentions performance.

## 2. Results and discussion

In this study, a kind of polymer/polymer-ceramics/polymer hybrid sandwich structure was designed to deal with two important issues for the electrolytes in lithium metal batteries, low ionic conductivity and the chemical instability of  $\text{Ti}^{4+}$  ions in LLTO against lithium metal. The schematic diagram for the fabrication process of the sandwich electrolytes (SWEs) is shown in Fig. 1a. In this design of SWEs, the introduction of LLTO nanowires filled PEO layer can not only provide higher ionic conductivity, but also increase the ionic transfer number. On the other hand, the PVDF layer can avoid the chemical reaction of the LLTO and suppress lithium dendrite growth as shown in Fig. 1b. The as prepared electrolytes are listed in Table 1.

LLTO-PEO interlayers with varying contents of LLTO nanowires (NWs) were made as shown in Table 1. The LLTO NWs were prepared by the electrospinning with various PVP contents (the detail please see Supporting information). The morphologies of the LLTO nanowires were examined by the scanning electron microscopy (SEM) as shown in Fig. S1-S3. Larger aspect ratio and higher yield can be obtained using the precursor with 15 wt% PVP, which is chosen as the optimized precursor for LLTO nanowires in this work. As displayed in Fig. 2a, the SEM image of the precursor fibers have the smooth surface and the

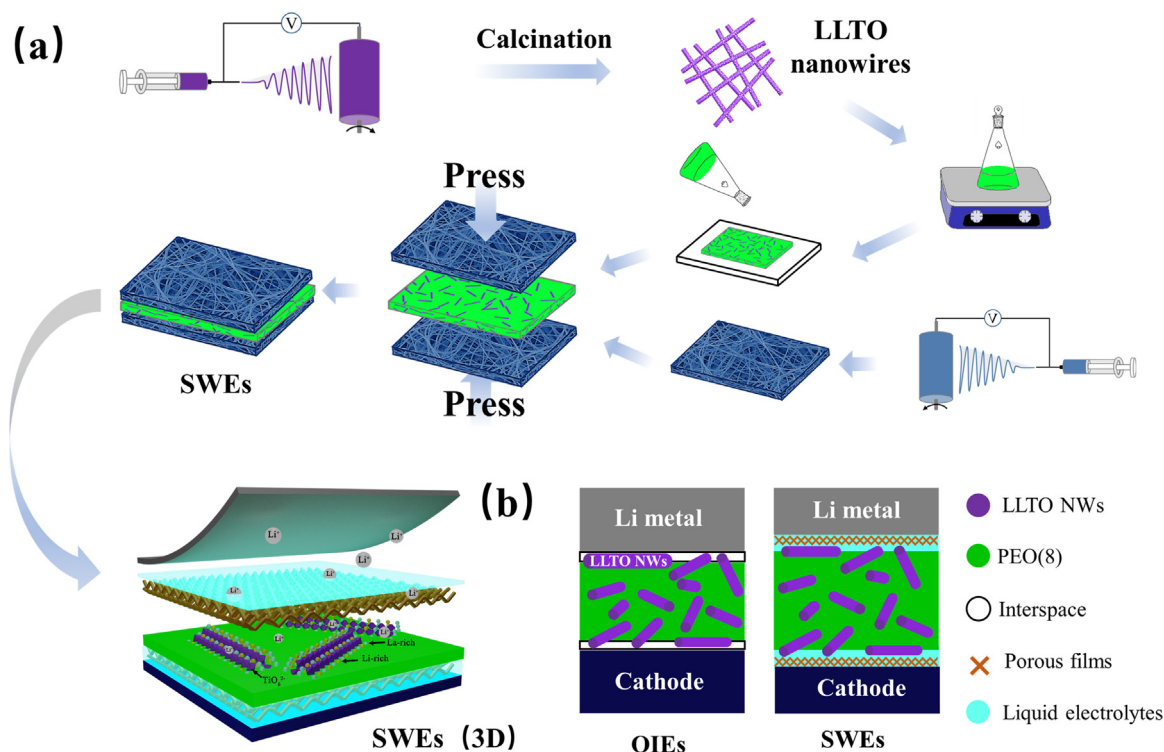


Fig. 1. (a) A schematic diagram for the fabrication process of the sandwich structure composite electrolytes (SWEs). (b) Sectional diagrammatic of the lithium metal batteries using interlayer electrolyte and sandwich structure composite electrolytes.

Download English Version:

<https://daneshyari.com/en/article/7019910>

Download Persian Version:

<https://daneshyari.com/article/7019910>

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