



An all-solid-state Li-organic battery with quinone-based polymer cathode and composite polymer electrolyte



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ABSTRACT

Despite having promising Li storage properties such as multielectron reactions and fast kinetics, organic electrode materials exhibit poor cycling stability, which is partly caused by their tendency to dissolve in liquid electrolytes. In this work, an all-solid-state Li-organic battery with excellent cycling stability and high discharge voltage was designed, in which poly(2-chloro-3,5,6-trisulfide-1,4-benzoquinone) (PCTB) and poly(ethylene glycol) (PEO)-based composite polymer electrolyte (CPE) served as the cathode and electrolyte respectively. The PEO-LiClO₄-10 wt% Li_{0.3}La_{0.566}TiO₃ (LLTO) electrolyte has an excellent ionic conductivity of $7.99 \times 10^{-4} \text{ S cm}^{-1}$ at 343 K. Furthermore, the all-solid-state battery exhibited a high discharge capacity of 104 mAh g⁻¹ with an average potential of 2.72 V at 343 K. After 300 cycles, 90% of the maximum capacity was retained. These results shed light on the application of carbonyl compounds in conjunction with PEO-based electrolytes for Li-ion batteries.

1. Introduction

Quinone and its derivatives are well known organic electrode materials and their applications have been reported by many research groups [1]. However, many challenges remain for the practical application of quinone materials, such as their tendency to dissolve and low discharge voltage plateaus [2]. Our group recently reported a quinone-based polymer cathode, PCTB, that showed a high average voltage of 2.72 V [3]. However, after 100 cycles in a 1 M LiPF₆ DEC/EC (v/v 1:1) electrolyte, only 63% of the maximum capacity was retained. This capacity fading may have been due to the dissolution of PCTB in the electrolyte, as we noticed that the separator became light gray in color after 100 cycles.

A number of effective strategies have been developed to suppress the dissolution of organic electrode materials such as the use of anchoring [4–6], polymerization [7,8], nanostructures [9,10], and solid-state electrolytes [11–14]. Unlike other strategies, the use of all-solid-state electrolytes to produce solvent-free Li-organic batteries inherently prevents the dissolution of organic electrode materials. Therefore, in order to obtain excellent cycling performance, it is of great importance to develop Li-organic batteries with reliable all-solid-state electrolytes.

PEO is an ideal material for composite polymer electrolytes (CPEs) [15,16]. However, PEO has low ionic conductivity. One effective method to improve its conductivity is the incorporation of fillers into PEO to form a composite electrolyte [15,17]. Compared to inactive

fillers (TiO₂ [18] and SiO₂ [19]), active fillers (e.g., Li_{3-x}La_{2/3-x}TiO₃ [20,21] and Li₇La₃Zr₂O₁₂ [22]) usually provide higher ionic conductivity. Among the active filler materials, Li_{0.3}La_{0.566}TiO₃ (LLTO) is well known to exhibit high lithium ionic conductivity [23].

Here, LLTO nanoparticles were synthesized through a Pechini-type polymerizable precursor method that acted as active fillers within PEO to form an electrolyte for all-solid-state Li-organic batteries. The physicochemical properties of the electrolyte and electrochemical performance of the battery were characterized.

2. Material and methods

2.1. Preparation

2.1.1. Synthesis of PCTB

First, 2,3,5,6-tetrachloro-1,4-benzoquinone (TB) (0.62 g) was reacted with Na₂S·9H₂O (2.40 g) in 10 mL aqueous solution and stirred at 373 K for 3 h to obtain the sodium salt. Then, TB (0.62 g) in *N,N*-dimethylformamide (DMF) (10 mL) was added to the sodium salt solution (after cooling to 363 K), which was then stirred for 10 h. After filtration, the sample was washed with distilled water and ethanol, and dried at 393 K for 12 h.

2.1.2. Synthesis of LLTO

Titanium (0.135 g) was dissolved in a solution containing 10 mL of

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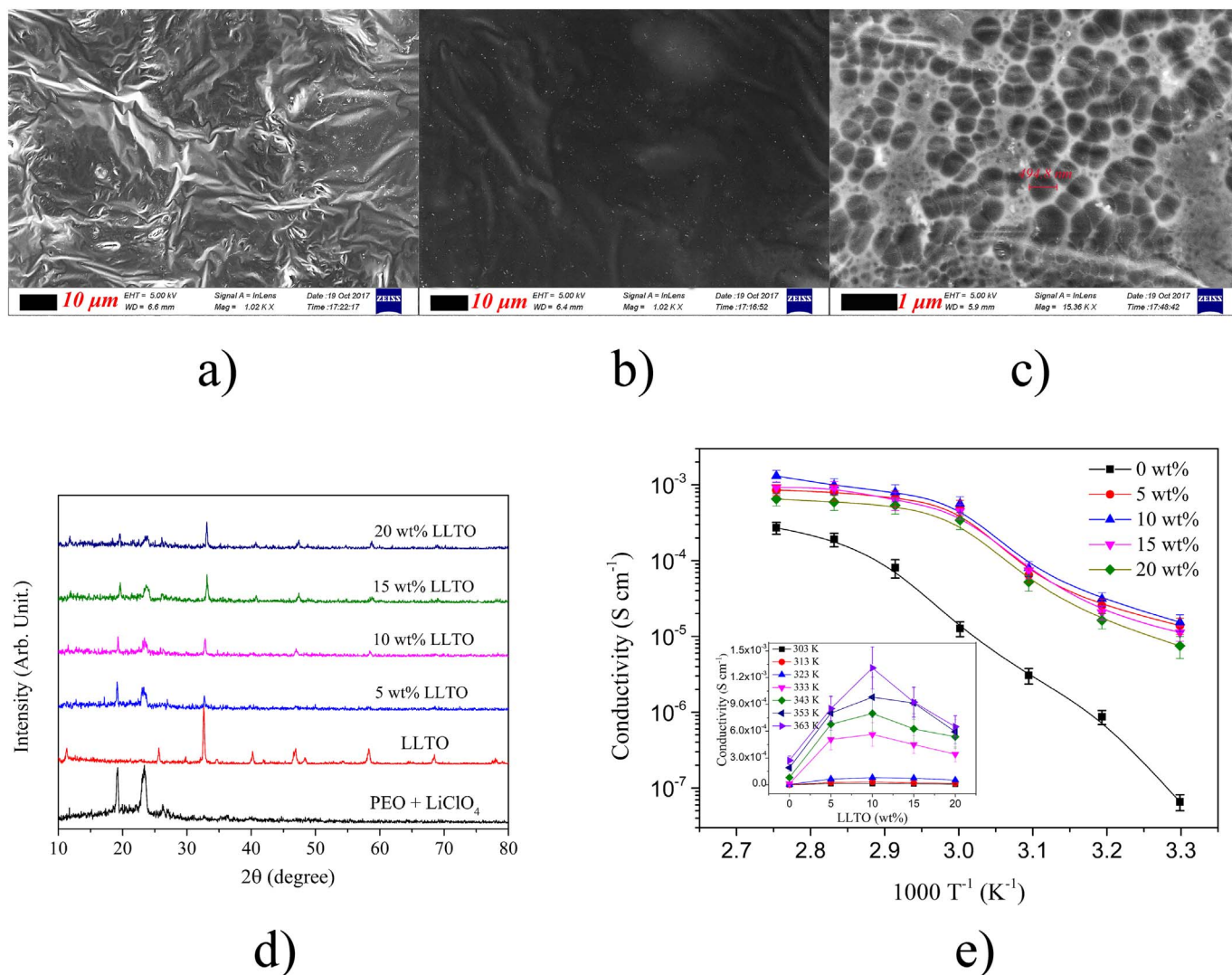


Fig. 1. a, b) SEM images of PEO and PEO-LiClO₄-10 wt% LLTO membranes. c) SEM images of LLTO in PEO-LiClO₄-10 wt% LLTO. d) XRD spectra of the electrolytes. e) Variable temperature conductivities of electrolytes with various LLTO contents.

H₂O₂ (AR, 30 wt% in H₂O) and 2.5 mL ammonia solution (AR, 35 wt% in H₂O). Citric acid (9.60 g) was then added. Li₂CO₃ (0.031 g) and La₂O₃ (0.261 g) were dissolved in 15 mL of HNO₃ (AR, 30 wt% in H₂O) after being heated at 393 K for 12 h. This mixture and ethylene glycol (12.5 g) were added to the above solution, which was then stirred for 1 h. After being heated at 433 K for 12 h, a stable polymer precursor was obtained. The precursor was then heated to 633 K to obtain a gray powder precursor. Finally, the powder precursor was calcinated in air at 1173 K for 2 h to acquire the final Li_{0.3}La_{0.566}TiO₃ powder [23].

Preparation of the electrolyte.

The required amount of the LLTO filler was added to acetonitrile (6 mL) and subjected to magnetic stirring and ultrasonic treatment for 1 h. PEO (Aladdin, M_v ~400,000, 0.4 g) and LiClO₄ (0.05 g) were then dissolved in the solution acquired above. The mixture was stirred at 303 K for 48 h to obtain a homogeneous slurry, which was then cast on a Teflon plate. The sample was dried under vacuum at 333 K for 48 h to form an electrolyte film with a thickness of approximately 130 μm.

2.2. Characterization

The morphologies of the samples were observed using scanning electron microscopy (SEM) with a Sigma 300 microscope (Zeiss, Germany). The Fourier transform infrared (FTIR) spectra were acquired

using a Nicolet 6700 (ThermoFisher, America). The X-ray diffraction (XRD) patterns were collected using a D8-FOCUS X-ray diffractometer (Bruker, Germany) with Cu Kα (λ = 1.54 Å) radiation.

2.3. Electrochemical measurements

The electrode slurry was prepared by mixing 50 wt% of PCTB, 30 wt% of conductive carbon, and 20 wt% of PVDF in NMP, with an aluminum mesh as the current collector. The mass loading of the electrode was ~1.33 mg cm⁻². The batteries were cycled using a CT2001A battery test system (Land, China) at 343 K. Cyclic voltammetry (CV) measurements were conducted using a three-electrode battery (Li/Li/PCTB) on an Interface 1000E (Gamry, America) at 343 K. The electrochemical impedance spectroscopy (EIS) measurements were obtained using a Reference 600 (Gamry, America) in the frequency range 10⁵ to 10⁻² Hz at an amplitude of 10 mV. The ionic conductivity of the electrolyte was analyzed by EIS in the range 303–363 K at intervals of 10 K. The electrochemical stability of the electrolyte was evaluated using linear sweep voltammetry (LSV) using a stainless steel (SS)/film/Li cell configuration at a scan rate of 1 mV s⁻¹.

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