



# Structure and electrochemical properties of composite polymer electrolyte based on poly(vinylidene fluoride)–hexafluoropropylene/titania–poly(methyl methacrylate) for lithium-ion batteries



Jiang Cao<sup>a,b</sup>, Li Wang<sup>b,e</sup>, Mou Fang<sup>b,e</sup>, Xiangming He<sup>b,c,\*</sup>, Jianjun Li<sup>b,e</sup>, Jian Gao<sup>b,e</sup>, Lingfeng Deng<sup>d</sup>, Jianlong Wang<sup>b</sup>, Hong Chen<sup>a,d,1</sup>

<sup>a</sup> State Key Laboratory for Powder Metallurgy, Centre South University, Changsha 410083, PR China

<sup>b</sup> Institute of Nuclear and New Energy Technology, Beijing Key Lab of Fine Ceramics, Tsinghua University, Beijing 100084, PR China

<sup>c</sup> State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China

<sup>d</sup> College of Material Science and Engineering, Central South University of Forestry and Technology, Changsha, Hunan 410004, PR China

<sup>e</sup> Huadong Institute of Lithium Ion Battery, Zhangjiagang, Jiangsu 215600, PR China

## HIGHLIGHTS

- Titania–PMMA organic/inorganic hybrid is synthesized via in situ polymerization.
- The hybrid increases the porosity, uptake efficiency of the PVdF–HFP membrane.
- The hybrid increases the ionic conductivity of the PVdF–HFP based CPE.
- The hybrid enhances the performance of LiCoO<sub>2</sub> cycled between 4.4 and 2.75 V.

## ARTICLE INFO

### Article history:

Received 25 May 2013

Received in revised form

18 July 2013

Accepted 29 July 2013

Available online 8 August 2013

### Keywords:

Poly(vinylidene fluoride)

–hexafluoropropylene

Composite polymer electrolyte

Organic/inorganic hybrid material

Lithium-ion batteries

## ABSTRACT

Titania–poly(methyl methacrylate) (PMMA) organic–inorganic hybrid material is synthesized via in situ polymerization. The hybrid material is employed to prepare poly(vinylidene fluoride)–hexafluoropropylene (PVdF–HFP) composite polymer electrolyte. The effect of the hybrid material is investigated by SEM, TG–DSC, AC impedance and charge/discharge cycling tests. The results demonstrate that the inorganic–organic hybrid material as additive increases the porosity, pore size and electrolyte uptake of the PVdF–HFP composite polymer electrolyte membrane, so that the ionic conductivity of the composite polymer electrolyte membrane is improved. The performance enhancement of the composite polymer electrolyte is confirmed by an electrochemical test using LiCoO<sub>2</sub>/Li cells in the voltage range of 2.75–4.4 V. This study shows that titania–PMMA hybrid material is a promising additive for PVdF–HFP composite polymer electrolyte for Li-ion batteries.

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## 1. Introduction

With the increasing safety demands on the lithium-ion battery, more and more attention is paid to polymer electrolytes. Due to the fact that they have superior performance compared to traditional

liquid electrolytes in terms of no-leakage, high flexibility to cell geometry and high physical and chemical stability, polymer electrolytes are widely regarded as promising electrolytes for advanced Li-ion battery [1–3]. Gel polymer electrolyte (GPE) has been used in Li-ion batteries because it can provide higher ionic conductivity of about  $10^{-3} \text{ S cm}^{-1}$  compared to the solid state polymer electrolyte [4–8]. However, the mechanical properties and electrode/electrolyte interfacial stability of GPE need to be further improved to make it extensively applicable in Li-ion battery [9,10].

Because it has excellent chemical stability and plasticity [11–14], poly(vinylidene fluoride–co-hexa-fluoropropylene) (PVdF–HFP) is considered as a promising candidate polymer matrix material for polymer electrolyte. Nano-sized ceramic fillers added into PVdF–

\* Corresponding author. State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China. Tel.: +86 10 89796073; fax: +86 10 89796031.

E-mail addresses: [hexm@tsinghua.edu.cn](mailto:hexm@tsinghua.edu.cn), [hexiangming@tsinghua.org.cn](mailto:hexiangming@tsinghua.org.cn) (X. He), [chenhongcs@126.com](mailto:chenhongcs@126.com) (H. Chen).

<sup>1</sup> Powder Metallurgy Research Institute, Centre South University, Changsha 410083, PR China. Tel.: +86 731 85623086; fax: +86 731 85623038.

HFP casting solution improve not only the mechanical properties, but also the ionic conductivity and interfacial properties between composite polymer electrolyte and electrode [15–18]. However, as a result of high surface energy of the inorganic nanoparticles, it is very difficult to disperse nanoparticles into polymer solution. Moreover, the aggregated nano-particles will negate any benefits associated with the nano scale dimension [19,20]. Valeriy V. Ginzburg [20] revealed that nanoparticle-rich phase would segregate from the polymer even at very low particle concentrations regardless of the polymer composition because of the role of strong entropic surface tension. Kim et al. [21] reported that TiO<sub>2</sub> nanoparticles cannot be well dispersed, even under conditions such as ultra-sonication and the subsequent ball-milling. Therefore, the main issue in obtaining an applicable inorganic/polymer composite electrolyte may be how to improve the interface compatibility between polymers and inorganic nanoparticles.

In this study, an organic/inorganic hybrid material is designed to improve the compatibility of titania with PVdF–HFP. In detail, poly(methyl methacrylate) (PMMA) is grafted onto the surface of titania particles by in-situ polymerization with vinyl triethoxy silane as coupling agent to form titanium–PMMA hybrid. Then a composite polymer electrolyte that composed of PVdF–HFP matrix and titanium–PMMA additive is successfully prepared via phase inversion. The influences of titanium–PMMA hybrid material on the pore structure of the porous membrane, and the electrochemical performance of PVdF–HFP composite polymer electrolyte-casted PE separator used in 4.4 V LiCoO<sub>2</sub>/Li cells are investigated by SEM, TG-DSC and AC impedance, etc.

## 2. Experimental

### 2.1. Material and its pretreatment

(PVdF–HFP) is commercial fluoro-copolymer KynarFlex 2801 (Atofina Chemicals, 12 mol% HFP). Analytical grade *N,N*-dimethyl formamide (DMF) is used as solvent. Tetrabutyl titanate (TBOT) is used as the starting material to prepare titania sol by hydrolysis. Methyl methacrylate (MMA) is washed with 5 wt% NaOH solution before it is used to remove the inhibitors. Benzoyl peroxide, as initiator, is purchased from Tianjin Fuchen Chemical in China.

### 2.2. In situ preparation of titania–PMMA organic–inorganic hybrid material

10 mL TBOT is mixed with 50 mL ethanol to prepare “A” solution. A certain amount of deionized water is added into another 50 mL ethanol to prepare “B” solution, in which the pH of “B” solution is adjusted to 3–4 by using concentrated nitric acid. Then the “A” and “B” solution are mixed together to make a mixture in which the mole ratio of Ti to H<sub>2</sub>O is around 1:4. The obtained mixture is then hydrolyzed at 65 °C to form titania sol. After that, vinyl triethoxy silane and MMA monomer are added into the titania sol one by one at 80 °C and polymerizes with benzoyl peroxide, as initiator. It should be mentioned that PMMA is grafted onto sol nano-titanium oxide particle surface under the effect of coupling agent vinyl triethoxy silane. The hydrolyzed vinyl triethoxy silane contains more groups of –Si–OH and –C=C–, and –Si–OH can react with –Ti–OH to form –Si–O–Ti–, then –C=C– can be polymerized with MMA monomer to form in situ sol–gel nano-titanium oxide/PMMA hybrid material.

### 2.3. Preparation of sandwich type porous membranes

PE separator is used as supporting membrane [22], and PVdF–HFP based porous membranes are fixed to both sides of it. The

procedure is as follows: First, pristine PVdF–HFP or PVdF–HFP with titania–PMMA hybrid additive (10 wt%) is dissolved in *N,N*-dimethyl formamide (DMF) to form a homogenous solution, with concentration of 15 wt%. Then the solution is casted on both sides of PE separator to form sandwich-type film at room temperature. After casting, the sandwich-type composite membranes are submerged into distilled water bath immediately. The characterization of the sandwich porous membranes is carried out after further submerged in absolute alcohol for 2 h and then dried in vacuum oven at 60 °C for 2 days. The dry thickness of the resulting membranes is about 40 μm.

### 2.4. Sample characterization

The chemical species of the titania–PMMA hybrid material is examined by FT-IR (Jasco Co., FT-IR470). The structure and morphology of porous membranes are analyzed by a scanning electron microscope (SEM, JSM6301F) with an accelerating voltage of 20 kV. Thermal analysis is performed using Q2000 TA Instruments, under nitrogen atmosphere in a temperature range from 30 to 400 °C with a heating rate of 10 °C min<sup>-1</sup>.

Liquid uptake is measured by weighting method. The dry pristine PVdF–HFP or PVdF–HFP and Titania–PMMA blends composite membranes are cut into identical round pieces. After being carefully dried and weighted, the pieces are submerged in propylene carbonate (PC). After a certain period of time (5 min), the fully swelling pieces are taken out, and the excess liquid is sucked away by filter papers. Then the pieces are weighted, and the liquid uptake is calculated using the following formula [23]:

$$\text{Membrane liquid uptake} = \frac{w_t - w_0}{w_0} \times 100\%$$

where  $w_0$  is the weight of the dry piece,  $w_t$  is the weight of the piece after fully swelling. In this paper, liquid uptake is the mean value of 5 parallel samples.

### 2.5. Electrochemical measurement

As-prepared composite membranes are cut into identical round pieces, then submerged in the liquid electrolyte, which is prepared by 1.0 M LiPF<sub>6</sub> dissolving in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC), to form composite polymer electrolyte. Ionic conductivity of the composite polymer electrolytes are tested by AC impedance technique [11] in the frequency range from 1 Hz to 1 MHz and at different temperatures (–5, 5, 15, 25, 35, 45, 55, 65 °C). A thermostatic bath with ±0.1 °C precision is utilized to precisely control the temperature.

The test of the LiCoO<sub>2</sub>/Li 2032-type coin cell is performed galvanostatically at room temperature at charge–discharge rate 0.5 C in the voltage range of 2.75–4.4 V using Land Battery Test System (Wuhan Land Electronic Co. Ltd) [24,25]. The cathode consists of 85 wt% LiCoO<sub>2</sub> (Shanshan Co. Ltd), 10 wt% carbon black, and 5 wt% binder. The cell assembly is carried out in an argon filled glove box, with oxygen content less than 2 ppm and H<sub>2</sub>O content less than 1 ppm.

## 3. Results and discussion

The FTIR spectra of vinyl triethoxy silane, titania sol, and titania–PMMA hybrid material are shown in Fig. 1(A), (B) and (C), respectively. Titania is confirmed by –Ti–O–Ti– absorption band at 500–720 cm<sup>-1</sup> [26–28]. The characteristic absorption peaks of vinyl triethoxy silane, which are 1295, 1276, 1106 and 1082 cm<sup>-1</sup>, appeared in the spectrum of titania–PMMA hybrid material but

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