



# Microporous organic polymer-based lithium ion batteries with improved rate performance and energy density



Chong Zhang<sup>a, b</sup>, Xiao Yang<sup>a</sup>, Wenfeng Ren<sup>b</sup>, Yanhong Wang<sup>b, \*\*</sup>, Fabing Su<sup>b, \*\*\*</sup>, Jia-Xing Jiang<sup>a, \*</sup>

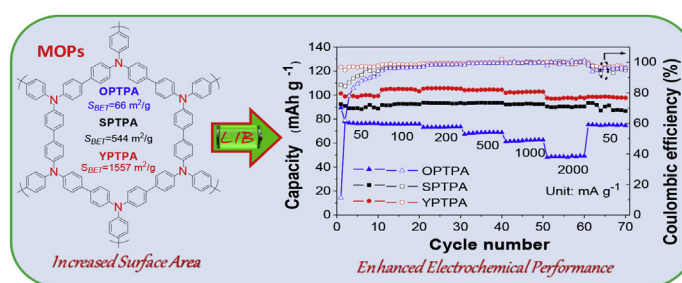
<sup>a</sup> Key Laboratory for Macromolecular Science of Shaanxi Province, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, Shaanxi, 710062, PR China

<sup>b</sup> State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, PR China

## HIGHLIGHTS

- Porous polymers were employed as cathode materials for lithium ion batteries.
- The surface area of the polymer affects the electrochemical properties.
- The polymers with high surface area exhibit improved electrochemical properties.
- YPTPA can deliver 97.6 mAh g<sup>-1</sup> within less than 3 min at 2000 mA g<sup>-1</sup>.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 10 November 2015

Received in revised form

22 February 2016

Accepted 21 March 2016

Available online 1 April 2016

### Keywords:

Triphenylamine

Microporous organic polymers

Organic cathode materials

Electrochemical characteristics

Lithium ion batteries

## ABSTRACT

Microporous organic polymers with triphenylamine segments were employed as cathode materials for lithium ion batteries. YPTPA with the highest surface area exhibits a discharge plateau at ~3.6 V vs. Li/Li<sup>+</sup>, an initial Coulombic efficiency of 96.8% at 50 mA g<sup>-1</sup> and a discharge capacity of 105.7 mAh g<sup>-1</sup> at 200 mA g<sup>-1</sup>. Compared to the homo-coupled polymer of OPTPA with relatively low surface area (66 m<sup>2</sup> g<sup>-1</sup>), SPTPA and YPTPA with higher surface area (544 and 1557 m<sup>2</sup> g<sup>-1</sup>, respectively) show enhanced rate performances and energy densities. YPTPA can deliver 97.6 mAh g<sup>-1</sup> within less than 3 min at high rate of 2000 mA g<sup>-1</sup> and the energy density of 334 Wh kg<sup>-1</sup> under an ultrahigh power density of 6816 W kg<sup>-1</sup>, while OPTPA only presents 48.2 mAh g<sup>-1</sup> at 2000 mA g<sup>-1</sup> with an energy density of 155 Wh kg<sup>-1</sup> under 6414 W kg<sup>-1</sup>. The great improvement in electrochemical properties of SPTPA and YPTPA demonstrates that increasing surface area of polymer cathodes by interweaving the redox-active units into microporous polymer skeleton is an efficient way to develop advanced polymer cathode materials with outstanding electrochemical performance.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Rechargeable batteries have been playing a key role in power source for portable consumer electronics, tools and electric vehicles. Among various rechargeable batteries, lithium ion batteries (LIBs) are undoubtedly one of the most popular and promising

\* Corresponding author.

\*\* Corresponding author.

\*\*\* Corresponding author.

E-mail addresses: [wangyanhong@ipe.ac.cn](mailto:wangyanhong@ipe.ac.cn) (Y. Wang), [fbsu@ipe.ac.cn](mailto:fbsu@ipe.ac.cn) (F. Su), [jjaxing@snnu.edu.cn](mailto:jjaxing@snnu.edu.cn) (J.-X. Jiang).

energy storage devices because of their high energy density and cyclability [1–4]. Currently, the leading technology of LIBs is based on the combination of lithium metal oxide or phosphate (e.g.  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFePO}_4$ ) cathode [3,5,6] and carbon anode. However, as a result of relatively slow intercalation kinetics of  $\text{Li}^+$  in the inorganic cathode materials, most of these conventional inorganic cathodes exhibited low rate performance, which is one of the most important challenges for practical applications. To achieve a sustainable and environmentally acceptable energy storage process, it is desirable to develop fast, high energy density and heavy metal-free cathode materials for the next generation of “green battery” [2,6–8]. Recent studies have revealed that organic cathode materials including organic molecules and polymers could be promising for LIBs because of their high energy/power densities, environmental friendliness, structural diversity and controllability, and resource renewability [2,9,10]. These organic compound-based cathode materials for LIBs mainly include organosulfur compounds [11–13], organic carbonyl compounds [14,15], conducting polymers [9,16,17,19], and organic free radical compounds [10,18,21].

However, the dissolution of small organic molecules in non-aqueous electrolyte will lead to the fast fading of electrochemical capacity, which is one of the most problems in practical applications. Some strategies have been developed to overcome this issue [8,15,22,23]. Among various approaches, it is a common and efficient strategy to design active materials with intrinsic insolubility, which mainly includes metal organic salts [22,24–26] and organic polymers [8,10,13,28]. Although utilization of metal organic salts and polymers can decrease the dissolution in electrolytes, organic salts bulk [24,26] and dense packed polymers [21] hinder the contact between active sites within the organic materials and electrolyte, resulting in low utilization ratio of active materials and slowing the diffusion of  $\text{Li}^+$ , which sequentially decreases the practical specific capacity and seriously compromises their advantage of intrinsic fast reaction kinetics on rate performance of LIBs [21,24,26,29–31]. High surface area of active materials allows for improved contact area with the electrolyte, more surface sites available for reversible reactions with  $\text{Li}^+$  and shorter  $\text{Li}^+$  diffusion pathways, which in turn lead to enhanced battery kinetics and specific capacity [26,27,29,30]. For example, Zhang et al. [27] reported that the P-doped  $\text{Li}_{2.05}\text{Mn}_{0.95}\text{P}_{0.05}\text{Si}_{0.95}\text{O}_4/\text{C}$  sample showed smaller particle size, higher surface area and electrochemical performances compared to  $\text{LiMnSiO}_4/\text{C}$ . Wang et al. [26] reported that the croconic acid disodium salt (CADS) nanowire with smaller size and higher surface area showed higher specific capacity and rate performance than CADS micropillar and CADS microwire. Chen et al. [24] synthesized organic tetralithium salts of 2, 5-dihydroxyterephthalic acid ( $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ ,  $\text{Li}_4\text{DHTPA}$ ) with different morphology (bulk, nanoparticles and nanosheets) and surface area, and  $\text{Li}_4\text{DHTPA}$  nanosheets with the highest surface area exhibited the best electrochemical performance among these materials. Zhang et al. [21] synthesized a polytriphenylamine terminated with ferrocene, the introduction of ferrocene segment hindered the dense packing of the resulting polymer, leading to the improved specific capacity and rate performance of LIBs.

Microporous organic polymers (MOPs), as a kind of advanced porous materials, show some features such as large specific surface area, high chemical and thermal stability, insolubility in most solvents, and synthetic diversity. These advantages make MOPs broad potentials in a variety of applications, such as gas adsorption [32–34], light emitting [35,36], energy storage [28,37–42] and heterogeneous catalysis [43–46]. There are, however, only a few reports on MOPs applied as electrode materials of LIBs. Jiang et al. [28] synthesized hexaazatrinaphthalene conjugated microporous polymers with built-in redox-active skeletons and permanent nanopores for cathode materials of LIBs. Sakaushi et al. [41]

obtained high power and long life all-organic energy storage devices by employing bipolar porous polymeric frameworks. Yang et al. [39] investigated the lithium storage of conjugated microporous polymers based on carbazole and benzothiadiazole. Chang et al. [47] developed a promising energy-storage system of porous polyimides as cathode materials for LIBs. These results demonstrated that MOPs could be promising candidates of electrode materials for the new generation of “green battery”.

Recently, we reported two microporous organic polymers (SPTPA and YPTPA) based on triphenylamine (TPA) for gas adsorption [33]. In this work, we employed both of the polymers as cathode materials for LIBs since both polymers combine high surface area with redox-active TPA units, which will lead to the improvement of electrochemical performances of LIBs. For comparison, another polymer of OPTPA was also synthesized via ferric chloride-catalyzed oxidative coupling reaction of *N, N, N', N'*-tetrphenylbenzidine. The three porous polymer networks possess the same repeating units (TPA), and thus the equal theoretical capacity, although they were produced from different polymerizations. Owing to the higher surface area, SPTPA and YPTPA display higher rate performance and energy density over a wide range of power density compared with OPTPA. In addition, YPTPA with higher surface area exhibits better electrochemical properties than SPTPA, indicating that increasing surface area of polymer cathodes by interweaving the redox-active units into microporous polymer skeleton is an efficient way to develop advanced polymer cathode materials with outstanding electrochemical performances.

## 2. Experimental section

### 2.1. Materials and synthesis

Ferric chloride ( $\text{FeCl}_3$ , analytical grade), methanol, chloroform and *N*-methylpyrrolidone (NMP, analytical grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Acetylene black and polyvinylidene fluoride (PVDF) are commercially available. The monomers of *N, N, N', N'*-tetrakis(4-bromophenyl)biphenyl-4,4'-diamine [48] and tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine were synthesized according to the literature [49].

OPTPA was prepared by  $\text{FeCl}_3$ -catalyzed oxidative coupling reaction of *N, N, N', N'*-tetrphenylbenzidine in chloroform. Typically,  $\text{FeCl}_3$  (648 mg, 4 mmol) was added into the solution of *N, N, N', N'*-tetrphenylbenzidine (488 mg, 1 mmol) in 20 mL chloroform. The mixture was stirred 18 h at room temperature under nitrogen atmosphere, and then 100 mL methanol was added into the mixture. The resulting precipitate was collected by filtration and washed with methanol. The desired polymer was collected and dried in vacuum oven at 80 °C overnight.

### 2.2. Characteristic and electrochemical measurement

The thermal properties and structure characteristic of YPTPA and SPTPA have been published in our previous work [33]. For OPTPA, the Fourier-transform infrared spectroscopy (FT-IR) spectrum of OPTPA was collected in transmission on a Spectrum GX FT-IR spectrometer (Fig. S1). The thermal properties was evaluated by EXSTAR TG/DTA 6300 (Seiko Instruments, Japan) with a heating rate of 10 °C  $\text{min}^{-1}$  in nitrogen atmosphere (Fig. S2). The porosity of OPTPA, SPTPA [33] and YPTPA [33] was determined by nitrogen adsorption and desorption at 77.3 K using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer (Fig. S3). The microscopic features of the sample were carried out on a field-emission scanning electron microscopy (SEM) (SU8020, Hitachi, Tokyo, Japan) and a high-resolution transmission electron

Download English Version:

<https://daneshyari.com/en/article/1286139>

Download Persian Version:

<https://daneshyari.com/article/1286139>

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