



Flexible polyimides through one-pot synthesis as water-soluble binders for silicon anodes in lithium ion batteries



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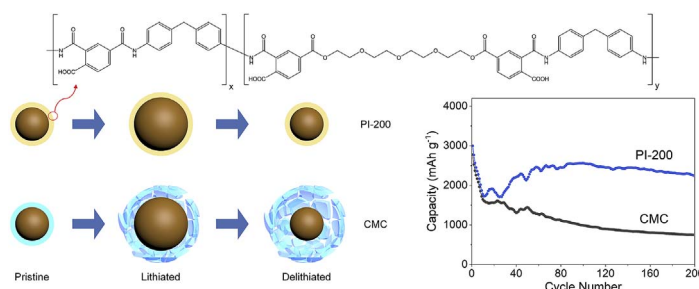
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HIGHLIGHTS

- Flexible polyimide binders were prepared through one-pot method.
- Water-soluble binders were used for silicon anodes in lithium ion batteries.
- The high capacity and cycling stability were achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of polyimides, which contain polyethylene glycol (PEG) segments with different molecular weight in the polymer chains, are synthesized through a facile one-pot method and characterized by Fourier transform infrared spectroscopy and hydrogen nuclear magnetic resonance spectroscopy. The main part of polyimides is originated from trimellitic anhydride chloride (TMAC) and 4,4'-methylenedianiline, onto which PEG segments are introduced through an esterification reaction with TMAC. These obtained polyimides, which acquire excellent water solubility after being neutralized by triethylamine, are applied as water-soluble binders to silicon negative electrodes for lithium ion batteries, and significantly improve the electrochemical performance of silicon anodes. Specially, the PI-200 (polyimide copolymerized with PEG-200) based silicon electrode exhibits a high initial discharge capacity of 2989.7 mAh g⁻¹ and remains about 2235.5 mAh g⁻¹ after 200 cycles at the current density of 0.1 C (420 mA g⁻¹).

1. Introduction

Various electrode materials have been investigated to improve the energy density of lithium-ion batteries in order to satisfy the expanding demands for portable electronic devices, electric vehicles and large-scale energy storage system [1–6]. Among these materials, silicon is considered as a promising anode material for next generation lithium-

ion batteries due to its high theoretical specific capacity of 4200 mAh g⁻¹ [7,8], which is over 10 times higher than currently used graphite (372 mAh g⁻¹) [9,10], and natural abundance. However, the cycle life of silicon anode is limited by the enormous volume change during charging-discharging cycles, resulting in repeatedly formed solid electrolyte interfaces, pulverization of electrodes, and continuous capacity fading [11–13]. Efforts regarding to these challenges have been tried by

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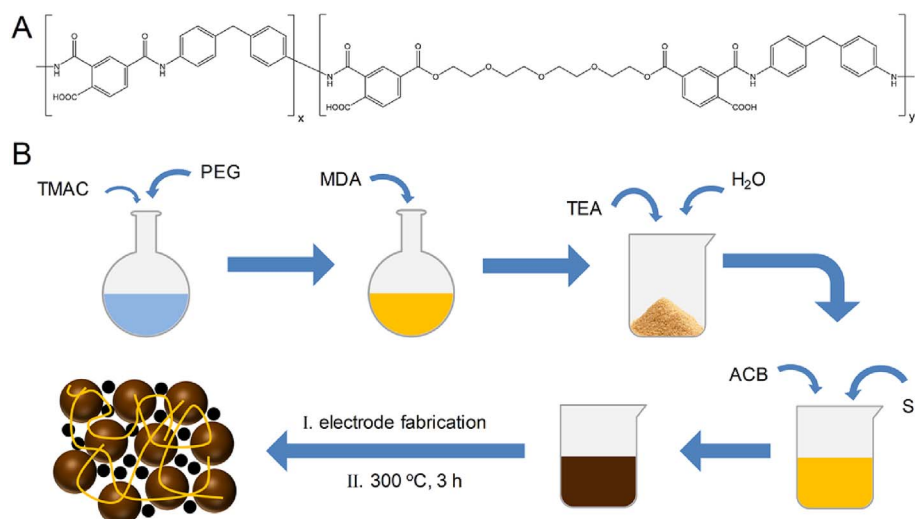


Fig. 1. (A) Molecular structure of PI-200. (B) Synthesis of polymer binders and fabrication of electrodes. The one-pot reaction was separated into two steps, esterification and polymerization. The synthesized polymer was dissolved and neutralized by the mixture of triethylamine (TEA) and water. The obtained solution was mixed with silicon powder and conductive acetylene carbon black (ACB) to get an electrode slurry. The slurry was then used for electrode fabrication. A heat treatment was needed to finish the imidization process after slurry coating. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

many researchers during last decade. For example, silicon particles can be relieved of fracture on the first lithiation process when the particle size is below the critical diameter of about 150 nm [12]. Liu et al. [14,15] designed a yolk-shell structure Si/C composite to reserve enough space for the expansion of silicon core. Consequently, this smart design protected the solid electrolyte interface from repeatedly destruction during charge-discharge processes. Yao et al. [16] fabricated a kind of hollow silicon nanosphere as electrode material for lithium-ion batteries, which reached a high discharge capacity of 2725 mAh g^{-1} in the first cycle and an outstanding capacity retention over 92% for the following every hundred cycles.

Although these methods achieved higher specific capacity than conventional graphite electrodes and improved the cyclic performance of silicon anodes, there is still an urgent demand of developing a facile and cost-efficient method to prolong the cycle life of silicon anodes for further large-scale production. Even though binders possess a relative small proportion in silicon electrode composites, it has been reported that they have a significant influence on the cycle performance of silicon anodes [17,18]. Many kinds of polymer binders have been developed in recently years, such as mussel-inspired binder [19], polyacrylic acid [20,21], polysaccharides [17,22–27], polyacrylonitrile [28], self-healing polymer binders [29], conductive binders [30–36], and so forth. In Zhang's work [26], a three-dimensional alginate binder was fabricated by using calcium ion as crosslinking agent. The volume expansion of silicon particles was restricted by the robust alginate network, thus significantly improving the electrochemical performance of silicon anodes. Sun et al. [29] designed a self-healing elastic polymer as carbon/silicon anode binder. The elastomer can be stretched over 4 times of original length with a tensile strength of $\sim 1.2 \text{ MPa}$ and maintain a tensile strength of 0.5 MPa after healing for 16 h, ensuring a high reversible specific capacity for stretchable electrodes.

As a kind of well-known engineering polymer, the polyimide has been applied in many fields due to its excellent comprehensive performance including superior mechanical properties, remarkable chemical and thermal stability as well as outstanding solvent resistance [37–39]. However, most of polyimides are insoluble or only soluble in strong polar organic solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethyl acetamide (DMAC), N,N-dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) [40,41], which are harmful to environment. In consideration of environmental protection requirements, most researchers mainly focus on improving the solubility of polyimides. It has been reported that a series of polyimides, which are attained from trimellitic anhydride chloride and aromatic diamine by solution condensation, are soluble in alkaline water such as the mixture solvent of water and triethylamine before imidization [42,43]. These polyimides

that haven't imidized contain at least one carboxyl group in each segment, which is reactive for neutralization. Consequently, the carboxylic ions in the polymer chains enable the neutralized polymer to be soluble in water.

In this study, a convenient one-pot solution condensation polymerization method was developed to synthesize polyethylene glycol modified polyimides with high molecular weight of hundreds of thousands of daltons. By introducing polyethylene glycol moieties into polyimides chains, the elongation at break was improved, which helps inhibit the silicon electrode from pulverization, and finally improved the specific capacity and cycle life of polyimide based silicon negative electrodes.

2. Experimental section

2.1. Materials

Trimellitic anhydride chloride (TMAC) and 4,4'-methylenedianiline (MDA) were purchased from J&K. Polyethylene glycol (PEG) with different molecular weight from 200 to 800 were obtained from Aladdin (Shanghai). DMAC was dried by calcium hydride overnight and then distilled before using. Silicon powder, conductive acetylene carbon black (ACB), and carboxymethyl cellulose (CMC) were purchased from Kejing Star Technology Co., Ltd. (Shenzhen). Polyacrylic acid (PAA) with average $M_v \sim 450,000$ was purchased from Sigma-Aldrich. Sodium alginate (SA) was purchased from Shandong Jiejing Group Corporation (China). Other reagents were all analytical pure.

2.2. Preparation of polymer binders

Esterification of PEG and polymerization were manipulated through a one-pot method as shown in Fig. 1. First, 1 mmol of anhydrous PEG and 2.32 g (11 mmol) of TMAC were dissolved in 20 mL of anhydrous DMAC, and then reacted for 24 h with N_2 protection. Next, 1.98 g (10 mmol) of MDA was added to the above solution and polymerized for 6 h under N_2 protection at ambient temperature. The obtained polymer was precipitated by 500 mL ethanol and then washed by 200 mL ethanol for 3 times. After drying in a vacuum oven at 40°C overnight, the product was milled to gain fine light yellow powder. Specially, the pure PI was directly polymerized by 2.11 g (10 mmol) TMAC and 1.98 g (mmol) MDA for 6 h without adding PEG.

2.3. Characterization of polymer binders

Fourier transform infrared (FTIR) spectroscopy and hydrogen

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