



Anthraquinone-based polyimide cathodes for sodium secondary batteries

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ARTICLE INFO

Article history:

Received 31 July 2015

Received in revised form 29 August 2015

Accepted 30 August 2015

Available online 3 September 2015

Keywords:

Sodium secondary batteries

Organic materials

Polyimide

Anthraquinone

Connection unit

ABSTRACT

Two polyimides using redox-active anthraquinone group as the connection unit are synthesized and characterized as cathodes for sodium secondary batteries. Sodium cells based on these two polyimide cathodes provide reversible capacities as high as 165 and 192 mAh g⁻¹, respectively, with excellent cyclabilities. A reversible four-electron transfer can occur for both of these two polyimides in the voltage range of 1.2–3.2 V with cyclic voltammetry measurements. These results suggest that anthraquinone is a promising connection unit for designing polyimide-based cathodes with high capacities for sodium secondary batteries.

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1. Introduction

Redox-active organic compounds are attracting an increasing attention as promising alternatives to inorganic electrode materials for electric storage batteries because of their environmental benignity, natural abundance, and structural diversity [1–6]. As sodium resources are inexhaustible, it would be greatly beneficial for large-scale electric storage applications if sodium secondary batteries could be built from renewable organic materials [7–10]. Moreover, organic compounds are structurally more flexible than inorganic materials and thus could accommodate the large-sized Na⁺ ions, which are advantageous over inorganic materials for the operation of sodium secondary batteries.

Although various kinds of organic electrode materials have been reported, the conjugated carbonyl compounds draw continuous research interest, because of their high redox reversibility and structural stability [4–9,11]. It has been well demonstrated that direct application of small molecular conjugated carbonyl compounds is difficult due to the serious dissolution in electrolyte, and polymerization is efficient to construct a stable and flexible framework to obtain a better cyclability [2–7,9,11]. However, although some polymers are prepared by directly connecting the redox-active groups [4,6], most polymers contain redox-inactive connection unit, which is not favorable for the enhancement of specific capacity. Therefore, it is urgently demanded to design new

organic electrode materials with high specific capacity and good cyclability.

Herein, two new polyimides (PI) are synthesized, using redox-active anthraquinone group as the connection unit, as this method is effective for the enhancement of specific capacity [11]. As shown in Fig. 1a, **PI1** and **PI2** have theoretical capacities of 383 and 342 mAh g⁻¹, respectively (based on a six-electron transfer for each unit). In this paper, the syntheses and properties of the PI cathodes for sodium secondary batteries were investigated.

2. Experimental

PI1 and **PI2** were prepared as follows: a mixture of 5 mmol of pyromellitic dianhydride (PMDA, Aladdin, 99%) or 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA, Aladdin, 96%), 5 mmol of 2,6-diaminoanthraquinone (Aladdin, 97%), and 50 mL of *N*-methyl-2-pyrrolidone (NMP) was heated under stirring in nitrogen atmosphere at 180 °C for 24 h. The solid was separated from the mixture and Soxhlet extracted using *N,N*-dimethylformamide for 24 h to remove the soluble oligomer. Then the insoluble solid product was dried under vacuum at 120 °C for 12 h and annealed in nitrogen atmosphere at 350 °C for 8 h. The chemical structure of the PI was characterized by Fourier transform infrared spectrometer (FTIR, VERTEX 70). The surface morphology was observed by scanning electron microscope (SEM, Sirion, 2000, FEI). Thermogravimetry (TG) was conducted on a TGA Q500 thermogravimetric analyzer (TA Instruments) in nitrogen at 10 °C min⁻¹.

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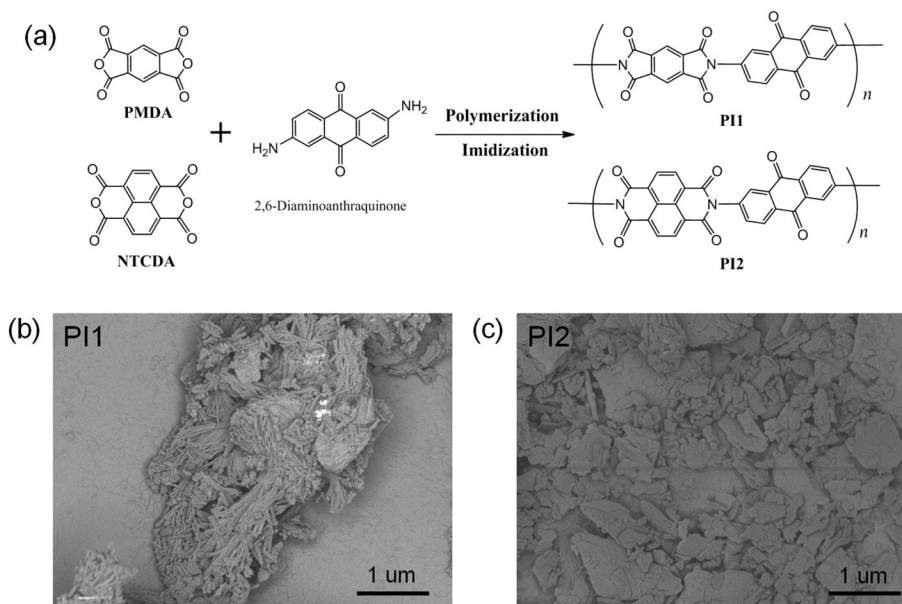


Fig. 1. (a) Synthesis and structures of **PI1** and **PI2**; SEM images of (b) **PI1** and (c) **PI2**.

The composite cathode was prepared by mixing 40 wt% PI, 40 wt% conductive carbon black (Ketjen Black, Wuhan Battery Plant), and 20 wt% polyvinylidene fluoride (PVDF, Arkema) together and dissolving the mixture into NMP to form a homogeneous slurry, then coating the slurry on aluminum foil (20 μm thick, ATL, China), drying at 80 $^{\circ}\text{C}$ for 12 h under vacuum. The average loading of PI on each electrode sheet (ϕ 12 mm) is around 0.8 mg cm^{-2} .

CR2032 cells were assembled in an argon-filled glove box (Mikrouna, super, H_2O and $\text{O}_2 < 0.1$ ppm), using the PI-containing electrode as cathode, a glass microfiber film (Whatman, GF/A) as separator, and Na foil as anode. NaPF_6 dissolved (saturated) in a mixture of dimethoxyethane (DME) and dioxolane (DOL) (1:1, by vol.) was used as the electrolyte. The specific capacities were calculated according to the net mass of PI in the electrodes. The cycling performances were tested using a charge–discharge apparatus (Land, CT2001A) at a constant current mode, with the voltage range of 1.5–3.5 V. Cyclic voltammograms (CVs) were measured on a CHI 600a electrochemical workstation (Shanghai, China) at a scan rate of 0.1 mV s^{-1} with the voltage range of 1.2–3.2 V.

3. Results and discussion

PI1 and **PI2** were synthesized by a simple and high-yield (94% for **PI1** and 91% for **PI2**) polymerization of PMDA or NTCDA with 2,6-diaminoanthraquinone (Fig. 1a), followed by annealing process for a complete imidization. Compared with the reaction of ethylene diamine with PMDA or NTCDA [4], the present reaction is easier to handle because of the nonvolatility of 2,6-diaminoanthraquinone, which confirms the 1:1 molar ratio of diamine and dianhydride, resulting in a higher molecular weight for PI and thus a better cyclability. The as-prepared **PI1** and **PI2** samples both appeared as brown powders, almost insoluble in common organic solvents. It was further revealed by SEM that **PI1** emerged as aggregated silks with the length of about 5 μm (Fig. 1b), and **PI2** appeared as platelets with an average size of about 1 μm (Fig. 1c).

PI could be best characterized by FTIR spectra (Figs. 2a and b). As shown in Fig. 2a, the 1238 cm^{-1} band of PMDA, which is ascribed to the stretch of the C–O band for dianhydride, decreases obviously upon polymerization. The band at 1362 cm^{-1} (**PI1**) is attributed to the stretch of C–N, suggesting the polymerization is successful [4]. The shift of the

carbonyl from 1770 cm^{-1} (PMDA) to 1726 cm^{-1} (**PI1**) also indicates a conjugation of the structure [4,9,12]. The new band at 1593 cm^{-1} (**PI1**) is originated from the carbonyl of anthraquinone unit. Similar results were also observed for **PI2** (Fig. 2b). The C–O band of NTCDA at 1166 cm^{-1} decreases sharply and the C–N band for **PI2** appears at 1344 cm^{-1} . The carbonyl band shifts from 1760 cm^{-1} (NTCDA) to 1674 cm^{-1} (**PI2**). The anthraquinone carbonyl band is found at 1583 cm^{-1} (**PI2**). TG results (Fig. 2c) reveal that both of **PI1** and **PI2** show much better thermal stabilities than the reactants (PMDA, NTCDA, and 2,6-diaminoanthraquinone), indicating the success of the synthesis [7,11].

PI1 and **PI2** were tested as cathodes for sodium secondary batteries, using galvanostatic charge–discharge cycling. Fig. 3a shows the typical charge–discharge curves for Na/**PI1** and Na/**PI2** cells at 50 mA g^{-1} . As seen in the figure, both cells show sloping discharge profiles. The average discharge voltage of **PI2** (2.01 V) is slightly higher than that of **PI1** (1.97 V), due to the larger conjugated structure of **PI2**, which lowers the lowest unoccupied molecular orbital energy and thus increases the average discharge voltage. Upon subtracting the capacity contributed by the conductive carbon (18 mAh g^{-1} for Ketjen Black, data not shown), the discharge capacities are 162 (**PI1**) and 179 (**PI2**) mAh g^{-1} , corresponding to 2.6 and 3.4 electrons per unit for **PI1** and **PI2**, respectively.

Fig. 3b shows the cycling performance of the Na/**PI1** and Na/**PI2** cells. As seen in the figure, both of the cells generally show good cyclabilities. The discharge capacities of the Na/**PI1** cell decrease slightly in the first 20 cycles and remain stable at about 165 mAh g^{-1} during the following 130 cycles, corresponding to a capacity retention rate of 92% after 150 cycles. On the other hand, the Na/**PI2** cell shows a stable reversible capacity of 192 mAh g^{-1} with 95% capacity retention after 150 cycles, indicating a relatively better cycling performance. Such a difference is also reflected by the coulombic efficiency. Good interface stabilities are indicated by the coulombic efficiencies of about 100% for both cells, but **PI2** shows coulombic efficiencies relatively more stable than **PI1**.

Figs. 4a and b show the CV curves of **PI1** and **PI2** electrodes, respectively. As shown in Fig. 4a, the main CV features of **PI1** appear as two pairs of redox peaks with similar areas at 1.30/1.75 and 1.75/2.25 V, resembling very much the CV patterns of poly(anthraquinonyl sulfide) [13]. It has been well demonstrated that a reversible two-electron

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