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Synthesis of three dimensional extended conjugated polyimide and application as sodium-ion battery anode

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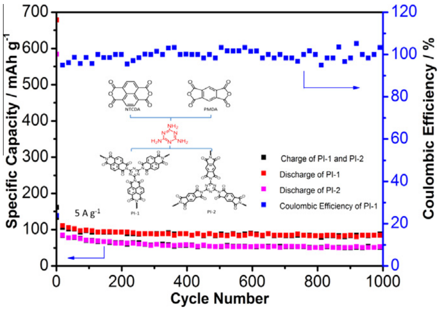
HIGHLIGHTS

- Three dimensional extended conjugated polyimides have been facilely prepared.
- The capacitance of obtained polymer is 88.8 mAh g^{-1} after 1000 cycles at 5.0 A g^{-1}.
- Synergistic effect exists in electron withdrawing amide groups and triazine rings.
- As-made polyimide is a promising candidate for Na-ion battery anode.

GRAPHICAL ABSTRACT



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ABSTRACT

Two covalent polyimides with different conjugated subunits have been synthesized as sodium-ion batteries anode. The melamine and two commercially available dianhydrides have been adopted as building blocks to fabricate 3D extended covalent frameworks, which are consisted of electron withdrawing amide groups and triazine rings to coordination with Na ions. The results revealed that cross-linked polymer exhibits excellent durability and rate capacity (88.8 mAh g^{-1} at a current density of 5.0 A g^{-1} after 1000 cycles), which provides a promising candidate for high performance Na-ion battery anode.

1. Introduction

Lithium-ion batteries (LIBs) are considered to be promising candidates of energy-conversion and energy-storage systems because of their high energy density, long cycling life in the past two decades [1–4]. However, the use of lithium is hampered by cost restriction and the resources of lithium would run out in future. Recently, increasing attentions are turning to Na-ion batteries (NIBs) as low-cost alternative technology other than LIBs. The abundance in the earth and low cost of Na become great advantageous when large amount of electrode materials are demanded for energy storage [5]. Furthermore, NIBs can utilize inexpensive aluminum current collectors for anodes because Al does not alloy with Na, whereas LIBs have to use expensive copper [6–8].

Currently, there has been great fascinating in developing advanced electrode materials for NIBs, and a large number of materials involving transition metal oxides have been proposed as cathodes, similar to those explored for LIBs [9–12]. Cao et al. reported a fabrication of single crystalline $Na_4Mn_9O_{18}$ nanowires with a high reversible capacity (128 mAh g^{-1} at 0.1 C, 1 C corresponds to 120 mA g^{-1}) and exceptional cycling performance as NIBs cathode

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[11]. Yang and co-workers synthesized a $Na_4Fe(CN)_6/C$ nanocomposite with exceptional cycling stability and high rate capability as NIBs cathode [12]. However, with regard to anodes, the commercial LIBs anode, i.e. graphitic carbon, does not perform well in NIBs due to its terrible capacity (31 mAh g^{-1}) [8]. The reason is that the Na-ion is larger than Li-ion (diameter: 2.32 vs 1.80 Å), which may increase the difficulty of insertion/extraction into the conjugated layers of graphitic during cycling [13]. Built upon the success of LIBs, intercalation-type inorganic anodes have been investigated for NIBs, where the performance is typically inferior than their LIBs counterparts due to the larger size of Na ions and the associated more dramatic and frequent structural changes during electrochemical cycling [14]. Meanwhile, covalent organic materials, owing to their abundance, design flexibility and environmental benignancy, especially the flexibility of structure facilitate the higher mobility of large-sized sodium ions, have lately enjoyed a renewed interest as electrodes in rechargeable sodium batteries [15].

Remarkably, organic carbonyl compounds are considered to be prospective electrode materials for NIBs due to their distinguish advantages, including lightweight, redox stability, multi-electron reactions, and availability from easily accessible natural sources [16]. Recently, coordination compounds 4,4′-Biphenyldicarboxy late sodium as anodes for Na-ion batteries elucidated the correlation between the structural properties of organic anodes and their electrochemical performances (200 mAh g^{-1}, 20 mA g^{-1}) have been investigated by Kyu Tae Lee and co-workers [17]. Xia and co-workers [18] reported a polyimide just delivers a reversible capacity of 140 mAh g^{-1} at the rate of 1 C (140 mA g^{-1}) and 84 mAh g^{-1} at the rate of 30 C (2520 mA g^{-1}). Zhang and co-workers demonstrated the use of aromatic carbonyl derivatives polyimides as cathode materials for NIBs (135.7 mAh g^{-1}, 24 mA g^{-1}) for the first time, which lays the foundation for future researches [19]. However, most of them were tested in a slow charge/discharge process (e.g. 20 mA g^{-1}, which takes a very long time for a charge/discharge) [7–9], and those tested under fast charge/discharge process often led to significant performance degradation. This phenomenon maybe ascribed to the poor conductivity of molecules and dissolve of the active material into electrolytes during cycling [9,19,20].

Herein, we utilize two commercially available dianhydrides (Fig. 1) namely pyromellitic dianhydride (PMDA) and naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCDA) as building blocks to polymerize with melamine for fabricating dianhydride-based polyimides (PIs). The electron withdrawing amides and triazine rings in the monomers could coordinate with Na ions to increase the storage capability. The amino-groups of melamine located on three directions could effectively build up 3D expended cross-linked network. After solution treatment, the active oligomers polymerized in depth at high temperature to constructed highly stable and conjugated framework, which could provide an effectively path to overcome these problems that mentioned above. With the improvement on the electrochemical stability and electronic conductivity, these materials could afford more reactive sites for electrode–electrolyte interaction and accelerate electron and ion transportation during reversible sodiation/desodiation processes. The electrochemical experiment data revealed that a high capacity, stable cycling life and ultrafast rechargeable anode for NIBs has been obtained.

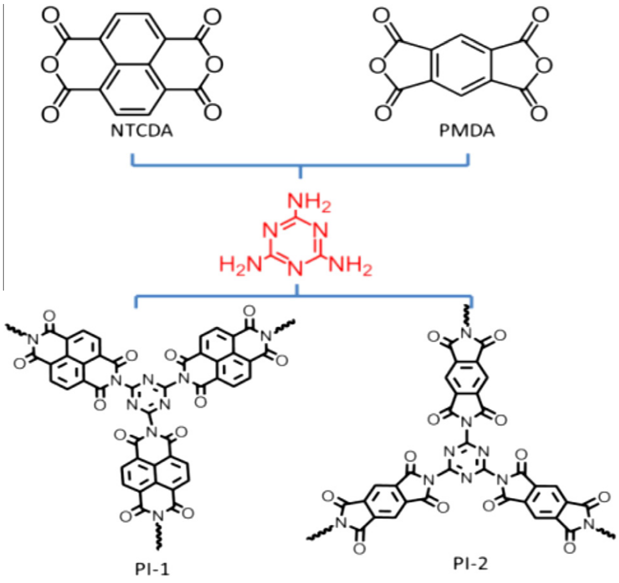

Fig. 1. Synthetic pathway of the polyimides.

2. Experimental

2.1. Materials preparation

All chemicals were commercially available grade and used without further purification. All of the solvents were dried by 4A molecular sieve before use.

2.2. Preparation of PI-1 and PI-2

A mixture of melamine (10 mmol) and dianhydride (NTCDA or PMDA) (15 mmol) were refluxed in N,N-Dimethylformamide (DMF, 30 mL) for 15 h under Ar protection at 150 °C. After reaction, the precipitates were filtrated and washed with ethanol for three times then dried at 75 °C in vacuum oven for 5 h. Then, the oligomers were heated at 330 °C in nitrogen for 6 h. Finally, the solid was washed by acetone twice and water (60 °C) twice to obtain the final products. The polyimide that prepared from NTCDA and PMDA is labeled as PI-1 and PI-2, respectively.

2.3. Analysis instruments

The chemical structures of the samples were characterized by Fourier transform infrared spectrometry (FTIR, Thermo Nicolet NEXUS 670, USA). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALab250Xi, Al Kα) was used to characterize chemical structure in further. The XRD pattern of the polyimides was recorded on an X'Pert PRO MPD X-ray diffractometer equipped with a monochromatized Cu Kα radiation from 10° to 75°. The stabilization of monomer and polymer were determined by thermogravimetric analysis (TGA, Netzsch STA 449C, Germany).

2.4. Electrochemical measurement

Working electrodes were prepared by mixing 50 wt% active materials, 30 wt% carbon black and 20 wt% binder in N-methyl-2-pyrrolidinone (NMP) for 20 min grinding in a mortar to form homogeneous slurry, which was then coated onto an aluminum foil current. The prepared working electrode was dried at 120 °C under vacuum for 8 h to remove the solvent before fabrication. Finally, the electrodes were cut into disks, and CR2032 cells were assembled in an argon-filled glove box with sodium metal foil as counter and reference electrode, Glass microfiber filters (GF/D) as separator, and 1 M $NaClO_4$ in ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 v/v) as electrolyte. Galvanostatic charge–discharge cycles were conducted on a LAND CT2001A battery tester at different current densities in the voltage range from 0.05 V to 2.5 V. The cyclic