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Polyimide as anode electrode material for rechargeable sodium batteries

Long Chen, Wangyu Li, Yonggang Wang, Congxiao Wang, Yongyao Xia*

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of New Energy, Fudan University, Shanghai 200433, China

Abstract

A polyimide synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and ethylene diamine (EDA) was evaluated as new anode material for sodium ion batteries (SIB).The polyimide delivers a discharge specific capacity of 140mAhg^{-1} at an average potential of 2 V vs. Na^{+}/Na with an initial coulombic efficiency of 97.6% and exhibits an excellent cycleability with a capacity rention of 90% over 500 cycles. A full SIB with polyimide anode and $Na_3V_2(PO_4)_3$/C cathode and $Na_4Fe(CN)_6$/C cathode were proposed.

Keywords:

Polyimide; Anode materials; Sodium-ion batteries

1. Introduction

Lithium-ion batteries have been investigated substantially in the past few decades and used widely in many aspects of our society [1]. However, the large-scale production of lithium-ion batteries for vehicle applications will eventually drive the cost of lithium higher in the near future. In this background, room-temperature sodium-ion batteries with abundant sodium resources and potentially low cost have been reconsidered particularly for such large-scale applications. While a number of promising cathode materials such as $Na_3V_2(PO_4)_3$ [2], Na_2FePO_4F [3], $Na_4Mn_9O_{18}$ [4], $Na_4Fe(CN)_6/C$ [5], $NaCrO_2$ [6] have already been invented, the anode remains the main obstacle impeding the application of this system. In earlier development, the anodic materials used were mostly hard carbon materials [7, 8]. Recently, Qian et al. reported a Sb/C nanocomposite [9] and amorphous phosphorus [10] as anode materials for sodium ion batteries. Hu et al. [11] reported the spinel $Li_4Ti_5O_{12}$ can also store Na ions. However, their long term cycling stability and initial coulombic efficiency are much inferior to those in lithium ion batteries.

Organic materials have recently attracted much more attention as alternative active materials for rechargeable Li-ion batteries [12-14]. Aside from abundant resources, organic electrode materials also have several advantages of chemical diversity, tunable redox property, mechanical flexibility and possible high energy density, offering a wide selection for battery applications. However, a few organic electrode materials for Na-ion batteries were reported, but exhibit poor electrochemical performance such as limited cyclic ability and poor initial coulombic efficiency [15-18].

In our opinion, dissolution of organic electrode materials in the electrolyte is the main reason for these problems, and the polymer has a better insolubility than small molecules [19]. Recently Deng et al. reported the poly(anthraquinonyl sulfide) (PAQS) as anode material for Na-ion battery with an excellent cycleability [20]. Based on this, polyimide is proposed herein for its stable and inactive framework which can avoid the unwanted dissolution. Its application as an electrode material for Li-ion batteries has been mentioned [21], further more it was also served as anode materials in aqueous LIB and SIB [22].

In this paper, we prepared 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (i.e. PNTCDA) which was introduced as a novel electrode material for Na-ion batteries. When PNTCDA is used as the anode material, its reduction and oxidation are accompanied by the association and disassociation of Na^+ ions with oxygen. Ideally, each formula unit is able to transfer four electrons through two steps (**Scheme 1**), which may allow a high theoretical specific capacity. The similar mechanism of Lithium ion battery was mentioned before [21]. Furthermore, the as-prepared PNTCDA anode was coupled with $Na_3V_2(PO_4)_3$/C and $Na_4Fe(CN)_6$/C cathode, respectively, to form 1.2 V full sodium ion batteries.

2. Experimental Section

2.1 Material synthesis

PNTCDA was synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and ethylene diamine (EDA) [21, 23]. Equimolar NTCDA and EDA reacted under reflux in the solvent of N-methylpyrrolidone (NMP) for 6 hours. The product was filtrated, washed with ethanol and NMP for several times, dried at 120°C in air for 12 hours, then heated in nitrogen atmosphere for 8 hours at 300□.

The $Na_3V_2(PO_4)_3/C$ samples were synthesized by a sol-gel method. An aqueous precursor containing stoichiometric $Na_2HPO_4.12H_2O$, $NH_4H_2PO_4$, NH_4VO_3 and sucrose was stirred at a constant temperature of 90℃ until the water was evaporated. Then, the resulting deposit was placed in a porcelain boat and heated at 800℃ for 10 h under N_2 flow in a tube furnace to form $Na_3V_2(PO_4)_3/C$ product.

$Na_4Fe(CN)_6/C$ composite was prepared, according to a previous report [5], by ball-milling dehydrated $Na_4Fe(CN)_6$ powder with Super P carbon in a mass ratio of 6:4 for 1 h.

2.2 Material characterization and electrochemical measurements

The as-prepared PNTCDA was characterized by fourier transform infrared spectroscopy (FTIR) measurements through a NICOLET 6700 FI-TR Spectrometer using KBr pellet. The PNTCDA-based composite electrodes were prepared by mixing active materials, carbon black, and binder (polyvinyl difluoride) (PVDF) in N-methylpyrrolidinone (NMP) at a weight ratio of 30:50:20. Subsequently, the slurry was cast uniformly on aluminum foil. The electrode film was vacuum-dried at 80□ for 10 h to remove the solvent before roll-pressing. The electrode film was then punched into discs with diameters of 12 mm dried at 120℃ in air for 12 h. Galvanostatic charge/discharge tests were carried out in CR2016 type coin cells, and the cells were assembled in a glove-box filled with Ar atmosphere. For the half-cell test, metallic sodium was used as the anode. The electrolyte solution was 1M $NaClO_4$-ethylene carbonate (EC)/ diethyl carbonate (DEC) (1:1 by volume). The cut-off voltages were 1.2V and 3.2V. The galvanostatic electrochemical test was evaluated under an automatic battery testing system (LAND CT2001A model). The cyclic voltammetry (CV) tests were carried out on CH Instruments electrochemical workstation (CHI 660D) at the rate of 1 mV s^{-1} between 1.2V and 3.2V.

3. Results and discussion

Fig.1a gives the FT-IR spectra of as-prepared PNTCDA, where all the characteristic absorption bands of the imide group can be detected clearly. These bands at 1703 cm^{-1}, 1670 cm^{-1} and 771 cm^{-1} were assigned to ν_{as}(imide C=O), ν_s(imide C=O) , and δ(imide C=O). The bands at 1350 cm^{-1} and 1582 cm^{-1} can be indexed to ν (imide C-N) and naphthalene, respectively. The result from FT-IR is consistent with previous reports, and thus demonstrates the successful synthesis of the target product (i.e. PNTCDA). **Fig. 1b** shows the cyclic voltammetry (CV) results of the PNTCDA. From the CV curves it is obvious that both the oxidation and reduction processes consist of two continuous steps, which are possibly associated with the formation of the radical anion (I^-), the dianion (I^{2-}) [24], respectively, in a similar manner as that for it in Li-ion battery [21]. The results of CV are quite consistent with the charge-discharge profiles in the **Fig. 1c**, in which there are two slope voltage curves of about 2.1V and 2.4V in the charge profile, and two slope voltage curves of about 1.8V and 2.25V in the discharge profile. As shown in **Fig. 1c**, at the low current density of 70 mA g^{-1}, PNTCDA displays a reversible capacity of 150 mAh g^{-1} which is only approximately the half of the theoretical capacity of PNTCDA (279.2 mAh g^{-1} calculated according to the reaction shown in **scheme 1**). Ideally, each formula unit will transfer two electrons in each step, and two steps are involved, so there should be four steps in CV curves. However, the experimental results of CV do not support this reaction mode given in **Scheme 1**. Obviously, the full electron transfer can not be achieved over the discharge/charge process. According to those previous studies about this material for Li-ion batteries [21], the full capacity may be obtained at a deeper discharge below 1.2 V, while which is accompanied by serious structural damage.

Fig. 1d shows the charge–discharge curves of PNTCDA electrode at varying currents from 140 mA g^{-1} (1C) to 2520 mA g^{-1} (30 C), and the capacities achieved at different currents were summarized in **Fig. 1e**. As shown in **Fig. 1d** and **1e**, the PNTCDA electrode delivers a reversible capacity of 140 mAh g^{-1} at the rate of 1C (140 mAh g^{-1}) . Even at high rate of 30 C (2520 mA g^{-1}), which corresponds to a time of 2 min to fully discharge, the capacity was about 60% of that at the 1 C rate, implying that the present electrode material is suitable for high-power battery application. Obviously, the voltage gap between charge and discharge increases with the growth of current densities (**Fig. 1d**), which is owing to the internal resistance of the PNTCDA electrode. The cyclic performance of the PNTCDA electrode at the rate of 1C (140 mA g^{-1}) is given in **Fig. 1f**. It can be observed that the initial coulombic efficiency is as high as 97.6% which is much superior to that of those small molecule or monomer organic electrode materials. Furthermore, the PNTCDA electrode exhibits a very stable cyclic performance with almost indiscernible capacity decay and kept its coulombic efficiency around 100% during successive 500 cycles. It can be assumed that the excellent cyclic ability arises apparently from the electrochemical reversibility of the conjugated carbonyl group and the structural stability of the polyimide chains.

Encouraged by the suitable redox activities of PNTCDA polymer, we used this anode material to construct two full Na-ion batteries with $Na_3V_2(PO_4)_3$/C cathode and $Na_4Fe(CN)_6$/C cathode, respectively, which have been invented as promising cathode materials for sodium battery [2,5]. **Fig. 2a** shows the charge/discharge curves of the $Na_3V_2(PO_4)_3$/C-Na half-cell at a current rate of 1 C in the voltage range of 2.5–4.0 V, **Fig. 2b** displays the charge/discharge profiles of $Na_4Fe(CN)_6$/C-Na half-cell between 2.0-3.8 V at the current rate of 1C. As shown in the **Fig. 2,** the experimental capacity of $Na_3V_2(PO_4)_3$/C and $Na_4Fe(CN)_6$/C were 85 mAh g^{-1} and 75 mAh g^{-1}, hence the full cell can be assembled with a mole ratio of $Na_3V_2(PO_4)_3$/C (cathode) to PNTCDA (anode) 1.65:1, and $Na_4Fe(CN)_6$/C (cathode) to PNTCDA (anode) 1.87:1. The electrolyte solution was 1.0 mol L^{-1} $NaClO_4$-ethylene carbonate (EC)/ diethyl carbonate (DEC) (1:1 by volume). Coin type PNTCDA-$Na_3V_2(PO_4)_3$/C and PNTCDA- $Na_4Fe(CN)_6$/C full cells are measured at the voltage interval of 0–2.3 V and the achieved results are summarized in **Fig. 3**. As shown in **Fig. 3a** and **Fig. 3c** the cell works very well with an average voltage of about 1.2 V and fully realizes the reversible capacity both the anode and cathode materials, the capacities were calculated based on the anode materials. If based on the sum of anode and cathode materials, the capacity should be about 75mAh g^{-1} and 70 mAh g^{-1} of PNTCDA-$Na_3V_2(PO_4)_3$/C and PNTCDA- $Na_4Fe(CN)_6$/C full cells respectively. In addition, these two cells also exhibit a good cycling stability with 75% and 65% capacity retention over 100 cycles at 1C rate (**Fig. 3b**, **Fig. 3d**). While in the full aqueous sodium ion battery with PNTCDA as anode material, its cycle stability is not so good for the poor cycle performance of cathode material [22].

4. Conclusion

In summary, we propose the use of PNTCDA, a kind of polyimide, as anode material for rechargeable sodium batteries. The two-electron transfer of each monomer unit results in a specific discharge capacity of around 140 mAh g^{-1}, a discharge voltage of 1.7–2.4 V, and a superior high rate capability with 60% capacity delivery at a 32C rate. Moreover, the intrinsic stability and insolubility of the polyimide ensures that it is not dissolved in the electrolyte, and thus allows an excellent cycling stability and a high initial coulomb efficiency of 97.6%. And we have successfully constructed two 1.2V full Na-ion batteries by use of PNTCDA anode, which present a good cyclability and reversibility. Particularly, the environmental friendliness and low cost of this anodic material enable it to be used for large-scale electric storage applications.

Acknowledgements

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Figures and Captions

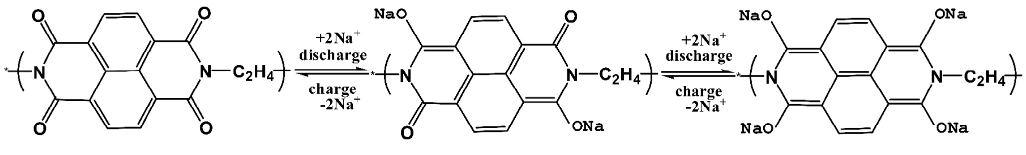
Scheme 1. Possible electrochemical redox mechanism of PNTCDA

Fig. 1 (a) FTIR spectra of PNTCDA (KBr pellets). (b) CV curve of PNTCDA. (c) Charge/discharge curves of Na/PNTCDA at 70 mA g^{-1} (0.5C). (d) Charge/discharge curves of PNTCDA at varying currents from 140 mA g^{-1} (1C) to 2520 mA g^{-1} (30 C). (e) Discharge capacities of Na/PNTCDA at different currents. (f) Cycle performance of Na/PNTCDA

Fig. 2 (a) Charge/discharge curves of $Na_3V_2(PO_4)_3$/C-Na half-cell at 85 mA g^{-1} (1C). (b) Charge/discharge curves of $Na_4Fe(CN)_6$/C-Na half-cell at 75 mA g^{-1} (1C)

Fig. 3 Electrochemical performances of full Na-ion batteries (a) Charge/discharge curves of PNTCDA- $Na_4Fe(CN)_6$/C at 1C rate (140 mA g^{-1}); (b) Cycling performance of PNTCDA- $Na_4Fe(CN)_6$/C at 1 C rate; (c) Charge/discharge curves of PNTCDA-$Na_3V_2(PO_4)_3$/C at 1C rate (140 mA g^{-1}); (d) Cycling performance of PNTCDA-$Na_3V_2(PO_4)_3$/C at 1 C rate.

Scheme 1



PNTCDA

Figure 1

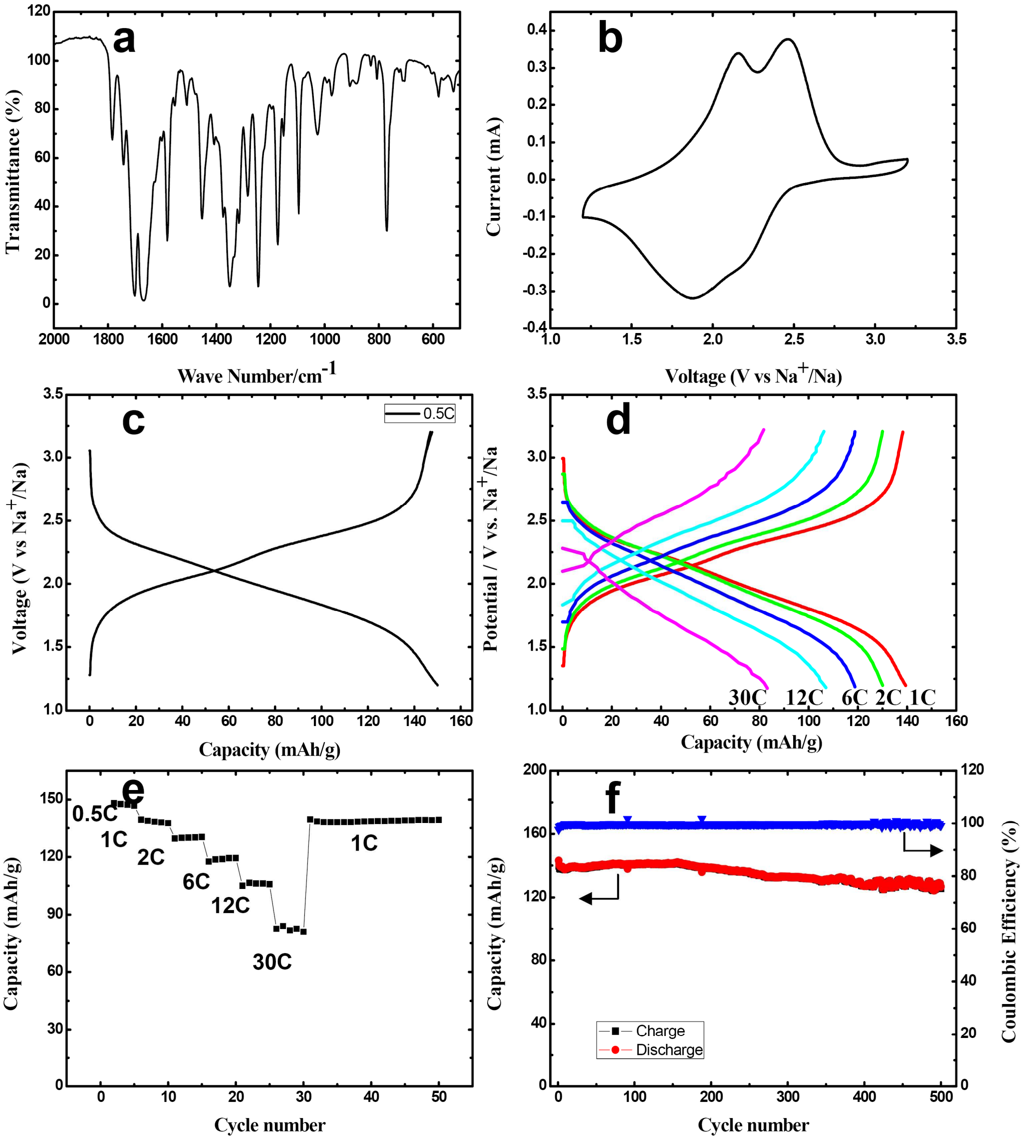

a
Transmittance (%)
Wave Number/cm^{-1}
2000 1800 1600 1400 1200 1000 800 600
0 20 40 60 80 100 120
b
Current (mA)
Voltage (V vs Na$^+$/Na)
1.0 1.5 2.0 2.5 3.0 3.5
-0.4 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.3 0.4
c
0.5C
Voltage (V vs Na$^+$/Na)
Capacity (mAh/g)
0 20 40 60 80 100 120 140 160
1.0 1.5 2.0 2.5 3.0 3.5
d
Potential / V vs. Na$^+$/Na
Capacity (mAh/g)
30C 12C 6C 2C 1C
0 20 40 60 80 100 120 140 160
1.0 1.5 2.0 2.5 3.0 3.5
e
Capacity (mAh/g)
Cycle number
0.5C
1C
2C
6C
12C
30C
1C
0 10 20 30 40 50
0 30 60 90 120 150
f
Capacity (mAh/g)
Coulombic Efficiency (%)
Cycle number
Charge
Discharge
0 100 200 300 400 500
0 40 80 120 160 200
0 20 40 60 80 100 120

Figure 2

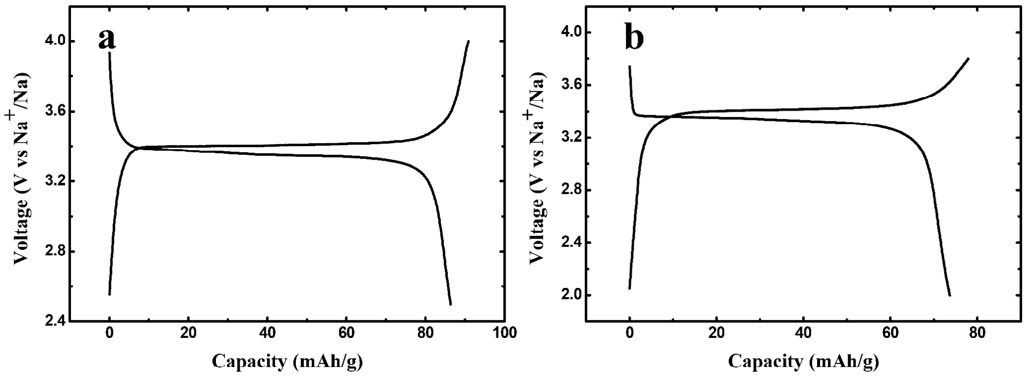
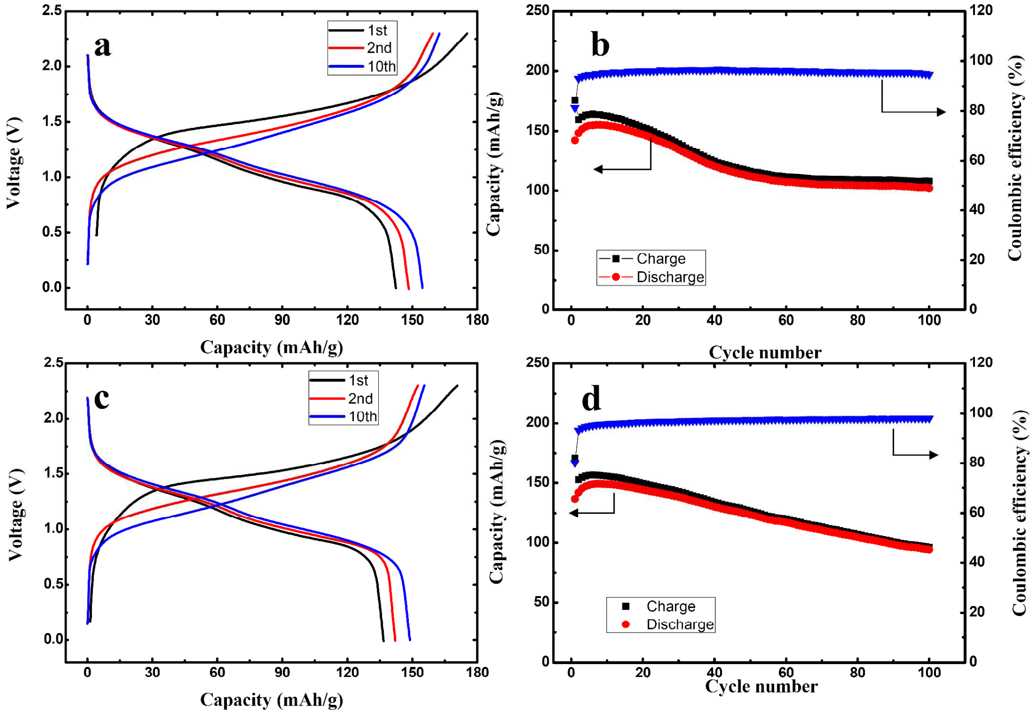

a
b
Voltage (V vs Na$^+$/Na)
Capacity (mAh/g)
2.4
2.8
3.2
3.6
4.0
0
20
40
60
80
100
2.0
2.4
2.8
3.2
3.6
4.0
0
20
40
60
80

Figure 3


a
b
c
d
Voltage (V)
Capacity (mAh/g)
1st
2nd
10th
2.5
2.0
1.5
1.0
0.5
0.0
0
30
60
90
120
150
180
Capacity (mAh/g)
Coulombic efficiency (%)
Cycle number
Charge
Discharge
250
200
150
100
50
0
20
40
60
80
100
120

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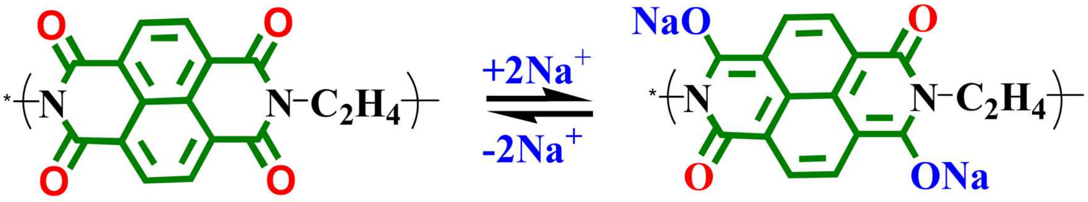
TOC



Polyimide served as anode material for sodium ion battery with large reversible capacity and excellent cycling stability.
