

Sulfonyl-based polyimide cathode for lithium and sodium secondary batteries: Enhancing the cycling performance by the electrolyte



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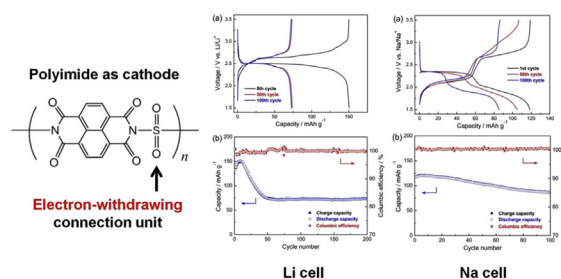
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HIGHLIGHTS

- Polyimide with electron-withdrawing sulfonyl connection unit is synthesized.
- Li cell based on this polyimide cathode provides a flat discharge plateau at 2.5 V.
- Increasing electrolyte concentration can enhance the cycling performance.
- Na cell gives a flat discharge plateau at 2.3 V and a sloping plateau at 1.9 V.

GRAPHICAL ABSTRACT



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ABSTRACT

A sulfonyl-based polyimide has been synthesized and investigated as cathode for lithium and sodium secondary batteries. The lithium cell delivers a flat discharge plateau at 2.5 V with an average discharge voltage of 2.45 V. Increasing the lithium salt concentration can largely enhance the cycling performance. A stable discharge capacities of 120 mAh g⁻¹ is obtained for long-term cycling (450 cycles) with concentrated electrolyte. The sodium cell provides two plateaus with an average discharge voltage of 2.0 V. The capacity retention rate of the sodium cell is 70% at 100th cycle (86 mAh g⁻¹).

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1. Introduction

Pressing concerns about environmental issues have led to an urgent demand for sustainable electric energy storage techniques. Existing electric energy storage materials mostly rely on non-

renewable mineral resources dealt via energy requiring ceramic processes, which have serious cost and resource limitations that hinder their large-scale applications [1]. As an attractive alternative to inorganic materials, redox-active organic compounds have recently attracted great attention as electrodes for lithium and sodium secondary batteries, because of their advantages such as environmental benignity, structural diversity, and availability from easily accessible natural resource [2–3]. In particular, organic sodium secondary batteries are favorable for large-scale applications due to the natural abundance of sodium resources [4–8]. Moreover, organic compounds are structurally more flexible than inorganic

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materials and thus could accommodate the large-sized Na⁺ ions, which are advantageous for the operation of sodium secondary batteries. In spite of the advantages, organic cathodes usually show relatively low discharge voltage than inorganic materials, and an ordinary method to improve the discharge voltage is introducing electron-withdrawing group to the organic compounds [9,10]. However, additional group will increase the formula weight and result in a decrease in specific capacity, which is not favorable for the enhancement of energy density. Therefore, a new strategy is demanded to design organic electrode materials more wisely.

Although a variety of organic electrode materials have been reported, conjugated carbonyl compounds draw continuous research interest because of their high redox reversibility and structural stability [6–8,11–14]. 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 indispensable to construct a stable framework to obtain a better cyclability [2,3,7,8,11–13]. However, polymerization usually introduces connection unit, which increases the formula weight and reduces the energy density. As sulfonyl is a well-known electron-withdrawing group widely used for designing lithium conducting salts and ionic-liquid electrolytes [15–17], it is thought that using electron-withdrawing sulfonyl group as the connection unit for conjugated carbonyl polymers might be a feasible strategy to improve the discharge voltage without affecting the capacity much, because no additional functional group is introduced.

On the other hand, it is found that previous works have asymmetrically focused on improving the cycling performance by modification of the electrodes, and not much effort has been devoted to investigating the effects of electrolytes on organic lithium and sodium secondary batteries. It will be much simpler if the cycling performance could be enhanced by optimization of the electrolytes, and more selections of electrode materials could be provided for organic batteries.

In the present study, an electron-withdrawing sulfonyl group-connected polyimide (**PI**, Fig. 1) was synthesized and characterized as cathode for lithium and sodium secondary batteries. The effects of the electrolyte on the electrochemical properties were also investigated to enhance the long-term cyclability.

2. Experimental

The **PI** was prepared as follows: A mixture of 5 mmol of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA, Aladdin, 96%), 5 mmol of sulfamide (Aladdin, 97%), and 50 mL of *N*-methyl-2-pyrrolidone (NMP) were heated under stirring (about 120 rpm) in nitrogen atmosphere at 150 °C for 24 h and then at 200 °C for 12 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 yield was 72%. 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 Instrument) in nitrogen atmosphere at 10 °C min⁻¹ from 50 to 800 °C. The polyimide with ethylene as the connection unit was synthesized in the same manner, using ethylene diamine instead of sulfamide.

The composite cathode was prepared by mixing 60 wt% **PI**, 30 wt% conductive carbon black (super P, Timcal), and 10 wt% polyvinylidene fluoride (PVDF, Arkema) together and dissolving the electrode mixture into NMP to form a homogeneous slurry, then coating the electrode slurry on aluminum foil (20 μm thick, ATL, China), drying at 80 °C for 12 h under vacuum. The average loading of the **PI** on each electrode sheet (Φ 12 mm) is around 1.2 mg cm⁻².

CR2032 cells were assembled in an argon-filled glove box (Mikrouna, super, H₂O and O₂ < 0.1 ppm), using the **PI**-containing electrode as cathode, a glass microfibre film (Whatman, GF/A) as separator, Li foil or Na foil as anode. LiTFSI (lithium bis(trifluoromethanesulfonyl)imide, Aldrich, 1.0, 2.0, and 3.0 mol L⁻¹) dissolved in a mixture of dimethoxyethane (DME) and dioxolane (DOL) (1:1, by vol.) was used as the electrolytes for lithium cells. NaPF₆ dissolved (saturated) in a mixture of DME/DOL (1:1, by vol.) was used as the electrolyte for sodium cells. The specific capacities of the cells were calculated according to the net mass of **PI** in the electrode. The cycling performances of the cells were tested using a charge–discharge apparatus (Land, CT2001A) at a constant current mode, with the voltage limited between 1.5 and 3.5 V. Cyclic voltammograms were measured on a CHI 600a electrochemical workstation (Shanghai, China) at a scan rate of 0.1 mV s⁻¹ with the voltage range from 1.5 to 3.5 V.

3. Results and discussion

The sulfonyl-based polyimide was synthesized by a simple polymerization of NTCDA with sulfamide (Fig. 1), followed by annealing process for a complete imidization [12]. It was found that the reaction time and annealing process are important for the cycling performance of **PI**. The obtained **PI** was a dark brown powder and almost insoluble in common organic solvents. It is revealed by the SEM image (Fig. 2a) that **PI** appears as platelets with the size of about 10 μm. The infrared spectra of NTCDA and **PI** are shown in Fig. 2b. The 1122 cm⁻¹ band of NTCDA, which is ascribed to the stretch of the C–O band, decreases obviously upon polymerization. The bands at 1348 and 1267 cm⁻¹ (**PI**) are attributed to the stretch of C–N and sulfonyl, respectively, suggesting the polymerization is successful. The shift of the carbonyl from 1760 to 1680 cm⁻¹ also indicates a conjugation of the structure [8,11,12]. TG results (Fig. 3) reveal that **PI** shows much better thermal stabilities than NTCDA, indicating the success of the synthesis [7,11,18,19], and the remaining product at high temperature might be **PI** with higher molecular weight and higher thermal stability.

Electrochemical redox properties of **PI** as cathode for lithium secondary batteries were characterized by cyclic voltammetry (CV) and galvanostatic charge/discharge cycling. Fig. 4 shows the CV profiles of the **PI** electrode in 1.0 mol L⁻¹ LiTFSI in DME/DOL (1:1, by

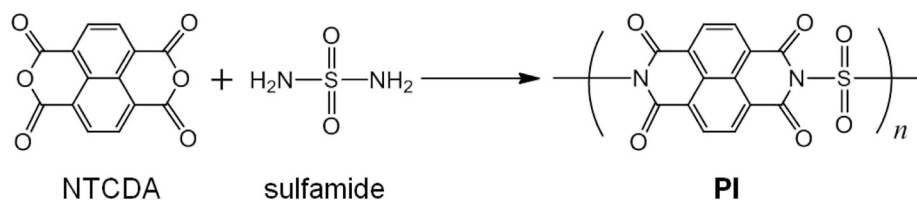


Fig. 1. Synthesis and structure of the sulfonyl-based polyimide (**PI**).

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