



Short communication

Poly(diphenylaminesulfonic acid sodium) as a cation-exchanging organic cathode for sodium batteries

Y.F. Shen^a, D.D. Yuan^a, X.P. Ai^a, H.X. Yang^a, M. Zhou^{a,b,*}^a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China^b College of Materials Science and Engineering, Huangzhong University of Science and Technology, Wuhan 430074, China

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ABSTRACT

A Na-rich poly(diphenylaminesulfonic acid sodium) (PDS) is prepared by oxidative polymerization and tested as an organic Na-host cathode for Na-ion batteries. Due to the highly self-doped benzenesulfonic anions grafted on the polyaniline backbones, this redox-active polymer demonstrates a reversible capacity of 100 mAh g⁻¹ at an average potential of ~3.4 V, reaching its theoretical value of reversible 1 Na insertion/extraction reaction. In addition, this polymer cathode also exhibits considerable rate capability and cycling stability, possibly serving as a low cost and sustainable cathode of Na-ion batteries for widespread electric storage applications.

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1. Introduction

Organic electrode materials for electric storage batteries have attracted great attention because of their low cost, resource sustainability and structural diversity. A large variety of polymer hosts have been reported for electrode-active materials of rechargeable lithium batteries [1,2], however, few of them have been investigated for sodium-ion batteries. As an attractive alternative to Li ion technologies, Na-ion batteries possess distinct advantages of resource abundance and environmental benignity [3,4]. In particular, if Na-ion batteries could be built from renewable organic materials, it would be greatly beneficial for large scale electric storage applications.

Redox-active polymers have flexible frameworks that should be capable of accommodating larger Na ions for reversible insertion reaction. In recent years, a number of n-type organic molecules [5–7] and polymers [8,9] have demonstrated considerable anodic Na-storage capacities; however, only a very few of organic cathodes is reported to have cathodic Na-storage performances [10,11]. Though a number of p-doped polymers have been used as cathodes of Na-ion batteries, they undergo their charge/discharge reactions through a reversible p-doping/dedoping mechanism of electrolyte anions, which cannot act as a Na host to construct “rocking chair type” Na-ion batteries [9,12].

To solve this problem, we recently proposed a new strategy to create a polymeric Na-host cathode by grafting ionizable sodium sulfonate on

redox-active polypyrrole backbones, by which this self-doped polypyrrole can undergo its redox reaction through a Na⁺ insertion/extraction mechanism, acting as a Na⁺-rich cathode [10]. However, due to the low doping density (21%) of the sodium salt of the grafted organic group on the polypyrrole backbones, this self-doped polypyrrole did not give high capacity utilization with a partial capacity contribution from reversible p-doping of electrolyte anions.

To enable high density Na storage in polymeric host, we synthesized a Na-rich polymer, poly(diphenylaminesulfonic acid sodium) (PDS), which contains nearly 1 Na per diphenylamine unit. Due to the high redox activity and high redox potential of diphenylamine moiety, the PDS polymer exhibits a fully reversible 1 Na insertion capacity (100 mAh g⁻¹) at a high voltage of 3.4 V and a good cyclability at various high rates. In this paper, we describe the synthesis and electrochemical properties of the PDS material as an organic cathode host for Na-ion batteries.

2. Experimental

The PDS polymer was synthesized by chemical oxidative polymerization of diphenylaminesulfonic acid sodium in acetonitrile using anhydrous FeCl₃ as the oxidant. The experimental procedure was to dissolve 2 mmol diphenylaminesulfonic acid sodium in 15 mL acetonitrile and then add dropwise anhydrous FeCl₃ (10 mmol in 5 mL acetonitrile) into the above solution to initiate the polymerization. The polymerization was carried out at 0 °C for 12 h. The polymeric precipitate was washed several times with ethanol and finally dried at 60 °C under vacuum for 24 h.

* Corresponding author at: College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China. Tel.: +86 27 68754526; fax: +86 27 87884476.

E-mail address: minzhou-ec@whu.edu.cn (M. Zhou).

Elemental analysis of the chemical composition of the polymer was carried out on VarioEL III (German). ICP-AES analysis was performed with IRIS Intrepid III XSP. FT-IR spectra were recorded on a NICOLET AVATAR 360 FT-IR spectrometer.

Electrochemical performance characterization was carried out using 2016-type coin cells with a film cathode (containing 50 wt.% PDS, 20 wt.% carbon fibers (VGCF, Showa Denko Co), 20 wt.% carbon black (Ketjenblack, Wuhan Battery Plant) and 10 wt.% polytetrafluoroethylene binder) and a sodium disk anode. The electrolyte is 1 mol L⁻¹ NaPF₆ in a mixture of ethylene carbonate and diethyl carbonate (EC/DEC = 1:1 by volume, Shinestar battery materials co. Ltd, China). 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 2.5 to 4.2 V.

3. Results and discussion

The as-prepared PDS sample appeared as a dark greenish black powder, almost insoluble in commonly used organic electrolyte. Fig. 1 shows the SEM image and the FT-IR spectrum of the PDS sample. As shown in Fig. 1a, the PDS polymer emerged as aggregated particles with an average size of ~60 nm. The FT-IR spectrum in Fig. 1b reflects all the characteristic absorptions of the PDS polymer. The adsorption bands at 1134 and 1363 cm⁻¹ are assigned to the in-plane bending vibrations of benzene and sulfonate-grafted benzene rings, respectively. The 1174 and 1035 cm⁻¹ bands are characteristic of the symmetric and antisymmetric stretchings of the S=O double bond and the 701 and 652 cm⁻¹ bands are attributed to the stretching vibrations of the S–O bond in sulfonate groups, respectively. Usually, polyaniline and its derivatives consist of two principal units: benzenoid ring and quinonoid ring [13]. In our PDS sample, the characteristic stretching modes of the benzenoid (N–B–N) and quinonoid (N=Q=N) structures are well defined at 1490 and 1593 cm⁻¹, the relative intensity (*I*₁₄₉₀/*I*₁₅₉₃) of

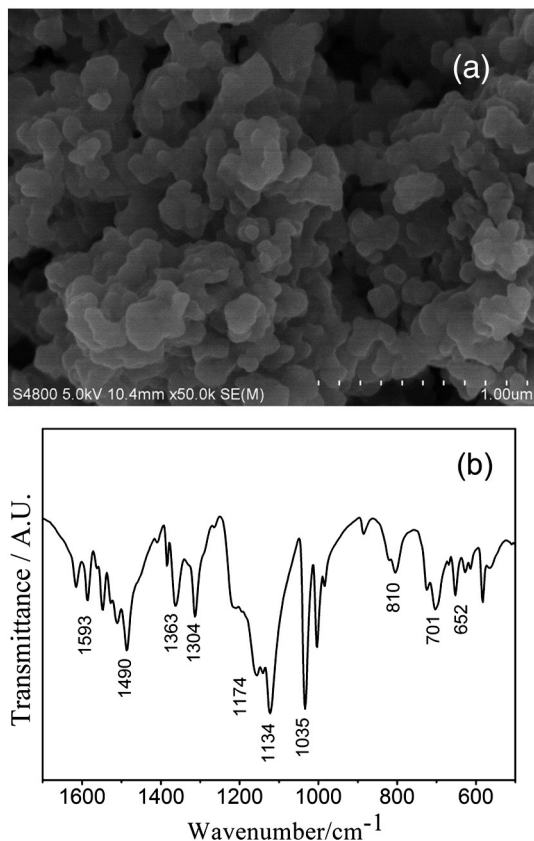


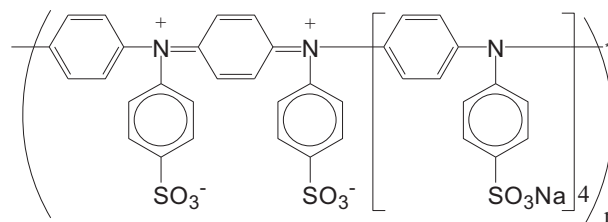
Fig. 1. (a) SEM and (b) FT-IR spectrum of the as-prepared PDS material.

which is sufficiently high, suggesting that the PDS polymer existed in a reduced state. Combined with elemental composition analysis and ICP characterization, the chemical composition and structure of the PDS polymer can be determined as Scheme 1.

Electrochemical redox properties of the PDS polymer were characterized by cyclic voltammetry (CV) and galvanostatic charge–discharge cycling. Fig. 2a shows the CV curves of the PDS electrode in 1.0 mol L⁻¹ NaPF₆ in a mixed solvent of EC + DEC. As shown in the figure, the main CV features of the polymer appear as two pairs of redox peaks at 3.5/3.3 V and 3.7/3.6 V, resembling very much the CV patterns of polyaniline previously reported [13,14]. According to previous studies of the redox mechanism of polyaniline [14,15], its two pairs of CV bands are attributed to reversible doping/dedoping reactions of PF₆⁻ anions into/from its polymer chains, respectively. However, in our PDS sample, the benzenesulfonate anions are already chemically grafted on the polyaniline backbones and only disassociable Na⁺ ions could be moved out and in from the polymer for charge counterbalance. Therefore, the redox reaction of the PDS electrode may proceed through a reversible Na⁺ insertion mechanism rather than a conventional p-doping/dedoping mechanism of electrolyte anions. In addition, the CV current in Fig. 2a shows a gradual increase in the first ten cycles and then kept stable in the subsequent cycles, apparently involving an activation process of the polymer electrode.

In accordance with its CV features, the PDS electrode showed sloping charge/discharge profiles in the voltage region of 4.0–3.0 V (Fig. 2b), which are actually an overlap of two steps of charge/discharge with similar slopes. Correspondingly, the reversible capacity of this PDS electrode also shows a gradual increase from its initial 30 mAh g⁻¹ to a stable value of 99 mAh g⁻¹ at the 10th cycle, which is close to its theoretical capacity (100 mAh g⁻¹) as expected from 1 Na⁺ insertion/extraction into/from each diphenylaminesulfonate unit. In comparison with the organic Na⁺ insertion cathodes recently reported, this PDS material delivers a much higher capacity than sodium sulfonate-grafted polypyrrole [10] and a much higher working voltage than polyimide cathodes [11], demonstrating a combined advantage of high voltage and high capacity.

In addition, the PDS cathode also exhibits a remarkable high rate capability. Fig. 3a shows the charge and discharge curves of the PDS cathode in a Na⁺ electrolyte at various current rates. As shown in the figure, the PDS electrode delivers a reversible capacity of 92 mAh g⁻¹ at 100 mA g⁻¹ and 75 mAh g⁻¹ at 200 mA g⁻¹. Even at a very high rate of 400 mA g⁻¹, this electrode can still release a capacity of 43 mAh g⁻¹, exhibiting a considerable high-rate capability. To evaluate the practical possibility of the PDS cathode for Na-ion battery applications, 2016-type Na-PDS coin cells were assembled and cycled at constant and varying current rates. As shown in Fig. 3, the reversible capacity of the PDS cathode rises up to 100 mAh g⁻¹ quickly in the first 10 cycles and then decreases at 72 mAh g⁻¹ after 100 cycles with a capacity retention of 70%, showing a considerable capacity stability at the galvanostatic cycling at 50 mA g⁻¹. When cycled at changing rates as shown in Fig. 3b, the PDS electrode can still keep its capacity steadily without much capacity degradation. After 65 cycles at various high rates from 50 to 800 mA g⁻¹, the polymer cathode can still deliver 85 mAh g⁻¹, about 85% of its initial capacity, demonstrating an excellent high-rate cyclability.



Scheme 1. The formula of pristine polymer.

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