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A sulfonated polyaniline with high density and high rate Na-storage performances as a flexible organic cathode for sodium ion batteries

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A Na-rich cathode is developed by grafting electron-withdrawing -SO₃Na group on polyaniline chains. Due to the immobile doping and effective activation of the sulfonate group, this polymer demonstrates a high capacity (133 mAh g⁻¹) and excellent cyclability through cation-exchanging reaction, offering a low cost and sustainable cathode for SIBs.

Sodium ion batteries (SIBs) have recently captured worldwide interest as the most attractive alternative to lithium ion batteries (LIBs) owing to the distinct advantages of resource abundance and environmental benignity.^{1,2} However, an overwhelming majority of host materials developed so far for SIBs are based on transition-metal compounds,³⁻⁵ which have serious cost and negative environmental impacts. In contrast, redox-active organic materials have competitive advantages of low cost, resource sustainability and structural diversity.^{6,7} Moreover, compared to the rigid inorganic lattices, the flexible frameworks of the organic materials are particularly favorable for the reversible insertion/extraction of the relatively large Na⁺ ions. If SIBs could be constructed of renewable organic materials, it would bring about a great benefit for large-scale energy storage applications in upcoming electrical vehicles and renewable power stations.

Over the past years, a series of n-type organic molecules and polymers have been studied as anodic hosts for SIBs with considerable success;⁸⁻¹⁴ however, only a few organic cathodes demonstrate acceptable Na-storage performances.¹⁴⁻¹⁶ In principle, p-type electroactive polymers are promising cathode candidates for SIBs due to their high redox potential (above 3.0 V vs Na/Na⁺) and high theoretical capacity. However, their practical energy density is limited by the low p-doping degree as well as the consumption of large amounts of electrolyte anions.^{12,17} In addition, most organic cathodes cannot act as a Na reservoir to supply Na⁺ ions for Na⁺

deficient anodes and cannot be used to build “rocking-chair type” SIBs.

To construct a Na-rich organic host, a feasible strategy is to graft ionizable organic sodium salts on the polymer chains,^{18,19} so that the Na⁺ ions can be extracted from and inserted back into the polymeric framework during charge and discharge, respectively, changing the redox reaction mechanism from conventional p-doping/dedoping to reversible Na⁺ insertion/extraction reactions. In our recent work,¹⁹ we synthesized a self-doped polyaniline, poly(diphenylaminesulfonic acid sodium)(PDS), exhibiting reversible Na-storage performances as a high voltage organic cathode (3.4 V vs Na/Na⁺). Unfortunately, the reversible capacity (100 mAh g⁻¹) is not sufficiently high for battery applications due to the large size and high formula weight of the doping group (benzene sulfonic sodium). To further improve the electrochemical capacity as well as cyclability of the polymer, we proposed to graft smaller group with stronger electron-withdrawing ability onto the redox-active polyaniline chains.^{20,21} In this paper, we report a sulfonated polyaniline, poly(aniline-co-aminobenzenesulfonic sodium) (PANS), as a novel Na-storage cathode for the first time. Benefiting from its high Na density and strong electron-withdrawing ability of the grafted -SO₃Na group, this Na-rich polymer can deliver a high reversible capacity of 133 mAh g⁻¹ and an excellent cycling stability with capacity retention of 96.7% over 200 cycles, possibly serving as a high capacity and cycling-stable cathode with low cost and environmental benignity.

The PANS polymer was synthesized via chemical oxidative copolymerization (see details in ESI†). The as-prepared PANS is in the form of dark purple powder and appeared as flake-like structure with an average size of 5 μm as observed in SEM (Fig. S1, ESI†). To reduce the particle size and improve electronic conductivity, the bulk PANS sample was ball-milled with Ketjen Black (KB). Fig. 1a show that after ball-milling, the PANS particles emerges as an irregular aggregate of 200 nm particles surrounded by KB (uniformly distributed size of 60 nm), thus forming a better electronic and ionic conducting network that establishes abundant electrochemically active areas for Na⁺ insertion/extraction reactions. The Brunauer-Emmett-Teller (BET)

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See

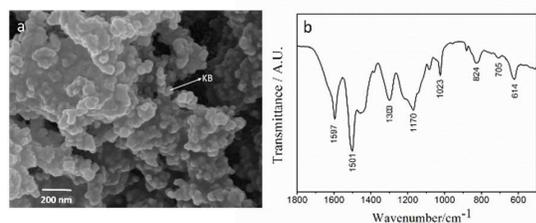


Fig. 1 Structure characterizations: (a) SEM image of the ball-milled PANS/C composite; (b) FT-IR spectrum of the as-prepared PANS.

specific surface areas of the bulk PANS and ball-milled PANS/C were measured to be 37.1, 235.4 m² g⁻¹, respectively (Fig. S2, ESI[†]). XRD pattern of the sample features an amorphous structure of the polymer (Fig. S3, ESI[†]). The FT-IR spectrum in Fig. 1b reflects all the characteristic absorptions of the sulfonated polyaniline: such as the C-N stretching of the aromatic amines (1300 cm⁻¹), the in-plane (1170 cm⁻¹) and out-plane (824 cm⁻¹) bending vibration of benzene. The bands at 1023, 705 and 614 cm⁻¹ can be assigned to the symmetric and antisymmetric stretching of the sulfonate groups. The characteristic stretching modes of the benzenoid (N-B-N) and the quinoid (N=Q=N) structures are well defined at 1501 cm⁻¹ and 1597 cm⁻¹. The relative intensity of I₁₅₀₁/I₁₅₉₇ is sufficiently high, indicating that the PANS polymer exist mainly in a reduced state. Furthermore, the binding energy for the Na 1s electrons in the PANS appeared at 1071.4 eV from the X-ray photoelectron spectroscopic measurements (Fig. S4, ESI[†]), confirming the presence of -SO₃Na group in the polymer. Combined with elemental composition analysis and ICP characterization (Table S1, ESI[†]), the chemical composition of PANS polymer can be determined to be [C₆H₄N. C₆H₄NSO₃Na]_n, indicating a 50% sulfonation degree.

To reveal the electrochemical redox activity, the PANS electrode was firstly evaluated by cyclic voltammetry. As shown in Fig. 2a, the main CV features of the self-doped polymer appeared as two pairs of well-defined redox peaks located at 3.6/3.4 V and 3.0/2.8 V (vs

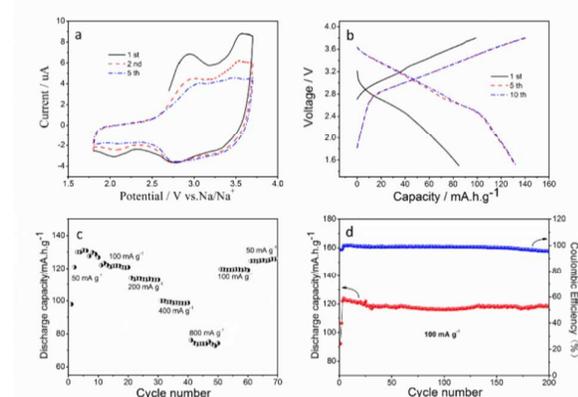


Fig. 2 Electrochemical performances of the PANS/C electrode in 1.0 mol L⁻¹ LiPF₆ + EC-DEC(V:V=1:1) electrolyte: (a) CV curves measured in a voltage range of 1.8 to 3.7 V at a scan rate of 0.1 mV s⁻¹; (b) the charge-discharge profiles in the first ten cycles at a current density of 50 mA g⁻¹; (c) reversible capacities at various current densities; (d) cycling performances at a constant current density of 100 mA g⁻¹.

Na/Na⁺), resembling very much the CV patterns of polyaniline electrodes in organic electrolytes.^{17,19} As the PANS polymer was chemical-grafted by the sulfonate anions, the redox reaction in the polymer can be attributed to reversible insertion/extraction of the ionizable Na⁺ for the charge counterbalance. It is noteworthy that the obvious peaks occurring at 2.05 V in the initial two negative scan, which disappeared in the subsequent cycles, can be ascribed to the carbon additive (KB), according to the CV features of KB presented in Fig. S5 (ESI[†]).

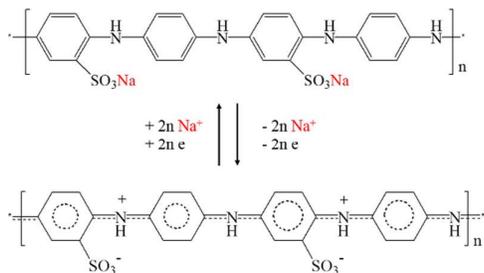
To ensure the practical feasibility of PANS as a cathode material for SIBs, 2025 coin-type Na/PANS cells were assembled and cycled galvanostatically with a voltage range between 3.8 V and 1.5 V. As given in Fig. 2b, the charge/discharge capacities of PANS in the first cycle are 98.7/85.0 mAh g⁻¹, respectively, corresponding to an initial columbic efficiency of 86.1%. The reversible capacity rapidly increased to a stable value of 133 mAh g⁻¹ in the subsequent cycles, with the columbic efficiency rising up to ~96%. Compared to other Na-rich organic cathodes, the PANS demonstrates a much higher reversible capacity than its analogues (80 mAh g⁻¹ for PP-PS,¹⁸ 100 mAh g⁻¹ for PDS¹⁹), and higher working voltage than the tetrasodium salt (2.2 V for Na₄DHTPA¹⁴). Derived from the charge and discharge profiles of the carbon additive (KB) in Fig. S6 (ESI[†]), the capacity contribution from KB is calculated to be ~10 mAh g⁻¹.

In addition to its high reversible capacity, the PANS cathode also exhibits a remarkable rate capability and cyclability. Fig. 2c shows the reversible capacities of the PANS electrode at various rates. The electrode delivers a reversible capacity of 123, 113, 99, 76 mAh g⁻¹ at 100, 200, 400 and 800 mA g⁻¹, respectively. Furthermore, after 60 cycles at various high rates, the PANS electrode regains a reversible capacity of 125 mAh g⁻¹, about 94.0% of its initial capacity. The outstanding rate capability should be ascribed to the flexible polymer matrix which favors the Na⁺ insertion/extraction with less restrictions. The cycling performance of PANS was further evaluated at a constant current density of 100 mA g⁻¹. As shown in Fig. 2d, the reversible capacity of PANS cathode remained stable at 118 mAh g⁻¹ after 200 cycles, corresponding a capacity retention of 96.7%. The superior cyclability is hardly seen in other organic cathode, probably due to the high stability of the PANS framework benefiting from the steric effect of the sulfonate group.²⁰

To confirm the Na storage reaction in the polymer cathode, we conducted quantitative ICP characterization of the Na contents in the cycled PANS at different depths of charge and discharge (Table S2, ESI[†]). At the first charge to 3.8 V, almost no discernible amount of Na⁺ ions, indicating the complete removal of Na⁺ ions from the polymer electrode. When discharged to 3.0 V, the Na contents in the polymer were calculated to be 5.74% wt., corresponding to 0.706 Na⁺ inserted to per PANS unit (C₁₂H₈N₂SO₃Na). Once the electrode was fully discharged to 1.5 V, the Na contents were calculated to be 1.06 Na⁺ ions bound in each PANS unit. The ICP evidence strongly suggests that the redox reaction of the PANS polymer took place dominantly through Na⁺ insertion/extraction processes during charge/discharge cycles (Scheme 1).

It is noticeable that the theoretical reversible capacity of PANS should be ~95 mAh g⁻¹ if calculated from the reaction mechanism in Scheme 1. However, the realized reversible capacity (133 mAh g⁻¹) is considerably higher than the expected value. In other words, the

high capacity cannot be only ascribed to a Na^+ insertion reaction in the



Scheme 1 The main reaction mechanism of the PANS

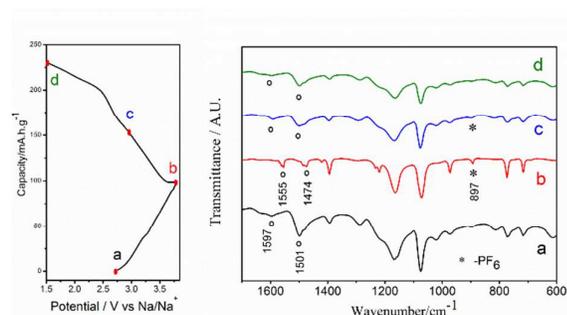


Fig. 3 FT-IR spectra of the PANS electrode (right) recorded at different potentials as indicated in the charge and discharge curve (left): a. as-prepared PANS electrode; b. charged to 3.8 V; c. discharged to 3.0 V and d. discharge to 1.5 V.

PANS polymer. To further reveal the underlying chemistry of the electrochemical performances of the PANS electrode, the changes in the bonding states of the PANS backbones at different depths of charge and discharge were characterized by FT-IR analysis. As shown in Fig. 3, when first charged to 3.8 V, the PANS electrode shows similar FT-IR pattern to its pristine state except for the band at 1597 (N=Q=N), 1501 (N-B-N) cm^{-1} shifting to 1555 cm^{-1} , 1474 cm^{-1} and an enhanced intensity ratio of I_{1555}/I_{1474} , suggesting the conformational change of the benzenoid structure to quinonoid structure of the polyaniline backbone. In addition, a new 897 cm^{-1} band featuring the P-F bond vibration in PF_6^- anions also appeared noticeably, implying that the charging reaction involved the doping of PF_6^- into the polymer matrix. When discharged to 3.0 V, the relative intensity of I_{1597}/I_{1501} decreased obviously, suggesting a partial reduction of the quinonoid structure to the benzenoid structure. At the fully discharged state (1.5 V), the intensity ratio of I_{1597}/I_{1501} decreased to an even lower value and the band at 897 cm^{-1} (P-F) vanished, which reflect a total reduction of the polymer backbone accompanying with Na^+ insertion and PF_6^- extraction. Based on the reaction mechanism stated above, the high discharge capacity observed from the PANS electrode can be satisfactorily accounted for a reversible Na-insertion/extraction reaction, followed with a PF_6^- doping/dedoping process, thus resulting in a higher utilization of the polyaniline backbone (above 50%). This also

reveals the fact that introduction of the self-doped sulfonate group promotes the electrochemical activation of the polyaniline chains.

In summary, we synthesized a Na-rich polymer cathode, Poly (aniline-co-aminobenzenesulfonic sodium) (PANS) and investigated it as a novel Na-host cathode. This sulfonated polyaniline exhibits a remarkable electrochemical performances dominantly through a Na^+ insertion/extraction reaction with a high reversible capacity of 133 mAh g^{-1} , an outstanding rate capability and excellent capacity retention of 96.7% over 200 cycles, all of which make it a promising cathode material for sodium-ion batteries. Particularly, the self-doping method described in this work is facile and easily extendable to other polymer chains, thus providing a new strategy for creating p-type cation-exchanging polymers for widespread electric storage applications.

This work was supported by the Natural Science Foundation of China (Grant 51307069), 973 Program (2015CB258400) and the National Thousand Talents Program of China.

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