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Water Dispersed Conducting Polyaniline Nanofibers for High-Capacity Rechargeable Lithium−Oxygen Battery

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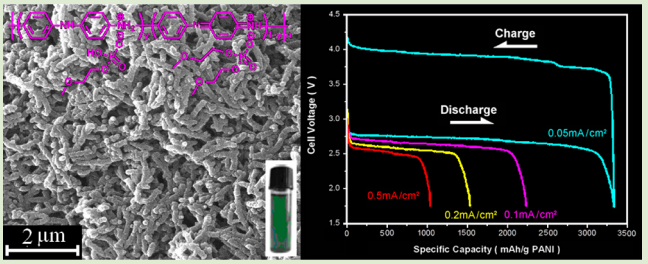
Supporting Information

ABSTRACT: Water dispersed conducting polyaniline nanofibers doped with phosphate ester have been synthesized and characterized by scanning electron microscopy (SEM), wide-angled X-ray diffraction (WAXD), X-ray photoelectron spectroscopy (XPS), UV−visible spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. Next, a systematic and careful electrochemical test was carried out to deeply investigate their potential application for lithium−oxygen battery. The experimental result showed us that this low cost and easily produced material could catalyze the discharge reaction independently, and after an initial degradation from 3260 to 2320 mAh/g PANI during the first three cycles at current density of 0.05 mA/cm^2, its discharge capacity kept relatively stable in the next 27 cycles with only a 4% loss, which may provide a new choice for fabrication of high-capacity rechargeable lithium−oxygen battery for practical application.



Today, with the vast amount of portable electronics being used, such as mobile phones, personal computers, and cordless tools, in our daily life and startup of the pure electric vehicle project, electrical energy storage becomes more important than at any time in the past.[1−5] As one of the most common and significant storage tools for the electrical energy, battery has developed into a huge family with several large series and more than three thousands of members to date, and it is continuing to grow at a more surprising and unprecedented speed.[6,7] Among all types of these battery systems, the lithium−oxygen battery, which is also called lithium−air battery, attracts more and more attention of the scientists because of its high theoretical specific energy (>3500 mAh/g), proper cell voltage (≥3.0 V), and achievable environment-friendly components (heavy metal is unnecessary in both cathode and anode).[8−12]

The discharge reaction in lithium−oxygen battery occurs between Li and O_2 to yield Li_2O_2 or Li_2O. On the one hand, this reaction gives the lithium−oxygen battery the chance to utilize the abundant oxygen resource in the air. On the other hand, it requires that the battery cathode needs to possess some special properties compared with the other battery electrodes.[13−16] In order for the oxygen to expediently leave and enter the battery during the charge and discharge processes, the cathode should have a porous structure. Besides that, an ideal cathode should also have catalytic effect for this reaction to enhance the battery high discharge current performance. Surrounding these two aspects, a lot of research work has been done or is ongoing, and some of the work has indeed achieved amazing results.[17−20] However, there are still some grievous problems that need to be dealt with for the further development of the lithium−oxygen battery. These include, for example, simplifying the cathode preparation, improving the high rate discharging performance, increasing the electrochemical cycle life, and so on.

As a typical conducting polymer, polyaniline (PANI) has long been a very favorable material in various electrical devices due to its ease of synthesis, adjustable conductivity, perfect processability, and special redox activity.[21−24] Recently, as a candidate of the electrode material, polyaniline is utilized more and more widely in the research fields of battery and supercapacitor.[25−29] Via its prominent features mentioned above, polyaniline had improved the performance of these energy storage devices in many respects, but few of these research work focused on its application in lithium−oxygen battery. Herein, we synthesized the water dispersed conducting polyaniline nanofibers to investigate its potential applications for the rechargeable lithium−oxygen battery for the first time. It was found that the polyaniline nanofibers cathode could (1) efficiently catalyze the discharge reaction without any additive, (2) give the lithium−oxygen battery much higher discharge capacity compared with the nonfibrous polyaniline cathode, and (3) keep relatively good cycle stability after an initial degradation.

Water dispersed conducting polyaniline nanofibers were prepared by a synthetic approach outlined in Figure 1. First, the aniline monomer in nitric acid dilute solution was initiated by ferric nitrate to form the conducting polyaniline nanofibers doped with nitric acid. At this time, the polymer was not water

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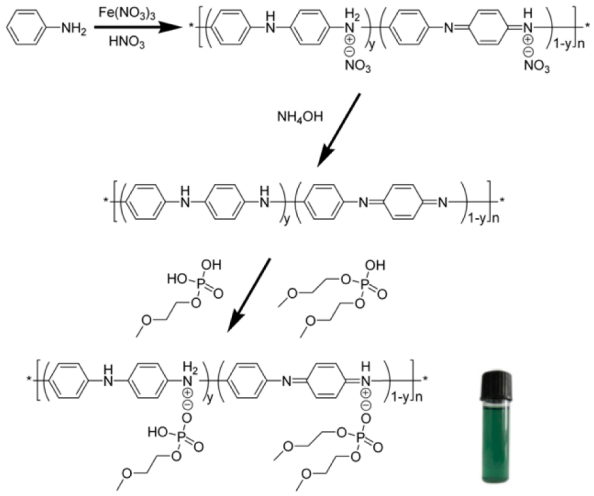

Figure 1. Synthesis of water dispersed conducting polyaniline nanofibers.

dispersed and that would seriously affect its even combination with the cation aqueous polyurethane resin adhesion agent during the subsequent electrode preparation. To address this problem, we ameliorated its dispersed property by changing the variety of dopant. After dedoping the polyaniline nanofibers in ammonium hydroxide solution, the formed polyaniline emeraldine base was then added into the fresh-prepared phosphate ester bearing one ethylene glycol to stir for 72 h at 60 °C. After that, the phosphate ester as anion was linked with polyaniline backbone, where the ethylene glycol hydrophilic segment assured the stability of the polyaniline nanofibers water dispersion. For a comparison, we also synthesized equivalent nonfibrous conducting polyaniline powder by a general chemical route.[30]

The morphologies of the two types of polyaniline were studied by scanning electron microscopy (SEM) image. As shown in Figure 2a, the mean diameter of the polyaniline nanofibers is approximate 150 nm, though the fiber surface is not very smooth, no obvious pores exists. By means of irregular pile-up, these one-dimensional nanofibers constructed a complex three-dimensional porous microstructure, and the Brunauer–Emmett–Teller (BET) surface area of this 3-D material is approximately 70 m^2/g. In contrast, as shown in Figure 2b, the nonfibrous polyaniline consists of micrometer-sized solid particles, and there are large spaces among these blocks. A same measurement showed us that the BET surface area of this kind of polyaniline is only about 15 m^2/g. It is no doubt that this difference between the two kinds of polyaniline would result in the distinct performances of the battery cathodes made by them. Besides the SEM image, other characterization methods, such as the wide-angled X-ray diffraction (WAXD), X-ray photoelectron spectroscopy (XPS), UV–visible spectroscopy, and Fourier transform infrared (FTIR) spectroscopy, were carried out for the polyaniline nanofibers, which could be found in Supporting Information.

To fabricate the polyaniline cathode for lithium–oxygen battery, 7.5 mg water dispersed polyaniline nanofibers (or the same amount of nonfibrous polyaniline powder), 1.5 mg carbon black (Super Li), 1 mg cation aqueous polyurethane resin adhesion agent, and 0.2 g deionized water were mixed to make a homogeneous (or a relatively homogeneous) mixture at

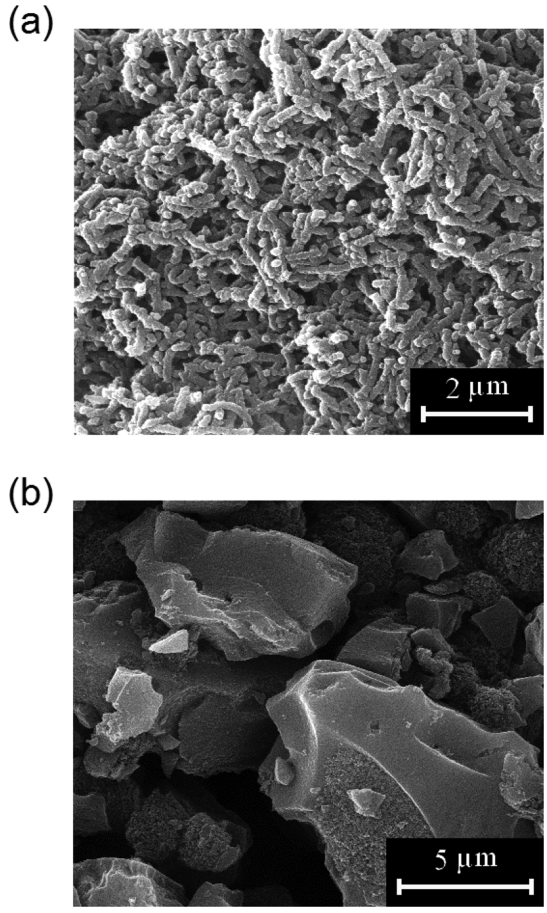

Figure 2. SEM images of (a) polyaniline nanofibers and (b) nonfibrous polyaniline.

ambient temperature. This mixture was coated and pressed on a foam nickel and then dried at 55 °C for 72 h in vacuum oven. After that, a lithium–oxygen battery cathode which contained 7.5 mg polyaniline component was produced. The 2032-type coin cell was used for the electrochemical test with a thin lithium film as the battery anode. The electrolyte was 1 M $LiBF_4$ in propylene carbonate solution. A Whatman GF/D glass microfiber filter paper was used as the separator, its high intensity could avoid the battery short circuit caused by the forming of lithium dendrite during charge process.[31]

The cyclic voltammetric (CV) curves of the electrodes made by two types of polyaniline are shown in Figure 3a. The polyaniline nanofibers electrode has considerably higher redox currents than the nonfibrous one, indicating that more effective surface areas of the polyaniline nanofibers are accessible for the electrolytes. This result is consistent with not only the SEM analysis, but also the subsequent battery discharge investigation. Another characteristic that can be clearly seen in Figure 3a is that the two kinds of polyaniline electrodes are both electrochemical inert in the potential range of battery discharging (below 3.2 V vs Li/Li^+), and the top limits of their electrochemical stability windows are both higher than 4.3 V versus Li/Li^+. Therefore, the voltage range between 1.75 and 4.2 V (vs Li/Li^+) was chosen as the continuous charge–discharge cycling process. Figure 3b shows the discharge curves of lithium–oxygen battery from the nonfibrous polyaniline cathode. To compare the capacity data more clearly, here we normalized them with respect to the corresponding PANI. The

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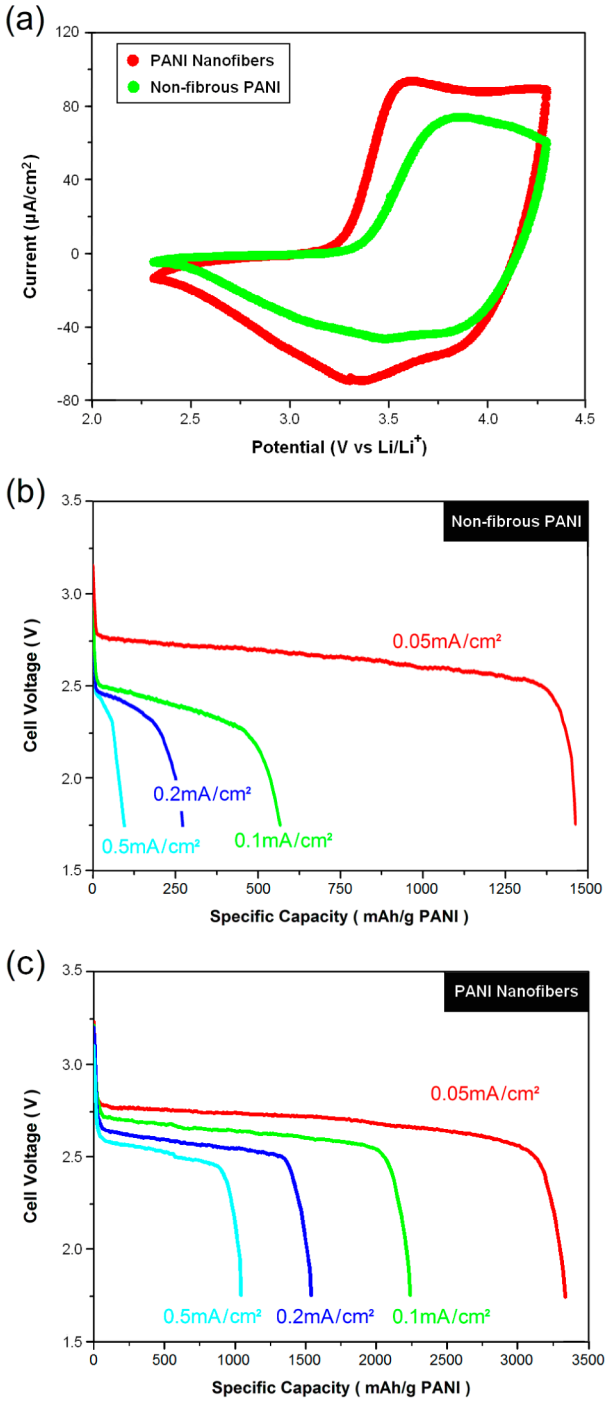

Figure 3. (a) Cyclic voltammograms of the two types of polyaniline electrodes; (b, c) discharge curves of corresponding lithium−oxygen batteries. Scan rate for cyclic voltammograms: 20 mV/s.

discharge capacity at current density of 0.05 mA/cm^2 reached 1380 mAh/g PANI, however, it dropped fast to less than 100 mAh/g PANI with increasing current density to 0.5 mA/cm^2, indicating that the nonfibrous polyaniline could catalyze the discharge reaction independently, but the number of its surface active sites can not satisfy the high current discharge requirement. In the case of the lithium−oxygen battery based on polyaniline nanofibers cathode, however, the discharge capacity at current density of 0.05 mA/cm^2 could reach 3280 mAh/g PANI at the first cycle, and it still maintained approximate 1000 mAh/g PANI at 0.5 mA/cm^2 current density, which was almost an order of magnitude higher than that from nonfibrous polyaniline cathode.

The galvanostatic charge and discharge curves of lithium−oxygen battery based on polyaniline nanofibers cathode are shown in Figure 4a, the current density is 0.05 mA/cm^2, and

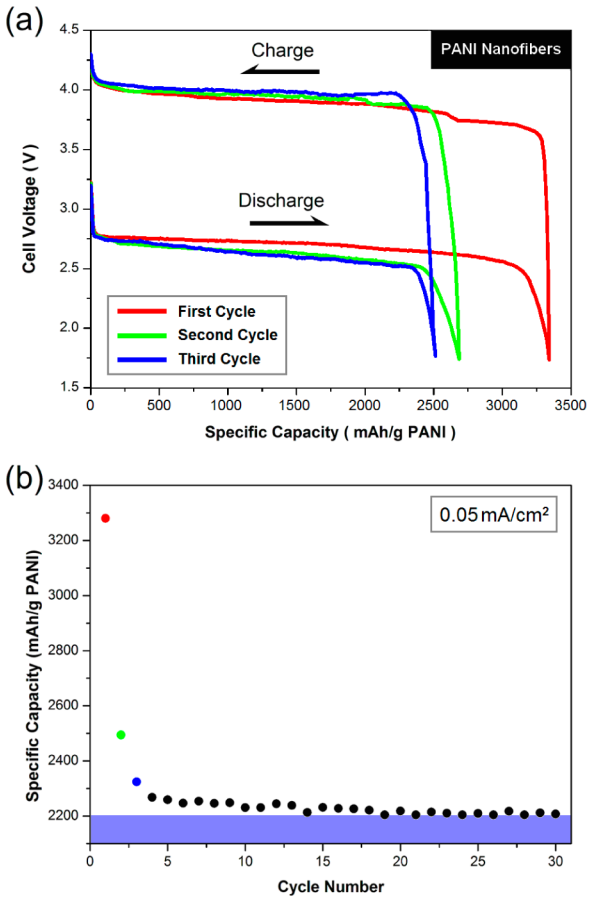

Figure 4. (a) Charge−discharge curves and (b) discharge capacities vs cycle number for the lithium−oxygen battery based on polyaniline nanofibers cathode at current density of 0.05 mA/cm^2.

the voltage window is between 1.75 and 4.2 V. During charge process, the charging potential was much higher than that on discharge, indicating that the battery had a bad charge−discharge efficiency. This is a long-term unsolved major disadvantage in lithium−oxygen battery.[17,19,32] The discharge capacity versus cycle number is shown in Figure 4b. After an initial degradation from 3260 to 2320 mAh/g PANI during the first three cycles, the discharge capacity kept relatively stable in the next 27 cycles with only a 4% loss. The large degradation, we think, is due to the morphological and chemical changes of the polyaniline nanofibers in battery cathode after the initial charge−discharge cycles. More detailed discussion on this question is made in Supporting Information.

In conclusion, water dispersed conducting polyaniline nanofibers have been synthesized and employed in lithium−oxygen battery for the first time. This low cost and easily produced material could be directly utilized as the battery cathode without any additional catalyst. Its high specific capacity at different discharge current density and good cyclic stability may provide a new choice for fabrication of high-capacity rechargeable lithium−oxygen battery for practical application.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental section, WAXD spectra, XPS spectra, UV−visible spectra, and FTIR spectra of the polyaniline nanofibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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