



Electrochemical performance of all-solid lithium ion batteries with a polyaniline film cathode

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ARTICLE INFO

Article history:

Received 17 March 2015

Revised 2 June 2015

Accepted 3 June 2015

Available online 3 September 2015

Keywords:

Lithium ion batteries

Cathode

Conducting polymer

Polyaniline

Flexible battery

ABSTRACT

We have prepared a high-density polyaniline (PANI) paste (50 mg/mL), with similar physical properties to those of paints or pigments. The synthesis of PANI is confirmed by Fourier transform infrared (FT-IR) spectroscopy. The morphologies of PANI, doped PANI, and doped PANI paste are confirmed by scanning electron microscopy (SEM). Particles of doped PANI paste are approximately 40–50 nm in diameter, with a uniform and cubic shape. The electrochemical performances of doped PANI paste using both liquid and solid polymer electrolytes have been measured by galvanostatic charge and discharge process. The cell fabricated with doped PANI paste and the solid polymer electrolyte exhibits a discharge capacity of $\sim 87 \mu\text{Ah}/\text{cm}^2$ (64.0 mAh/g) at the second cycle and $\sim 67 \mu\text{Ah}/\text{cm}^2$ (50.1 mAh/g) at the 100th cycle.

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1. Introduction

Thin, flexible, lightweight, and environmentally friendly batteries for high-performance sportswear, wearable displays, and new classes of portable power have become focused. For such electronic applications, a liquid electrolyte should be avoided and the electrode materials should have adequate mechanical flexibility for solid-stated flexible. Especially, printed electrodes offer more flexibility than common electrodes. As cathode materials, conducting polymers offer many advantages, such as high conductivity, mechanical flexibility, light weight, and cost-efficiency, compared to the metal-containing materials.

Among the conducting polymers, polyaniline (PANI) is particularly useful because of its low cost, simple polymerization, and high yield. Additionally, PANI is highly stable in its conductive form and satisfies most of the basic requirements of electrode materials for light-weight batteries. Several techniques have been used in the fabrication of thin films such as thermal evaporation, electro-polymerization [1–5], spin-coating [6], dipping [7], electrophoretic patterning [8], and printing [9]. However, it is difficult to apply these techniques to produce PANI films due to its insolubility in common solvents.

Recent breakthroughs in the synthesis and fabrication of dispersed PANI in solvents have focused on overcoming these processing difficulties. However, the fabrication of these electrodes requires a re-print process and a large amount of binder to obtain suitable

density and thickness. In addition, the dispersants in the PANI solution degrade the electrochemical performance and lower the solution viscosity as impurities.

Recently published papers for flexible devices based on the conducting polymers have focused on the development of different aspects of the various applications such as flexible sensors, organic solar cells, display applications, and thin film manufacturing processes [10–14]. Current studies are investigating lithium secondary batteries with the PANI cathode and a gel polymer electrolyte. Nevertheless, these devices still contain non-solid-state components [3,15].

In this study, therefore, we aimed to fabricate a high-density (50 mg/mL) PANI paste with suitable physical properties for printing. The PANI-pasted substrates printed via screen printing had a smooth surface without rough particles. PANI paste can be used as a conducting material in various applications, including plastic, clothes, and flexible substrates. We measured the electrochemical performance of both doped PANI and doped PANI paste with a liquid electrolyte and a solid polymer electrolyte. Furthermore, we measured the charge and discharge capacities of doped PANI paste as a function of electrode thickness to investigate the marginal efficiency of electrodes.

2. Experimental

2.1. Materials

Aniline (>99.5%, Aldrich) monomers were purified by filtration through aluminum oxide (~ 150 mesh, 58 Å) and distillation before being stored in a refrigerator. Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$,

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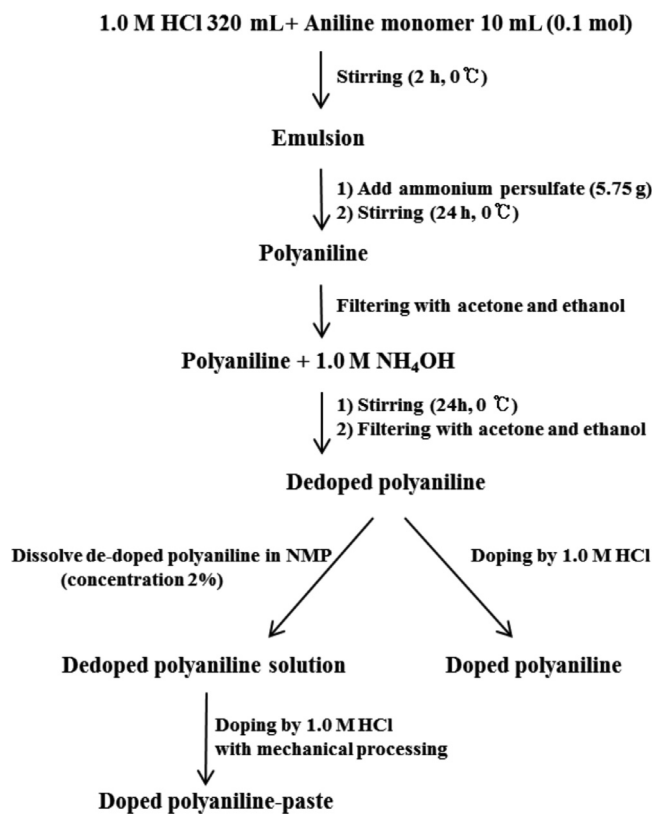


Fig. 1. Fabrication processes of doped PANI and doped PANI paste.

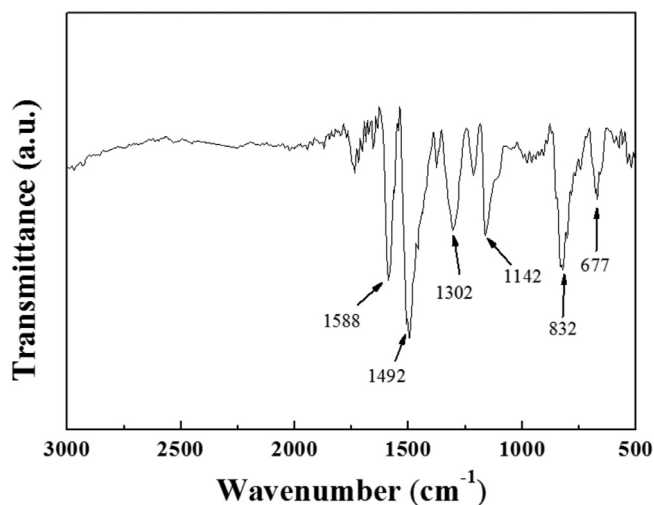


Fig. 2. FT-IR spectrum of PANI-EB.

98%, used as an initiator), hydrochloric acid (HCl, 37%), and *N*-methyl-2-pyrrolidinone (NMP, 99.5%) were purchased from Aldrich.

2.2. Instrumentation

A ball-mill (pulverisette 6, FRITSCH) was used for mixing. The electric conductivities were measured by 4-point probe (CMT-SR1000N, AIT Co.) after coating the polymer electrolytes onto a pre-patterned ITO cell. The crystallinity of the doped PANI and doped PANI paste was characterized with X-ray powder diffraction (XRD, Rigaku UltraX, Rigaku Co.) diffractometer equipped with Cu K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range of 10° – 60° with a step size of $0.02^{\circ}/s$. A centrifuge (HA12, Hanil Co.) was used to separate

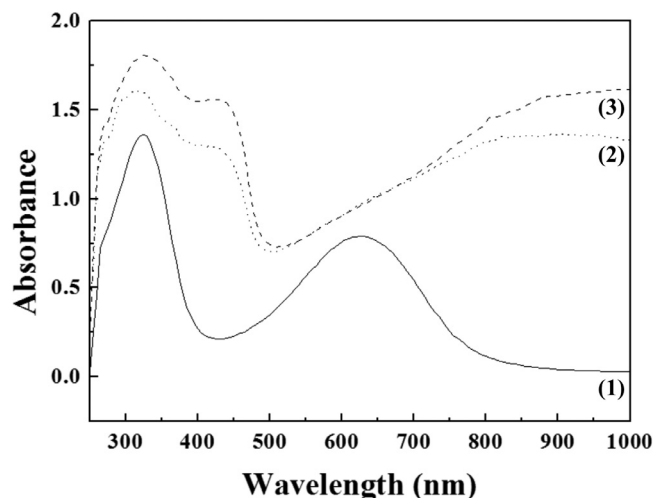


Fig. 3. UV-vis spectra of (1) PANI-EB, (2) doped PANI, and (3) doped PANI paste.

the PANI paste from the colloidal solution. A screen printing system (Simple Silky, Jaesung Engineering) was used to print the PANI paste. Ultraviolet–visible spectroscopy (UV-vis) was performed using an Optizen analyzer (Mecasys Co.). A Varian FT-IR 1000 instrument was used for the Fourier transform infrared (FT-IR) spectroscopy. The morphology and particle size information were obtained from field emission scanning electron microscopy (FE-SEM) (Supra 40, Carl Zeiss Co., Ltd.) analysis. The electrochemical performance was estimated by galvanostatic charge and discharge process and cycling tests (WBCS3000, WonAtech). The electrochemical stability window of the solid polymer electrolyte was measured by cyclic voltammetry (CV, Ivium Tech., IVIUMnSTAT). A stainless steel plate was used for the working electrode and lithium foil (FMC Co.) was used for the counter and reference electrodes. These test cells were assembled by sandwiching the solid polymer electrolyte between two electrodes. The ionic conductivity was measured by an impedance analyzer (Zahner Elektrik, model IM6) with an amplitude of 10 mV in a frequency range from 1 Hz to 1 MHz. The electrochemical impedance spectroscopy (EIS) measurements were conducted using a SP-300 (Biologic) at a fully discharged state over the frequency range from 100.0 kHz to 0.01 Hz at an amplitude of 10 mV at room temperature.

2.3. Synthesis of PANI and the processing method for PANI paste

PANI was synthesized via the chemical oxidative polymerization method: after 10 mL of aniline monomer (10.22 g, 0.1 mol) was dissolved in 350 mL of 1.0 mol/L HCl, 5.75 g of ammonium persulfate in 20 mL of 1.0 mol/L HCl solution was slowly added dropwise into the suspension at the reaction temperature of 0–5 °C until the dark suspension turned green, which indicated that polymerization of the aniline monomer had commenced. After 24 h polymerization, the solution was filtered and washed several times with water and acetonitrile until the filtrate became colorless. PANI (emeraldine base, EB) was obtained by stirring the polymer in 1.0 mol/L NH₄OH for 10 h and the solution was filtered and vacuum dried at 60 °C overnight. Finally, doped PANI powder was prepared by stirring in 1.0 mol/L HCl solution.

At the same time, PANI-EB was dissolved in NMP to form a PANI solution (2%), which was doped with 1.0 mol/L HCl and mixed for 2 h. The doped PANI solution was concentrated into PANI paste with a density of 50 mg/mL using the centrifuge. The density of PANI paste was measured from the dried weight of 1 mL of PANI paste. Fig. 1 shows an outline of the processing method for doped PANI and doped PANI paste.

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