



# Preparation and electrochemical properties of polyaniline nanofibers using ultrasonication



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## ABSTRACT

Polyaniline nanofibers have been successfully prepared by applying ultrasonic irradiation during oxidative polymerization of aniline in dilute hydrochloric acid and evaluated for suitability in lithium cells after doping with lithium perchlorate salt. Polyaniline nanofibers are confirmed by Fourier transform infrared spectroscopy, Fourier transform Raman spectroscopy, and transmission electron microscopy, and the efficiency of doping is confirmed by DC conductivity measurements at different temperatures. Electrochemical properties of nanofibers are evaluated, of which a remarkable increase in cycle stability is achieved when compared to polyaniline prepared by simple oxidative polymerization of aniline. The cell with nanofibrous polyaniline doped with LiClO<sub>4</sub> delivers an initial discharge capacity value of 86 mA h g<sup>-1</sup> at 1 C-rate which is about 60% of theoretical capacity, and the capacity is slightly lowered during cycle and reaches 50% of theoretical capacity after 40 cycles. The cell delivers a stable and higher discharge capacity even at 2 C-rate compared to that of the cell prepared with bulk polyaniline doped with LiClO<sub>4</sub>.

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## 1. Introduction

The field of electrically conducting polymers has developed and expanded at a rapid pace since the discovery made by H. Shirakawa, A. Heeger, and A. MacDiarmid in the late 1970s. They were awarded the Nobel prize in 2000 for both the discovery of metal-like conductivity of polyacetylene after doping with iodine vapor, and for the subsequent development and investigation of new conducting polymer systems [1]. The preparation, characterization, and application of electrochemically active and electronically conducting polymeric systems are still at the forefront of research in chemistry. Among conducting polymers, polyaniline (PANI) and polypyrrole are most noted for their allocations in atmospherically stable rechargeable batteries. The conductivity of

conducting polymers results from mobile charge carriers introduced into the conjugated  $\pi$ -system through the doping process.

In 1862, Letheby reported the first PANI synthesis using electrochemical polymerization of aniline in sulfuric acid at oxidation potentials [2]. However, no effort was made to characterize the structure of the as-prepared PANI at the early stages. After 40 years, Green and Woodhead postulated that oxidation of aniline yielded a molecule comprising alternative amine imine segments that is capable of oscillating between distinct oxidation states [3,4]. In 1968, Surville and Jozefowics measured the conductivity of PANI near 20 S cm<sup>-1</sup> [5]. Heeger and co-workers reported the enhanced conductivity after doping with secondary dopants [6]. PANI has been found to have applications in a wide range of emerging areas such as light-emitting or electrochromic devices, electromagnetic radiation absorbers, antistatic coatings, conducting molecular wires, gas sensors, separation membranes, anticorrosion coatings, super capacitors, and lithium secondary batteries [7–15]. Among these applications, lithium secondary battery is one of the most important applications of conducting polymers. In 1993, Miller reported the study of conducting polymers as an electrode material for secondary batteries [16].

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Synthesis of PANI is well established and many different methods are used for the preparation of PANI; electrochemical polymerization, vapor phase polymerization, enzyme-catalyzed polymerization, photochemically initiated polymerization, and chemical polymerization such as interfacial polymerization and self-stabilized dispersion polymerization are a few of the methods used for PANI synthesis [17–23]. To date, chemical synthesis has been the major commercial method for producing PANI. Among these methods, interfacial polymerization method can produce nanofibrous structured PANI. It has been proved that the application of nanostructured material could enhance the performance of batteries to a remarkable extent.

In this work we have developed a novel method for the preparation of nanofibrous structured PANI through a simple and cost effective method. Ultrasonication was used during the first 4 h of chemical preparation of PANI to achieve nanofibers. The effect of temperature of the reaction medium on the structural properties of PANI nanofibers and their electrochemical properties after doping with  $\text{LiClO}_4$  were studied.

## 2. Experimental

### 2.1. Synthesis of PANI

Aniline (Aldrich) was purified by distillation under reduced pressure. 6.25 mL of aniline was dissolved in 125 mL of 1 M HCl and taken in 500 mL three necked flask and cooled to 0 °C using an ice bath. A pre-cooled solution of 19.5 g of ammonium persulphate (APS) in 62 mL 1 M HCl was added to the above solution with mechanical stirring. The addition of solution was controlled to be slow and careful in order to avoid overheating of the reaction mixture (exothermic reaction). The polymerization reaction was further preceded by stirring at 30 °C for 24 h. The green colored precipitate was filtered with 1 M HCl three times and added into the same flask containing 1 M aqueous ammonia solution and mechanically stirred for 3 h to ensure complete dedoping of PANI from HCl. The resultant blue emeraldine base was filtered and washed successively with water, ethanol, and acetone to remove the unreacted starting materials and oligomers. PANI was dried at 60 °C for 12 h and further dried at 80 °C for 24 h under vacuum.

### 2.2. Preparation of PANI nanofibers

Ten milliliters of aniline were dissolved in 200 mL of 1 M HCl. The solution was kept inside the sonicator and the temperature was controlled by adding ice to the sonicator bath. A solution of 31.24 g of APS dissolved in 250 mL of 1 M HCl was kept in a dropping funnel and added very slowly to the above solution. Addition of APS solution was completed in 2 h. During the addition of APS solution to the aniline solution, the reaction mixture was exposed to ultrasonication. Ultrasonication was applied further for 2 h without any mechanical agitation to the reaction mixture. Later, the reaction mixture was magnetically stirred for 20 h. The precipitate was filtered and washed 3 times with 1 M HCl, then added to 1 M ammonia solution, and magnetically stirred for 3 h. The blue colored PANI nanofibers were filtered, washed successively with water, ethanol, and acetone. PANI nanofibers were dried at 60 °C for 12 h and then dried further at 80 °C under vacuum for 24 h.

### 2.3. Doping of PANI

One gram of PANI or PANI nanofibers prepared at different temperatures were kept in separate vials containing 5 mL of 1 M lithium perchlorate ( $\text{LiClO}_4$ ) in ethyl carbonate/dimethyl carbonate (EC/DMC, 1/1 volume ratio, Aldrich). The reaction mixture was kept

without agitation in a glove box having argon atmosphere for 72 h. Resultant PANI emeraldine salt was filtered, washed with diethyl ether, dried at 60 °C for 12 h, and then vacuum dried at 80 °C for 24 h.

### 2.4. Cell assembly

The electrode was prepared by mixing PANI- $\text{LiClO}_4$  with conducting agent carbon black (Super-P) and binder poly(vinylidene fluoride) (PVdF) in 70:15:15 weight ratio. The ingredients were mixed together in *N*-methylpyrrolidone (NMP) solvent for 1 h at room temperature to get a homogeneous slurry. The slurry was cast on aluminum foil and dried at 60 °C for 12 h and then dried further at 80 °C under vacuum for 24 h. The film was cut into circular discs of diameter 11 mm. Two electrode Swagelok cells were assembled with lithium metal (300 m thickness, Cyprus Foote Mineral Co.) as anode, Celgard<sup>®</sup> 2400 separator, 1 M  $\text{LiClO}_4$  in EC/DMC (1:1, v/v) electrolyte and PANI- $\text{LiClO}_4$  composite as cathode. The cell assembly was performed under argon atmosphere in a glove box with  $\text{H}_2\text{O}$  level <10 ppm.

### 2.5. Characterizations

Branson 3210-DTH sonicator (120 W, 47 KHz) was used for the preparation of PANI nanofibers. Transmission electron microscope (TEM-JEOL JEM-2010) operating at an acceleration voltage of 200 kV was used to characterize the morphology of the samples. Chemical characterization and doping level confirmation was done by Fourier transform Raman spectroscopy (FT-Raman, Bruker IFS 66 equipped with a FRA 106 Raman module using 1064 nm line of Nd:YAG laser as excitation source; laser power set to 150 mW and resolution of 4  $\text{cm}^{-1}$ ) and Fourier transform infrared spectroscopy (FTIR, VERTEX 80 v (Bruker Optics) spectrometer). The DC conductivity of PANI nanofiber samples were measured from 80 °C to 0 °C in a gold-plated cell using a Novocontrol broadband dielectric spectrometer. Electrochemical performance tests were conducted using an automatic galvanostatic charge discharge unit, using WBCS3000 battery cycler (WonA Tech. Co.) between 1.5 and 4.0 V at room temperature at a current density corresponding to 1 C or 2 C-rate.

## 3. Results and discussion

Polymerization of aniline was performed using two different techniques for a comparative study. PANI was prepared using conventional mechanical stirring at low temperature. By the addition of APS solution, the color of the reaction mixture gradually changed. An immediate appearance of pink color was noticed, which turned into deep blue and after 5 min, green colored PANI-HCl emeraldine base began to precipitate from the solution. Fig. 1 shows the TEM images at different magnifications of PANI prepared by mechanical stirring. From the TEM image, it is clear that the PANI particles tend to agglomerate during the formation of PANI in the reaction mixture. The particle size of PANI is in the range of 500 nm–1.2  $\mu\text{m}$ .

With ultrasonication method, PANI nanofibers were successfully produced and preserved. Violet color in the reaction mixture was observed during the initial addition of APS solution. The color changed to green within 10 min on the topside of the reaction vessel. Gradually the color spread through the entire medium and the formation of PANI started. The ultrasonication in the first 4 h was enough to produce aligned PANI. The reaction was carried out for further 20 h with magnetic stirring to ensure the completion of the reaction. Fig. 2 shows the TEM images of PANI prepared using ultrasonic irradiation at different temperatures. From TEM images, it is clear that PANI was prepared in the form of nanofibers. PANI

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