



Enhanced electrochemical performances of PANI using redox additive of $K_4[Fe(CN)_6]$ in aqueous electrolyte for symmetric supercapacitors



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ABSTRACT

Polyaniline (PANI) particles were prepared by reflux assisted chemical oxidative polymerization method with the aid of ammonium per sulfate/ferric chloride as oxidants and HCl/H_2SO_4 as the medium. Amorphous nature and the emeraldine state of PANI were revealed from X-ray diffraction and Fourier transform infrared analysis. Moreover, ultra violet–visible spectra attributes to the polaron band – π^* transition of polyaniline. The scanning electron microscopic image shows that the particle size is in the range of 0.2–2 μm . The electrochemical performances of the material were investigated in 1 M H_2SO_4 and 0.08 M $K_4[Fe(CN)_6]$ added 1 M H_2SO_4 aqueous electrolytes. Cyclic voltammetry and galvanostatic charge–discharge studies were carried out to find its suitability as a supercapacitor electrode material. The charge discharge analysis of the fabricated symmetric supercapacitors revealed the fact that the electrolyte containing redox additive (0.08 M $K_4[Fe(CN)_6]$) delivered an enhanced specific capacitance of $228 F g^{-1}$ ($\sim 912 F g^{-1}$ for single electrode) than that of 1 M H_2SO_4 ($100 F g^{-1}$) at $1 mA cm^{-2}$. Further cycling stability is performed at $5 mA cm^{-2}$ ensures the durability of the supercapacitor.

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1. Introduction

The growing demands on energy consumption offered a new scope to identify new materials or the modifications of the existing materials for the energy storage and conversion devices. Specifically conducting polymers used in electrochemical capacitors have contributed much in this area. Conducting polymers have several advantages such as ease of preparation, light weight, flexible and environmental compatibility over the other metal oxide electrodes are the factors supported to be a promising candidate for supercapacitor application. Especially electronically conducting polymers including PANI, PPy, PEDOT and polythiophene and so on are widely used. It has comparatively good electronic conductivity as metals due to its conjugated π orbital and promotes charge transfer in conduction process. Among them, PANI is widely used due to its high conductivity. Other than supercapacitors, PANI has numerous applications in rechargeable batteries [1], sensors [2], anti-corrosion coatings [3], photo switch [4], electromagnetic interference shielding [5] and so on. Advantages over other conducting polymers are the requirement of simple reaction conditions, very stable against moisture, electrochromic behavior, and electrochemical performance, non toxic and mechanical

flexibility. In addition, the color change during reaction process indicates variable oxidation states of PANI [3]. PANI has been prepared by various methods such as chemical polymerization [6], electrochemical polymerization [7], interfacial polymerization [8], solution method [9], microwave assisted polymerization [10], solid state polymerization [11] aqueous polymerization [12] and so on.

In recent years PANI were investigated as an active electrode material for pseudocapacitor due to its better electrochemical performances [13]. In this context, by template synthesis, Li et al. has prepared PANI nanofiber using binary oxidant system and reported the specific capacitance of $428 F g^{-1}$ at $2 mA cm^{-2}$ [14]. Self-doped PANI nanofiber film deposited on Pt electrode by reverse pulse voltammetric method possesses a capacitance of $480 F g^{-1}$ at $5 mA cm^{-2}$ [15] compared to PANI film. An open ended PANI nanotube array was grown on titanium nanotube template using electrochemical polymerization method and showed a capacitance of $740 F g^{-1}$ (current density of $3 A g^{-1}$) with 13% loss in SC over 1100 cycles [16]. Ordered PANI nanowhiskers were grown on the surface of the mesoporous carbon exhibited the capacitance of $900 F g^{-1}$ at a current density of $0.5 A g^{-1}$ [17]. Higher capacitances for this kind of synergetic composite material find its application in supercapacitors. All the available evidences regarding higher capacitive material used either template- assisted growth or made into composite with some other metal oxide or carbon based materials. Post-processing techniques was necessary to separate the PANI product from the template residues. Hence it

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is a need to find out the strategy to enhance the capacitance through simple techniques for application purposes.

With this knowledge, here it is reported that the preparation of PANI through reflux assisted chemical oxidative polymerization method. Since, Reflux treatment is a simple and convenient method due to its relative low temperature operation and applicable for large scale production. It is well documented that the reflux method is a novel method to prepare porous inorganic structures without employing any template or surfactants [18–20]. Also, the obtained products were high pure. Further, to enhance the specific capacitance of prepared PANI, new kind of strategy is employed i.e., addition of electrochemically active materials into the conventional electrolyte. In doing so, the electrochemical performance is enhanced tremendously. In the recent past, Roldan et al. has employed some of the electrochemically active materials such as indigo carmine, methylene blue and hydroquinone into the aqueous electrolytes to improve the specific capacitance of the material [21–23]. Generally, Redox additive added electrolyte was used to enhance the electrochemical performance of carbon material [24–28]. Though polymer exhibits high theoretical capacity, it decreases upon cycling. This is due to the low p doping level of counter ions in the polymeric matrices and a diffusive solution of the anions to the electrolyte [29]. To address this drawback, redox ions can be added into the electrolyte. As a result, incorporation of redox additives provides more active sites for electrochemical reaction to occur and enhances the capacitance. In the recent past, there were very few report explains the performance of conducting polymers in redox additive added electrolyte medium. Chen et al. [30] have studied the morphology-dependent electrochemical performance of PANI (nanofibers, nanospheres and nanotubes) in 0.4 M hydroquinone added 1 M H₂SO₄ and reported the higher capacitance of 896 F g⁻¹ at 1 A g⁻¹ than the conventional 1 M H₂SO₄ electrolyte (502 F g⁻¹). Similarly, Xie et al. [31] have studied the electrochemical performance of PANI in 0.04 M hydroquinone dissolved in 1 M H₂SO₄ (HQ–H₂SO₄) as electrolytes and reported the enhanced specific capacitance of 584 F g⁻¹ at 0.5 A g⁻¹ from 403 F g⁻¹ in the redox additive electrolyte. SnO₂/PANI composite has been synthesized by Zhu et al., and performed the electrochemical analysis in 1 M H₂SO₄ and 0.1 or 0.4 M HQ dissolved in 1 M H₂SO₄ electrolyte. The calculated specific capacitance is 857 F g⁻¹ in HQ–H₂SO₄ and 356 F g⁻¹ in 1 M H₂SO₄ electrolytes [32]. Considering the above, here we have used 0.08 M K₄[Fe(CN)₆] as the redox additive to the conventional 1 M H₂SO₄ electrolyte and studied the capacitive performance of PANI.

2. Experimental methods and materials

The starting precursors for the preparation of PANI were aniline monomer, ammonium per sulfate (APS) and ferric chloride (FeCl₃) as oxidants, hydrochloric acid and sulfuric acid as medium. The procedure for the synthesis of PANI is as follows. 0.05 mol of aniline monomer solution was dissolved in 3 M HCl/3 M H₂SO₄ acidic medium and the resultant solution was taken in a round bottom flask and kept under reflux treatment at 60 °C. After 5 min stirring, APS/FeCl₃ solution (0.05 mol dissolved in 50 ml double distilled water) was added drop by drop into the above prepared solution. During the course of time the colorless solution changes to green which indicates the initiation of polymerization process. Then the mixture was continuously refluxed along with stirring for about 2 h at constant temperature. Finally the precipitate was washed several times with double distilled water and methanol before dried at 60 °C for 12 h. The PANI samples prepared under reflux by APS in the presence of 3 M HCl/3 M H₂SO₄ acid were named as PANI-1 and PANI-2 respectively. Similarly samples prepared using FeCl₃ in 3 M HCl/3 M H₂SO₄ were named as PANI-3 and PANI-4,

respectively. In addition, the PANI prepared using APS in HCl medium without reflux treatment is named as PANI-1a.

The XRD patterns of the materials were obtained by using XPERT-PRO diffractometer through Cu K α radiation. FT-IR spectral studies were carried out in the frequency range 4000–400 cm⁻¹ by FT-IR interferometer (PerkinElmer make model RXI instrument). UV–visible spectral analyses were done by using the double beam bio spectrometer (ELICI-BL-198). The working electrodes for evaluating the electrochemical performances were prepared by coating the slurry of the material onto the graphite substrate over the area of 1 cm². The slurry was prepared by mixing 70% of the active material, 25% of carbon black, and 5% of PVDF binder in 0.3 ml NMP solution. Then these electrodes were dried in air oven for overnight and used for electrochemical study. The electrolyte used to fabricate the supercapacitor is 1 M H₂SO₄ and 0.08 M K₄[Fe(CN)₆] added 1 M H₂SO₄. The electrochemical characterization i.e., cyclic voltammetry (CV) of the synthesized PANI materials were performed in a three electrode system with a 4 mg of mass loading of PANI in graphite current collector as a working electrode, Pt wire and Ag/AgCl electrodes were used as counter and reference electrodes respectively. The electrochemical performance of the samples was investigated using Biologic SP 150 workstation.

3. Results and discussion

3.1. Structural and morphological properties

Fig. 1(a)–(d) shows the XRD pattern of PANI 1–4 samples. The pattern does not show any sharp peaks suggesting an amorphous nature of PANI. However the polymer displays a diffuse broad peak ranging from 10° to 30°, which is consistent with the results obtained by previous reports [14–20]. All the samples shows a diffraction peak centered at 2 θ = ~25° ascribed to the periodicity perpendicular to the polymer chains. Further the peak at 2 θ = ~20° indicates the periodicity parallel to the polymer chain in all samples except PANI-1 [33]. Here the absence of the peak at 2 θ = ~20° in PANI-1 shows the material is highly amorphous than other prepared PANIs. It is believed that the amorphous may be more favorable for high capacitance [34]. Also it reveals the highly doped emeraldine salt form of PANI. The similar type of observation was noticed by Abdiryim et al. [11].

Fig. 2(a)–(d) displays the FT-IR spectra of PANI and used to identify the functional groups present in the material. The observed bands and their corresponding assignments are shown

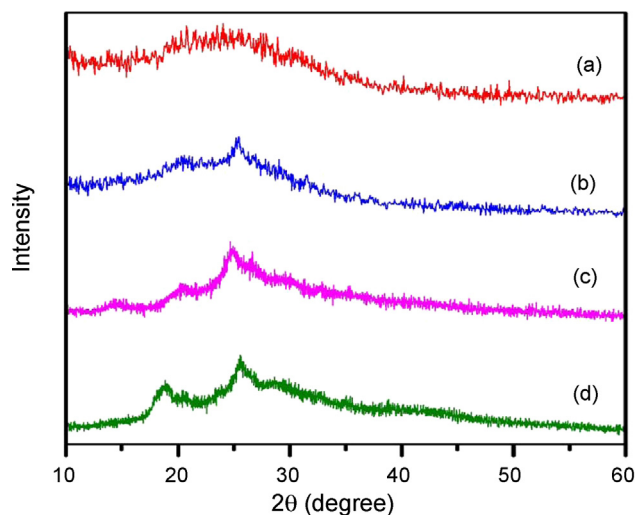


Fig. 1. XRD patterns of PANI-1 (a), PANI-2 (b), PANI-3 (c) and PANI-4 (d).

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