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Identification of the best chemical equivalent ratio to produce emeraldine salt exhibiting better pseudo capacitance

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ABSTRACT

This work details the effect of varying the ratio of concentrations of oxidant-to-monomer, in the process of synthesizing Polyaniline (PANI) in emeraldine salt (oxidation state) form for pseudo capacitor application. The formation of emeraldine salt is confirmed by analytical characterizations such as Fourier Transform Infrared spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Raman analysis techniques. The UV/Vis spectroscopic (UV) technique was employed to elucidate the optical band gap of variants. Both DC and AC measurements have shown a maximum total conductivity of 1.296×10^3 S cm^{-1}. The cyclic voltammetry (CV) of variants exhibit reversible redox reactions due to back and forth transitions between emeraldine and pernigraniline oxidation states and high diffusion of ions in the fabricated polyaniline thin films. The electrochemical impedance spectroscopy has shown their low solution resistances and charge transfer resistances behaving like a near ideal capacitor and the specific capacitances of CER variants have been calculated by performing constant current discharge cell test showing a maximum specific capacitance of 30.2 Fg^{-1}. The variants also exhibit better coulombic efficiencies.

1. Introduction

Considering energy storage devices, supercapacitors synergistically inherit properties of high energy dense batteries and high power dense capacitors. Subclasses of supercapacitors are pseudo-capacitor and Electric Double Layer Capacitors (EDLC). The former stores energy by means of intercalation, redox reactions or electrosorption [1] and the latter ones by the formation of Helmholtz double layer. Among seven basic conducting polymers [2], PANI is one of the polymers that possess π backbone which is made up of a chain of repeating benzenamine molecules that can easily coordinate with metal ions [3] attributing to good electrical [4], optical [5] and sensing properties [6].

PANI can be dissolved and casted as thin films, by doping it in an acidic solvent like HCl [7] during preparation and PANI is a cost-effective polymer with high storage capacity [8] making it potentially viable for pseudo-capacitor application [9]. Based on the oxidation states of PANI, it has been classified into seven different interconvertible forms, in which the emeraldine salt form is the only conducting form [10]. The pH of the solvent used during PANI synthesis determine its oxidation state, which when altered gives another form of PANI. The pH at which interconversion takes place is called transition pH [11]. Henceforth, the oxidation state decides the end applications of PANI. Some of the PANI applications include pseudo capacitors [12], electromagnetic interference shielding, filtering membranes [13], solar cells [14], gas sensors, battery electrodes, corrosion resistant coats and much more. Each one of these applications demand certain physicochemical characteristics of PANI. For instance, in a dye sensitized solar cell (DSSC), the photo conversion efficiency has been enhanced by adapting conducting polymer fabricated FTO photo anode instead of typical Pt fabricated ones [15]. In another instance, migration of electrochemical product between electrodes in a DSSC is avoided by the use of sulfonated PANI electrolyte which also enhances the photo conversion efficiency [16].

PANI is doped using acids at the time of polymerization of aniline, producing PANI-dopant complexes. The properties of PANI-polymer complexes like presence of defects, conductivity, morphology and oxidation state are the core deciding factors for its viability as a supercapacitor. The defects may be in form of polarons

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or bipolarons which can be identified collectively by UV/Vis spectroscopy and Electron Spin Resonance (ESR) measurement [6]. Methods to produce ordered morphological PANI (using liquid crystal soft template) with high electrical conductivity [17], composites of PANI with metals [18–20], carbon nanotubes [19], graphene [21–24], co-polymers, ferrite [25] to enhance conductivity have been addressed.

These studies suggest researchers to produce PANI either by electro-polymerization [26] or by wet chemical oxidative synthesis. As in case of sensors, catalysts, bio-remediation and energy storage materials, PANI had been produced electrochemically [27] or had been spun as fibres [27] (sequential polymerization and electrospinning), nonetheless both methods have their own demerits; former limits the quantity of end product PANI-dopant complex, latter necessitates addition of external material to increase the viscosity of PANI. This work details a technique (wet chemical polymerization of aniline), producing PANI with better homogeneity, morphology, conductivity which is achieved by optimization of Chemical Equivalent Ratio (CER) (ratio of concentrations of oxidant-to-monomer), through the use of a biphasic medium (isopropanol: water) and oxidizing agent ($FeCl_3$) that has weakest oxidation potential (for reducing agglomeration of nanoscale PANI) facilely producing emeraldine salt, alleviating the need of adding templates (hard and soft) and/or adding foreign substance thereby, enhancing the total conductivity, coulombic efficiency, pseudo-capacitance simultaneously bringing down the average particle size of PANI, which is deployable as a supercapacitor.

2. Experimental

2.1. Chemical and reagents

The reagents used are aniline (monomer), Iron (III) chloride (weak oxidant), iso-propanol, hydrochloric acid (protonating acid) supplied by Aldrich and other chemicals from SRL.

2.2. Apparatus

PANI samples of different CER are checked for their optical absorbance by UV/Vis spectroscopy using Perkin Elmer's Lambda 35 UV Visible spectrometer at room temperature (30 °C) to record the absorbance of CER variants. Also, aliquots of solid PANI are compressed into circular discs with dried potassium bromide (KBr) for FTIR transmittance analysis using Spectra RX1 instrument Perkin Elmer instrument operating in the frequency range of 4000 cm^{-1} - 400 cm^{-1}. The oxidation state and surface composition of powder PANI are identified by thermo scientific XPS spectrometer with Al Kα X-ray source (1486.6 eV photons). Powdered PANI fractions adhered to double sided tapes mounted on sample holder were used. An X-Ray source of 12 KV and 10 mA from an electron gun with Al as target were used.

Laser Raman spectroscopic measurements were carried out by Renishaw InVia Raman microscope excited using a semiconductor diode laser at 785 nm utilizing only 5% of total laser power. The surface morphology of the polyaniline samples are electron micrographed using a Carl Zeiss MA15/EVO18 electron microscope having a resolution of 3.0 nm accelerating at 30 KV with single electron detector. The energy dispersive analyses were done using Oxford Instruments Nano Analysis INCA Energy 250 microanalysis system. Electrical characterizations and I–V studies were carried out in Keithley 4200 instrument at room temperature (30 °C).

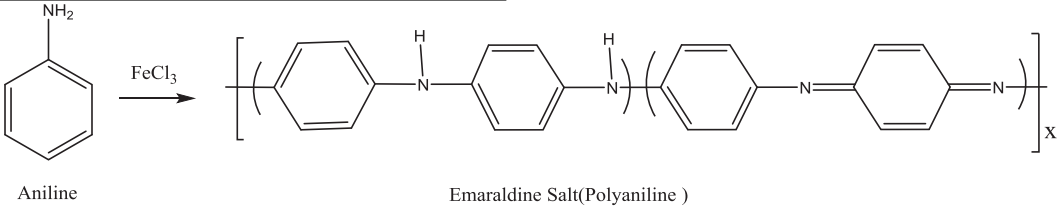
The electrochemical studies such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and constant current discharge (CCD) supercapacitor cell tests were carried out using a 3-cell electrode system interfaced to CH instrument model CHI608C. The sweep rates for CV were varied from 10, 20, 50 and 100 mVs^{-1}. EIS measurements were done in open circuit voltage with AC voltage amplitude of 5 mV having frequency ranging 0.01 Hz–10^5 Hz. Constant current discharge supercapacitor cell test was performed in a 3-cell electrode system with Pt foil as current collector, single calomel electrode as reference and 0.5 M H_2SO_4 as electrolyte. The working electrode used had been fabricated from a thin film of active material as described in section 2.4 and the potential was swept from 0 to +0.6 V with constant current of 3 mAg^{-1}

2.3. Polymerization of aniline

The work involves polymerization of aniline in biphasic medium containing distilled water and 2- propanol in a 1:1 vol/vol (v/v) ratio. This biphasic medium reduces the quick oxidation of aniline thereby reducing cross-linking formation in PANI. In addition to this, the oxidant $FeCl_3$ possessing weak oxidizing potential decreases the oxidation rate of aniline which attributes towards linear polymer chain formation in PANI.

The synthesis involves two major steps such as oxidation and subsequent protonation as shown in the reaction scheme that follows.

a) Polymerization:



Aniline Emaraldine Salt(Polyaniline)

b) Protonation: