Polyaniline / copper nanocomposites for enhanced electrode applications

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Abstract

Electrode materials influence the energy density, power density, durability and efficiency of energy storage capacitors. PANI and PANI/CuCl2 composites were synthesized by chemical oxidation method. PANI/ CuCl2 composite is found to have enhanced electrical properties compared to pure PANI. Incorporation of nano CuCl2 in the PANI polymer matrix was confirmed by XRD. The XRD pattern indicated the crystalline phase of CuCl2. Evaluation of electrical properties of 2, 3 and 4 wt% of Cu doped PANI showed that AC conductivity increased exponentially above critical frequency. In agreement with this observation, the impedance value is found to decrease. 4 wt % Cu doped PANI(PC3) samples were showing almost stable phase conductivity and impedance over a wide range of frequency, with specific capacitance of 56.25F/g, which suggests its suitability as an effective material for electrode application in electrochemical storage devices.

Keywords: Specific capacitance; Cyclic voltammetry; polaron conduction; Electrode material; emeraldine polyaniline; nanocomposite; ac conductivity.

Introduction

Efficient energy storage devices are highly in demand in all walks of technology, for the effective operation of various portable and flexible electronic devices. Lot of research is going on in the design and development of new charge storage devices. Electrode materials influence the energy density, power density, durability and efficiency of energy storage and conversion devices. It is essential to develop clean and efficient energy devices to meet the energy demands without endangering our environment. The electrode materials play a significant role in the performance of the energy storage. Carbon species, metal compounds and conducting polymers are three main types used as electrode materials[1- 4]. In recent years, conducting polymers have attained a great attention in a wide range of areas due to their ease of synthesis, environment stability, and excellent electrochemical, optical and magnetic properties. Polayaniline (PANI), which is an inherently conducting polymer has become an advanced electrode material including super capacitors, lithium ion batteries and thermoelectric devices due to its high conductivity, easy synthesis, environment friendly, excellent capacity for energy storage and low cost. PANI has the highest specific capacitance due to multi-redox reactions and good electronic properties due to protonation. PANI is used as an electrode material because of its conjugated system ie. the PANI macromolecule has a backbone chain of alternating double and single bond. PANI is known as a mixed oxidation state polymer composed of reduced benzoid units and oxidized quinoid units. Delocalization of electrons in the resonance structure of benzoid and quinoid groups in PANI is responsible for its interesting electrical and optical properties. The overlapping of p orbitals contributes to the formation of a system of delocalized π electrons which results in an extended p orbital along the polymer chain through which the electrons are free to move about. Polyaniline exists in four oxidation states. They are Leucoemeraldine base, Emeraldine base, Emeraldine salt and Pernigraniline[5-7]. The PANI used in electrodes is a mixture of its three oxidation states and have highest portion of PANI-EB (half oxidized emeraldine base) in the mixture to contribute to the best performance. PANI can be synthesized by the oxidation of monomer aniline through chemical or electrochemical methods. When it is used as an active material, stores charge by redox reaction as the PANI transition between various oxidation states, it has been able to achieve high specific capacitance through the entire volume in storage of charge. It can be doped in a non-redox reaction in acidic medium which results in an emeraldine salt and the capacitance value of the PANI can be maximized[8-11].

EXPERIMENTAL

PREPARATION OF POLYANILINE

Polyaniline has been synthesized by using chemical polymerization technique. In chemical oxidation polymerization, a monomer(aniline) is polymerized using Ammonium persulphate as an oxidant. Chilled monomer(15ml aniline) of definite molarity is added to the pre-cooled acidic solution(250ml water+ 35ml HCl). The reaction is carried out in low temperature range by placing the beaker in ice bath, to achieve better yield and better quality of polyaniline and to avoid the formation of oligomers. Ammonium persulphate (2.85g + 100ml water) taken in a 0.1 M is added to the above solution slowly drop by drop, and the resulting solution stirred using magnetic stirrer for 5-6 hr in order to ensure the completion of the reaction.

The reaction mixture is then filtered using vacuum pump. Polyaniline in the form of flakes or powder was obtained which was green in color. The polymer was washed with distilled water several times and also washed with acetone till the filtrate obtained was colour less and neutral in nature. The polyaniline samples obtained in powder form were dried first at room temperature for few hours and then finally dried in an oven kept at 60oC- 90OC for 4-5 hours. The dried polymer powder was then mixed in an agate mortar pestle and then pelletized.

COPPER DOPED POLYANILINE

PREPARATION OF COPPER DOPED POLYANILINE

Copper chloride salt of various doping levels of 2, 3, and 4(wt %) each prepared in 5 ml deionized water, was added into the bulk solution prepared for the synthesis of PANI, just before the stirring stage. After the polymerization, the whole solution was again filtered, washed with deionized water and ethanol several times and dried at 600C in order to form doped PANI samples, PC1(2%), PC2(3%), PC3(4%).

RESULTS AND DISCUSSIONS

A diffraction pattern is a distribution of scattered intensity as a function of scattering angle. In the present work, X-ray diffract grams were taken for the pure PANI sample (PP), using Cu Kα radiation (λ=1.5420A0) on Rigaku instrument and the pattern obtained (Fig. 1) exhibited peaks at 2θ values of 11.650, 14.80, 20.770, 29.140, 31.140 and 33.430. In our observations, the X-ray peak at value of 14.80 and 20.770 is the strongest. The X-ray diffracts grams for PANI doped with copper is also shown in Fig.1 as PC1, PC2 and PC3. The figure shows peaks at 2θ values of 11.650, 14.80, 20.770, 29.140, 31.140 and 33.430. The strongest peak is obviously for 2θ as 14.80and 20.770. The studies on X-ray diffraction characterization indicate almost identical nature for all samples being whether PANI or its derivative. The Cu doping slightly changes the major crystalline nature in the PANI samples and it seems that metal compounds get trapped between PANI pockets uniformly.

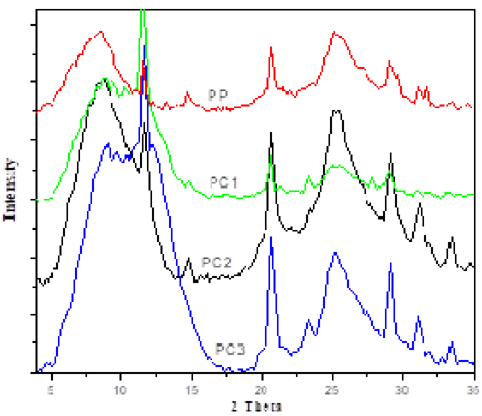

Fig.1: The electrical measurements were carried out using Keysight E4980 LCR meter. The frequency dependent conductivity of PANI/CuCl2 composite is shown in Fig.2. It is evident that the AC conductivity is frequency dependent and is enhanced and almost constant with increase in the frequency. The doping of conjugated polymers generates high conductivities by increasing the carrier concentration[12-14]. The polymer is oxidized by the acceptors (removal of electron), thereby producing a radical cation (hole) on the chain that does not delocalize completely, but is delocalized only over a few monomeric units deforming the polymeric structure. This hole site moves through the polymer and it results in conductivity. Bipolarons are formed by removal of a second unpaired electron on a chain already having a negative or positive polaron. As these polarons and bipolarons are mobile they can move along the polymer chain, resulting in polaron conduction [15-16].

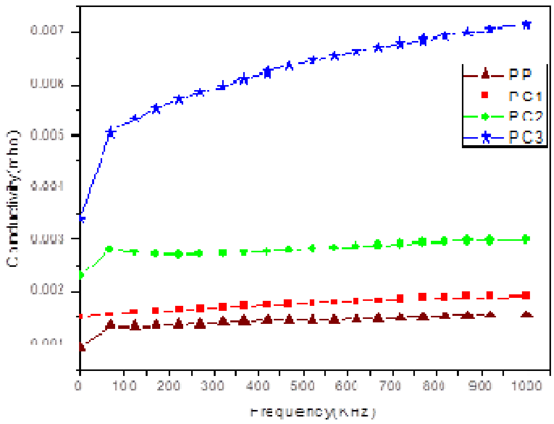

Fig.2: The conductivity increases because of the contribution of polarons

As the frequency increases, the conductivity increases because of the contribution of polarons which are moving along shorter distances in the polymer chain. This indicates that there may be charge carriers which can be transported by hopping through the defect sites along the polymer chain. The ac conductivity becomes saturated above a certain frequency. The variation of the impedance with frequency for pure and Cu doped PANI is shown in Fig.2. It can be seen from this curve that the impedance decreases with increasing frequency, and it remains almost constant for copper doped PANI sample PC3 [16,17,-21].

shows the variations phase angle for pure and Cu doped PANI at various frequencies. At low frequencies, the sample exhibited high phase which decreased with frequency. It is observed that phase is almost constant at high frequency. The plots exhibit two linear portions of different slopes. This shows different polarization mechanisms in the low and high-frequency ranges. The phase at high frequencies is associated with dipolar relaxation and at low frequencies; the phase is associated with interfacial polarization and DC conductivity [22].

The increase in the phase at low frequencies reveals that system exhibits strong interfacial polymerization. Interfacial polarization occurs when there is an accumulation of charge between the two conductive and insulating regions within the material when electric field is applied. This interfacial polarization is particularly dominant at low frequencies and in conjugated polymers. At high frequencies, the variation in the field is very rapid for the dipoles to align themselves hence results in less phase angle change. Here also sample PC3 shows an almost stable phase relationship [23].

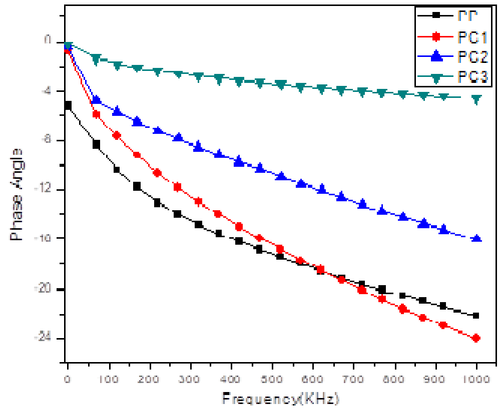

Fig 3: Variation of Phase angle with Frequency for pure and Cu doped PANI

Cyclic Voltammetry measurements were carried out using CHI660E series electrochemical workstation, at National Institute of Technology, Calicut [24]. A specific capacitance of 56.25 F/g and specific energy 112.5 kW/kg was calculated for 0.4g of PC3(4wt% Cu doped PANI) sample from cyclic voltammetry measurements, with a scan rate 0.1V/s, potential window with initial potential -1V and final potential 1 V. Area of loop is determined from CV graph of Fig.5 and the specific capacitance Csp is calculated by using the formula [25].

CONCLUSIONS

PANI and PANI/CuCl2 composites were synthesized by chemical oxidation method. The incorporation of nano CuCl2 in the PANI polymer matrix was confirmed by XRD. The XRD pattern indicated the crystalline phase of CuCl2. Cu doped PANI exhibited increased values of ac conductivity and low impedance. A specific capacitance of 56.25 F/g and specific energy of 112.5kW/kg was obtained for 4 wt % Cu doped PANI PC3, showing almost stable phase conductivity and impedance over a wide range of frequency, suggesting its potential as an effective material for electrode application in electrochemical storage devices.

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