Study and Characterization of Polyaniline at Various Doping of LiCl wt.% Using Electrical Measurements and XRF Analysis

Faten Adel Ismael Chaqmaqchee* and Amera Ghareeb Baker

Department of Physics, Faculty of Science and Health, Koya University, Daniel Mitterrand Boulevard, Koya 45, Kurdistan Region, Iraq

Abstract: Polyaniline PANI samples were synthesized *via* chemical polymerization method. The mechanism of charge transport in these composites has been studies by measuring the DC conductivity at various lithium chloride LiCl wt.%. It shows that their activation energy decreases with increasing LiCl concentration and thus, the conductivity increases at 15 %wt. In addition, X-ray Fluorescence XRF was used to analysis the elements of PANI regarding to LiCl concentration. The elements positively detected by the XRF are Cl, Kr, SO_3, Al_2O_3, SiO_2, and ZrO_2. The XRF data show a relative systematic error typically independent of the concentration. The accuracy is determined by comparing the XRF data with various LiCl wt.%.

Keywords: PANI, X-ray Fluorescence, conductivity, lithium chloride, activation energy.

1. INTRODUCTION

Polyaniline PANI is known as highly tunable conducting polymer due to its electrical conductivity, mechanical strength, easy to handle and high thermal stability [1, 2]. The polymers were studied earlier, to be the most important industrial conducting polymer today. Their doping level can be controlled through using an acid doping over base dedoping [3]. PANI has been extensively used in wide area of applications such as solar energy conversion, rechargeable batteries, electrochemical sensor and capacitor [4, 5]. This is to their lower density, low synthetic cost, and easy for fabrication and processing environmental stability. In addition, Nanostructured polyaniline of nanorods, wires and fibers has been used in sensor applications. It has better sensitivity and quicker time response comparing to its conventional bulk counterpart. However, this kind of sensors has not been widely exploited because it needs reliable techniques for making high quality conducting polymer nanostructures [6].

Modern instrument such as X-ray Fluorescence XRF is often purchased with commercial program and fundamental parameters methods that combined with calibrations by reference materials. XRF is commonly used for the detection almost the whole elements from periodic table using different types of samples such as liquids, soils, metals and plastics [7, 8]. The XRF method generally has errors depending on element and concentration.

*Address correspondence to this author at the Department of Physics, Faculty of Science and Health, Koya University, Daniel Mitterrand Boulevard, Koya 45, Kurdistan Region, Iraq; Tel: (+964) 7504860521;
E-mail: faten.chaqmaqchee@koyauniversity.org

In this work, PANI samples with various lithium chloride LiCl wt% have been characterized using D.C electrical measurements. XRF technique was also used to analysis the spectra of energy. Their mass% concentrations for several representative elements plus Cl mass% in different LiCl wt% were compared.

2. MATERIALS AND METHODS

PANI materials were purchased from Hopkin and Williams and BDH. Polymerization of aniline is prepared to produce polyaniline disc and solution at different lithium chloride LiCl wt%. All the electrical measurements of D.C conductivity were done on disc shape of polyaniline samples using the mechanical balanced (Mettler H35AR) of accuracy (10^4-0.35 g). Polyaniline powder was pressed into a pellet of 1.5 to 2 mm thickness and 13 mm diameter under 10 ton/cm² pressure using hydraulic press.

In this work, the chemical composition of the polyaniline samples was measured with a Rigaku NEX CG X-ray florescence (XRF) spectrometer. XRF is an effective method of analyzing metals, thin films and polymers. The polymers samples were place in the chamber and measured by 20 mm diaphram in vacuum. X-ray spectra were obtained using RX9, Cu, Mo and Al conditions. In these analyses, the X-ray tube current were set to approximately 1 mA for the RX9 target and into 0.5 mA for other targets. The X-ray tube voltage has been set to 25 kV only for the RX9 and 50 kV for Cu, Mo and Al targets. The X-ray measuring time was only 200 s for the Al target and 100 s for other targets.

3. PREPARATION OF POLYANILINE

Pure Polyaniline PANI salt was prepared *via* different conditions. A three-necked round bottomed

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flask equipped with a thermometer. Electromagnetic stirrer and condenser were used to polymerize Polyaniline. The preparation of PANI is based on oxidation of (0.2M) aniline hydrochloride with (0.25M) ammonium peroxydisulphate in aqueous medium. Both solutions are mixed in a round bottomed flask and gentle stirring to polymerize the mixture. The reaction is found to be exothermic, in which their temperature as a function of time was recorded through the polymerization processes. The mixture was then left to rest for one day. The precipitate PANI was collected on filter papers and washed with three 100 mL of different HCl molarities and 150 mL of acetone. PANI was then dried in air and in vacuum oven (80°C) for one hour and 6 hours, respectively.

The selected samples were doped with various weight percentage of 5, 10, 15 and 20 LiCl wt% of total materials weight used in reaction. The cooled distilled water was used to solve aniline and ammonium in two different beakers, and be refrigerating about 15 mint using thermometer. When temperature of the thermometer reaches -5˚C, the solutions were mixed together in the round bottomed flask. The space surrounding of the round was kept in ice and sodium chloride salt to reach -5˚C.

4. RESULTS AND DISCUSSION

The resistances of the polyaniline pellet have been measured as a function of temperature at various LiCl wt% concentration using an electrical circuit. Figure **1** shows the variation of conductivity for doped polyaniline in the range from 293 to 423 K. The figure shows that the conductivity of polyaniline increases with increasing the concentration percentage of 5, 10 and 15% LiCl, while the conductivity decreases with

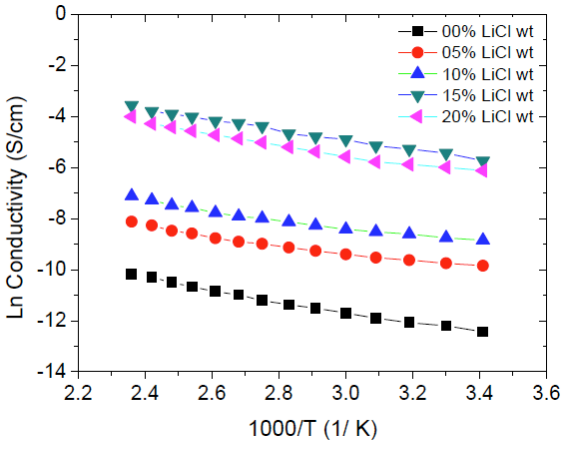

Figure 1: Temperature dependence of electrical conductivity of different LiCl ratio prepared by polyaniline.

20% LiCl. This is due to adding LiCl to PANI, where above 15% leads to increase its interchain distance, which makes hopping between chains more difficult, causes a reduction of conductivity and increasing the activation energy.

Figure **2** shows the variation of activation energy as a function of LiCl wt.%. Activation energy decreases with increasing LiCl concentration. This behavior can be explained as a result of adding LiCl to PANI. Therefore, when LiCl concentration less than 20%, the conductivity increases due to the charge carrier concentration, and when LiCl reaches to the 20%, the interchain distance may dominate, and lead to decrease the conductivity of the sample. In addition, activation energy decreases with an increasing conductivity as confirms in an inset Figure **2**.

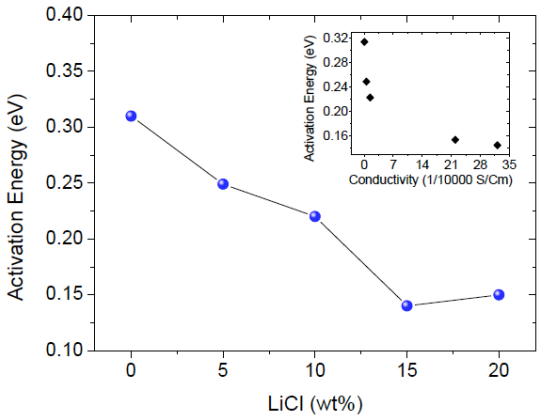

Figure 2: The activation energy as a function of LiCl wt. % for polyaniline.

XRF analyses were used to identify the changes on polyaniline by different LiCl wt%. When these samples are irradiated with x-rays, the intensity as a function of energy for RX9 Cu, Mo and Al targets can be calculated using computer software. XRF spectra were measured over the energy range 1-10 keV. Figure **3** shows two distinct peaks in the range 2 to 3 at 2.3 and 2.6 keV corresponding to S kα and Cl kα lines. Note that the intensity of Cl-kα for PANI samples increases from pure 00% LiCl wt. to 15% LiCl wt. for higher conductivity applications, while the intensity decreases at 20% LiCl wt.

As for the quantitative results, Figure **4** displays mass% concentrations (given in mg of the element per m^2) for several representative elements (Cl, Kr, SO_3, Al_2O_3, SiO_2, and ZrO_2) in 10% LiCl wt. sample. It can be seen that, Cl element of 1.63 mg/m^2 has higher concentration mass% than oxide elements of SO_3, Al_2O_3, SiO_2, and ZrO_2. Moreover, Figure **5** presents a mass% concentration, but only for Cl, in five samples,

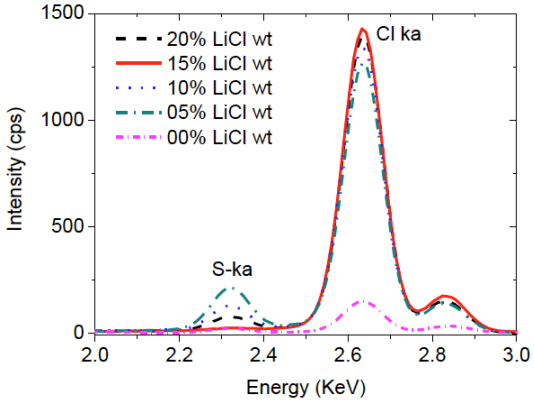

Figure 3: Intensity versus energy for various LiCl wt% using XRF technique.

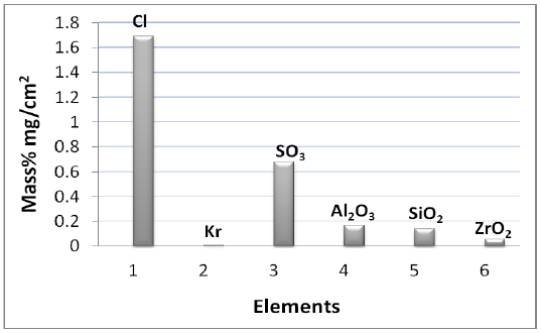

Figure 4: Comparison of mass % concentrations of selected elements (Cl, Kr, SO_3, Al_2O_3, SiO_2, and ZrO_2) in the same 10% LiCl wt. sample, and determined by XRF.

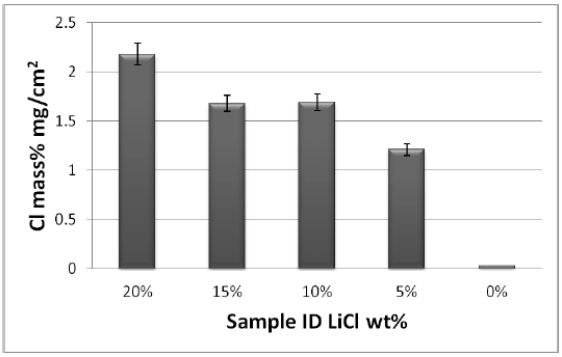

Figure 5: Cl mass% in different LiCl wt% concentration determined by XRF under the same operating conditions.

in which mass% of 20% LiCl wt. has high concentration than other PANI samples.

5. CONCLUSIONS

This study has demonstrated the conductivity of PANI samples with different LiCl concentrations using DC electrical measurements. An activation energy decreases with increasing LiCl wt% and consequently, the conductivity increases at 15 %wt concentration. Moreover, XRF analysis was used to identify PANI elements corresponding to their mass concentrations and into kα lines elements, respectively. The elements that detected with Rigaku NEX CG are included Cl, Kr, SO_3, Al_2O_3, SiO_2, and ZrO_2, where the accuracy is compared with the XRF data using various LiCl wt.%.

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