Structural and DC Conductivity Studies of $CoCl_2$ - PEO Doped Polyaniline Complexes.

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Abstract

The present study deals with the synthesis of polyethylene oxide (PEO) complexes with conducting Polyaniline (PANI) and Cobalt Chloride salt ($CoCl_2$) by insitu polymerization method with different weight percentage(wt%). The newly prepared composites were confirmed by Fourier transform infrared spectroscopy (FTIR) studies onPANI:$CoCl_2$:PEO complexes, and the peak at 1122 cm^{-1} is considered to be measure of the degree of electron delocalization, 1487 $cm^{-1}$is due to C=C stretching of benzonoid ring, 1558 cm^{-1} is C=N quinonoid stretching mode of vibration. DC conductivity studies show thermally activated behavior of all the composites. The conductivity was found to increase with the increase in temperature indicating the semiconducting behavior of all the complexes. Maximum conductivity was observed in 30 wt% of Cobalt Chloride salt complexes with conducting Polyaniline and polyethylene oxide.

Key Words: Polyaniline, Cobalt Chloride salt, Polyethylene oxide, complexes, DC conductivity.

I. Introduction:

The solid polymer salt complexes are of technological interest due to their possible application as solid electrolytes in different devices such as batteries, fuel cells, electro-chromic display devices/smart windows and photo-electrochemical solar cells, etc.,.Solid polymer electrolytes that do not contain low molecular liquids and represent polymer (or polymer mixture)–salt systems are the most inert to cathode materials. In addition, their component composition remains unchanged with time. At the same time, the transport characteristics of solid polymer electrolytes are not high enough. The principles of developing such materials can be chosen on the basis of fundamental research into the mechanisms of ionic transport in solid polymer electrolytes. The ionic conductivity in high molecular weight polyethylene oxide (PEO) doped with sodium and potassium salts were first reported by Wright [1-8]. The

technological implications of these PEO based electrolytes, such as their use in lithium batteries were realized and suggested by Armand [9-10]. These reports related to these solid electrolytes have been reported in reviews by many researchers [11,12].

It was found that the amorphous part of a polymer electrolyte accounts for their high conductivity [13-14]. Consequently, it is more efficient to use amorphous polymers in building polymer electrolytes.

II. Materials And Method:

All Chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate (APS) ($(NH_4)_2S_2O_8$), Hydrochloric acid (HCl), and $CoCl_2$,PEOwere procured from sigma and were used as received.

a) Synthesis of Polyaniline:

The synthesis was based on mixing aqueous solutions of aniline hydrochloride and ammoniumpersulphate at room temperature, followed by the separation of polyaniline hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equi molar volumes of aniline and hydrochloric acid) was dissolved in distilled water in a volumetric flask to 100 mL of solution. Ammonium persulphate (0.25M) was dissolved in water also to 100 mL of solution. Both solutions were kept for 1 hour at room temperature (25°C), then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 300-mL portions of 0.2 M HCl, and similarly with acetone. Polyaniline (emeraldine) hydrochloride powder was dried in air and then in vacuum at 60°C to achieve the constant weight [15].

b) Synthesis of PANI: $CoCl_2$:PEO complexes

The 0.1 mole aniline monomer is dissolved in 1 mole nitric acid to form polyaniline hydronitride. Fine graded pre-sintered $CoCl_2$ +PEO (AR grade, SD-Fine Chem.) powder in the weight percentages (wt%) of 10,20,30,40and 50wt% is added to the polymerization mixture with vigorous stirring in order to keep the $CoCl_2$:PEOpowder suspended in the solution. To this reaction mixture, APS as an oxidant is added slowly with continuous stirring for the period of 4 hrs at temperature 5^0C. Polymerization of aniline takes place over fine grade $CoCl_2$ +PEO particles. The resulting precipitate is filtered and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any uncreated aniline.

After washing, the precipitate is dried under dynamic vacuum at 60^0C for 24 h to achieve constant weight of resulting complexes [15]. In this way, five different polyaniline / $CoCl_2$ +PEO complexes with different weight percentages of $CoCl_2$ +PEO (10, 20, 30, 40 and 50wt%) in polyaniline have been synthesized. All the complexes are crushed into fine powder in an agate mortar in the presence of acetone medium.

The powders of polyaniline and polyaniline – $CoCl_2$ +PEO complexes so obtained from synthesis techniques discussed in the early sections are crushed and finely in the presence of acetone medium in agate mortar. This powder is pressed to form pellets of 10 mm diameter and thickness which varies from 1 to 2 mm by applying pressure of 90 MPa in a hydraulic press. The pellets of polyaniline and its complexes so obtained from above mentioned techniques are coated with silver paste on either side of the surfaces to obtain better contacts.

III. Characterization

The FTIR spectra of all the samples are recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording FTIR spectra, powders are mixed with KBr in the ratio 1:05 by weight to ensure uniform dispersion in KBr pellets. The mixed powders are pressed in a cylindrical die to obtain clean discs of approximately 1 mm thickness. The DC conductivities are measured using two probe method.

IV. RESULTS AND DISCUSSIONS

A) FTIR

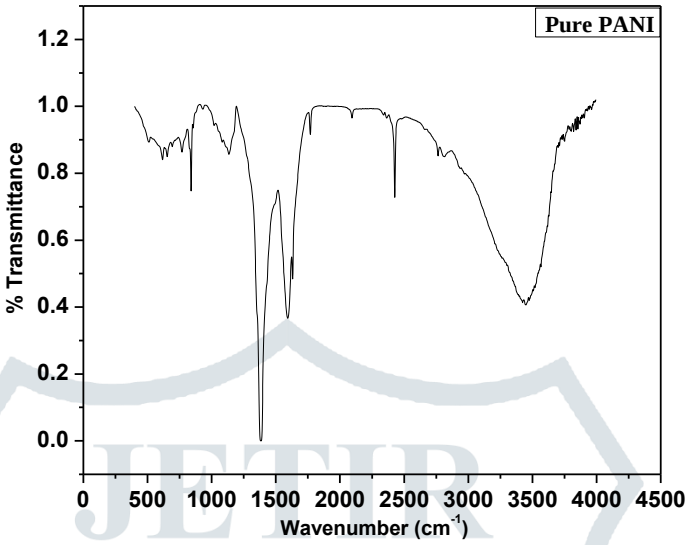

Figure: (1)FTIR Spectra of pure polyaniline.

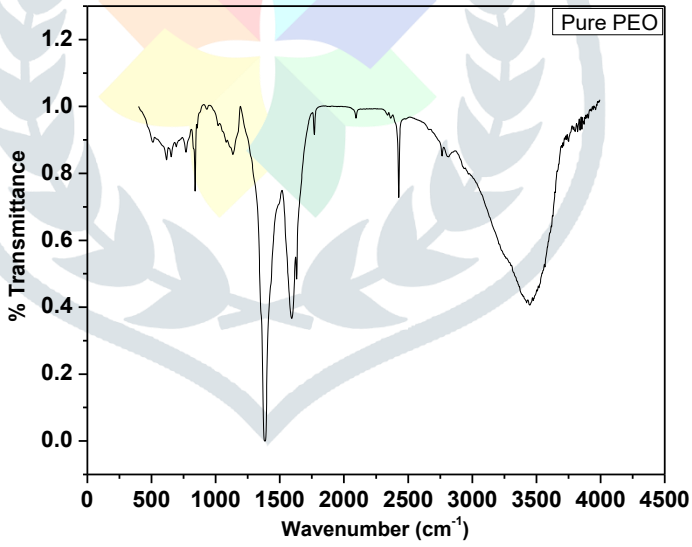

Figure:(2) FTIR Spectra of Pure Polyethylene oxide

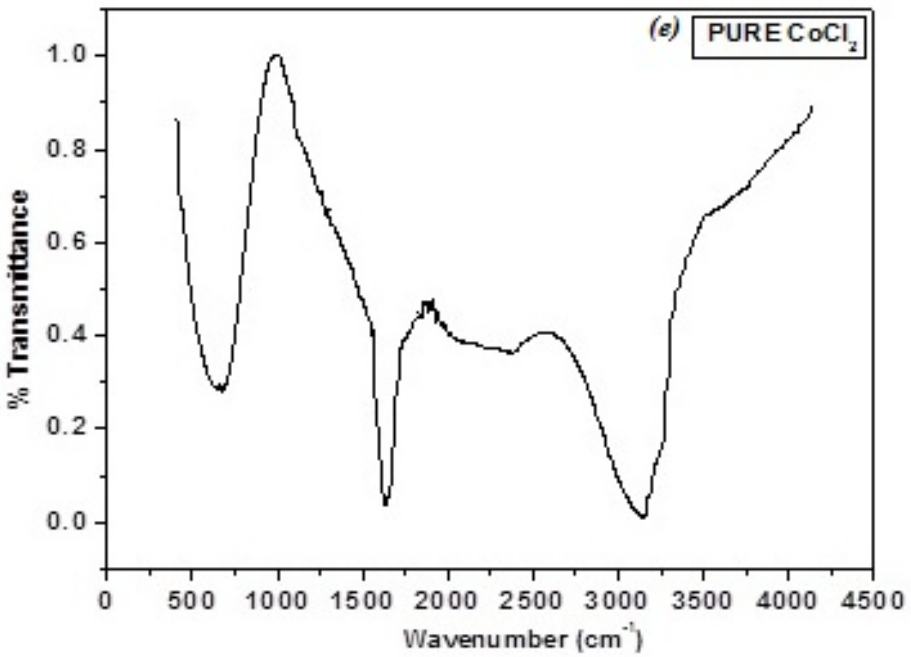

Figure:(3) FTIR Spectra of Cobalt Chloride salt.

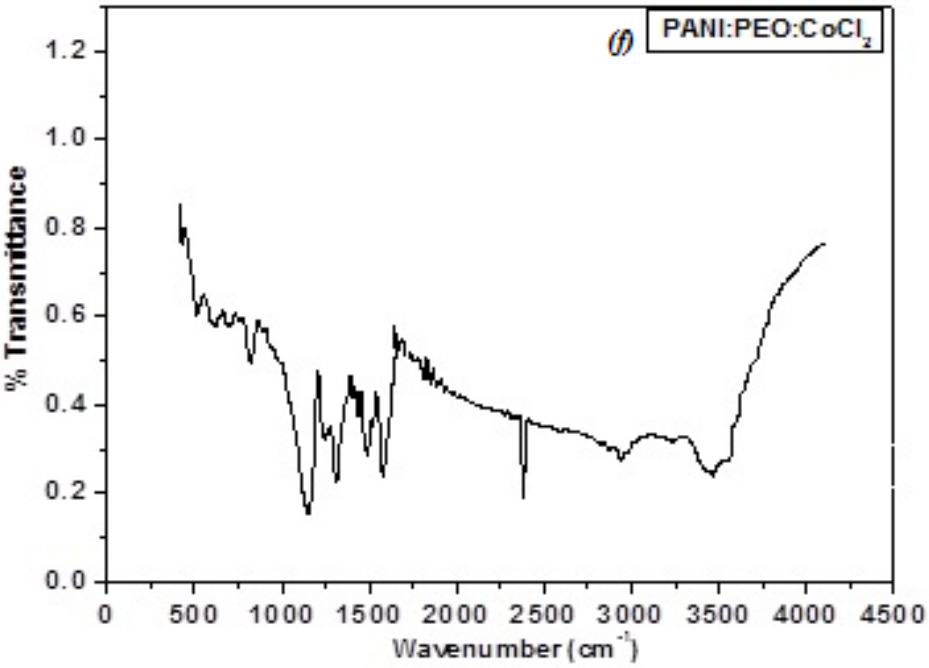

Figure: (4)FTIR Spectra of PANI:$CoCl_2$:PEOcomplexes

The prominent peak (Figure.1) shows FTIR spectra of pure polyaniline. The vibration of polyaniline is known to be in the region 1000 – 1500 cm^{-1}. The FTIR spectra of PANI shows vibrations around 814, 1024, 1122, 1240, 1300, 1487, 1556, 2860, 2924, 3447cm^{-1}. 814 cm^{-1} which corresponds to plane bonding of C-H bonding aromatic ring, 1024 cm^{-1} corresponds to S-O vibration, 1122 cm^{-1} is C-O-C stretching excess oxidant, 1240 is C-N stretching of benzonoid ring, 1303 cm^{-1} is C-N aromatic amines, 1487 cm^{-1} is C=C stretching of benzonoid ring, 2860 cm^{-1} and

2924 cm^{-1} are C-H stretching, 3447 cm^{-1} is N-H stretching vibration. Therefore, the above characteristic peaks confirm the formation of polyaniline[16].

Figure 2 shows the spectra of pure polyethylene oxide. In the pure PEO spectrum, a large broad band appears centered at 3442 cm^{-1}. This is possibly due to the hydration of PEO. It was known that the PEO is highly hydrophilic, thus it absorbs water vapor and gets hydrated. Pure PEO shows a large broad band of CH_2 stretching between 2950 and 2840 cm^{-1}. However, the band is split into two at 2922 cm^{-1} and 2359 cm^{-1} corresponding to asymmetric CH_2 stretching (n(CH_2)a) and symmetric CH_2 stretching (n(CH_2)s), respectively.

Two clear CH_2 vibrational modes also appear in PEO at 1467 cm^{-1} which, corresponds to asymmetric CH_2 bending (d(CH_2)a) and 1344 cm^{-1} which corresponds to symmetric CH_2 wagging and some C-C stretching (w(CH_2)s + n(CC)[17].

B) DC Conductivity

Conductivity Studies:

Polyaniline: Polyethylene oxide: Cobalt Chloride

Figure 5(b) shows the σdc conductivity as a function of temperature for PANI:PEO:$CoCl_2$ polymer complexes at various weight percentages. The dc conductivity is found to be constant up to 140^0C of all the composites and afterwards it increases steeply with temperature. Among all PANI: PEO: $CoCl_2$ polymer complexes, 30 wt% shows higher conductivity. This clearly indicates that the conductivity is not only the motion of ions ($CoCl_2$) but also hopping of charge carriers like polarons and bipolarons from one island to another.

It is also suggested here that the thermal curling effects of the chain alignment of the polyaniline, leads to the increase in conjugation length and that brings about the increase of conductivity. Also, there will be molecular rearrangement on heating which make the molecules favorable for electron delocalization. The conductivity varies directly with the temperature obeying an expression of the following form.

$$\sigma (T) = \sigma 0 \exp [- (T0/T)\ ¼] \text{ ----------(1)}$$

where σ is the conductivity, T is the temperature, and σ0 is the conductivity at characteristic temperature T0. Conductivity varying with various values of the exponent (T-1/4, T-1/3and T-1/2) has been reported and different models have been used to interpret this data.

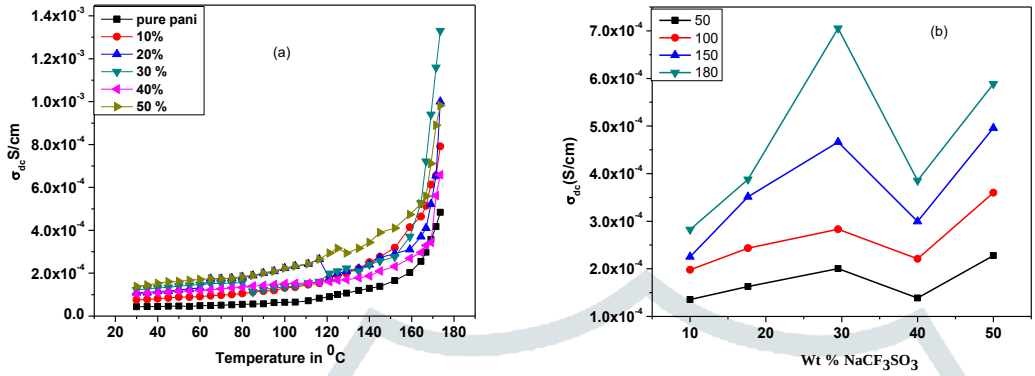

Figure 5(a) Variation of σ_{dc} conductivity of PEO/PANI/$CoCl_2$ composites at various weight percentages as a function of temperature,(b) shows the variation of dc conductivity as a function of different weight percentages.

Figure 5(b) shows the variation of dc conductivity as a function of different weight percentages of PANI-PEO-$CoCl_2$ polymer complexes at three different temperatures (50, 100 ,150 and 180^{0}C). It is observed that for 10 wt%, 20 wt% and 40 wt% of PANI-PEO-$CoCl_2$ polymer complexes, the conductivity decreases. However in 30 wt% and 50 wt% of PANI-PEO-$CoCl_2$ polymer complexes, conductivity increases which is due to the variation in distribution of PANI which may be supporting for more number of charge carriers to hopp between favorable localized sites causing increase in conductivity. The decrease in conductivity may be attributed due to the trapping of charge carriers. This can be well supported by VRH model[18].

V. Conclusion:

The alkyl salt $CoCl_2$: PEO doped polyaniline complexes has been prepared at different weight percentages (10, 20, 30, 40 and 50 wt %) where synthesized byinsitu polymerization method. The SEM image reveals the presence of PEO-$CoCl_2$ particles which are uniformly distributed throughout the composite sample. The temperature dependence of the conductivity of the composites exhibits a typical semiconductor behavior and hence can be expressed by the 1D-VRH model proposed by Mott. The decrease in the conductivity of the composites may be due to the trapping of charge carriers in the matrix, which may be confirmed by the percolation theory. This result indicates that the $CoCl_2$: PEO

doped polyaniline complexes has an electrochemical stability and sis thus suitable for application in solid-state batteries. Maximum conductivity was observed in the composite of 30 wt% of $CoCl_2$: PEO doped polyaniline complexes.

Reference

1. Armand, M.B., Chabagno, J.M. and Duclot, M. (1979), in Fast Ion Transport in Solids (Edited by Duclot, M.J.; Vashishta, B.; Mundy, J.N.; and Shenoy, G.K.), North-Holland,Amsterdam
2. Wright, P.V.(1975). Electrical conductivity in ionic complexes of poly(ethylene oxide).British,PolymerJournal,7(5),319-327.
3. Maccallum, J.R.; and Vincent, A. (1987). Polymer electrolyte review. Amsterdam,131.
4. Hasmi, S.A.; Chandra A.; and Chandra S. (1992). In: Solid State Ionics: Materials and Applications. (Edited by Chowdari; B.V.R. et al.), World Scientific.Singapore-567.
5. Owen, J.R. (1989). Superionic solids and solid electrolytes-recent trends. Edited by Lasker, A.L.; and Chandra, S., Academic Press, New York, 111.
6. Gray, F.M. (1987). Polymer electrolytes. Royal Society of Chemistry, England. And Kumar, B.; and Rodrigues, S.J. (2001).Poly(ethyleneoxide)-based composite electrolytes: Crystalline Amorphous transition.Journal of the Electrochemical Society, 148(12), A1336 – A1340.
7. Chandra, A. ;Srivastva, P.C. ; and Chandra S. (1992). In :Superionic solids state ionics: Materials and applications. (Edited by B.V.R. Chowdary et al.), WorldScientific,Singapore,397.
8. Maccallum, J.R.; and Vincent, C.A. (1981). Polymer electrolyte reviews. Elsevier, Amsterdam In this paper, the authors have reported the Synthesis, characterization and studies onDC conductivity, dielectric constant and dielectric loss of PANI:$CoCl_2$:PEOcomplexes.

9. Wright, P.V, "Electrical conductivity in ionic complexes ofpoly(ethylene oxide)", British Polymer Journal, 7(1975)319.
10. Armand, M.B., Chabagno, J.M. and Duclot, M, "Fast Ion Transport in Solids" (Edited by Duclot, M.J.; Vashishta, B.; Mundy, J.N.; and Shenoy, G.K.), North-Holland, Amsterdam,(1979).
11. A. Bhide and K. Hariharan, "Ionic transport studies on$(PEO)_6$:$NaPO_3$ polymer electrolyte plasticized with PEG400,"European Polymer Journal,43(2007)4253.
12. Wright, P.V, "Electrical conductivity in ionic complexes ofpoly(ethylene oxide)", British Polymer Journal, 7(1975)319.
13. Armand, M.B., Chabagno, J.M. and Duclot, M, "Fast Ion Transport in Solids" (Edited by Duclot, M.J.; Vashishta, B.; Mundy, J.N.; and Shenoy, G.K.), North-Holland, Amsterdam,(1979).
14. A. Bhide and K. Hariharan, "Ionic transport studies on$(PEO)_6$:$NaPO_3$ polymer electrolyte plasticized with PEG400,"European Polymer Journal,43(2007)4253.
15. Chakradhar Sridhar B,Sasikala M , Jakeer Husain , M.V.N, Pradeep and M.V.N. Ambika Prasad, "Synthesis, characterization, Electrical and Sensor Behavior of PANI/In_2O_3 Nano Composites," Ferroelectrics,502(2016)159.
16. Chakradhar Sridhar B,Nagesh Gunvanthrao Yernale, and M. V. N. Ambika Prasad,Hindawi Publishing Corporation ,Synthesis, Spectral Characterization, and Antibacterial and Antifungal Studies of PANI/V_2O_5 Nanocomposites, International Journal of Chemical Engineering, 2016,Article ID 3479248.
17. Rui Yang, Shichao Zhang, Lan Zhang, WenboLiu;"Electrical properties of composite polymer electrolytes based on PEO-SN-$LiCF_3SO_3$", Int. J. Electrochem. Sci., 8 (2013) 10163.
18. Chakradhar Sridhar B, Jakeer Husain and M.V.N. Ambika Prasad ,Studies on DC Conductivity and LPG Sensing Behavior of PANI/V_2O_5 Nanocomposites, IJAET, 7(2014) 532.