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Synthesis, characterization and conductivity measurement of poly (2-vinyl pyridine) complex in nano fine state

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Summary

The objective of the present work is to prepare Poly (2-vinyl pyridine)-I_2 complex in nano fine state. The compounds were characterized by IR, UV, SEM and TGA techniques. Conductivities were determined from 30 to 150°C in solid state within a frequency range 42Hz to 500kHz. Conductivity of the complex formed in nano fine state is more stable and shows dramatic improvement compared to the bulky one.

Introduction

Poly (2-vinylpyridine), P2VP and its derivatives like salts and complexes, hold a unique position in the field of solid state batteries [1-4]. Specifically, P2VP–I_2 is used to prevent the degradation of lithium electrodes in solid state batteries[5]. From the literature it is found that batteries with metallic electrodes like Li have a limited life-cycle due to the degradation of outer surface of the electrode. The formation of high surface area lithium powder is undesirable because it reacts violently with moisture and air, resulting in downgraded cell performance. Composite anode alternatives have been suggested to overcome such problems, but they are prone to a large loss of capacity as compared to metallic lithium. Lithium alloy active materials have a relatively short cycle life due to mechanical degradation of the electrode.

The lithium/iodine battery used for implantable devices exhibits high internal impedance that increases as the cell is discharged, due to the increasing thickness of the solid electrolyte and the decreasing electronic conductivity of the cathode material. Therefore it is not capable of delivering high power.

In lithium-ion batteries energy is stored through the movement of lithium ions whereas in lithium-iodine batteries it is through the iodide ion. As lithium ion is smaller so the lithium-ion batteries give high current density than that of lithium-iodine batteries. However, in both cases the batteries are sensitive to temperature and they become inactive above 60°C [6, 7].

Therefore what is needed is a cell construction with a suitable method of operation, which overcomes the problems of passivation in order of the cell. This problem can be addressed by the synthesis of a suitable material which is stable above 60°C.

To increase its conductivity, the method of preparation of the P2VP-I_2 complex needs to be improved. Assuming that if the P2VP-I_2 complex is formed in a nano fine state, the problem might be solved. It is also important that to prepare P2VP-I_2 complex in nano fine state the starting material P2VP must be in nano fine state. The main object of this paper is to synthesis P2VP in nano fine state by electrolysis of P2VP-HCl salt. Then, P2VP-I_2(N) complex is synthesized by the interaction of, P2VP(N) with iodine in vapor state. The polymer so formed is characterized by IR, UV, SEM, TGA and conductivity studies.

Experimental

Materials

Preparation of Poly (2-vinylpyridine), P2VP and P2VP-HCl salt

2VP (Acros Organics) was purified by distillation under vacuum. Acetone (Ranbaxy) and hydrochloric acid (Ranbaxy) were used without further purification. Benzene (Ranbaxy) was purified as reported in the literature [8]. P2VP and P2VP-HCl salt were prepared as reported earlier [9].

Preparation of P2VP-I_2 from P2VP

P2VP prepared from 2VP is dissolved in chloroform, treated with iodine solution in ethanol and kept over night in the dark. After precipitation in acetone, it was washed with chloroform to remove last traces of P-2VP and then was stored in a desiccator.

Preparation of Poly (2-vinylpyridine) nano, P2VP(N) thin film by electrolysis

Pure P2VP(N) was deposited on copper plate (thickness: 150µm) by electrolysis of P-2VP-HCl salt[10]. Both anode and cathode are made of copper plate were inserted in to a 20% (w/v) P2VP-HCl solution in distilled water. A 3volt DC power supply was used along with a 22k ohms current limiting resistance in series to limit the current around 100µA. A very low current is applied to facilitate a slow reaction for the formation of the compound in nano state. The deposition time was 6h and a thin film of P-2VP with a thickness of 0.1µm was deposited on the cathode after the completion of the electrolysis. After the deposition of P2VP(N) thin film, the copper plate was washed with distilled water repeatedly to remove the last traces of P-2VP-HCl salt and then it was stored over P_2O_5 in a desiccator.

Preparation of P2VP-I_2(N) from P2VP(N)

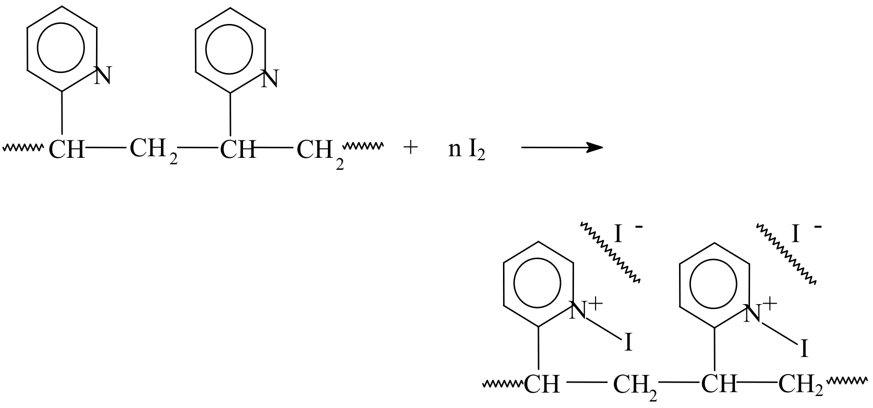
Copper plate with the deposited P-2VP(N) thin film was fixed on a Petri dish (size 94x17mm) with glue and the dish was kept inverted on a 250ml beaker as a lid. An excess of solid iodine pieces were kept inside the beaker so that during sublimation, the solid iodine slowly reacted with the P2VP(N) film on the top of the beaker. After about 16 hours at 25°C, the brown colored P2VP(N) had been converted to a violet colored film of P2VP-I_2(N).

Physical measurement

IR spectra were recorded with a Bruker Vector 22 FTIR in a reflectance mode. Ultraviolet spectra were obtained on a Shimadzu UV-1601 spectrophotometer. The SEM of the polymers was carried out in a scanning electron microscope (Model: LEO 1430VP). TGA was performed using a Perkin-Elmer thermal analyzer in nitrogen at a heating rate of 10°C/min using 5±1 mg samples. The bulk electrical conductivity of these compounds was evaluated from the complex impedance-admittance plots recorded at different temperatures using a HIOKI 3520, frequency response analyzer. The plots were recorded in the frequency range from 40 Hz to 500 kHz keeping the signal amplitude of 20 mV. The geometry of the cell for the measurement of conductivity was Pt|polymer film|Pt, where platinum plates were used as electrodes. The experiment was carried out under a relative humidity of 57% [11].

Results and Discussion

It is proposed that the following reactions take place between P-2VP and I_2 for the formation of P2VP-I_2.



The IR spectra of P2VP-I_2(N), (Figure1(b)) indicates that the peak at 1550 cm^{-1} is due to the incorporation of iodide ion[12] in to the pyridine molecule which is absent in P2VP(N) (Fig1(a)).

From the UV spectra (Figure 2), a blue shift is observed for P2VP(N) and P2VP-I_2(N) with respect to P2VP and P2VP-I_2. The wave length is 218.8nm, 208.7nm, 194.4nm and 191.5nm for P2VP, P2VP-I_2, P2VP(N) and P2VP-I_2(N) respectively. This indicates the formation of P2VP(N) and P2VP-I_2(N) particles in nano fine state. The SEM photographs of P2VP(N) and P2VP-I_2(N) are presented in Figure 3 and Figure 4 respectively. SEM analysis indicates that the particle size of P2VP(N) is within the range of 108.6 to 125.8nm and that for P2VP-I_2(N) is within 144.4nm to 204.2nm.

The conductivity curves (Figure 5) for both P2VP(N) and P2VP-I_2(N) show a gradual increase of conductivity with rise of temperature and they are stable even up to 150°C. The curves show that the conductivity of P2VP-I_2(N) is less than that of P2VP-I_2

which is contrary to expectation. On thorough examination it is found that the presence of excess amount of Iodine associated with P2VP-I_2 accounts for the higher conductivity than that of P2VP-I_2(N)[13].

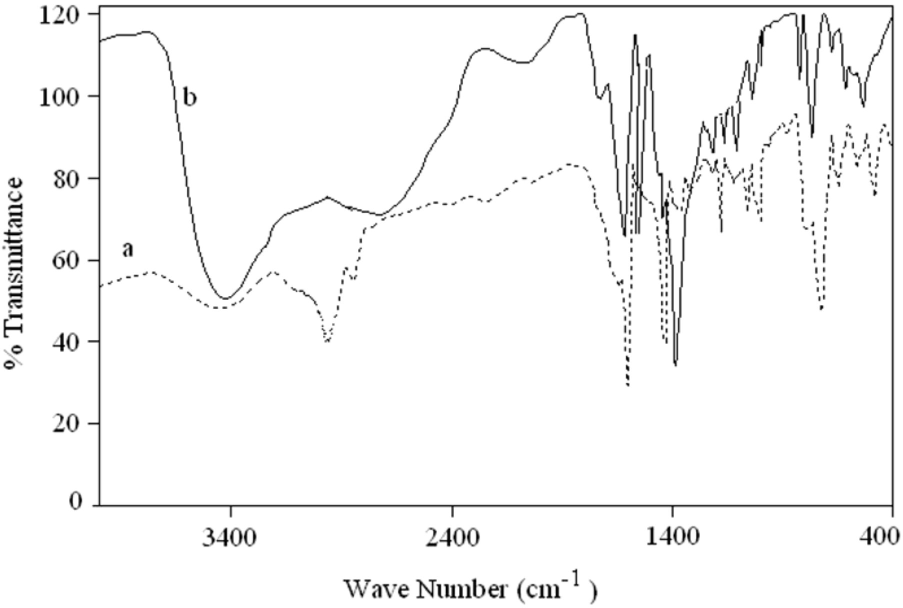


Figure 1. IR Spectrum of a. P2VP, b. P2VP-I_2.

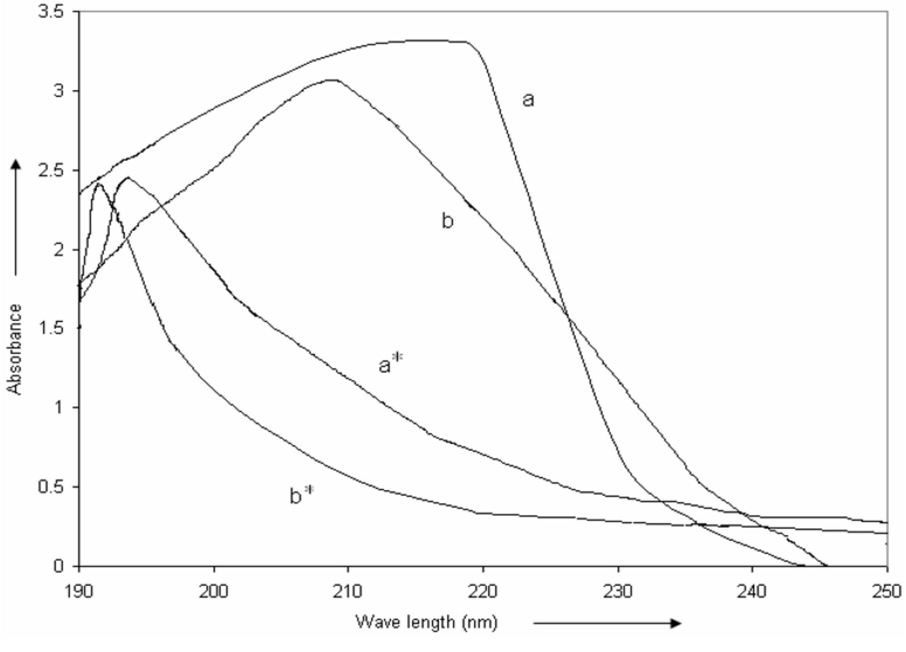


Figure 2. UV Spectrum of a. P2VP, a*. P2VP(N), b. P2VP-I_2 and b*. P2VP-I_2(N).

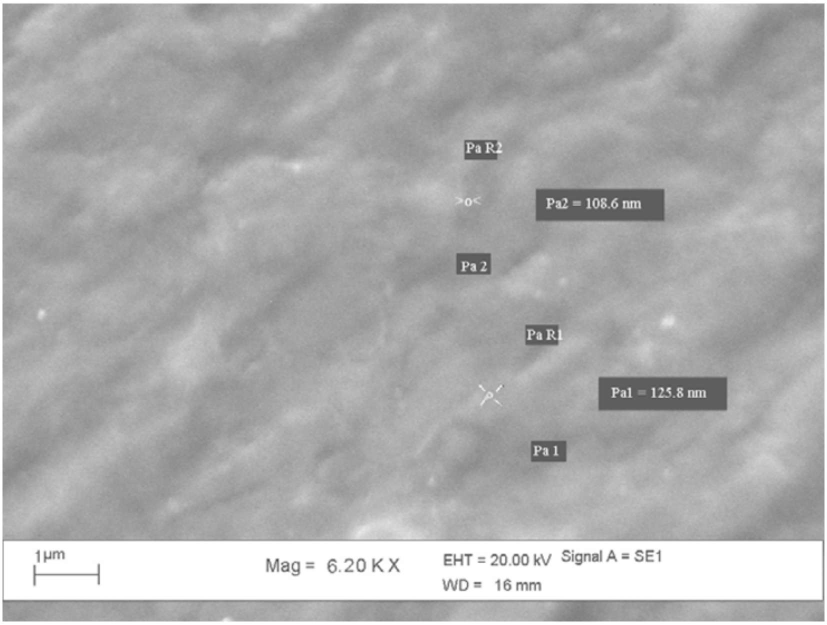


Figure 3. SEM photograph of P2VP(N).

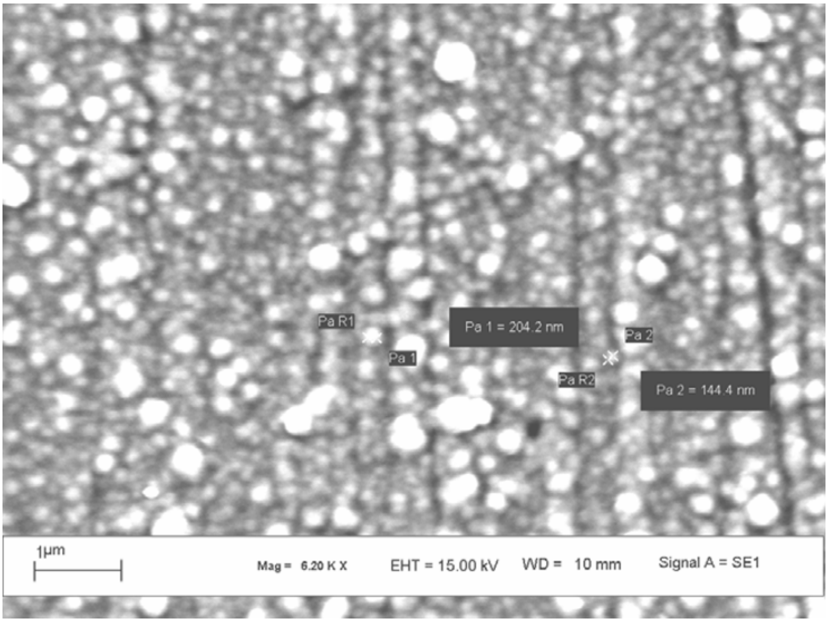


Figure 4. SEM photograph of P2VP-I_2 (N).

However, the cases of P2VP and P2VP-I_2 show a sudden rise of conductivity at around 90°C and this may be due to an annealing effect [14] at this temperature for these bulk films. This observation indicates that the nano compounds are uniformly composed and are thermally more stable.

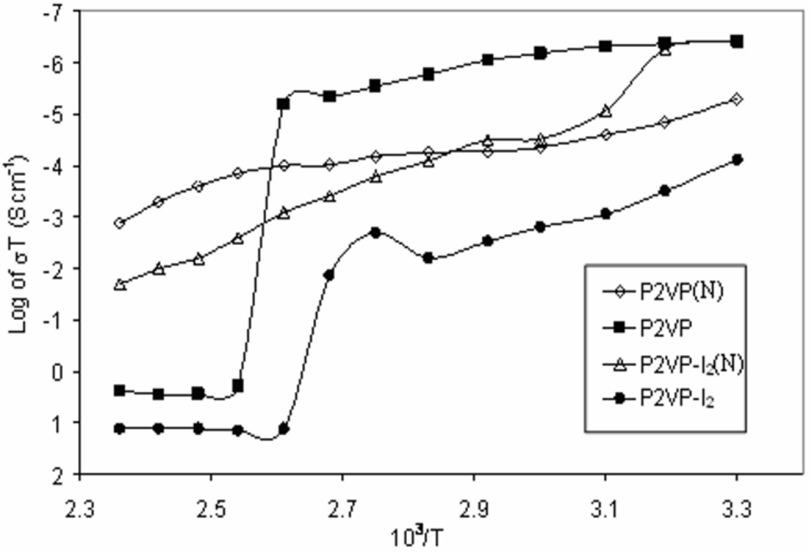


Figure 5. Log of σT vs. 1/T curves.

The activation energies for the conduction of these compounds are as follows:
P2VP(N) = 0.3517ev; P2VP-I$_2$(N) = 0.9691ev; P2VP = 0.329ev and P2VP-I$_2$ = 1.0761ev
The activation energies for the conduction of the nano compounds are less than that of the bulky compounds. This is due to the orderly arrangement of the molecules in nano fine state whereas in the bulky case the arrangement is random.

In the impedance vs. temperature curves (Figure 6) P2VP(N) and P2VP-I$_2$(N) show very smooth curves compared to those of the bulky compounds for both low and high frequency. There was a sudden decrease of impedance in case of P2VP and P2VP-I$_2$ in the temperature range 80-120°C induced by the applied frequency and can be termed

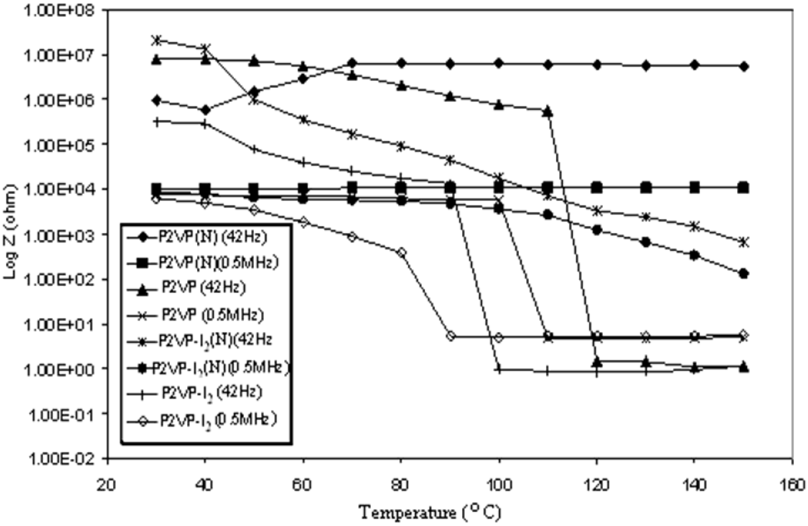


Figure 6. Log Z vs. Temperature curves.

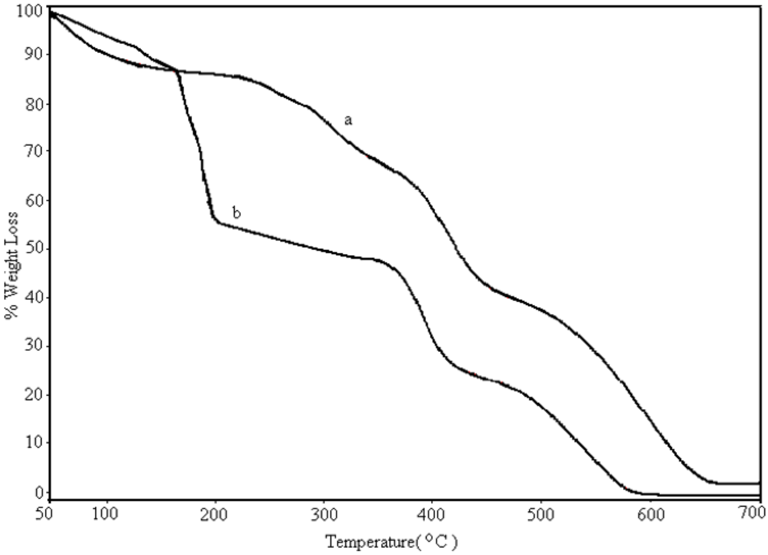


Figure 7. TGA curves of: a. P2VP-I_2 (N) and b. P2VP-I_2 under nitrogen at a heating rate of 10°C/min.

as 'break down temperature' of these materials. No such behaviour is seen in case of the nano materials and they are stable through out the temperature and frequency range. The TGA curves (Figure 7) of P2VP-I_2 and P2VP-I_2(N) complex also support this explanation. From the curves it is found that P2VP-I_2(N) is more stable compared to P2VP-I_2. This may be due to the nano fine structure of P2VP-I_2(N).

It appears that the nano material synthesized may be a potential candidate for the lithium/iodine battery.

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