Int. J. Electrochem. Sci., 10 **(2015)** 2663 - 2684

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrical Conductivity and Thermal Stability Studies on Polyaniline Sn(IV)tungstomolybdate Nanocomposite Cation-Exchange Material: Application as Pb(II) Ion-Selective Membrane Electrode

Zeid Abdullah ALOthman[1], *Mohammad Mezbaul Alam*[1,*], *Mu. Naushad*[1], *Rani Bushra*[2]

[1] Advanced Materials Research Chair, Chemistry Department, Building#5, College of Science, King Saud University, Riyadh 11451, Kingdom of Saudi Arabia
[2] Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India
[*] E-mail: alamohammad@ksu.edu.sa (M.M. Alam)

Received: 1 December 2014 / *Accepted:* 9 January 2015 / *Published:* 19 January 2015

Conducting polymeric-inorganic composite ion-exchange materials are now considered as an advanced class of materials due to their excellent ion-exchange behavior as well as their analytical and electroanalytical applications. In this study, electrically conductive nanocomposite of polyaniline Sn(IV) tungstomolybdate (PSTM) was synthesized by sol–gel method via the blend of inorganic precipitate of Sn(IV)tungstomolybdate into the matrix of polyaniline gel having good ion-exchange capacity and electrical conductivity behavior. The so obtained composite was characterized by using several sophisticated instrumental analyses; such as FTIR, TGA-DTA, XRD, SEM and TEM. Electrical conductivity behavior of this composite material was investigated by using 4-probe-in-line DC electrical conductivity measuring technique and the electrical conductivity was found in semiconductor region; i.e., 10^{-2} S cm^{-1}, which followed Arrhenius equation for its temperature dependence. The thermal stability of the PSTM composite material in terms of dc electrical conductivity retention was studied under isothermal and cyclic techniques and electrical conductivity of the composite was found to be sufficiently stable under ambient temperature conditions. The dependence of the electrical conductivity on the concentration of conducting phases i.e., polyaniline exhibited that the increase in electrical conductivity followed the percolation threshold. Using this electroactive composite cation-exchanger, a novel heterogeneous precipitate based ion-selective membrane electrode was developed for the determination of Pb(II) ions in solutions. The membrane electrode has a quick response time with mechanically stable and can be used within a varied pH range. The selectivity coefficients for various cations evaluated by mixed solution method were found to be less than unity. The electrode was also found to be suitable in electrometric titrations.

Keywords: Electrical conductivity, Thermal stability, Polyaniline Sn(IV) tungstomolybdate, Nanocomposite cation-exchanger, Pb(II) ion-selective membrane electrode.

1. INTRODUCTION

Composites of conducting polymers and inorganic oxides are considered as heterogeneous disordered systems with a complementary behavior between the polymeric matrix phase and the inorganic dispersed phase. These types of hybrid organic-inorganic composites are advanced class of materials due to their extraordinary properties within a single molecular composite; organic polymeric part of the composite provides mechanical, electrical and chemical stabilities whereas inorganic part supports the thermal stability and also increases the electrical conductivity [1-4].

Electrically conducting polymers such as polyparaphenylene, polyaniline, polypyrrole, polyacetylene, polythiophene and their derivatives have received extensive attention of researchers for the last few decades because of their fascinating electronic, magnetic and optical properties [5–7]. Among them, polyanline (PANI) is the most promising polymeric material which can be frequently used because of its easy synthesis, flexibility, high electrical conductivity, environmental stability, relatively low cost and effective material for sensing applications [8-12]. However, a major problem with conducting polymers is its poor mechanical strength and chemical stability which restricts their use in device fabrication. There is a wide scope for the enhancement by combining organic materials with inorganic counterparts to form organic-inorganic composites/nanocomposites [13-17].

Nanocomposites formed from oxide particles and intrinsically conducting polymers have attracted a great deal of interests because of their unique structural, electrical, thermal and mechanical properties [18–21]. Its original performance was improved because of introduction of inorganic particles. They have better performance than the single component and even show new function due to the effects of nanomaterials and the synergies between polymers and inorganic compounds. These compounds exhibit a number of useful physiochemical properties in addition to the possibilities for their use in energy storage devices, chemical stability, biological sensors, chemical sensors, actuators, gas sensors, corrosion protection, memory devices, catalysis etc. [22-30].

Over the last decade, conducting polymers based ion-exchange composite materials represent one of the most attractive developments in the material chemistry for variety of applications [31–34]. Various organic-inorganic nanocomposites prepared in different research laboratories have shown excellent ion-exchange behavior, electrical conductivity, high stability, reproducibility, selectivity for heavy toxic metal ions and sensing material for various toxic metals, organic vapors, hazardous gases and humidity [35-40]. Though researchers are continuously contributing their efforts to synthesize new composite materials, still much more studies needed to develop practically applicable composites based on conducting polymers and their derivatives.

In this regard, very recently, polyaniline Sn(IV)tungstomolybdate cation-exchange nanocomposite was synthesized in our laboratory and its excellent ion-exchange properties were examined [41] for the selective separation of toxic Pb^{2+} from the solutions that can be used in pollution control. In the present research work, detailed electrical conductivity and thermal stability studies have been investigated on our newly synthesized PSTM nanocomposite material and it exhibited better electrical conducting properties than pristine conducting polymer. An attempt has also been made to obtain a new heterogeneous precipitate based membrane electrode by using the PSTM composite cation-exchanger as electroactive material for the determination of Pb(II) ions present in the solutions.

2. EXPERIMENTAL

2.1. Reagents and instruments

Aniline ($C_6H_5NH_2$), potassium persulfate ($K_2S_2O_8$), stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) were the main reagents used for the PSTM nano-composite preparation. These reagents were purchased from BDH Chemicals Limited (Poole, England). All other chemicals and reagents were of analytical reagent standard. Solutions of aniline (10% solution, v/v) and potassium persulfate (0.1 M) was prepared in 1.0 M HCl and the solutions of 0.1 M stannic chloride pentahydrate, 0.1 M sodium molybdate and 0.1 M sodium tungstate were prepared with demineralized water (DMW). A solution of 0.1 M $Pb(NO_3)_2$ was prepared by dissolving $Pb(NO_3)_2$ salt in 100 ml demineralized water (DMW) while other standard $Pb(NO_3)_2$ solutions of 1×10^{-1} M to 1×10^{-10} M concentrations were prepared by subsequent dilutions.

A 4-in-line-probe electrical conductivity-measuring instrument, Scientific Equipment (Roorkee, India), was used for measuring the dc electrical conductivity. A digital electronic balance (ES 125S, Precisa Gravimetrics AG, Switzerland) was used for weighing purpose. A manual hydraulic press – 15 ton (GS15011**,** Specac’s Atlas Series Laboratory Hydraulic Press, Japan) instrument was used for making pellets of the composite material. A digital pH/mV meter (744, Metrohm, Switzerland) with a saturated calomel electrode as a reference electrode was used for the potential measurement at room temperature (25 ± 2 °C).

2.2. Synthesis

The polymeric-inorganic nanocomposite of polyaniline Sn(IV) tungstomolybdate was prepared by the combination of conducting polymer of polyaniline gel into the inorganic precipitate of Sn(IV) tungstomolybdate cation-exchanger that followed the method exactly similar to that of our previous work [41].

2.2.1. Polyaniline

Polyaniline gel was synthesized by polymerization of aniline monomer in the presence of hydrochloric acid using potassium persulphate (acts as an oxidizing agent) by chemical oxidative polymerization method. For the synthesis, solution of aniline was taken in a double wall flask at temperature below 10 °C and then solution potassium persulphate was added drop by drop in the double wall flask with continuous stirring for 2 h. In this way, green colored polyaniline gel was prepared.

2.2.2. Sn(IV) tungstomolybdate

Sn(IV) tungstomolybdate precipitate was synthesized by adding the mixture of aqueous solutions of sodium molybdate and sodium tungstate into the solution of stannic(IV) chloride at the flow rate of 2.0 mL min^{-1} with continuous stirring in different volume ratios and pH conditions. White gel type slurry was obtained. The resulting white precipitate so formed was allowed to stand for 24 h in the mother liquor for digestion.

2.2.3. Polyaniline Sn(IV) tungstomolybdate (PSTM)

PSTM composite cation-exchange material was prepared by the sol–gel mixing of polyaniline gel into the precipitate of Sn(IV) tungstomolybdate with a continuous stirring. The resulting mixture was changed slowly into greenish colored slurry. The slurry was kept for 24 h at room temperature. Subsequently, polyaniline based composite cation-exchanger gel was filtered off and washed thoroughly with DMW to remove excess acid and any adhering trace of potassium persulphate. The washed gel was dried over P_4O_{10} at 50 °C in an oven. Similarly, a numbers of samples of PSTM were prepared by varying their pH and volume ratios. The dried products were immersed in DMW to obtain small granules. They were converted to the H^+ form by keeping it in 1 M HNO_3 solution for 24 h with occasionally shaking intermittently replacing the supernatant liquid. The excess acid was removed after several washings with DMW. The materials were finally dried at 50 °C and then stored in air tight container.

Table 1. Preparation conditions of polyaniline Sn(IV) tungstomolybdate (PSTM) nanocomposite cation-exchange material.

Sample No.	Mixing volume ratio (v/v)						Appearance of beads after drying	Yield (g)	IEC for Na^+ ions (meq g^{-1})
	Sn (0.1M)	W (0.1M)	Mo (0.1M)	pH of the inorganic precipitate	$K_2S_2O_8$ (0.1M)	Aniline (10%)			
PSTM (M-4)	1	1	2	1.0	1	1	Green	7..58	1.77

For further studies, sample M-4 (Table (1)) [41] was selected on the basis of highest ion-exchange capacity (IEC), percent of yield, physical appearance and reproducibility for Na^+ ions.

2.3. Ion-exchange capacity (IEC) and Thermal Effect

The IEC which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation-exchanger was determined by standard column process. 1 g of the dry cation-exchanger sample (PSTM) in H^+-form was taken into a glass column having an internal diameter ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1M alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard 0.1 M NaOH using phenolphthalein indicator.

To study the effect of temperature on the IEC, 500 mg samples of the PSTM (M-4) cation-exchange nanocomposite sample in the H^+-form were heated at rising temperatures started from 50 °C till 900 °C in a muffle furnace for 1 h and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature.

2.4. Characterization

The infrared (IR) spectra was recorded on PSTM using FTIR Spectrometer, Perkin Elmer (1730, USA) using the KBr disk method. The scanning electron microscopy instrument (SEM; LEO, 435 VF) was used for SEM images of the material at different magnifications. Transmission electron microscopy (TEM) analysis was carried out using Jeol H-7500, Hitachi, Japan. Thermal analysis was carried out using an automatic TGA/DTA Analyzer (DTG-60, Shimadzu, Japan).

2.5. Electrical conductivity

For electrical conductivity measurement experiments, the nanocomposite sample M-4 (as prepared) was treated with 1M aqueous solution of HCl to induce protonic acid doping. The material was then washed for excess HCl with doubly distilled water repeatedly till the filtrate gave negative test for hydrogen ions and dried at 50 ^{o}C in an air oven for 48 hours. The dried material (200 mg) was finely ground in a mortar pastel and pellets were made at room temperature with the help of a manual hydraulic press at 25 kN pressure for 10 min. The thickness of a pellet was measured by a micrometer at five different points and the average thickness was taken as the thickness of the pellet sample. The optimum thickness of pellets was obtained ~0.2 mm.

Four-probe electrical conductivity measurements with increasing temperatures (between 30 and 200 °C) for the composite samples were performed on pressed pellets by using a 4-in-line-probe dc electrical conductivity-measuring technique. The sample to be tested was placed on the base plate of four-probe arrangement and the probes allowed to rest in the middle of the sample. A very gentle pressure was applied on the probes and then it was tightened in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply was then switched on, the temperature was allowed to increase gradually with current, and voltage was recorded with rise in temperature.

2.6. Thermal stability in terms of dc electrical conductivity retention

2.6.1. Isothermal technique

The isothermal stability of PSTM (M-4, HCl treated) in terms of DC electrical conductivity retention was carried out under isothermal condition on pressed pellet at 50, 70, 90, 110 and 130 °C in an air oven. The electrical conductivity measurements were carried out at an interval of 15 min.

2.6.2. Cyclic technique

The thermal stability of the PSTM composite (M-4, HCl treated) in terms of electrical conductivity retention was also studied by repeatedly measuring dc electrical conductivity on pressed pellet with increasing temperature from 30 to 200 ^{o}C. The measurements were repeated in this temperature range for 5 times at an interval of 45 minutes.

2.7. Environmental stability of the conductivity of composites

The stability of the PSTM composite material (M-4, HCl treated) in terms of electrical conductivity retention was studied by repeatedly measuring 4-in-line-probe dc electrical conductivity at room temperature on pressed pellet at an interval of five days by short-term exposure to laboratory air.

2.8. Fabrication of ion selective electrode

The composite cation exchanger (100 mg) was ground to a fine powder, and was mixed thoroughly with Araldite (Ciba-Geigy) (100 mg) on Whatman's filter paper No. 42, and a master membrane of 0.32 mm thickness was prepared. A piece of membrane was cut out and fixed at one end of a pyrex glass tube (0.8 cm O.D. x 0.6 cm I.D.) with Araldite. The tube was filled with 0.1 M lead nitrate. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE)	Internal electrolyte (0.1 M Cd^{2+})	Membrane	Sample solution	External reference electrode (SCE)

In advance of measurements of the electrode potential (at 25±2 °C) for a series of standard solutions of $Pb(NO_3)_2$ (10^{-10} M–10^{-1} M), the membrane of the electrode was conditioned by soaking in 0.1 M $Pb(NO_3)_2$ solution for 5 days and for 1 h at least before use. In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time and working pH range.

3. RESULTS AND DISCUSSION

Preparation of composite materials by the amalgamation of inorganic precipitate ion-exchangers of multivalent metal acid salts and organic conducting polymers, providing a new class of 'organic-inorganic' hybrid ion-exchange materials with better mechanical and granulometric properties, good ion-exchange capacity, high stability (chemical as well as thermal), reproducibility, selectivity for certain heavy metals and enhanced electrical conductivity behavior.

3.1. Synthesis and doping

Electrically conductive polyaniline based polyaniline Sn(IV)tungstomolybdate nano was chemically prepared by the combination of polyaniline into the inorganic polyvalent sites of Sn(IV) tungstomolybdate that contains two components: the inorganic component of the composite is the efficient ion-exchange material, whereas organic component is a good electrically conducting polymer. In general, a high electrical conductivity of conductive polymer is attained by dopants, which stabilize the polaron and bipolaron states as counter anions [42-45]. Thus, the dc electrical conductivity of composite ion-exchange material is due to the presence of sufficient amount of the conducting polymer and basically it is electronic conduction contributed by the conducting component, *i.e.* polyaniline by the charge-transfer reaction between polyaniline component of the composite and doping agent, HCl, as given:

[Polyaniline Sn(IV) tungstomolybdate] + nHCl → [Polyaniline($n\text{H}^+$)($n\text{Cl}^-$) Sn(IV) tungstomolybdate] ……… (1)

Controlling the doping process (*i.e.* treatment with aqueous solution of HCl), the electrical conductivity of these type of materials could be varied from insulator, through semiconductor to metal range and *vice-versa*. Schöllhörn and Zagefka [46] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides, which has further been supported by the work of Foot and Shaker [47]. On the basis of the disproportionation reaction of ammonia as suggested by above workers (equation-2), Mohammad [48] also has suggested an analogous disproportionation reaction for water (equation-3).

$8\ NH_3 \rightarrow 6\ NH_4^+ + 6\ e^- + N_2$ ……… (2)

$6\ H_2O \rightarrow 4\ H_3O^+ + 4\ e^- + O_2$ ……… (3)

The basic strength of water is very low, hence does not act as undoping agent in case of polyaniline. However, the neutralization reaction to undope polyanilne within polyaniline Sn(IV) tungstomolybdate composite material by ammonia may be suggested as follows:

[Polyaniline($n\text{H}^+$)($n\text{Cl}^-$) Sn(IV)tungstomolybdate] + $n\text{NH}_4^+$ + $n\text{e}^-$ → [Polyaniline Sn(IV)tungstomolybdate] + $n\text{NH}_4\text{Cl}$ ...……. (4)

3.2. Characterization

Among the PSTM samples prepared in our earlier studies [41], sample M-4 possessed better ion-exchange capacity, reproducible behavior and high mechanical and thermal stability. The ion-exchange capacity in meq g^{-1} for various monovalent and divalent metals, determined by standard column process, were as follows: Li^+, 1.21; Na^+, 1.77; K^+, 1.98; Mg^{2+}, 1.52; Ca^{2+}, 1.72; Sr^{2+}, 1.60; Ba^{2+}, 2.10; Pb^{2+}, 3.0; Cd^{2+}, 2.6; etc [41]. It was observed from the K_d (selectivity coefficient) values that PSTM nanocomposite material had the maximum selectivity toward Pb^{2+} ion because Pb^{2+} was significantly adsorbed in all solvents, while remaining metal ions are partially adsorbed on the surface of the composite material. The composite material (sample M-4) had good reproducible performance because it was synthesized in various batches and it did not show any considerable change in IECs and also there is negligible changes in IECs when this composite cation-exchanger (H^+-form) was repeatedly used in different cycles after regeneration with 1 M HNO_3. Moreover, as the ratio of sodium molybdate (anionic part) in the reaction mixture was increased, the ion exchange capacity also increased because the replaceable hydrogen groups were attached to this group which is an ionogenic group. It was also found that the IEC for Na^+ (1.13 meq g^{-1}) of the inorganic part (Sn(IV) tungstomolybdate) has been improved to 1.77 meq g^{-1} due to its granulometric properties when it was combined with the conjugated polymer of polyaniline [41].

PSTM shows reasonably good mechanical and chemical stability, as it was resistant to different acids of high concentrations and other organic solvents. This chemical stability is due to the presence of binding polymer, which can prevent the dissolution of heteropolyacid salt or leaching of any constituent elements into the solution. The nanocomposite showed steady weight loss that started from 50 °C and till 800 °C almost ~37% degradation took place (Table (2)).

Table 2. Effect of heating on PSTM (sample M-4) nanocomposite cation-exchange material at different temperatures for 1 h.

Temperature (°C)	Weight loss (%)	IEC (meq g^{-1})	% Retention of IEC
50	0.00	1.77	100.00
100	9.55	1.77	100.00
200	13.62	1.76	99.44
300	18.75	1.63	92.09
400	25.18	1.55	87.57
500	28.80	1.21	68.36
600	31.23	1.10	62.15
700	33.41	1.07	60.45
800	35.02	1.02	57.62
900	36.40	0.97	54.80

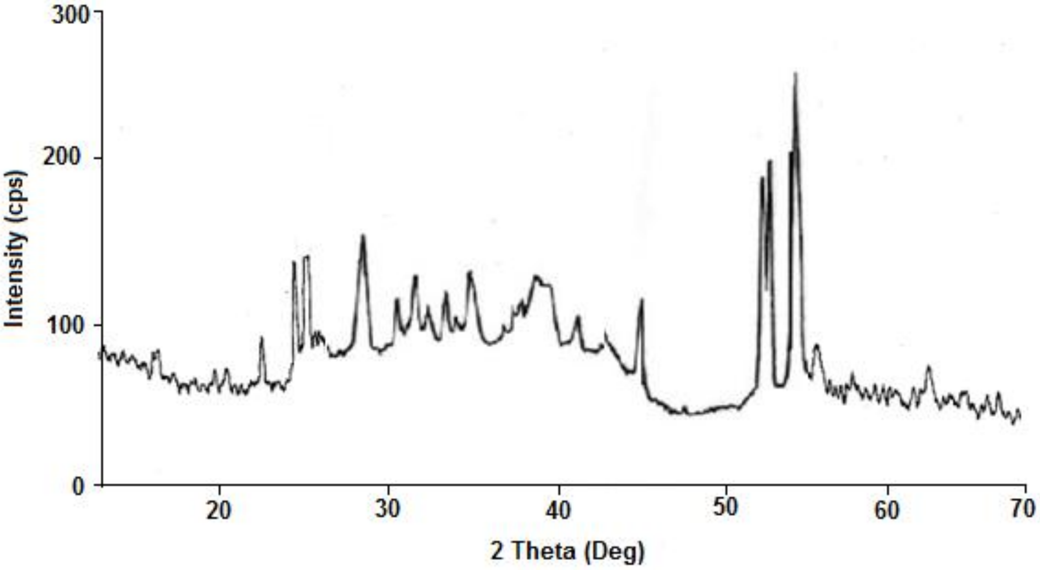

Figure 1. XRD of PSTM nanocomposite cation-exchange material.

It is evident from the XRD data as well as diffractograms recorded on powdered sample of so prepared PSTM composite cation-exchanger exhibited the semi-crystalline nature of this material. The XRD pattern of pure PANI [31] shows the broad diffraction peak, attributed to amorphous nature of PANI. The XRD diffraction peaks of STM reported in the literature [49] showed the crystalline nature of the inorganic precipitate. The PSTM composite in our study shows a decrease in crystallinity which may be attributed to the dominant amorphous nature of PANI. The broadening of peak of STM in PSTM nanocomposite (figure 1) suggests successful incorporation of STM in PSTM. The PSTM nanocomposite was also characterized by TGA, SEM and TEM studies (figures S1-S3) [41].

3.3. Electrical conducting behavior

The electrical conductivity is one of the properties of materials that varies most widely, from 10^{7} (Ω-m) typical of metals to 10^{-20} (Ω-m) for good electrical insulators. The conductivities in the range 10^{-6} to 10^{4} (Ω-m) belong to semiconductors. In metals, electrons are current carrier, and hence the conduction named as *electronic conduction*. In case of ionic crystals, ions are the charge carriers, thus the conduction named as *ionic conduction*. During the formation of a solid, the atoms come together, Coulomb forces help their valence electrons to interact, and also they are in the atmosphere of the electric field made by their own nucleus and that of the other atoms. Along this, two particular quantum mechanical effects occur. Firstly, via Heisenberg's uncertainty principle, the electrons are forced to a small volume raises their energy, which is termed promotion. Secondly, because of the Pauli’s Exclusion Principle, this limits the number of electrons that can have the same property (which comprise the energy). As a product of all these effects, wide valence bands are formed by the electrons of atoms when they create a solid. These bands are separated by gaps in which electrons cannot exist. The particular place of the bands and band gaps depends on the variety of atom (e.g., Si vs. Al), the distance between atoms in the solid, and the atomic arrangement (e.g., carbon vs. diamond).

In semiconductors and insulators, the valence band is filled, and any more electrons cannot be added which is following Pauli's principle. Electrical conduction requires that electrons be able to gain energy in an electric field; this is not possible in these materials because that would imply that the electrons are promoted into the forbidden band gap. In metals, the electrons occupy states up to the Fermi level. Conduction takes place by motivating electrons into the conduction band that starts at the Fermi level that is separated by the valence band by an insignificant amount. Conduction in metals is by electrons in the conduction band. In insulators, conduction happens by means of electrons in the conduction band and by holes in the valence band. Holes are empty states in the valence band that are created when an electron is removed.

In metals, just above the Fermi levels, there are vacant states where promotion of electrons can occur. The promotion energy is to some extent small so that at any temperature electrons can be found in the conduction band. The quantity of electrons contributing in electrical conduction is extremely small. In insulators, there is an energy gap between the valence and conduction bands, to promote an electron energy is needed to the conduction band. From heat or from active radiation, like light of adequately small wavelength, this energy may come.

A working explanation for the difference between semiconductors and insulators is that electrons can reach the conduction band in semiconductors at ordinary temperatures, whereas in insulators they cannot. The chance that an electron reaches the conduction band is about $exp(-E_g/2kT)$, where E_g is the band gap and kT has the usual meaning. If this probability is, say $< 10^{-24}$, one would not find a single electron in the conduction band in a solid of 1 cubic centimeter. This requires $E_g/2kT > 55$. At room temperature, $2kT = 0.05\ eV$; thus $E_g > 2.8\ eV$ can be used as the condition for an insulator. Besides having comparatively small E_g, semiconductors have covalent bond; conversely insulators usually are partly ionic bonded.

Semiconductors can be *intrinsic* or *extrinsic*. Electrical conductivity does not depend on impurities in *intrinsic* semiconductors, therefore *intrinsic* relates to pure. But in *extrinsic* semiconductors, the conductivity depends on the concentration of impurities. Hence, conduction is thru electrons and holes. Electrons and holes in an electric field travel in opposite direction because they have opposite charges. One finds that electrons move much faster than holes. A hole in an *intrinsic* semiconductor is produced by the promotion of each electron to the conduction band. Unlike *intrinsic* semiconductors, an *extrinsic* semiconductor may have diverse concentrations of holes and electrons. They are made by doping, the addition of a very small concentration of external (impurity) atoms. Diffusion and ion implantation are two common methods of doping.

Excess electron carriers are produced by substitutional impurities that have more valence electron per atom than the semiconductor matrix. The energy level of the donor state is close to the conduction band, so that the electron is promoted (ionized) easily at room temperature, leaving a hole (the ionized donor) behind. As this hole is not like a hole in the matrix, it does not travel effortlessly by capturing electrons from adjacent atoms. This means that the conduction occurs mainly by the donated electrons (thus *n-type*). Excess holes are produced by substitutional impurities that have fewer valence electrons per atom than the matrix. The energy level of the acceptor is close to the valence band, for that reason an electron may simply hop from the valence band to complete the bond leaving a hole behind, which indicates that conduction happens mostly by the holes (thus *p-type*). Temperature causes electrons to be promoted to the conduction band and from donor levels, or holes to acceptor levels. The dependency of conductivity on temperature is like other thermally activated processes: $\sigma = A \exp(-E_g/2kT)$; where A is a constant (the mobility varies much more slowly with temperature). Plotting $ln\ \sigma$ vs. $1/T$ produces a straight line of slope $E_g/2k$ from which the band gap energy can be calculated. In addition to this dependence, e*xtrinsic* semiconductors have one due to the thermal promotion of electrons from donor levels or holes from acceptor levels. The dependence of conductivity on temperature is also exponential but it eventually saturates at high temperatures where all the donors are emptied or all the acceptors are filled. This indicates that at low temperatures, larger conductivity takes place in *extrinsic* semiconductors than *intrinsic* semiconductors. Both the impurity levels and valence electrons are ionized at high temperatures, on the other hand since the impurities are very low in amount and they are exhausted, ultimately the performance is controlled by the *intrinsic* type of conductivity.

Thus, temperature plays a significant role in conductivity that increases the activity of a conducting species, though the temperature is not the driving force. The increase in conductivity with increase in temperature is the characteristics of "*thermal activated behavior*". Many phenomena in materials science and engineering are classified as *thermally activated processes* – they require thermal energy to occur. Some energy obstruction needs to be overcome in a thermally activated process in order for the process to happen. This barrier is referred to as activation energy. Extra thermal energy is provided by increasing the temperature so that more particles (these may be atoms, molecules, electrons, etc.) can exceed the activation energy. This ultimately causes the process to occur faster or more easily. The temperature dependence of all thermally activated processes can be represented by the Arrhenius equation, a general equation of the form:

$$z = A_o \exp\left(\frac{-E_A}{RT}\right) \qquad \text{...........}(5)$$

where z = the phenomenon that is thermally activated, E_A = the activation energy for the process, A_o = a constant, sometimes called the "pre-exponential constant", R = universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), T = absolute temperature (Kelvin). In order to easily fit data to an Arrhenius relationship, equation (5) can be handled by taking the log of both sides and then we obtain:

$$\ln(z) = \left(\frac{-E_A}{R}\right)\left(\frac{1}{T}\right) + \ln(A_o) \qquad \text{...........}(6)$$

Equation (6) is now in the familiar form of a straight line, $y = mx + b$; where $y = \ln(z)$, $x = (1/T)$, m = the slope of the line, which is equal to $(- E_A/R)$, b = the y-intercept of the line, which is equal to $\ln(A_o)$. A plot of data according to equation (6) [$\ln(z)$ vs. $(1/T)$], is called an Arrhenius plot, from which the activation energy and pre-exponential constant can be determined from the slope and intercept of the best-fit line through the data.

Furthermore, to explain the conduction mechanism in the conducting polymers, the concept of polaron and bipolaron was introduced. Low level of oxidation of the polymer gives polaron and higher level of oxidation gives bipolaron. Both polarons and bipolarons are mobile; and in the conjugated system, they could move along the polymer chain by the rearrangement of double and single bonds. Conduction due to polarons and bipolarons is supposed to be the dominant factors which determine the mechanism of charge transport in polymer with non-degenerate ground states.

Electrical conductivities of our PSTM composite samples were determined using the *four-probe* method of conductivity measurement for semiconductors. This is the most suitable technique as it overwhelms difficulties which are encountered in conventional methods of conductivity measurement (*i.e.*, *two-probe*), *e.g.* the rectifying nature of metal-semiconductor contacts and the injection of minority carriers by one of the current carrying contacts, which affects the potential of other contacts and modulate the conductance of the material, *etc.* It also permits the measurement of conductivity in samples having wide variety of shapes. After getting the current-voltage data by using a 4-in-line-probe dc electrical conductivity-measuring instrument at increasing temperatures for the determination of electrical conductivity of the composite samples were processed for calculation of resistivity (ρ_o) using the following equation:

$$\rho_o = (V/I) \times 2\,\pi S \qquad \text{……}(7)$$

where V is the voltage (V) and I is the current (A). Since the thickness of the sample is small compared to the probe distance a correction factor for it has to be applied and the corrected resistivity may be calculated as:

$$\rho = \rho_o/G_7\,(W/S) \qquad \text{……}(8)$$

where ρ is the corrected resistivity in ohm.cm., $G_7(W/S)$ is the correction factor used in the case of non-conducting bottom surface and it is a function of W, thickness of the sample under test (cm) and S, probe spacing (cm); *i.e.*,

$G_7 (W/S) = (2S/W) \log_e 2$ …… (9)

Thus, the electrical conductivity (σ) was calculated using the following equation:

$\sigma = 1/\rho$ …… (10)

where σ is the electrical conductivity in Scm^{-1}. Although the electrical conductivity measurements were carried out in the ambient conditions, the composite samples were thoroughly dried before making pellets and electrical conductivity measurements. So, the contribution of protonic conductivity in total electrical conductivity due to the presence of moisture may be minimal and may not be taken into consideration.

The magnitude of the conductivity is dependent on the number of charge carriers available and their mobility. With the increase in temperature, the mobility of charge carriers increases, hence a rise in conductivity. Another factor which also affects the electrical conductivity is the molecular alignment of the chains within the entire system. Parvatikar et al. [16,17] have explained the rise in electrical conductivity in their PANI/WO_3 and PANI/CeO_2 nanocomposites on the basis that thermal curing leading to a better alignment of the polymer chains, which increases the conjugation length, and hence an increase in electrical conductivity. Also, molecular rearrangement takes place during heating, which makes the molecular conformation favorable for electron delocalization [50]. Likewise, in our study, electrical conduction in PSTM nanocomposite material is also occurred by '*thermally activated process*', i.e., electrical conductivity increases with temperature and that can be described by the Arrhenius equation. The increase in conductivity would be due to the increase of efficiency of charge transfer between Sn(IV) tungstomolybdate and polymer chains with increase in temperature [51,52].

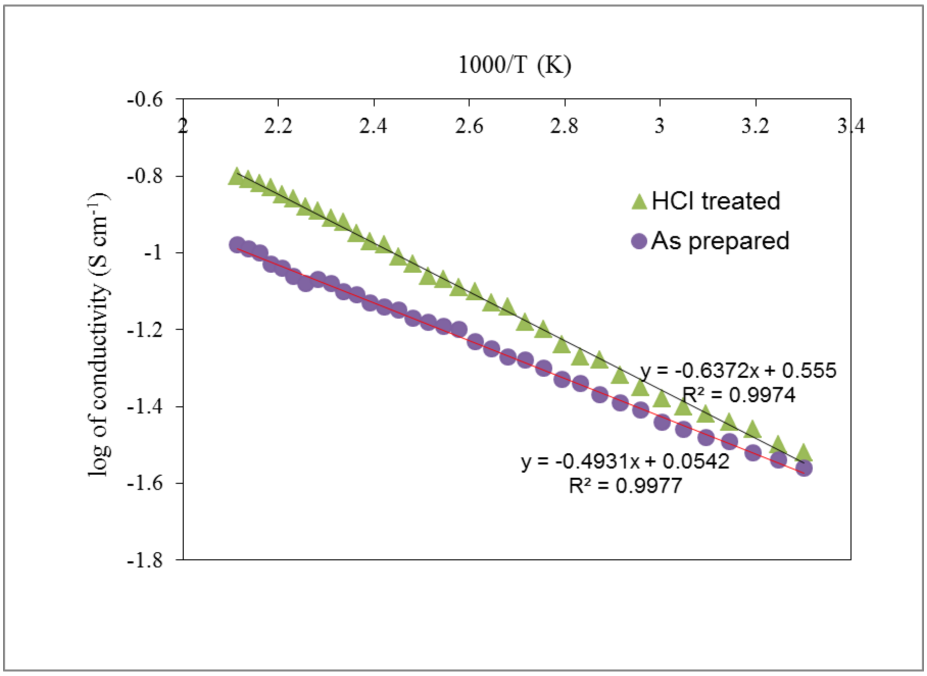

Figure 2. Arrhenius plots for polyaniline Sn(IV) tungstomolybdate composite material (as prepared and HCl treated).

The variations of electrical conductivity (*σ*) of the composite samples (as prepared and HCl treated), prepared with 10 vol.% aniline concentration, with increasing temperatures (between 25 and 200 °C) were studied. On investigation, it was found that the electrical conductivities of PSTM samples increase with the increase in temperature and the values lie in the order of 10^{-2} S cm^{-1}, i.e., in the borderline of conductor and semiconductor division. To define the nature of the dependence of electrical conductivity on temperature, plots of log *σ* versus 1000/*T* (K) were drawn (figure 2) and they followed the Arrhenius equation similar to other semiconductors [53]. It was also observed that the composite materials showed enhanced electrical conductivity on exposure to HCl as compared to as prepared form, due to the charge-transfer reaction between polyaniline component of the composite and HCl (doping agent) as mentioned above.

The effect on electrical conductivity of the different forms (Na^+, Li^+, Ca^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}) of PSTM composite cation-exchange material were also examined and presented in Table (3). It was observed that the electrical conductivity of the composite was affected negligibly, when treated with the alkali and alkaline metal nitrate solutions of (Li^+, Na^+, K^+, Ca^{2+}), while the electrical conductivities of Pb^{2+}, Cu^{2+}, Mn^{2+} forms of the composite were decreased to 10^{-6}, near semiconducting to insulator region.

Table 3. Four-probe DC electrical conductivity of different forms of polyaniline Sn(IV) tungstomolybdate composite systems at ambient temperature (prepared with 10% aniline monomer).

Sample No.	Sample treatment	Ambient temperature DC electrical conductivity (S cm^{-1})
1	As prepared	2.75×10^{-2}
2	HCl treated	3.02×10^{-2}
3	NaCl treated	1.68×10^{-2}
4	KCl treated	2.45×10^{-3}
5	LiCl treated	3.84×10^{-3}
6	$CaCl_2$ treated	1.76×10^{-2}
7	$Pb(NO_3)_2$ treated	2.34×10^{-6}
8	$MnCl_2$ treated	1.57×10^{-6}
9	$Cu(NO_3)_2$ treated	3.80×10^{-6}

The electrical conductivity of the composite is due to oxidized polyaniline maintained in its conductive state by Sn(IV) tungstomolybdate counter ions in excess. The room temperature conductivity of PSTM nano-composite (2.75×10^{-2} S/cm) synthesized presently is higher compare to that of the homopolymer of polyaniline (9.12×10^{-4} S/cm) prepared by chemical polymerization [1] with potassium persulfate as an oxidant at 10 °C may be due to the electron donating property of the Sn(IV) tungstomolybdate group. The conducting properties also depend on the percolation behavior [54] of the conducting phase. Major part of electrical conductivity of the composite is due to the addition of polyaniline in the composite. The dependence of the electrical conductivity through the biphasic system (polyaniline Sn(IV) tungstomolybdate composite; prepared with different concentrations of aniline monomers) on the concentration of conducting phase (i.e., polyaniline) was examined and the results are given in Table (4). A slight increase in electrical conductivity of the composite is followed at a certain aniline concentration by an immediate jump, which is again pursued by fair increase. At about 10% aniline concentration (critical concentration of conducting phase), the sharp rise in electrical conductivity is observed that could possibly be explained on the basis of percolation theory [54]. Thus, we can say that main factor that made the composites electrically conductive is the presence of polyaniline in sufficient amount. It was also observed that the ambient temperature conductivities of the composites for some concentrations of aniline monomers are greater than that of polyaniline (prepared as 10% aniline in 1 M HCl) as shown in Table (4).

Table 4. Values of DC electrical conductivity of various samples of PSTM composite with different concentrations of aniline monomer

Sample ID	Polyaniline (prepared with 10% aniline in 1 M HCl)	Polyaniline Sn(IV) tungstomolybdate (HCl treated)	
	Ambient temperature DC electrical conductivity (S cm^{-1})	Aniline monomer concentration (vol. %)	Ambient temperature DC electrical conductivity (S cm^{-1})
Sample-1	9.12×10^{-4} [Ref. 1]	2	2.40×10^{-5}
Sample-2	-	4	4.39×10^{-5}
Sample-3	-	6	6.62×10^{-4}
Sample-4	-	8	2.56×10^{-3}
Sample-5	-	10	3.02×10^{-2}
Sample-6	-	12	3.85×10^{-2}
Sample-7	-	14	4.28×10^{-2}
Sample-8	-	16	4.51×10^{-2}
Sample-9	-	18	4.69×10^{-2}
Sample-10	-	20	4.53×10^{-2}

3.4. Stability of composites in terms of DC electrical conductivity retention

It is generally considered for the thermal degradation of the usual polymers that the elimination of hydrogen/loss of dopant from the polymer chains occurs at high temperatures, and an oxygen molecule reacts with the generated radicals in air. In case of polyaniline, this would stop the extension of the π conjugation of polyaniline chain. Therefore, decrease in electrical conductivity occurs. Thus, the factors that influence the stability of the conductivity of composites are of considerable interest, both from fundamental and industrial perspectives. However, the stabilities of the composites were dependent on the preparation conditions employed.

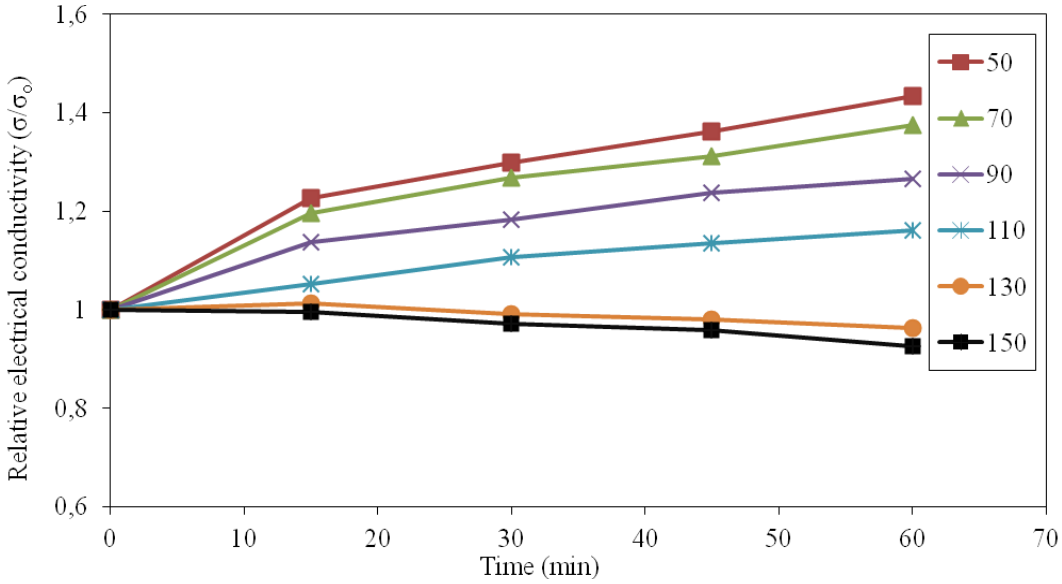

Figure 3. Isothermal stability of polyaniline Sn(IV) tungstomolybdate composite material (HCl treated) in terms of retention of DC electrical conductivity with respect to time at 50, 70, 90, 110, 130 and 150 °C.

The thermal stability of the PSTM (M-4) composite material (HCl treated) in terms of DC electrical conductivity retention was studied under isothermal condition (at 50, 70, 90, 110, 130 and 150 °C) measuring 4-in-line-probe dc electrical conductivity at an interval of 15 mins. The electrical conductivity investigated with respect to the time of accelerated ageing is presented in figure 3. It was observed that the electrical conductivity for the composite material is quite stable at 50, 70, 90 and 110 °C that supports the fact that the DC electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150 °C that may be attributed to the loss of dopant and the chemical reaction of dopant with the composite material. In terms of electrical conductivity validation, the stability of HCl treated composite material was also monitored for 5 cycles by repeatedly measuring linear four-probe dc electrical conductivity with increase in temperature at an interval of 45 minutes and the DC conductivity for each heating cycle was plotted as log σ versus $10^3 T^{-1} K^{-1}$ as shown in figure 4. It was observed for this composite material that each plot followed the Arrhenius equation for its temperature dependence similar to other semiconductors [53]. There was minor difference in their electrical conductivity even after repeating the experiment for five times that showed the good stability of the material during heating-cooling cycles under severe oxidizing conditions upto 200 °C.

These composite materials were also observed to be a stable material, *i.e.*, the room temperature conductivity is negligibly affected by short-term exposure to laboratory air as evident from figure 5. The materials of these types may often exhibit an increase in conductivity upon short-term exposure to oxygen, which is attributed to the formation of a charge transfer complex with oxygen and may involve O^{2-}.

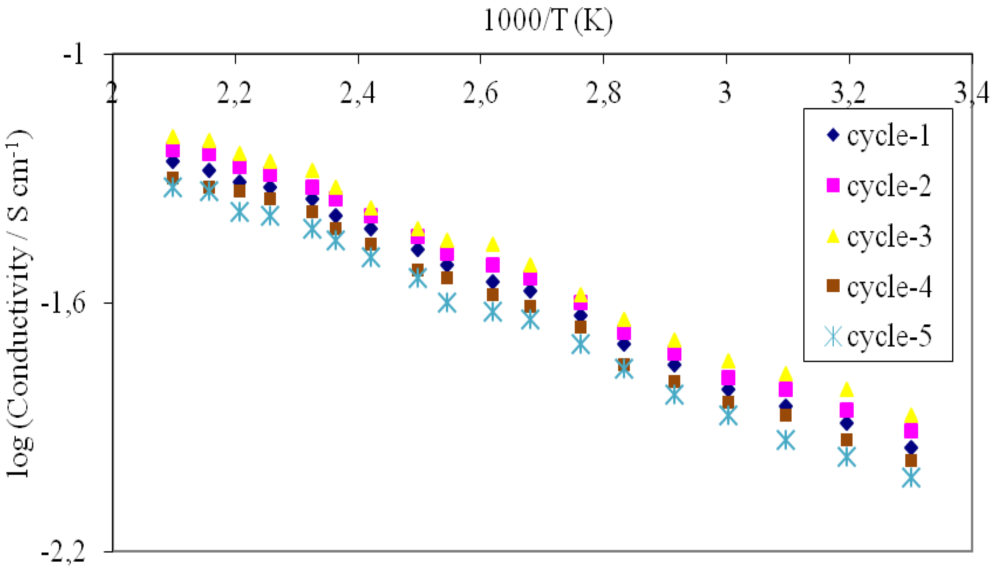

Figure 4. Arrhenius plots of retention of dc electrical conductivity for polyaniline Sn(IV) phosphate (HCl treated) during heating cooling cycles upto 200 °C.

Presumably, electron transfer from the polymer moiety to oxygen occurs, resulting in an increased extent of oxidation of the polymer chain. Thus short-term exposure to oxygen may increase the conductivity of the material by increasing the concentration of charge carriers. Oxygen can also produce a decrease in the conductivity of the material through a destructive reaction; *e.g.* exposure of the composite to oxygen results in a decrease in the conductivity due to an irreversible reaction that is believed to generate covalently bonded oxygen species. Axially bound water is also responsible for part of the conductivity loss during the ageing of the material.

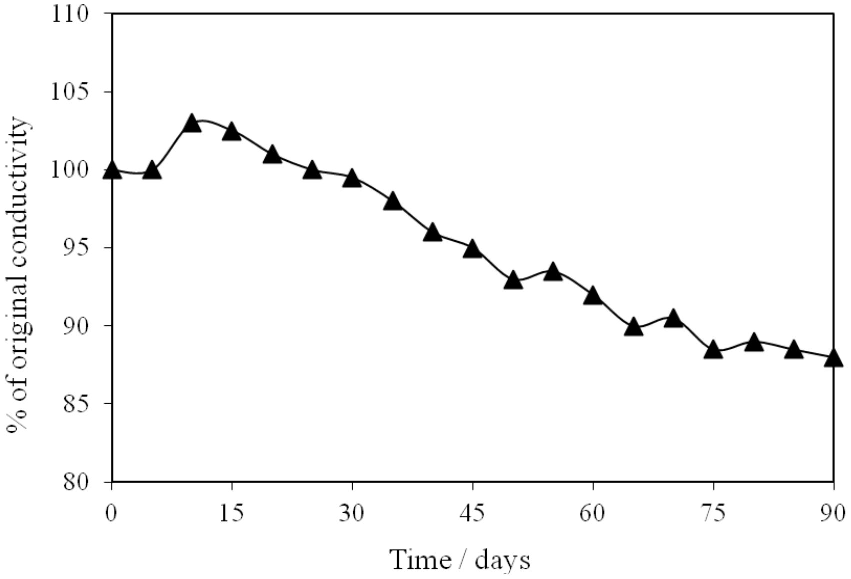

Figure 5. Conductivity versus time of exposure to laboratory air for polyaniline Sn(IV) tungstomolybdate composite material (HCl treated).

The analytical application of PSTM nanocomposite was investigated by fabricating heterogeneous precipitate Pb(II) ion-selective membrane electrode obtained from this electroactive cation-exchange material. Sensitivity and selectivity of the ion-selective membranes electrode depend upon the nature of electrically active material, composition of membrane and physico-chemical features of the membranes employed. It gives linear response (figure 6) in the given range of 1 x 10^{-1} – 1 x 10^{-6} with a slope of 29.4 mV per decade change in Pb(II) ion concentration and the slope value is very close to Nernstian value, 29.6 mV/ concentration decade for divalent cations. Below 1×10^{-6} M, a non-linear response was observed but the calibration curve could be utilized for the determination of Pb(II) down to 1×10^{-6} M. A constant potential was obtained after 15 s and it was also observed that the electrode potential remained unchanged within the pH range 2.5–8.5. The selectivity coefficients, $K_{Pb.M}^{POT}$ of a number of interfering cations intended for the Pb(II) ion-selective PSTM membrane electrode were determined by the mixed solution method [55] and this parameter indicates the extent to which a foreign ion (M^{n+}) interferes with the response of the electrode towards its primary ion (Pb^{2+}). The results reveal that the electrode is selective for Pb(II) in presence of interfering cations.

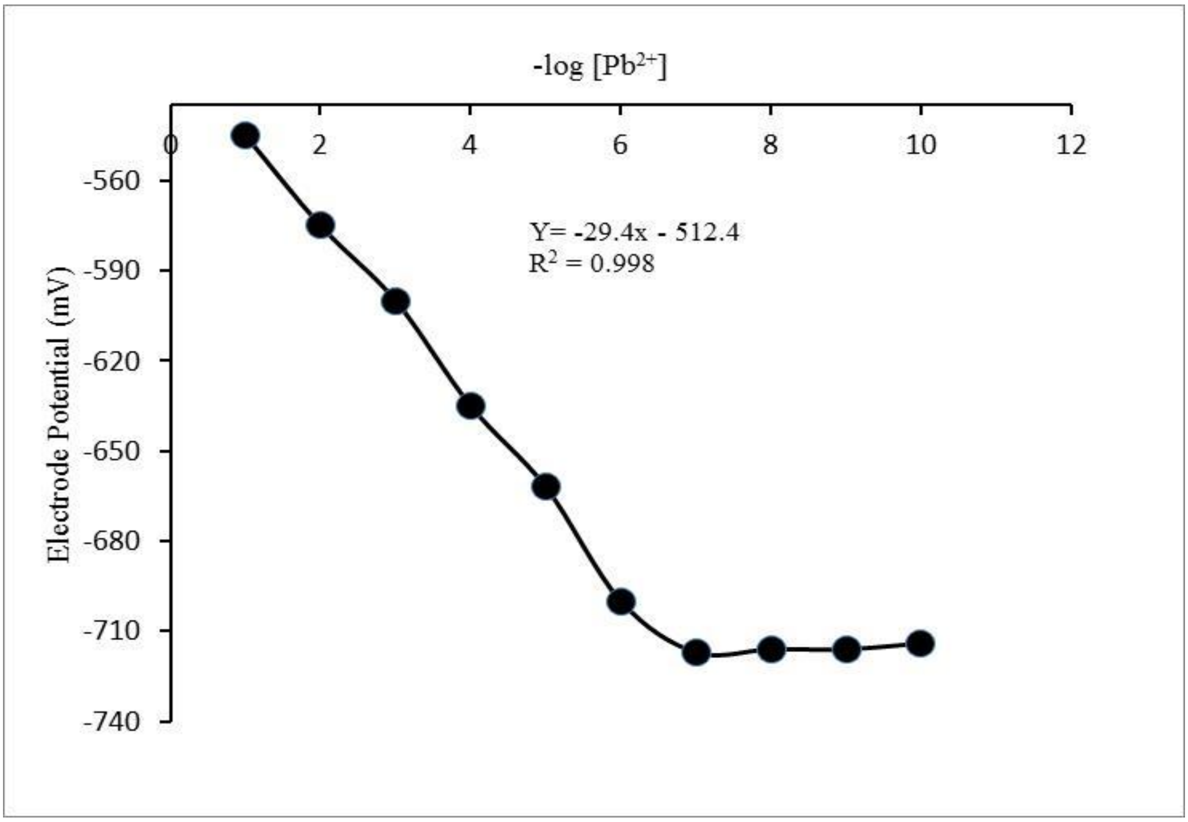

Figure 6. Calibration graph of Pb(II) ion-selective PSTM membrane electrode.

The practical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometric titration of synthetic solution of Pb(II) ions against EDTA (ethylenediaminetetraacetic acid disodium salt dihydrate) solution as a titrant. For this, pipetted out 10 ml of 0.05 M $Pb(NO_3)_2$ solution in a beaker. The volume of beaker was elevated upto 20 ml by DMW. The solution was titrated with 0.05 M EDTA solution and electrode potential was measured after each addition of 0.5 ml of EDTA solution. The essential modification of pH (~ 4) was completed before adding up the titrant. The accumulation of EDTA effects a decrease in potential as a result of the decrease in free Pb(II) ions concentration due to its complexation with EDTA (figure 7). The amount of Pb(II) ions in solution can be accurately determined from the resulting neat titration curve providing a sharp rise in the titration curve at the equivalence point.

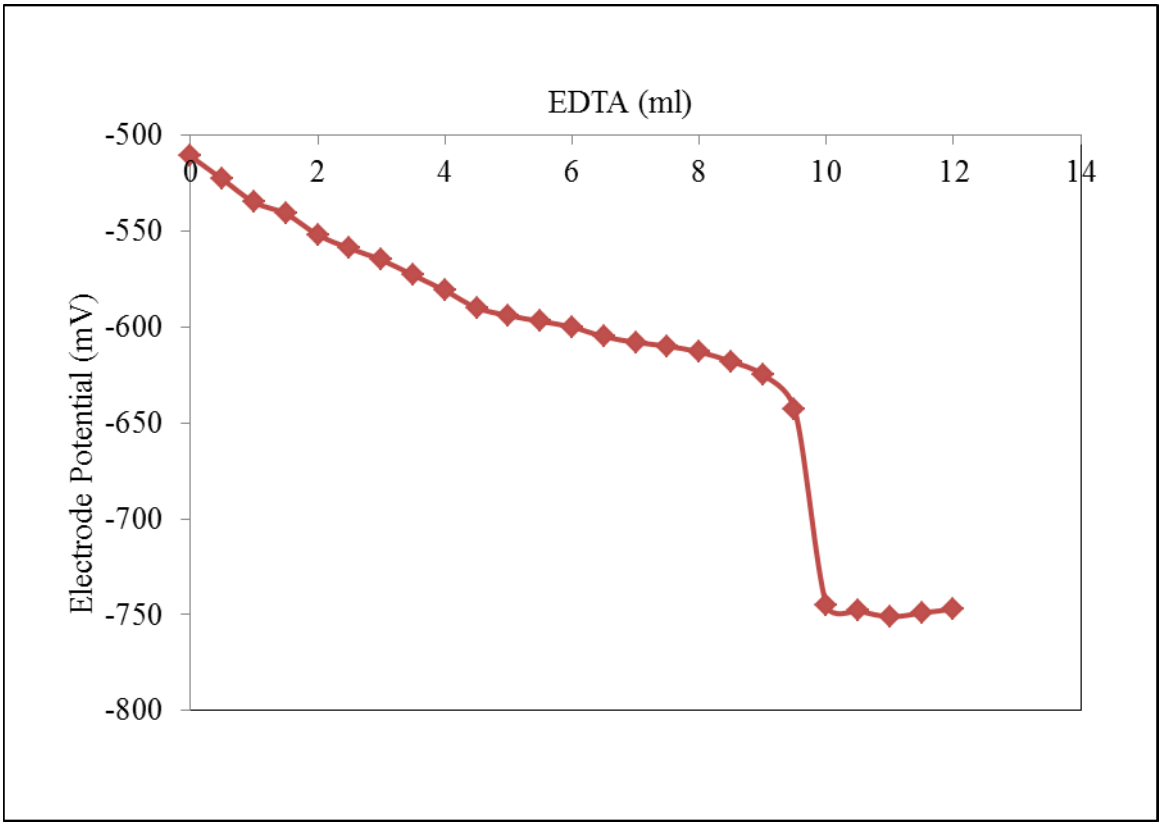

Figure 7. Potentiometric titration curve of solution of Pb(II) ions against EDTA solution.

4. CONCLUSIONS

A new organic-inorganic cation-exchange nanocomposite material, polyaniline Sn(IV) tungstomolybdate (PSTM) having good ion-exchange and electrically semi-conducting properties has been successfully prepared through the sol-gel reaction of polyaniline(PANI) and Sn(IV) tungstomolybdate (STM) cation-exchanger. The results of TEM, SEM, XRD and FTIR studies revealed that the composite formation has been effectively achieved and indicated that there is a strong interaction between PANI and STM particles. The DC electrical conductivity behavior of the nanocomposite at temperature range from 30 to 200 °C was recorded and concluded that the material showed ‘thermal activated behavior’. The chemical, thermal and mechanical strength of this electroactive material can be utilized to make its ion-selective membrane electrode for the selective determination and separation of heavy metal ions in the solutions. It is highly selective for Lead (a major toxic element), as shown from the selectivity studies [41] performed in our laboratory, which makes it important for the environmentalists. Compared with other composite materials of this class, the PSTM showed improved electrical conductivity, isothermal stability in terms of DC electrical conductivity retention and thermal degradation behavior. The PSTM nanocomposite can be used in electrical and electronic applications as a semiconductor below 130 °C under ambient conditions. This composite material was also utilized as an electroactive component for the preparation of ion-selective membrane for the determination of Pb(II) ions in solutions. The membrane demonstrated a working concentration range 1 x 10^{-1} – 1 x 10^{-6} M, response time 15 s, pH range 2.5–8.5, and selectivity in presence of other metal ions. The applied utility was determined as potentiometric sensor for the titration of Pb(II) using EDTA as a titrant. It has been also used in the determination of Pb(II) ions in some synthetic samples containing a number of different metal ions as well as samples obtained from electroplating units and the error has been found as ± 2–5%. Hence, this could be a material of interests for detection and removal of water pollution in heavy metal ion source of Pb.

ACKNOWLEDGEMENTS

This project was supported by NSTIP strategic technologies programs, project number (ADV 1285-02) in the Kingdom of Saudi Arabia.

SUPPLEMENTARY MATERIAL:

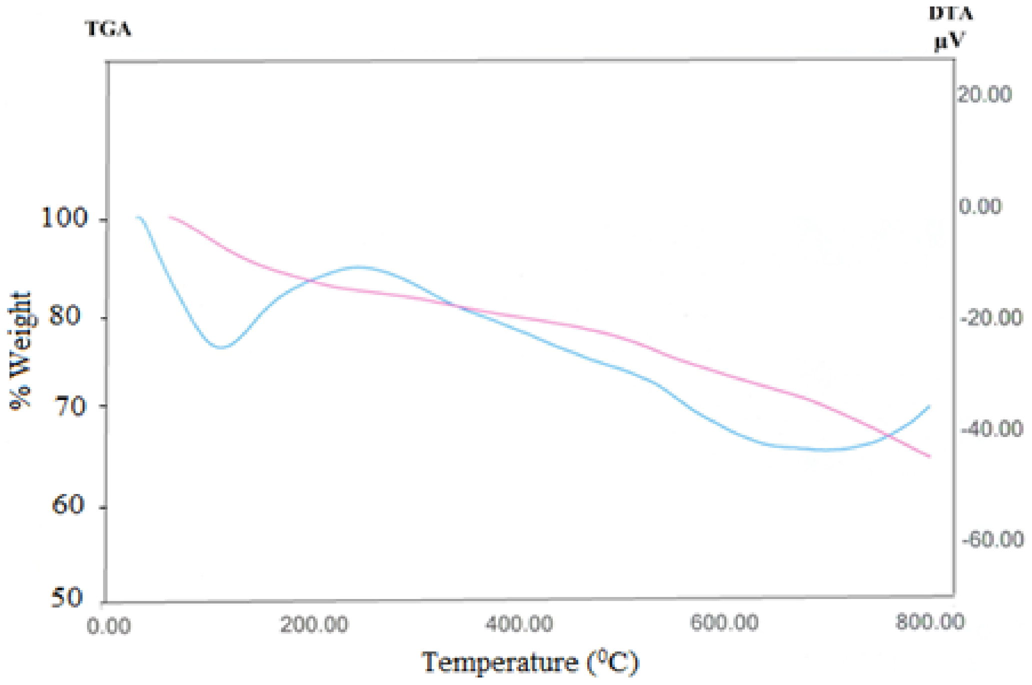

Figure S1. TGA of PSTM nanocomposite cation-exchange material [Ref. 41, with permission].

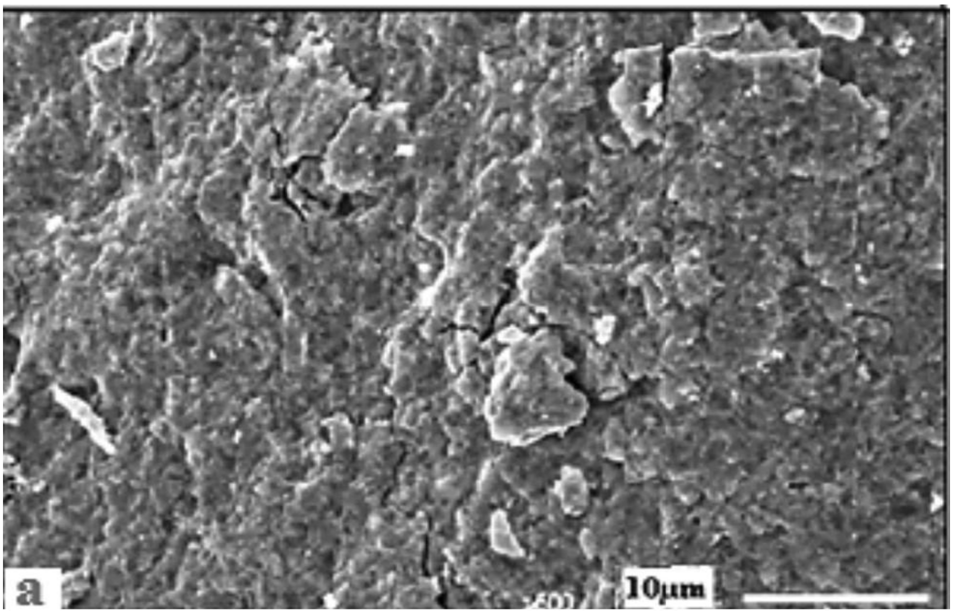

Figure S2. SEM of PSTM nanocomposite cation-exchange material [Ref. 41, with permission].

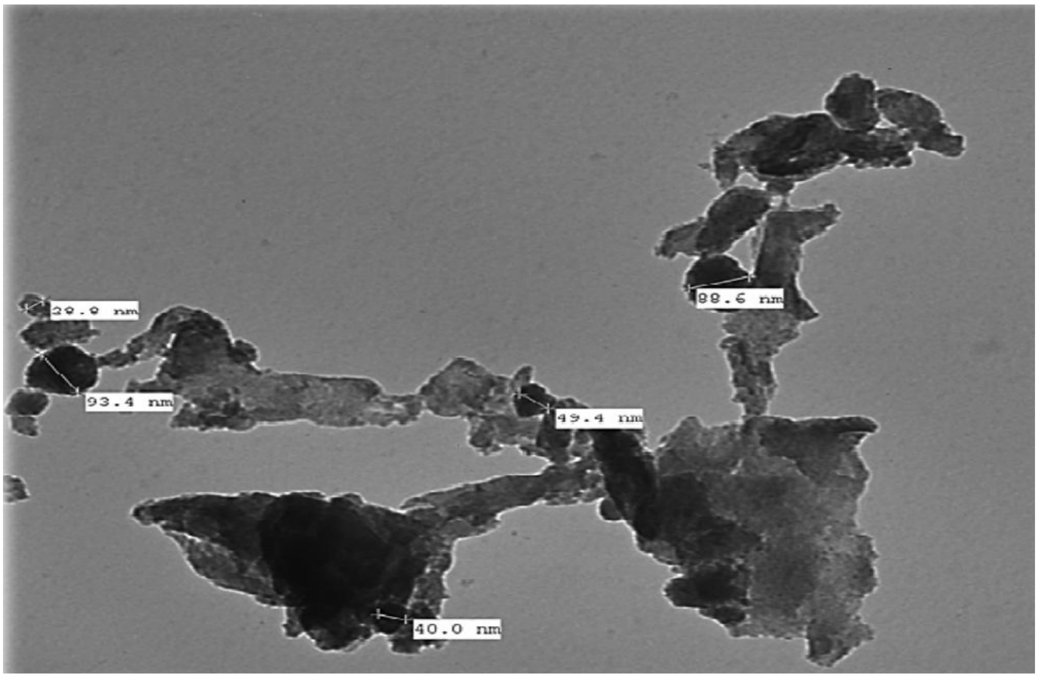

Figure S3. TEM of PSTM nanocomposite cation-exchange material [Ref. 41, with permission].

References

1. A. A. Khan , M. M. Alam and F. Mohammad, *Electrochim. Acta*, 48 (2003) 2463.
2. A. A. Khan and U. Baig, *Composites: Part B*, 56 (2014) 862.
3. Y. Moon, J. yun and H. Kim, *J. Ind. Eng. Chem.*, 19 (2013) 493.
4. Z. Alam, Z. A. AL-Othman, Mu. Naushad and S. A. Nabi, *J. Inorg. Organomet. P.*, 22 (2012) 379.

5. J. D. Stenger-Smith, *Prog. Polym. Sci.*, 23 (1998) 57.
6. H. Shirakawa, *Synthetic Met.*, 125 (2002) 3.
7. A. J. Heeger, *Synthetic Met.*, 125 (2002) 23.
8. S. Bhadra, D. Khastgir, K. Nikhil, Singh and J. H. Lee, *Prog. Polym. Sci.*, 34 (2009) 783.
9. D. N. Debarnot and F. P. Epaillard, *Anal. Chim. Acta*, 475 (2003) 1.
10. C. Yang and C. Chen, *Synthetic Met.*, 153 (2005) 133.
11. F. W. Zeng, X. X. Liu, D. Diamond and K. T. Lau, *Sensor. Actuat. B-Chem.*, 143 (2010) 530.
12. C. O. Baker, B. Shedd, P. C. Innis, P. G. Whitten, G. M. Spinks and G. G. Wallace, *Adv. Mater.*, 20 (2008) 155.
13. X. Li, G. Wang, X. Li and D. Lu, *Appl. Surf. Sci.*, 229 (2004) 395.
14. R. V. Ingle, S. A. Arote, M. B. Rajendra Prasad, V. S. Kadam, R. S. Mane, Inamuddin, Mu. Naushad, V. A. Tabhane and H. M. Pathan, *High Perform. Polym.*, 26 (2014) 660.
15. D. C. Schnitzler, M. S. Meruvia, I. A. Hümmelgen and A. J. Z. G. Zarbin, *J. Brazi. Chem. Soc.*, 3 (2004) 378.
16. N. Parvatikar, S. Jain, S. V. Bhoraskar and M. V. N. A. Prasad, *J. Appl. Polym. Sci.*, 102 (2006) 5533.
17. N. Parvatikar, S. Jain, S. Khasim, M. Revansiddappa, S.V. Bhoraskar and M.V.N.A. Prasad, *Composites*, 114 (2006) 599.
18. Inamuddin and M. M. Alam, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 45(2008) 1084.
19. A. Khan, A. M. Asiri, M. A. Rub, N. Azum, A. A. P. Khan, I. Khan and P. K. Mondal, *Int. J. Electrochem. Sci.*, 7 (2012) 3854.
20. Y. Guo, D. He, S. Xia, X. Xie, X. Gao and Q. Zhang, *J. Nanomat.*, 2012 (2012) 7 pages.
21. S. B. Kondawar, S. P. Agrawal, S. H. Nimkar, H. J. Sharma and P. T. Patil, *Adv. Mater. Lett.*, 3 (2012) 393.
22. J. Liu, E. N. Kadnikova, Y. Liu, M. D. McGehee and J. M. J. Frechet, *J. Am. Chem. Soc.*, 126 (2004) 9486.
23. C. Wang, Z. Wang, M. Li and H. Li, *Chem. Phys. Lett.*, 34 (2001) 431.
24. M. O. Ansari and F. Mohammad, *Sensor Actuat. B-Chem.*, 157 (2011) 122.
25. J. Huang, S. Virji, B. H. Weiller and R. B. Kaner, *Chem. (Weinheim an der Bergstrasse, Germany)*, 10 (2004) 1314.
26. P. Anilkumar and M. Jayakannan, *Langmuir*, 24 (2008) 9754.
27. M. Yufeng, S. R. Ali, A. S. Dodoo and H. He, *J. Phys. Chem. B*, 110 (2006) 16359.
28. K. Arshak, E. Moore, L. Cavanagh, J. Harris, B. McConigly and C. Cunniffe, *Composites: A*, 36 (2005) 487.
29. B. Zhang, X. Dong, W. Song, D. Wu, R. Fu and B. Zhao, *Sensor Actuat. B-Chem*, 132 (2008) 60.
30. D. W. Hatchett and M. Josowicz, *Chem. Rev.*, 108 (2008) 746.
31. A. A. Khan, U. Baig and M. Khalid, *J. Ind. Eng. Chem.*, 19 (2013) 1226.
32. A. A. Khan and U. Baig, *J. Ind. Eng. Chem.*, 18 (2012) 1937.
33. A. A. Khan and U. Baig, *Solid State Sci.*, 15 (2013) 47.
34. A. A. Khan and U. Baig, *Int. J. Comp. Mater.*, 3 (2013) 39.
35. A. A. Khan and T. Akhtar, *Electrochim. Acta*, 53 (2008) 5540.
36. A. A. Khan and Inamuddin, *Talanta*, 72 (2007) 699.
37. A.A. Khan and M.M. Alam, *React. Funct. Polm*, 55 (2003) 277.
38. A. A. Khan and A. Khan, *Mater. Sci. Eng. B*, 158 (2009) 92.
39. A. A. Khan M. M. Alam and F. Mohammad, *Electrochim. Acta*, 48 (2003) 2463.
40. A. A. Khan and M. Khalid, *J. Appl. Polym. Sci.*, 117 (2010) 1601.
41. R. Bushra, Mu. Naushad, R. Adnan, Z. A. ALOthman and M. Rafatullah, *J. Ind. Eng. Chem.*, In Press, 2014. http://dx.doi.org/10.1016/j.jiec.2014.05.022
42. M. Fukuyama, Y. Kudoh, N. Nanni and S. Yohimura, *Mol. Cryst. Liq. Cryst.*, 224 (1993) 1993.
43. J. C. Thieblemont, A. Brun, J. Marty, M. F. Planche and P. Calo, *Polymer*, 36 (1995) 1605.

44. L. F. Thompson, C. G. Willson and S. Tagawa, *ACS Symp. Ser.*, 537 (1994) 466.
45. J. C. Thieblemont, M. F. Planche, C. Petrescu, J. M. Bouvier and G. Bidan, *Synthetic Met.*, 59 (1993) 81.
46. R. Schöllhörn and H. D. Zagefka, *Angew Chem. Int. Ed. Engl.*, 16 (1997) 199.
47. P.J.S. Foot and N.G. Shaker, *Mater, Res. Bull.*, 18 (1983) 173.
48. F. Mohammad, *J. Phys. D. Appl. Phys.*, 31 (1998) 951.
49. H. K. Sharma and N. Sharma, *Der Chemica Sinica*, 4 (2013) 182..
50. A. Kobayashi, H. Ishikawa, K. Amano, M. Satoh and E. Hasegawa, *J. Appl. Phys.*, 74 (1993) 296.
51. M. Leclerc, G. D’Aparno and G. Zotti, *Synthetic Met.*, 55 (1993) 1527.
52. F. Zuo, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein, *Phys. Rev. B*, 36 (1987) 3475.
53. F. Mohammad, “*Handbook of Advanced Electronic and Photonic Materials and Devices*”, H.S. Nalwa (Ed.), Academic Press, New York, 2000.
54. D. Stauffer, “*Introduction to percolation theory*”, Taylor and Francis, London, 1985.
55. G. J. Moody and J. R. D. Thomas, “*Selective Ion Sensitive Electrode*”, Merrow, Watford, Herts, England, 1971.