Chapter 4

Electrical Conductivity Measurement
Studies on
Poly-o-toluidine Zr(IV) Phosphate
and
Poly-o-toluidine Ce(IV) Phosphate
Nano-Composite
Cation-Exchange Materials
4.1 Introduction

Research on hybrid organic-inorganic material is an expanding area in the materials science [1-10]. Therefore, organic-inorganic composite materials are of intensive interest in the field of contemporary materials chemistry as these materials can exhibit extraordinary properties such as electrical, magnetic and optical properties [11], which arise from the synergism between the properties of the organic and inorganic components. Thus, these materials have gained much interest due to their remarkable change in mechanical [12], thermal [13-16], electrical [17] and magnetic [18] properties compared to pure organic polymers. Additionally, the properties of the composite materials depend on the morphology of the phase’s viz. organic and/or inorganic network, which has to be controlled over several length scales. Therefore, the development of such materials is a ‘land of multidisciplinarity’, where chemists, physicists, material scientists and engineers have to work closely together to fully exploit this technical opportunity for creating materials and device with benefits for the best of two worlds namely inorganic and organic.

One important class of hybrid materials is that in which the inorganic fraction is composed by conducting polymers, in which new inorganic lattice structures are formed, resulting from cooperative interactions between the organic and inorganic components. In all cases, there is promise of developing new materials with properties not seen in purely organic or purely inorganic solids. In general, the formation of hybrids between conducting polymers and inorganic solids aims to obtained composite materials with synergetic or complementary behaviors between the polymer and the inorganic matrices. The properties of the designed composites will depend both on the characteristics of the polymer and on the nature of the inorganic matrices. This approach can be very useful to obtain materials with predominant properties. The electrical conductivity of the conducting polymers is due to the conjugated backbone, which is totally responsible for electroactive character. The electrically conducting polymers are the electro-chromic materials with chemically active surface [19-22]. But they are chemically sensitive and have poor mechanical properties and pose processibility problems. The inherent instability is also due to highly unsaturated backbone of conjugated polymers. Stability problems have, therefore caused many research groups to search for conjugated polymers of high stability. To meet the requirement of stability of materials of improve performance, explosive research is going on to synthesize the composites of ‘organic-
organic’ and ‘organic-inorganic’ nature. In the view of the above-mentioned facts, researchers have shown much interest in the study of electrically conducting behavior of ‘organic-inorganic’ materials [23-30].

In this chapter, we report the preparation of composite of conducting polymers (poly-o-toluidine) and polyvalent metal acid salts [Zr(IV) phosphate and Ce(IV) phosphate] by mixing fixed amounts (vol.%) of organic monomers with different volume of inorganic precipitates while Nylon-6,6 Sn(IV) phosphate is non-conducting composite. The electrical conductivity behavior of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite systems with increasing temperature was measured by using 4-in-line-probe DC electrical conductivity measuring instrument.

4.2 Experimental

4.2.1 Reagents and chemicals

The main reagents used for the synthesis were: Zirconium oxychloride, ZrOCl2.8H2O (99%), Cerium sulphate, Ce(SO4)2.4H2O (99% CDH India Ltd.), phosphoric acid, H3PO4 (88-93% Loba Chemie India Ltd.), Ammonium persulphate, (NH4)2S2O8 (95% CDH, India), di-sodium hydrogen orthophosphate, Na2HPO4 (CDH, India), ortho-toulidine, C7H9N (98%, E-Merch India Ltd.), hydrochloric acid HCI, 35% and Nitric acid, HNO3 (35% E-Merch India Ltd.). All other reagents and chemicals were of analytical reagent grade.

4.2.2 Instrumentation

- A 4-in-line probe electrical conductivity measuring instrument (Scientific Equipment Roorkee, India) was used for measuring DC electrical conductivity.
- A hydraulic pressure instrument was used for making pellets of sample materials.
- An electronic balance (digital) – Sartorius (Japan), model 21 OS.
- A mortar pastel.
- A micrometer having least counts 0.01 mm.

4.2.3 Preparation of the reagent solutions

0.1M solutions of Zirconium oxychloride (ZrOCl2.8H2O) and tin tetrachloride (SnCl4.5H2O) were prepared in 4M HNO3 while ammonium persulphate solution was prepared in 2M HCl. H3PO4 solutions of different moralities were prepared in
demineralized (DMW) water and 0.1 M Ce(SO₄)₂·4H₂O prepared in 1M H₂SO₄. Solutions of 20% ortho-toluidine of different concentration (v/v) were prepared in 2M HCl.

4.2.4 Preparation of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate nano-composites
Various samples of ‘poly-o-toluidine Zr(IV) phosphate’ and ‘poly-o-toluidine Ce(IV) phosphate’ were prepared through the method described in chapter – 2, Section- 2.2.3 by mixing different concentrations of ortho-toluidine into inorganic precipitates of Zr(IV) phosphate and Ce(IV) phosphate, respectively and samples S-5 and T-4 were selected for detailed conductivity studies (Table 2.1 and Table 2.2).

4.2.5 Electrical conductivity measurement studies
The measurements of electrical conductivity were carried out on various samples of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate nano-composites.

4.2.5.1 Treatment with HCl solution (acidic doping)
Poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate nano-composite materials were treated with 0.5M aqueous solution of HCl to induced protonic acid doping. The materials were washed for excess HCl with doubly distilled water repeatedly till the filtrate gave negative test for hydrogen ions. Then the samples were dried at 50 °C in an oven for 48 hours.

4.2.5.2 Sample (pellet) preparation
The dried sample materials were finely ground in a mortar pastel and then taken into a die with spatula. The pellets of different sample materials of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate for electrical conductivity measurement were made at room temperature with the help of a hydraulic pressure instrument, at 25 KN pressure for 20 minute. Thickness of each sample was measured by micrometer at five different points and the average thickness was taken as the thickness of the pellet sample.

4.2.5.3 Instrumental method of electrical conductivity measurements
Four probe DC electrical conductivity measurements with increasing temperature for the representative samples of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV)
phosphate (as prepared and HCl treated) 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.

4.2.5.4 Thermal stability of composites in terms of DC electrical conductivity retention

4.2.5.4.1 Isothermal technique

The isothermal stability of the poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite materials in terms of DC electrical conductivity retention were studied under isothermal condition using four-in-line-probe DC electrical conductivity measuring instrument. This study was carried out at 50, 70, 90, 110, 130 and 140 °C for poly-o-toluidine Zr(IV) phosphate at an interval of 15 min while for poly-o-toluidine Ce(IV) phosphate it was carried out at 50, 80, 110 and 150 °C at an interval of 15 min on the selected composite samples (S-5 and T-4, HCl treated).

4.2.5.5 Environmental stability of the conductivity of composites

The stability of the poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite materials (S-5 and T-4, HCl treated) in terms of electrical conductivity retention was studied by repeatedly measuring four-in-line probe DC electrical conductivity at room temperature on pressed pellets at an interval of 10 days by short-term exposure to laboratory air.
4.3 Results and Discussion

In this chapter, various samples of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate electrically conducting ‘organic-inorganic’ composite materials were chemically prepared by the incorporation of poly-o-toluidine conducting polymers into the inorganic matrices of Zr(IV) phosphate and Ce(IV) phosphate, respectively. Among these, sample S-5 and T-4 (Table 2.1 and Table 2.2 in Chapter 2) were selected for detail electrical conductivity studies.

These composite materials contain two components viz. inorganic and organic. The inorganic components of the composites are the efficient ion-exchange materials whereas organic components, poly-o-toluidine is good electronically conducting polymer. In general, a high electrical conductivity of conductive polymers is attained by dopant, which stabilizes the polaron and bipolaron states as counter anions [31-34].

Thus, the DC electrical conductivity of composite ion-exchange materials is due to the presence of sufficient amount of the conducting polymer and basically it is electronic conduction contributed by the conducting components, i.e. poly-o-toluidine by the charge-transfer reaction between poly-o-toluidine component of the composites and doping agents, HCl, respectively as given:

\[
\begin{align*}
\text{[POTZr(IV)P]} + n\text{HCl} & > \text{[POT (nH}^\text{+} \text{(nCl}^-) \text{Zr(IV) P}]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.1 \\
\text{[POTCe(IV)P]} + n\text{HCl} & > \text{[POT (nH}^\text{+}(n\text{Cl}^-) \text{Ce(IV) P}]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.2 \\
\end{align*}
\]

Controlling the doping process (i.e. treatment with aqueous solution of HCl), the electrical conductivity of these materials could be varied from insulator, through semiconductor to metal range and vice-versa. *Schollhorn and Zagefka* [35] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalocogenides, which has further been supported by the work of *Foot and Shaker* [36]. On the basis of the disproportionation reaction of ammonia as suggested by above workers (equation-4.3), *Mohammad* [37] also has suggested an analogous disproportionation reaction for water (Eq. 4.4).

\[
\begin{align*}
8\text{NH}_3 & > 6\text{NH}_4^+ + 6e^- + \text{N}_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.3 \\
6\text{H}_2\text{O} & > 4\text{H}_3\text{O}^+ + 4e^- + \text{N}_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.4 \\
\end{align*}
\]
The basic strength of water is very low, hence does not act as undoping agent in case of poly-o-toluidine. However, the neutralization reactions to undope poly-o-toluidine within poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite cation-exchange materials may be carried out by ammonia.

4.3.1 Electrical conductivity measurements

Electrical conductivities of the pellets of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite samples were determined from the measurement of conductivity of the samples using the four-probe method of conductivity measurement for semiconductors. That is the most satisfactory method as it overcomes difficulties, which are encountered in conventional methods of conductivity measurement (i.e; two probes), 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, measurement of conductivity in sample having wide variety of shapes. In order to use the four-probe method it is necessary to make the following assumptions:

- The conductivity of the material is uniform within the area of measurements. If there is minority carrier injection into the material to be tested by the current carrying electrodes, most of the carriers recombine near the electrodes so that their effect on the conductivity is negligible.
- The surface on which the probe rest is flat with no surface leakage.
- The four-probe used for conducting measurement must contact the surface at point that lie in straight line.
- The diameter of the contact between the metallic probes and the material should be smaller than the distance between the probes.
- The surface of the materials may be conducting or non-conducting.
- A conducting boundary is one in which the bottom surface of the material to be tested is of much higher conductivity than that of the material itself. This could be achieved by copper plating on the bottom surface of the semiconductor slice.
- A non-conducting boundary is produced when the bottom surface of the material to be tested is in contact with an insulator such as poly-tetrafluoroethylene in these measurements.
After the measurements of current-voltage data by a four-in-line probe DC electrical conductivity measuring instrument was processed for calculation by using the following Equations:

\[ \rho = \frac{\rho_0}{G_7(W/S)} \]  

where \( \rho \) is corrected resistivity (ohm cm), \( \rho_0 \) = uncorrected resistivity (ohm cm), \( G_7(W/S) \) is the correction factor used for the case of a non-conducting bottom surface, which is a function of \( W \), the thickness of the sample under test (cm) and \( S \), the probe spacing (cm); i.e.

\[ G_7(W/S) = (2S/W) \ln 2 \]  
\[ \rho_0 = \frac{V}{I} \times 2\pi S, \]  

\[ \sigma = \frac{1}{\rho} \]  

where \( I \) is the current (A), \( V \) is the voltage (V) and \( \sigma = \) DC electrical conductivity (S cm\(^{-1}\)). Although the electrical conductivity measurements were done under ambient conditions, the composite samples were thoroughly dried before making the pellets and performing the electrical conductivity measurements. Hence, the contribution of protionic conductivity to the total electrical conductivity due to the presence of moisture should be minimum and need not to be taken into consideration.

Poly-o-toluidine Zr(IV) phosphate composite material was treated with 0.5M NaCl, KCl, ZnCl\(_2\), Pb(NO\(_3\))\(_2\), MgCl\(_2\) and Cu(NO\(_3\))\(_2\) solutions, and electrical conductivity measurements were carried out on these different forms (Na\(^+\), K\(^+\), Zn\(^{2+}\), Pb\(^{2+}\), Mg\(^{2+}\), Cu\(^{2+}\)) of composite cation-exchange material.

The variations of electrical conductivity (\( \sigma \)) of poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composite samples (as prepared and HCl treated), prepared with 20% ortho-toluidine with increasing temperature (between 30 °C to 200 °C) were carried out. On examination, it was observed that the electrical conductivity of the composite samples increase with the increase in temperature and the values lie in the order of \( 10^{-2} \) to \( 10^{-3} \) S/cm for both poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate i.e; in the semiconductor region. To determine the nature of dependence of electrical conductivity on temperature plots of \( \log \sigma \) versus \( 1000 / T(K) \) were drawn (Figure 4.1 and Figure 4.2) and they followed Arrhenius equation similar to other semiconductors [38].
Figure 4.1 Arrhenius plots for poly-o-toluidine Zr(IV) phosphate nano-composite material

It was also observed that the composite materials showed enhanced electrical conductivity on exposure to HCl as compared to original form, due to the charge-transfer reaction between poly-o-toluidine component of the composites and doping agents, HCl as described above. The dependence of the electrical conductivity through the bi-phasic systems poly-o-toluidine Zr(IV) phosphate and poly-o-toluidine Ce(IV) phosphate composites (prepared with 20% concentrations of ortho-toluidine) on the concentration of conducting phases (i.e. poly-o-toluidine) was examined.
Thus, we can say that main factor that made the composites electrically conductive is the presence of poly-o-toluidine in sufficient amount. Thus, major part of electrical conductivity of the composite is due to the incorporation of poly-o-toluidine in the composites.

Poly-o-toluidine Zr(IV) phosphate nano-composite material was also treated with 1M NaCl, ZnCl₂, Pb(NO₃)₂, KCl, MgCl₂ and Cu(NO₃)₂ solutions, and electrical conductivity measurements were carried out on these different forms (Na⁺, Zn²⁺, K⁺, Pb²⁺, Mg²⁺, Cu²⁺) of material. It was observed that the sample S-5 treated with Pb(NO₃)₂ showed the higher electrical conductivity while treated with KCl and Cu(NO₃)₂ showed lower electrical conductivity at room temperature as given in Table 4.1.
Table 4.1 Four-probe DC electrical conductivity of different forms of poly-o-toluidine Zr(IV) phosphate composite system at ambient temperature (prepared with 20% o-toluidine monomers)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Poly-o-toluidine nano-composite</th>
<th>Zr(IV) phosphate</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>As prepared</td>
<td></td>
<td>1.08 X 10⁻²</td>
</tr>
<tr>
<td>2.</td>
<td>HCl treated</td>
<td></td>
<td>1.37 X 10⁻³</td>
</tr>
<tr>
<td>3.</td>
<td>NaCl treated</td>
<td></td>
<td>1.83 X 10⁻²</td>
</tr>
<tr>
<td>4.</td>
<td>ZnCl₂ treated</td>
<td></td>
<td>1.72 X 10⁻²</td>
</tr>
<tr>
<td>5.</td>
<td>KCl treated</td>
<td></td>
<td>8.10 X 10⁻⁴</td>
</tr>
<tr>
<td>6.</td>
<td>Pb(NO₃)₂ treated</td>
<td></td>
<td>4.19 X 10⁻²</td>
</tr>
<tr>
<td>7.</td>
<td>MgCl₂ treated</td>
<td></td>
<td>1.21 X 10⁻²</td>
</tr>
<tr>
<td>8.</td>
<td>Cu(NO₃)₂ treated</td>
<td></td>
<td>1.66 X 10⁻³</td>
</tr>
</tbody>
</table>

4.3.2 Stability of composites in terms of DC electrical conductivity retention

The thermal stability of the poly-o-toluidine Zr(IV) phosphate (S-5) and poly-o-toluidine Ce(IV) phosphate (T-4) composite materials (HCl treated) in terms of DC electrical conductivity retention was studied under isothermal condition at 50, 70, 90, 110, 130 and 150 °C for poly-o-toluidine Zr(IV) phosphate while at 50, 80, 110 and 150 °C for poly-o-toluidine Ce(IV) phosphate measuring four-in-line-probe DC electrical conductivity at an interval of 15 minutes. The electrical conductivity measured with respect to the time of accelerated ageing is presented in Figure 4.3 and Figure 4.4.
Figure 4.3 Isothermal stability of poly-o-toluidine Zr(IV) phosphate nano-composite in terms of DC electrical conductivity with respect to time at 50, 70, 90, 110, 130 and 150°C

Figure 4.4 Isothermal stability of poly-o-toluidine Ce(IV) phosphate composite in terms of DC electrical conductivity with respect to time at 50, 80, 110 and 150°C
It was observed that the electrical conductivity 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 for poly-o-toluidine Zr(IV) phosphate and decreases with time at 110 and 150 °C for poly-o-toluidine Ce(IV) phosphate that may be attributed to the loss of dopant and chemical reaction of dopant with the material.

These composite materials were also observed to be a stable materials, i.e; the room temperature conductivity is negligibly affected by short- term exposure to laboratory air as evident from Figure 4.5 and Figure 4.6. The materials of these types may often exhibit 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 $O_2^-$. Presumably, electron transfer from 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.

![Conductivity verses time on exposure to laboratory air for poly-o-toluidine Zr(IV) phosphate nano-composite material (HCl treated)](image)

Figure 4.5 Conductivity verses time on exposure to laboratory air for poly-o-toluidine Zr(IV) phosphate nano-composite material (HCl treated)
Figure 4.6 Conductivity versus time of exposure to laboratory air for poly-o-toluidine Ce(IV) phosphate composite material (HCl treated)
References