

# Facile Synthesis of $\gamma$ -Zirconium Phosphate-Fibrous Cerium Phosphate / Emeraldine Salt Nanocomposite Membrane

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**Abstract**  $\gamma$ -zirconium phosphate-fibrous cerium phosphate nanocomposite membranes  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.34}[\text{Ce}(\text{HPO}_4)_2]_{0.66}\text{.4.4H}_2\text{O}$  and  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.27}[\text{Ce}(\text{HPO}_4)_2]_{0.73}\text{.3.47H}_2\text{O}$  ( $\gamma\text{-ZrP}_{0.27}\text{-CePf}_{0.73}$ ), were prepared by mixing slurry aqueous solutions of  $\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4\text{.2H}_2\text{O}$  and nanofibrous  $\text{Ce}(\text{HPO}_4)_2\text{.2.9H}_2\text{O}(\text{nCePf})$  from wt/wt% required ratios, respectively, were characterized.  $\gamma$ -zirconium phosphate-fibrous cerium phosphate( $\gamma\text{-ZrP}_x\text{-CePf}_{1-x}$ ) /emeraldine salt nanocomposite membranes were prepared via in-situ chemical oxidation of the monomers, aniline and anilineHCl, that was promoted by the reduction of Ce(IV) ions present in the inorganic matrix (where  $x = 0.34, 0.27$ ) respectively. The resultant materials were characterized by TGA, elemental (C,H,N) analysis, FT-IR spectroscopy and scanning electron microscopy(SEM). Images SEM of the resulting nanocomposites reveal a uniform distribution of the polymer on the inorganic matrix, has needle like structure. The presence of Ce(IV) ions allows redox reactions necessary to oxidative polymerization to occur. The fibrous morphology present by this material makes molding possible, giving desired shape to the final emeraldine salt nanocomposite membranes. The self-supported sheet integrity is preserved. This result is interesting because the shape integrity makes the building of molded conducting device possible.

**Keywords**  $\gamma$ -Zirconium phosphate- fibrous cerium phosphate composites, Emeraldine salt nanocomposites

## 1. Introduction

Conducting polymers are a novel class of synthetic metals that combine the chemical, electrochemical and mechanical properties of polymers with the electronic properties of metals and semiconductor, generated tremendous interest due to their potential applications in various fields such as rechargeable batteries, electrochromic display devices, separation membranes, sensors and anticorrosive coatings on metals [1-11].

In recent years conducting polymers containing nitrogen atoms like polyaniline and polypyrrole, and their substituted derivatives have received increasing attention in various fields, electronics, industry and others. Their electrical and electrochemical properties show great promise for commercial applications. They provide an interesting and useful focus for expansion of the fields of polymeric reagent research and molecular engineering. They are electrically conductive which makes their use as metal replacement materials of some interest [12-16].

The proton conductivity of solid electrolytes organic

based polymers are today the most promising materials to improve the performance of proton exchange membrane fuel cells. The most notable property of these materials, electrical conductivity, results from the delocalization of electron along the polymer backbone [5, 8-10, 16].

Polyaniline is one of the most studied conducting polymers, has potential for applications, due to its light weight, conductivity, mechanical flexibility and low cost. Polyaniline is especially attractive because it is relatively inexpensive. It has certain advantages over other conducting polymers, including simplicity and rapidity of preparation by electrochemical and oxidative chemical polymerization methods, and the ability to be formed in aqueous electrolytic solutions. It has good environmental stability and its conductivity could be controlled with acid/base (doping/undoping) [12, 13, 17-30].

Inorganic layered nanomaterials are receiving great attention because of their size, structure, and possible biochemical applications [31, 32], that have been proven to be good carriers for organic polar molecules. Examples of these are zirconium phosphates. Taking advantage of the expandable interlayer space, prevent them from interacting with environment, avoiding denaturation and enhancing their shelf life [31, 32].

Crystalline cerium phosphates have been studied for a long time as ion exchangers, their structures remains

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unknown until recently [33-35]. The reason is that, the composition, the structure and the degree of crystallinity of their precipitates results from reaction of solutions containing a Ce(IV) salt is mixed with a solution of phosphoric acid of [(PO<sub>4</sub>) / Ce(IV) ratio], strongly dependent on the experimental conditions such as rate and order of mixing of the solutions, stirring, temperature and digestion time, this also implemented on fibrous cerium phosphate [36].

To date most of the work on fibrous cerium phosphate was carried out on its ion exchange [37], intercalation [38] and electrical conductance properties [39]. Studies on its polystyrene, polyacrylamide [40] and polyvinyl chloride-based polyvinyl (alcohol) [41] composites have been reported. Nanoscaled tetravalent metal phosphates and their organic polymer composites comprise an important class of synthetic engineering. However, research in such area is still in its infancy [42-45]. Nanotechnologies are at the center of numerous investigations and huge investments. However, chemistry has anticipated for long the importance decreasing the size in the search of new properties of materials, and of materials structured at the nanosize in a number of applications relate to daily life.

Synthetic membranes can be fabricated from a large number of different materials. It can be made from organic or inorganic materials including solids such as metal or ceramic, homogeneous films (polymers), heterogeneous solids (polymeric mixes, mixed glasses), and liquids. Ceramic membranes are produced from inorganic materials such as aluminum oxides, silicon carbide, and zirconium oxide. Their inorganic composite membranes are well known [46-49].

Recently a great deal of attention has been paid towards synthesis of inorganic composite membranes and inorganic-organic polymer composite materials. Organic-inorganic nanocomposite membranes have gained great attention recently [45, 50], The composite material may combine the advantage of each material, for instance, flexibility processability of polymers and the selectivity and thermal stability of the inorganic filler [43-45, 51]. Pyrrole polymerization by fibrous cerium phosphate has been reported [52, 53], polymerization of pyrrole and aniline on  $\alpha$ -Tin phosphate and copper zirconium phosphate was reported [54, 55].

The composite materials usually does not have either characteristic of original materials and can be considered as materials with almost new physical and chemical properties [56].

In our laboratory we are carrying systematic investigations on novel tetravalent metal phosphates / organic heterocyclic conducting polymers nanocomposite membranes. Recently we have reported the preparation and characterization of fibrous cerium phosphate / polybenzimidazole nanocomposite membrane and fibrous cerium phosphate/polyindole nanocomposite membrane[57, 58].

Here we are reporting the synthesis and characterization of  $\gamma$ -zirconium phosphate-fibrous cerium phosphate

nanocomposite membranes, that was utilized as novel self supported polymerization of monomers aniline and anilineHCl agent, to obtain novel  $\gamma$ -zirconium phosphate-fibrous cerium phosphate / emeraldine salt nanocomposite membranes.

## 2. Materials and Methods

### 2.1. Chemicals

Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, ZrOCl<sub>2</sub>·8H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>(85%) of BDH, aniline (99.5%) of Mindex UK. Other reagents used were of analytical grade.

### 2.2. Instruments Used for Characterization

X-Ray powder diffractometer Siemens D-500, using Ni-filtered CuK $\alpha$  ( $\lambda$ = 1.54056Å), TG/DTA SIIExtra6000 TGA Perkin Elmer thermo gravimetric analyzer (TGA7)US, CHN-Elemental analyzer, Vario Elemental-German. Fourier Transform IR spectrometer, model FT/IR-6100, Scanning electron microscopy (SEM) Jeol SMJ Sm 5610 LV and pH Meter WGW 521.

### 2.3. Preparation of Nanofibrous Cerium Phosphate Membrane, Ce(HPO<sub>4</sub>)<sub>2</sub>·2.9H<sub>2</sub>O (nCePf)

Nanofibrous cerium phosphate membrane was prepared from adding 300 ml of 0.05M CeSO<sub>4</sub>·4H<sub>2</sub>O in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, drop wise, to 300 ml of 6 M H<sub>3</sub>PO<sub>4</sub> at ~ 80°C with stirring. After complete addition the resultant material left to digest at that temperature for 4h. To that 3 liter of hot distilled water, (~60°C), was added with stirring for 1h., then kept in the resultant slurry aqueous form.

### 2.4. Preparation of $\gamma$ - zirconium Phosphate ( $\gamma$ -ZrP)

$\gamma$ -zirconium phosphate monoammonium form  $\gamma$ -Zr.PO<sub>4</sub>.NH<sub>4</sub>HPO<sub>4</sub>, was obtained by reacting 50ml of ZrOCl<sub>2</sub>·H<sub>2</sub>O (1.3M in 8M HF) with 450ml of 2M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> in plastic bottle at (~70°C) for 3days keeping the volume constant by addition of distilled water. The resultant product was filtered washed with distilled water up to pH 3.5, filtered and air dried.

The ammonium form was converted to hydrogen form using 1MHCl with vigorous stirring at 15°C for 24h (for every 2g of  $\gamma$ -Zr.PO<sub>4</sub>.NH<sub>4</sub>HPO<sub>4</sub> 400ml 1M HCl were required), to obtain crystalline lamellar  $\gamma$ -Zr.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O, found to be similar to that was reported by Alberti [59].

### 2.5. Preparation of $\gamma$ - zirconium Phosphate-Fibrous Cerium Phosphate Nanocomposite Membranes ( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>)

Slurry aqueous solution of 0.3 g  $\gamma$ -zirconium phosphate ( $\gamma$ -ZrP) in 150 ml distilled water was added gradually to slurry aqueous solution of 0.6g fibrous cerium in 450ml distilled water at 45°C, with stirring, the stirring was continued after complete addition and at 45°C for 24h. The

resultant product was filtered on filter paper using Buchner funnel, washed with distilled water (50ml) twice then left to dry in air, the resulted product was homogeneous thin film, good mechanical texture,  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4\text{.}]_{0.34} [\text{Ce}(\text{HPO}_4)_2]_{0.66} \cdot 4.4\text{H}_2\text{O}$  was obtained.

In similar manner, using the above experimental parameters, composite  $\gamma$ -zirconium phosphate-fibrous cerium phosphate membrane  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.27} [\text{Ce}(\text{HPO}_4)_2]_{0.73} \cdot 3.47\text{H}_2\text{O}$  ( $\gamma\text{-ZrP}_{0.27}\text{-CePf}_{0.73}$ ) was obtained by mixing slurry aqueous solution in wt/wt % ratio 25:75 of  $\gamma\text{-ZrP:nCePf}$ , where the mixing weight ratio is 0.2g:0.6g, respectively. After complete mixing of the above slurry aqueous solutions, at 45°C for 24h, the resultant product was filtered on filter paper using Buchner funnel, washed with distilled water and left to dry in air.

### 2.6. Preparation of $\gamma$ -zirconium Phosphate-Fibrous Cerium Phosphate/Emeraldine Salt Nanocomposite Membranes

$\gamma$ -zirconium phosphate-fibrous cerium phosphate/emeraldine salt nanocomposite membranes were prepared by different methods:

- (1) By immersion of self supported-sheet ( $\gamma\text{-ZrP}_{0.34}\text{-CePf}_{0.66}$ ), 150 mg in 15 ml of 4% aniline in ethanol at (~5°C), for 10 minutes, then kept at room temperature for 72h. The color change gradually from blue to dark green. The impregnated sheet was removed, washed with distilled water and ethanol and left to dry in air, designated as composite (I).
- (2) By immersion of self supported-sheet ( $\gamma\text{-ZrP}_{0.27}\text{-CePf}_{0.73}$ ), 150 mg in 15 ml of 4% aniline in ethanol at (~5°C), for 10 minutes, then kept at room temperature for 72h. The color changes gradually from blue to dark green. The impregnated sheet was removed, washed with distilled water and ethanol and left to dry in air, designated as composite (II).
- (3) By immersion of self supported-sheet ( $\gamma\text{-ZrP}_{0.34}\text{-CePf}_{0.66}$ ), 180 mg in 17.5 ml of 4% aniline in 1MHCl solution at room temperature for 72h. The impregnated sheet was removed, washed with distilled water and ethanol and left to dry in air. The color of the resulting product was green, designated as composite (III).
- (4) By immersion of self supported-sheet ( $\gamma\text{-ZrP}_{0.27}\text{-CePf}_{0.73}$ ), 180 mg in 17.5 ml of 4% aniline in 1MHCl solution at room temperature for 72h. The impregnated sheet was removed, washed with distilled water and ethanol and left to dry in air. The color of the resulting product was green, designated as composite (IV).

## 3. Results and Discussion

A variety of open-framework tetravalent metal phosphate(TVMP) materials have been synthesized and their structures elucidated in the last few years [31, 32]. of particular interest to us are nanosized  $\alpha$ -,  $\gamma$ -(TVMP) of general formulae,  $\alpha\text{-M}(\text{HPO}_4)_2\text{.H}_2\text{O}$ ,  $\gamma\text{-M.PO}_4\text{.H}_2\text{PO}_4\text{.2H}_2\text{O}$ ,

their pellicular membranes, (Where M=Ti, Zr, Hf.), and fibrous cerium phosphate membrane.

Nanosized cerium phosphate membrane,  $\text{Ce}(\text{HPO}_4)_2\text{.2.9 H}_2\text{O}(\text{nCePf})$ , was prepared and characterized by chemical, XRD, thermal analysis FT-IR and SEM. The ion exchange capacity of fibrous cerium phosphate found to be equal to 5.21 meq/g.

### 3.1. XRD

The XRD pattern of fibrous cerium phosphate membrane is shown in Figure 1. Its  $d_{001}$  found to be equal to 10.85Å .

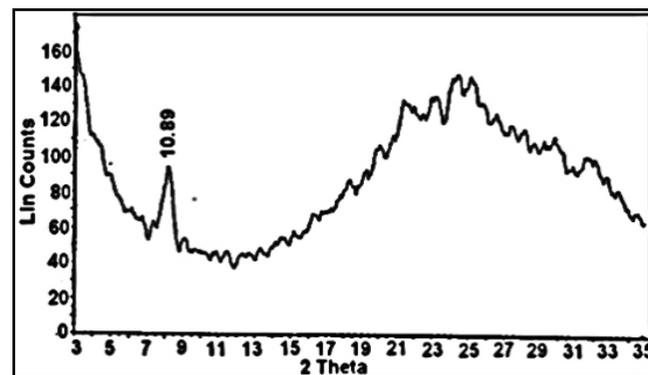


Figure 1. XRD of fibrous cerium phosphate

### 3.2. TGA

Its thermogram is shown in Figure 2. The thermal decomposition occurs in continuous process almost one step. The thermal analysis was carried out at temperatures between 10-750°C, the final product was  $\text{CeP}_2\text{O}_7$ , results from the loss of water of hydration between 60-200°C, followed by POH groups condensation. The total weight loss found to be equal to 19.09%.

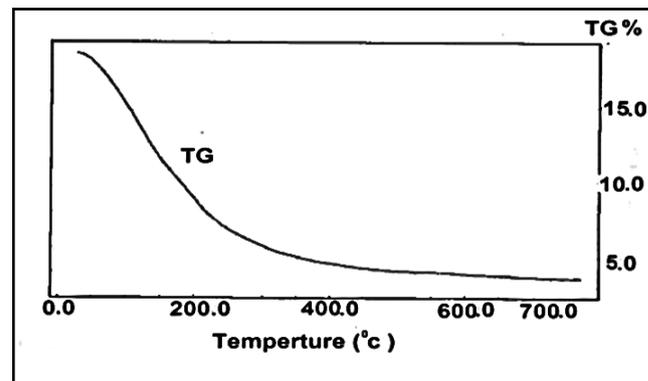


Figure 2. TG of fibrous cerium phosphate

### 3.3. FT-IR

FT-IR spectroscopy became a key tool to investigate structure of tetravalent metal phosphates [31, 32]. Figure 3, shows its FT-IR spectrum, with a trend similar to the IR spectra of M(IV) phosphates. Broad band centered at  $3350\text{cm}^{-1}$  is due to OH groups symmetric-asymmetric stretching of  $\text{H}_2\text{O}$ , small sharp band at  $1628\text{cm}^{-1}$  is due to H-O-H bending , sharp broad band centered at  $1045\text{cm}^{-1}$  is

related to phosphate groups vibration.

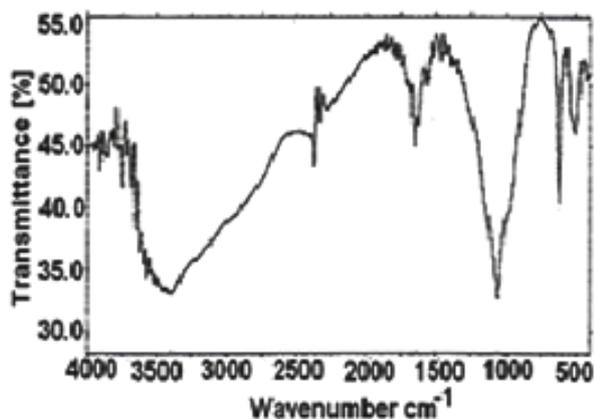


Figure 3. FT-IR spectrum of fibrous cerium phosphate

### 3.4. SEM

SEM morphology image of the nanosized fibrous cerium phosphate (nCePf) is shown in Figure 4. The photograph shows its average size is  $\sim 20.5$  nm.

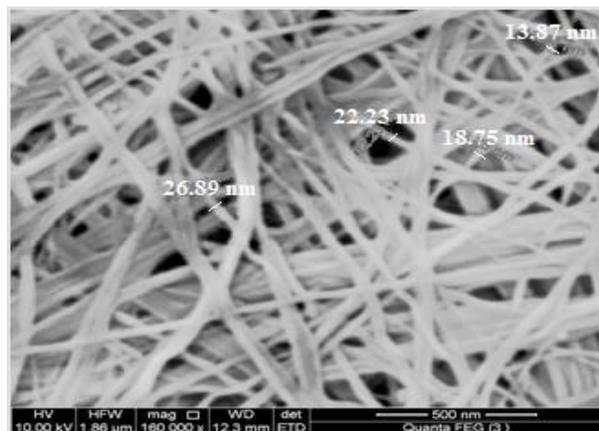


Figure 4. SEM image of fibrous cerium phosphate

### 3.5. XRD of ( $\gamma$ -ZrP)

Figure 5 shows the X-ray diffractogram (XRD), of  $\gamma$ -Zr.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O, with interlayer distance ( $d_{001}$ ) = 12.25 Å. Its ion exchange capacity found to be equal to 6.27 meq/g.

### 3.6. TGA of ( $\gamma$ -ZrP)

Thermal analysis is one of important tools utilized for characterization of (TVMP) [59].

Thermogram of  $\gamma$ -ZrP is given in figure 6. The thermal decomposition found to occur in three stages. The loss of water of hydration, two moles of water of hydration are lost at  $\sim 100^\circ\text{C}$ . At higher temperature a two stages condensation of POH groups occurs. The first is accompanied by loss of water at  $\sim 370^\circ\text{C}$  and yield  $\text{Zr}_3(\text{HPO}_4)_2(\text{P}_2\text{O}_7)_2$ . The second loss occurs between  $500$ - $700^\circ\text{C}$  resulting in formation of  $\text{ZrP}_2\text{O}_7$  as final product. So the total loss are 3 molecules of

water per unit formula.

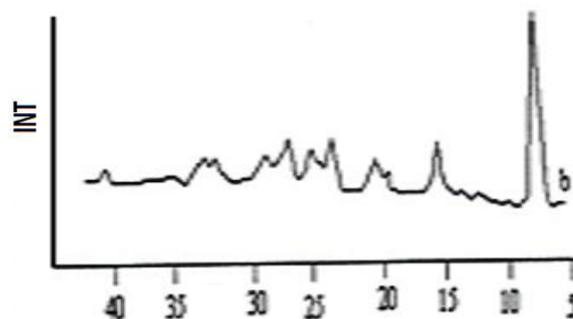


Figure 5. XRD of  $\gamma$ -Zr.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O

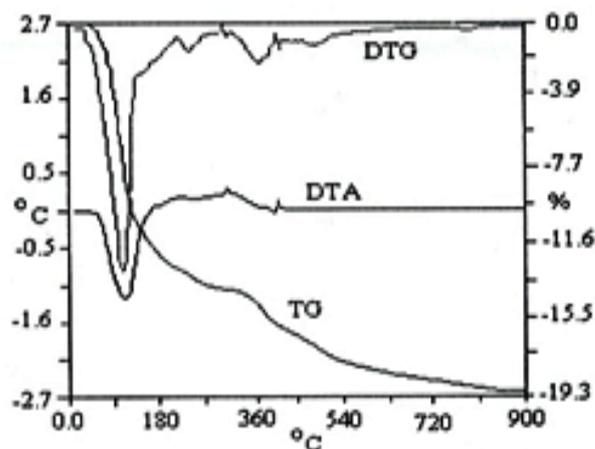


Figure 6. TGA of  $\gamma$ -Zr.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O

### 3.7. FT-IR of ( $\gamma$ -ZrP)

Figure 7, Shows FT-IR spectrum of  $\gamma$ -Zr.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O in the range  $4000$ - $400\text{cm}^{-1}$  wave number. Broad band centered at  $3560\text{cm}^{-1}$  assigned to vibrational modes of H<sub>2</sub>O and to (P)OH stretching mode of the hydrogen bond, suggest that water molecules are located at well defined crystallographic sites. These bands were also attributed to an O-H asymmetric modes of interlayer water molecules. The band at  $1635\text{cm}^{-1}$  also corresponds to H-O-H bending modes. The broad band centered at the region  $1030\text{cm}^{-1}$  corresponds to phosphate groups vibration.

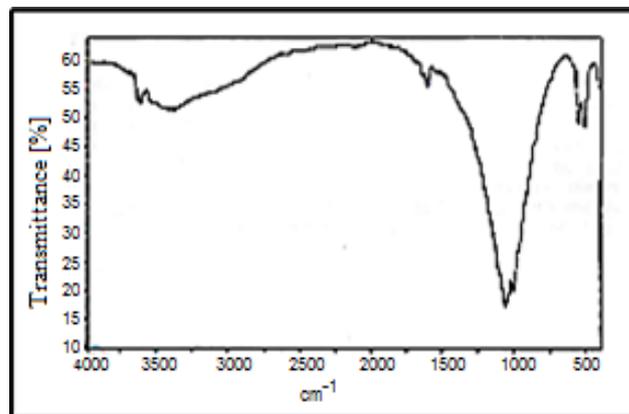


Figure 7. FTIR spectrum of  $\gamma$ -Zr.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O

### 3.8. $\gamma$ -zirconium Phosphate-Fibrous Cerium Phosphate Nanocomposite Membranes ( $\gamma$ -ZrP-nCePf)

Mixing slurry aqueous solution of crystalline  $\gamma$ -zirconium phosphate with slurry aqueous solution of fibrous cerium phosphate in wt/wt% mixing ratios 34:66, and 25:75%, results in the formation of composite membranes:  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.34}[\text{Ce(HPO}_4)_2]_{0.66}\text{.4.4H}_2\text{O}$  and  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.27}[\text{Ce(HPO}_4)_2]_{0.73}\text{.3.47H}_2\text{O}$  respectively. The resultant composites were homogeneous flexible thin films. They were characterized by XRD, TGA and FT-IR spectra. In the composite materials the XRD pattern retain, to certain extent, d spacing reflection of their parent  $\gamma$ -ZrP and nCePf. Metal(IV)phosphates are very insoluble materials, their composite materials retain wt/wt% mixing ratios of the original materials. Thermal analysis is a good tool for characterization of such type of materials. The final product results from thermal analysis of M(IV)phosphate composites are the pyrophosphate, e.g. the final product from the thermal decomposition of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4\text{.nH}_2\text{O}]_x[\text{Ce(HPO}_4)_2\text{.nH}_2\text{O}]_{1-x}$  is  $[\text{Zr}_x\text{Ce}_{1-x}]_2\text{P}_2\text{O}_7$ , where x, 1-x represents their original mixing of wt/wt% ratios, respectively.

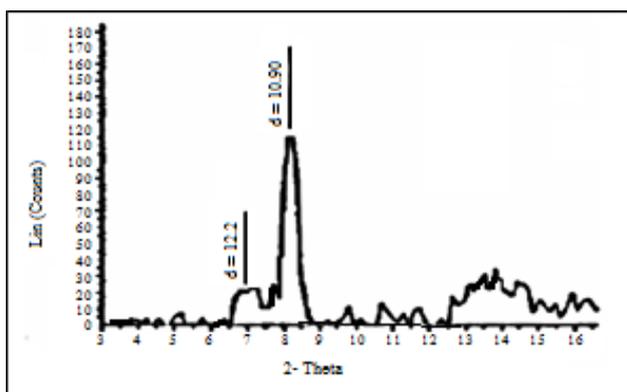


Figure 8. XRD of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.27}[\text{Ce(HPO}_4)_2]_{0.73}\text{.3.47H}_2\text{O}$

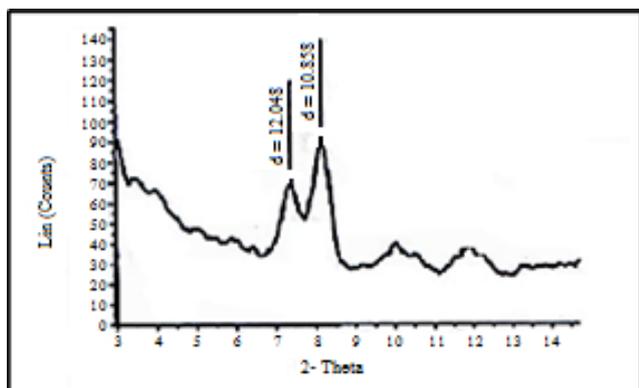


Figure 9. XRD of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.34}[\text{Ce(HPO}_4)_2]_{0.66}\text{.4.4H}_2\text{O}$

#### 3.8.1. XRD of ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>)

Figure 8 shows the x-ray diffractogram of the composite  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.27}[\text{Ce(HPO}_4)_2]_{0.73}\text{.3.47H}_2\text{O}$ , with d spacing reflections at 10.858Å and at 12.048Å, corresponds to x-ray diffraction pattern of parent materials of the

composite membrane contents, the fibrous cerium phosphate and  $\gamma$ -zirconium phosphate, respectively. Typical XRD pattern that expected for such type of composite membrane.

Figure 9 shows the x-ray diffractogram of the composite  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.34}[\text{Ce(HPO}_4)_2]_{0.66}\text{.4.4H}_2\text{O}$ , with d spacing reflections at 10.8Å and at 12.048Å, corresponds to x-ray pattern fibrous cerium phosphate and to that of  $\gamma$ -zirconium phosphate, respectively. Typical XRD pattern that expected for such type of composite membrane.

#### 3.8.2. TGA of ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>) and ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>)

Thermal analysis of the composite products were carried out between ~20-750°C. Thermogram of composite  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.27}[\text{Ce(HPO}_4)_2]_{0.73}\text{.3.47H}_2\text{O}$  is shown in Figure 10. The thermal decomposition occurs in four steps the first step due to loss of hydration water at temperature range 70-230°C followed by POH groups condensation at different steps, the final product was the pyrophosphate  $[\text{Zr}_{0.27}\text{Ce}_{0.73}]_2\text{P}_2\text{O}_7$ . The total weight loss found to be equal to 21.11%.

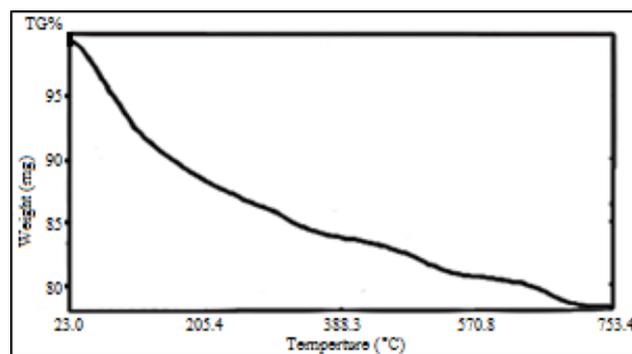


Figure 10. TGA of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.27}[\text{Ce(HPO}_4)_2]_{0.73}\text{.3.47H}_2\text{O}$

Thermogram of composite  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.34}[\text{Ce(HPO}_4)_2]_{0.66}\text{.4.4H}_2\text{O}$  is shown in Figure 11. The thermal decomposition occurs in four steps the first step corresponds to loss of hydration water at temperature range 70-220°C followed by POH groups condensation, at different steps, the final product was the pyrophosphate  $[\text{Zr}_{0.34}\text{Ce}_{0.66}]_2\text{P}_2\text{O}_7$ , the total weight loss found to be equal to 24.66%.

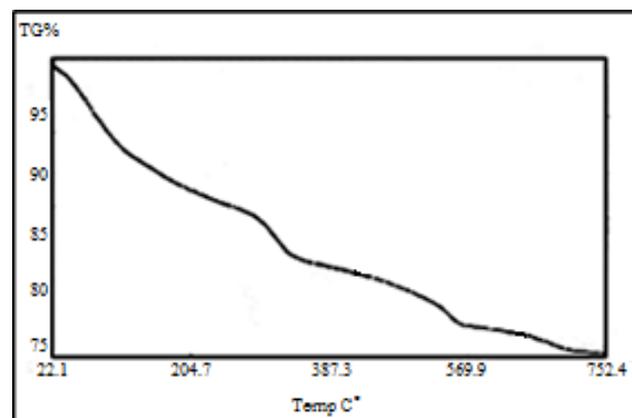


Figure 11. TGA of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_4]_{0.34}[\text{Ce(HPO}_4)_2]_{0.66}\text{.4.4H}_2\text{O}$

### 3.8.3. FT-IR of Composites ( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>)

The infrared spectra of composite compounds ( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>) are very similar and follow the same trend of FT-IR spectra of M(IV) phosphates. Typical FT-IR spectrum of the composite is given in figure 12. It consists of broad band centered at 3425cm<sup>-1</sup> due to OH groups symmetric-asymmetric stretching, small sharp band at 1665cm<sup>-1</sup> is related to H-O-H bending, sharp broad band centered at 1010cm<sup>-1</sup> corresponds to phosphate groups vibration.

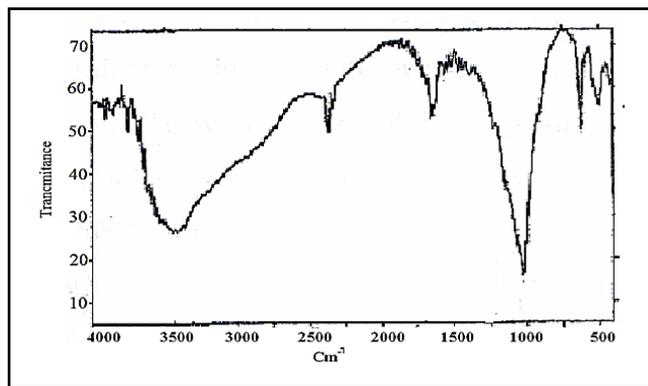


Figure 12. Typical FT-IR spectrum of ( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>)

This study shows that metal(IV)phosphate nanocomposite membranes can be obtained by mixing slurry aqueous solution of their membranes in required wt/wt% mixing ratios. The resultant composite compounds were flexible homogeneous thin films. XRD of composites show that it is possible to obtain tailor made inorganic membrane-membrane composites, of this type, where their XRD patterns shows two d spacing reflections which are related to the d spacing reflection of their parent compounds. The XRD retain the d spacing of their parent materials FT-IR spectra of every composite materials are very similar to the FT-IR spectrum of their original materials.

### 3.9. $\gamma$ -zirconium Phosphate-Fibrous Cerium Phosphate / Emeraldine Salt Nanocomposite Membranes

Novel  $\gamma$ -zirconium phosphate-fibrous cerium phosphate / emeraldine salt nanocomposite membranes were prepared via in-situ chemical oxidation of the monomers, aniline and aniline HCl, that was promoted by the reduction of Ce(IV) ions present in the inorganic matrix. The fibrous morphology present by this material makes molding possible, giving desired shape to the final nanocomposite membranes.

It was found that when nanosized  $\gamma$ -zirconium phosphate-fibrous cerium phosphate membranes ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>), ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>) were immersed in ethanolic solution of aniline the color gradually changes with time to (blue and finally to dark green) due to the formation of nanocomposite membranes( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>) / emeraldine salt composites, were designated as composites (I &II), where x= 0.34, 0.27, respectively.

On immersing of  $\gamma$ -zirconium phosphate-fibrous cerium phosphate composite membranes ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>),

( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>) in anilineHCl solution the color of self supported sheets gradually changes with time to pale blue and finally to light green due to the formation of nanocomposite membranes( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>) / emeraldine salt, were designated as composites (III& IV), where x= 0.34, 0.27, respectively. The green color of the resultant composites (I-IV) was due to formation of PANI salt. The self doping occurred in case of aniline, may be due to presence of H<sup>+</sup> of (=POH) groups. However, doping was expected when anilineHCl was used.

The polymerization was promoted by the reduction of Ce(IV) ions present in the inorganic matrix. Possible explanation is CePf present on the surface of the fiber, in  $\gamma$ -zirconium phosphate-fibrous cerium phosphate nanocomposite membranes, is attacked by the monomers, aniline (or anilineHCl), and converted to cerium(III) orthophosphate (CePO<sub>4</sub>). The presence of Ce(IV) ions allows redox reactions necessary to oxidative polymerization to occur. The self-supported sheet integrity is preserved.

#### 3.9.1. Elemental Analysis

From elemental (C,H,N) analysis, the amount of organic material present in ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>/emeraldine salt composite(I), found to be 18.3% in weight, where C =14.35, H = 1.95 and N = 2.76% in weight.

The % of elemental (C,H,N) related to the organic polymer of ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>) / emeraldine salt, composite (II), was 18.27% in weight, where C =14.25, H = 1.18 and N = 2.84% in weight.

The % elemental (C,H,N) analysis related to the organic polymer of ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>)/emeraldine salt, composite (III), found to be 12.91% in weight, where C=10.16, H=0.84, and N=1.90% in weight.

The % elemental (C,H,N) analysis related to the organic polymer of ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>)/emeraldine salt, composite (IV), found to be 11.25% in weight, where C=8.518, H=0.71, and N=1.969% in weight.

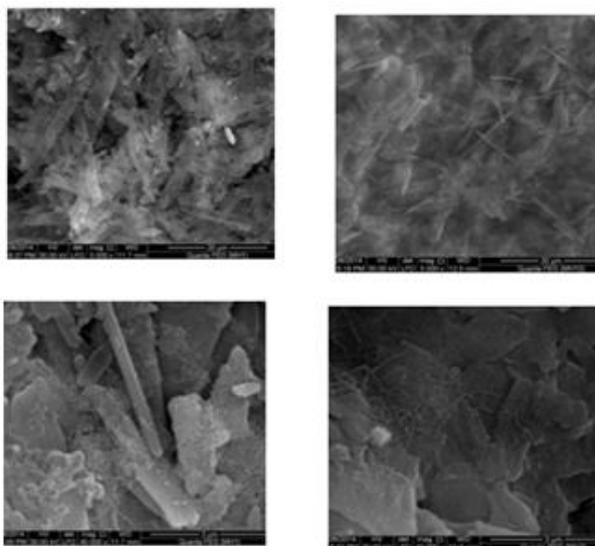
#### 3.9.2. SEM of ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>) ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>) /Emeraldine Salt Nanocomposite Membrane (I-IV)

Surface morphology of composites were studied using scanning electron microscopy (SEM). The SEM images, Figures (13-a,b,c,d) showed that the surface morphology of composite materials are totally different from their individual inorganic component (nZrP-nCePf). The morphology of the composite materials(I-IV) shows the polymer (ES) gets deposited over and between(nZrP-nCePf). in a uniform manner. The (ES) have a wide polydispersity, presumably due to increased rate of polymerization-pictures demonstrated the differences in surface morphology. Organic polymer in form of needle like structure, which is clear for composites (I, II, and III).

#### 3.9.3. FTIR of ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>)-, $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub> /Emeraldine Salt Nanocomposite Membranes (I-IV)

The chemical structure of obtained product was determined by FTIR spectrum. The FTIR spectroscopy has

provided valuable information regarding the formation of polyaniline/polystyrene composite. FTIR analysis has been done to identify the characteristic functional groups of product.



Figures (13 –a, b, c, d). SEM images of  $(\gamma\text{-ZrP}_x\text{-CePf}_{1-x})$ / emeraldine salt nanocomposites (I-IV), respectively

Figures (14-17) show FT-IR spectrum of nanocomposites (I-IV), (putting in consideration slight shifts of some bands in the region  $1700\text{-}1250\text{cm}^{-1}$ ). Broad band centered  $\sim 3440\text{cm}^{-1}$ , is due to OH groups symmetric stretching of  $\text{H}_2\text{O}$  super imposed with the N–H stretching of aromatic amines (expected at the range  $3500\text{-}3280\text{cm}^{-1}$ ). Small band around  $\sim 1630\text{cm}^{-1}$  is related to H-O-H bending, which represents the strongly bonded –OH groups in the matrix. Sharp broad band, centered at ( $\sim 1015\text{cm}^{-1}$ ) corresponds to phosphate groups vibration. Small band at  $\sim 2924\text{cm}^{-1}$  corresponds to C-H bonds, the presence of two bands in the range of  $1450, 1300\text{cm}^{-1}$  can be assigned to the non-symmetric  $\text{C}_6$  ring stretching modes. However the higher frequency vibration at  $\sim 1570\text{cm}^{-1}$  has a major contribution from the quinoid rings (C=C stretching vibration of quinoid ring), while the lower frequency mode at  $\sim 1490\text{cm}^{-1}$  depicts the presence of benzenoid rings (C=C stretching vibration of benzenoid ring). Thus FTIR spectra confirms the formation poly aniline composites [60-62].

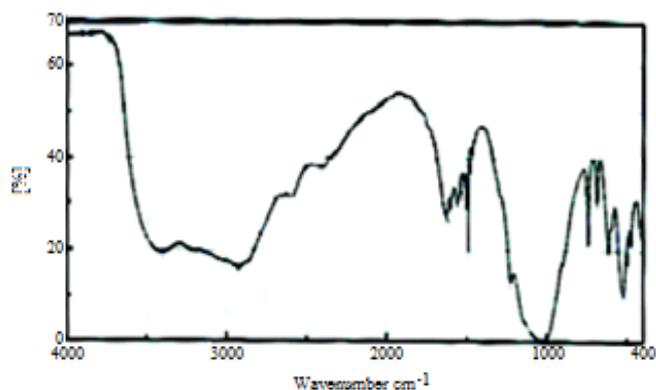


Figure 14. FT-IR spectrum of nanocomposite (I)

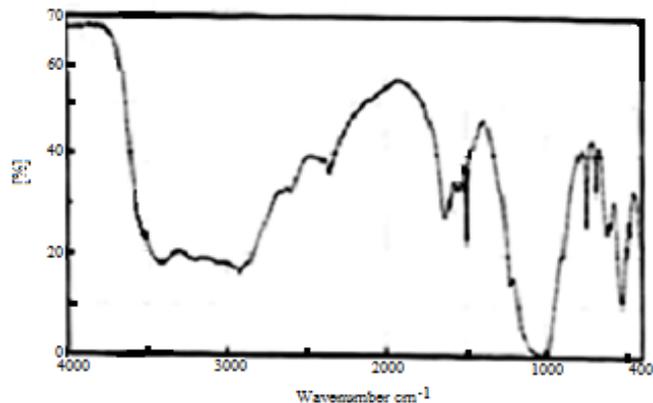


Figure 15. FT-IR spectrum of nanocomposite (II)

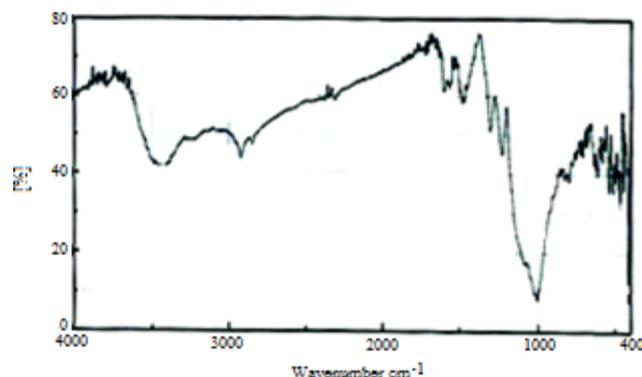


Figure 16. FT-IR spectrum of nanocomposite (III)

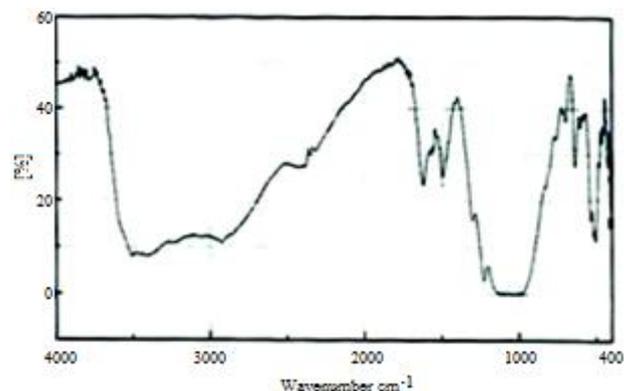


Figure 17. FT-IR spectrum of nanocomposite (IV)

### 3.9.4. TGA of $(\gamma\text{-ZrP}_{0.34}\text{-CePf}_{0.66})$ , $(\gamma\text{-ZrP}_{0.27}\text{-CePf}_{0.73})$ / Emeraldine Salt Nanocomposite Membranes (I-IV)

Thermal degradation is a very important process which helps in determining the influence of the polymer morphology on the thermal stability, the optimum temperature of operation and the activation energies related to the degradation processes [31, 59]. The thermal analysis ((TG/DTA) result of the composites (I-IV) are depicted in Figures 18-21 in respective manner. The weight loss up to  $150^\circ\text{C}$ , (7.668, 5.81, 13.52 and 14.91% in weight) is due to the removal of external water molecules of composites (I-IV), respectively. The weight loss occurs between  $150\text{-}800^\circ\text{C}$  corresponds to the decomposition of polyaniline (ES) and condensation of P-OH groups of the inorganic materials to

pyrophosphates ( $Zr_xCe_{1-x}$ ) $P_2O_7$ . The POH groups condensation found to superimpose with that of (ES) decomposition. Thermal decomposition was accompanied with four endothermic peaks. The total weight loss found to be equal to 25.973, 24.08, 26.26, and 26.16% in weight for composites (I-IV), respectively. From thermal and elemental

(C, H, N) analysis the resultant products were formulated as: ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>/(PANI)<sub>y</sub>·1.71H<sub>2</sub>O, ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>/(ES)<sub>y</sub>·1.28 H<sub>2</sub>O, ( $\gamma$ -ZrP<sub>0.34</sub>-CePf<sub>0.66</sub>/(ES)<sub>y</sub>·3.3 H<sub>2</sub>O and ( $\gamma$ -ZrP<sub>0.27</sub>-CePf<sub>0.73</sub>/(ES)<sub>y</sub>·3.37 H<sub>2</sub>O, where y= 18.30, 18.27, 12.91 and 11.25% in weight, respectively.

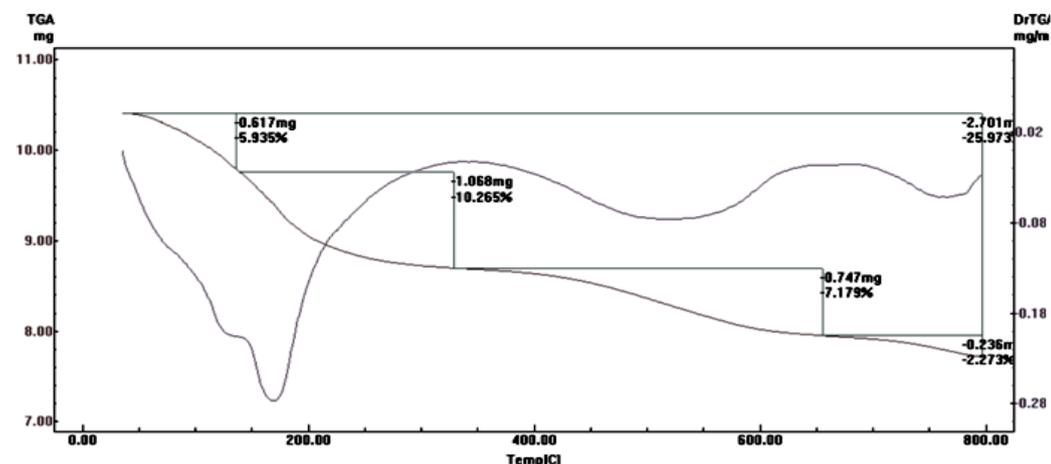


Figure 18. TG/DTA of nanocomposite (I)

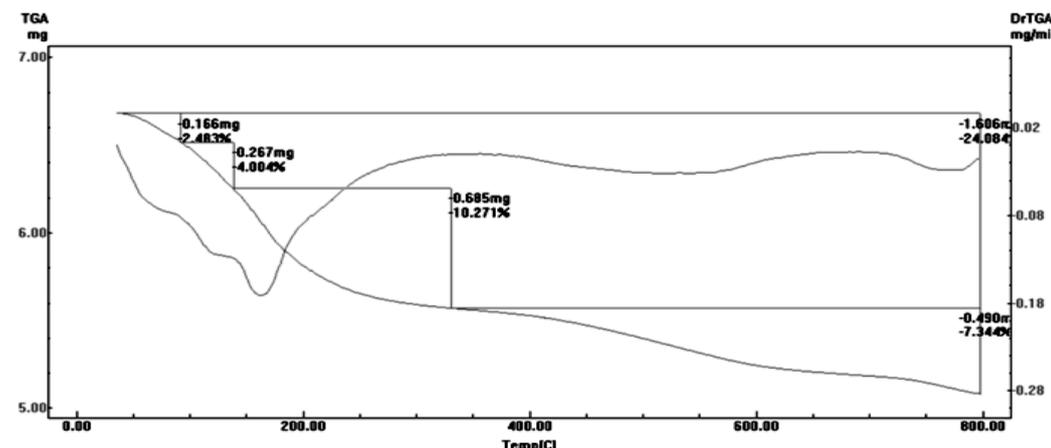


Figure 19. TG/DTA of nanocomposite (II)

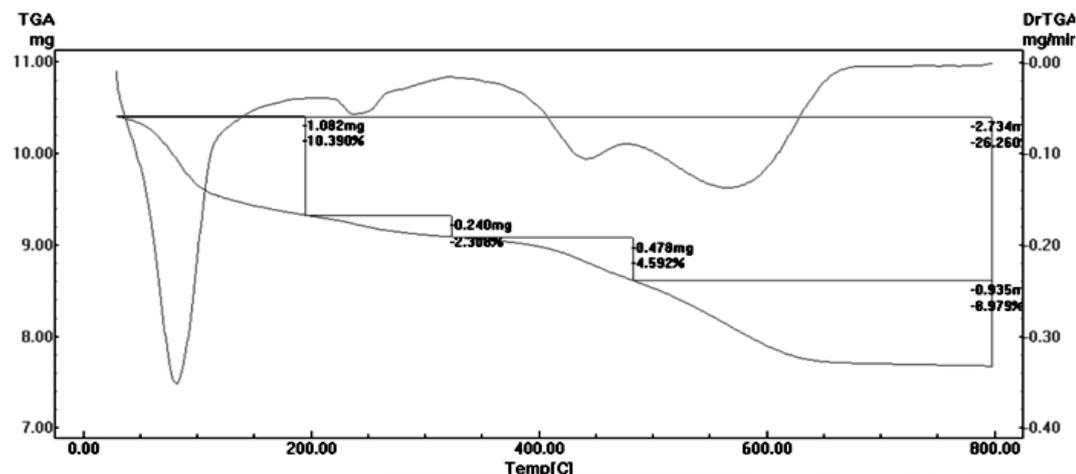


Figure 20. TG/DTA of nanocomposite (III)

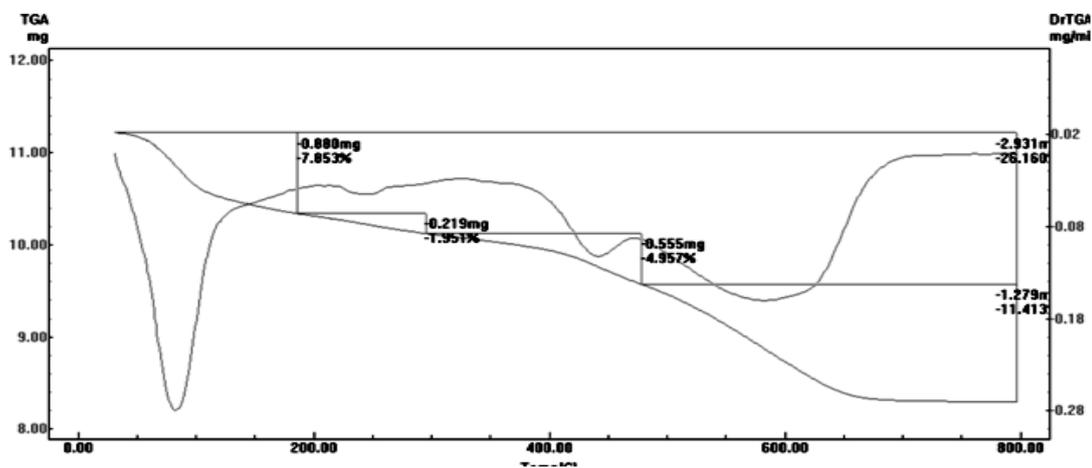


Figure 21. TG/DTA of nanocomposite (IV)

## 4. Conclusions

$\gamma$ -Zr<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and nanofibrous Ce(HPO<sub>4</sub>)<sub>2</sub>·2.9 H<sub>2</sub>O were prepared and characterized.

$[\gamma\text{-Zr}_2\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.34}[\text{Ce}(\text{HPO}_4)_2]_{0.66}\cdot 4.4 \text{ H}_2\text{O}$ , and  $[\gamma\text{-Zr}_2\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.27}[\text{Ce}(\text{HPO}_4)_2]_{0.73}\cdot 3.47 \text{ H}_2\text{O}$ , nano composite membranes were prepared and characterized. Novel ( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>)/emeraldine salt composites(I-IV), were prepared via in-situ chemical oxidation of the aniline to give (Composites I and II), with anilineHCl to give (composites II and IV), that was promoted by the reduction of Ce(IV) ions present in the inorganic matrix. The presence of Ce(IV) ions allows redox reactions necessary to oxidative polymerization to occur. The self-supported sheet integrity is preserved. This result is interesting because the shape integrity makes the building of molded conducting device possible. The formulation of the resultant composites was supported by thermal, elemental (C,H,N) analysis, FT-IR spectrum and SEM. The type of polyaniline composite and the degree of polymer loading found to be dependant on type of the monomer and of ( $\gamma$ -ZrP<sub>x</sub>-CePf<sub>1-x</sub>). emeraldine salt(PANI) is generally considered one of the most intriguing material for sensing devices due to its environmental stability, high conductivity. Thus by utilizing the beneficial properties of both  $\gamma$ -zirconium phosphate-cerium phosphate nanocomposite membranes and (PANI), their hybrid can be considered as novel conducting inorganic-organic composites, ion exchangers, solid acid catalyst, proton conductance and as sensors [60-62]. The color of the resultant composites(I-IV) are green, which was due to the formation of emeraldine salt. The self doping occurred on aniline polymerization, it may be due to presence of H<sup>+</sup> of (=POH)groups. However; doping was occurred, as expected, when anilineHCl was used. FT-IR spectra, CHN, TGA analysis and the changing in color support suggesting formulation of the resultant composites(I-IV).

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