American Journal of Chemistry 2014, 4(4): 109-115
DOI: 10.5923/j.chemistry.20140404.01

Synthesis and Characterization of Pellicular γ-Zirconium Phosphate Fibrous Cerium Phosphate Nanocomposite Membranes

S. K. Shakshooki*, S. R. EL-Tarhuni, A. M. EL-Hamady

Department of Chemistry, Faculty of Science, Tripoli University, Tripoli, Libya

Abstract Pellicular γ-zirconium phosphate, and nanosized fibrous cerium phosphate, γ-$Zr.PO_4(HPO_4).2H_2O$ (pγ-ZrP), $Ce(HPO_4)_2.2.9H_2O$ ($nCeP_f$), respectively, were prepared and characterized by chemical, thermogravimtricanalysi(TGA), Fourier Transform IR spectrometer(FT-IR), Scanning electron microscopy(SEM) and transmission electron microscopy (TEM). Pellicular γ-zirconium phosphate- fibrous cerium phosphate nanocomposite membranes were obtained by mixing slurry aqueous solution of pγ-ZrP and $nCeP_f$ at 45°C for 24h with stirring in wt/wt % ratio (67:33, 50:50 , 33:67 and 25:75 %, (pγ-ZrP:$nCeP_f$) respectively. The resultant composites found to be: $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.6}[Ce(HPO_4)_2]_{.0.4,}2.68H_2O$, $[\gamma\text{-}Zr.PO_4.H_2PO_4]_{0.51}$ $[Ce(HPO_4)_2]_{0.49}.3.56H_2O$, $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.34}[Ce(HPO_4)_2]_{0.66}.4.4H_2O$, $[\gamma\text{-}Zr.PO_4.H_2PO_4]_{0.27}$ $[Ce(HPO_4)_2]_{0.73}$. $3.47H_2O$, respectively.The resultant composites were homogeneous thin films with good mechanical texture and thermal stability.

Keywords Pellicular γ-zirconium phosphate, Fibrous cerium phosphate, Pellicular γ-zirconium phosphate-fibrous cerium phosphate nanocomposite membranes

1. Introduction

Metal phosphates chemistry recently has attracted attention in order to obtain materials with wide range of applications. Among these tetravalent metal phosphate which is very insoluble compounds. Other than amorphous [1], they exist in two dimensional (2-D) and three dimensional (3-D) structures [2].

Porous layered M^{IV} phosphates with α, θ and γ-structures [3-5], α-$M^{IV}(HPO_4)_2$. H_2O,θ-$M^{IV}(HPO_4)_2.5H_2O$ and γ-$M^{IV}.PO_4.H_2PO_4.2H_2O$, are well known compounds, (where M = Ti, Zr, Hf, Sn, Ce…..). These materials contain structural POH groups with labile protons and therefore potential conductance [6, 7], solid acid catalysts [8] and intercalates [9].

A number of organic membranes are available today. However, very little studies were carried out on inorganic membranes of tetravalent metals. Membranes consists of inorganic polymers such as membrane of M^{IV} phosphates are very attractive and could suitable for many processes of chemical technology such as waste disposal of metal ions, intercalates electrical conductance and solid acid catalysts.

* Corresponding author:
shakshooki2002@yahoo.com (S. K. Shakshooki)
Published online at http://journal.sapub.org/chemistry

Fibrous cerium phosphate has been reported [10]. Pellicular zirconium phosphate, $Zr(HPO_4)_2$. H_2O and pellicular hafnium phosphate, $Hf(HPO_4)_2$. H_2O were reported [11, 12]. The pellicular membranes are two dimensional (2-D) structure membranes.

In our laboratory we under taking systematic studies on different varieties of pellicular membranes with general formulae, $M^{IV}(HPO_4)_2$. H_2O [11, 13], $M^{IV}.PO_4.H_2PO_4.2H_2O$ [14] and $Zr_xTi_{(1-x)}(HPO_4)_2$. H_2O [15] that were prepared by different methods.

Recent years have seen upsurge interest in the study of inorganic solid-solid and inorganic solid-organic polymer composite materials. The resultant composite material usually does not have either characteristic of original materials and can be considered as materials with almost new physical and chemical properties [16].

Inorganic membranes-membrane composites are not recent invention, examples are SiO_2-TiO_2, SiO_2-ZrO_2, Pd-Al_2O_3, Pd thin filmdiposited on ceramic materials …etc [17, 18].

However, to date there are no reports about membrane-membrane composite materials of M^{IV} phosphates except the one reported by us [19] Here we are reporting the synthesis and characterization of novel pellicular γ-zirconium phosphate-fibrous cerium phosphate nanocomposite membranes.

2. Materials and Methods

Chemicals:

$ZrOCl_2.H_2O$, $CeSO_4.4H_2O$, H_3PO_4(85%) of BDH, HF (40%) of Reidel De-Haen. Other chemicals used were of analytical grade.

Instruments used for characterization

X-Ray powder diffractometer Siemens D-500, using Ni-filtered CuKα (λ = 1.54056Å), TG/DTA SIIExtra6000 TGA Perkin Elmerthermogravimetric analyzer(TGA)US, Fourier Transform IR spectrometer, model IFS 25 FTIR Bruker, Scanning electron microscopy (SEM) Jeol SMJ Sm 5610 LV, Transmission electron microscopy (TEM) Zeiss TEM 10CR, pH Meter WGW 52.

Preparation of fibrous cerium phosphate

100 ml 0.05M $CeSO_4.4H_2O$ in 0.5M H_2SO_4 were added drop wise to 100ml 6M H_3PO_4 at 80°C with stirring. The stirring was continued at that temperature for 4h. The resultant product was dispersed in 2 litre distilled water with stirring for 1h. Then subjected to washing by distilled water up to pH~3.5, then kept in 2 liter distilled water to be, as such, in slurry aqueous form.

Preparation of pellicular γ- zirconium phosphate membrane

γ-zirconium phosphate monoammonium form , γ-$Zr.PO_4.NH_4HPO_4$, was obtained by reacting 50ml of $ZrOCl_2.H_2O$ (1.3M in 8M HF) with 450ml of 2M $NH_4H_2PO_4$ in Pyrex round flask at 80°C with stirring for 24h. The resultant product was filtered washed with distilled water up to pH~3, filtered and air dried. The ammonium form was converted to hydrogen form using 1MHCl with vigorous stirring at 15°C for 24h. Flexible thin films, the pellicular γ-$Zr.PO_4.H_2PO_4.2H_2O$ (pγ-ZrP) membrane. The minor product (~10%) found to be crystalline γ-zirconium phosphate. (for every 2g ofγ-$Zr.PO_4.NH_4HPO_4$ 400ml 1M HCl were required).

Preparation of pellicular γ- zirconium phosphate-fibrous cerium phosphate nanocomposite membranes

Slurry aqueous solution of 0.3g of pellicular γ-zirconium phosphate (pγ-ZrP) in 150ml distilled water was added t gradually to slurry aqueous solution of 0.3g fibrous cerium in300ml distilled water at 45°C, with stirring , the stirring was continued after complete addition and at 45°C for 24h. The resulted product was filtered on filter paper using Buchnner funnel , washed with distilled water (50ml) twice then left to dry in air, the resulted product was homogeneous a thin films, with $[\gamma\text{-}Zr.PO_4.H_2PO_4]_{0.51}[Ce(HPO_4)_2]_{0.49}.3.56H_2O$.

In similar manner, using the above experimental parameters, composite pellicular γ-zirconium phosphate-fibrous cerium phosphate membranes: $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.6}[Ce(HPO_4)_2]_{.0.4,}2.68H_2O$, $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.34}$ $[Ce(HPO_4)_2]_{0.66}.4.4H_2O$ and $[\gamma\text{-}Zr.PO_4.H_2PO_4]_{0.27}[Ce(HPO_4)_2]_{0.73}.3.47H_2O$, were obtained by mixing slurry aqueous solution in wt/wt % ratio, 60:40, 33:67 and 25:75 of pγ-ZrP:$nCeP_f$, where the mixing weights ratio are 0.15g:0.1g, 0.15:0.3g and 0.1:0.3g, respectively. After complete mixing of the above slurry aqueous solutions, at 45°C the resultant products were filtered on filter paper using Buckner funnel, washed with distilled water and dried in air. They were homogeneous flexible thin films.

3. Results and Discussion

Nanosized cerium phosphate membrane, $Ce(HPO_4)_2.2,9H_2O(nCeP_f)$,was prepared and characterized by chemical, XRD, thermal analysis FT-IR, SEM and TEM.

X-ray diffractogram (XRD) of fibrous cerium phosphate membrane is shown in Figure 1 with d_{001}= 10.85Å.

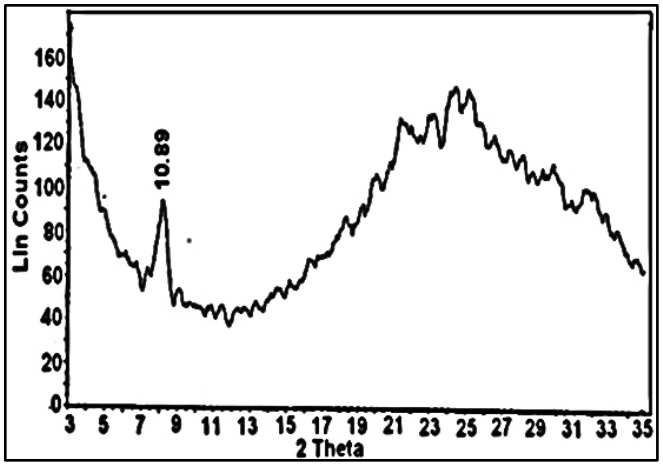

Figure 1. XRD of fibrous cerium phosphate

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 $CeP_2O_{7,}$ 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%.

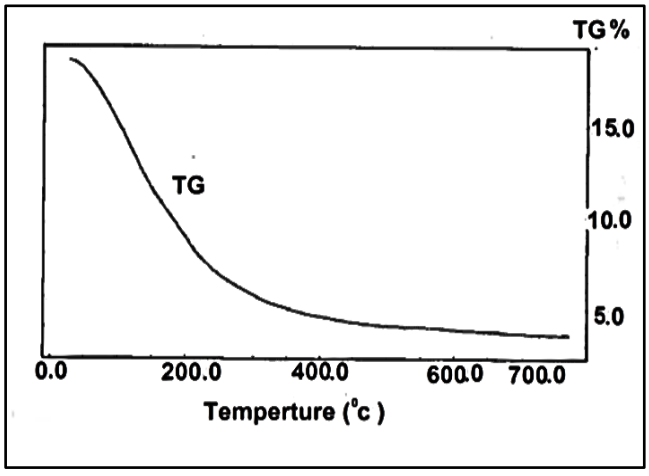

Figure 2. TG of fibrous cerium phosphate

Figure 3 shows its FT-IR spectra, with a trend similar to the IR spectra of M(IV)phosphates. Broad band centered at 3350cm^{-1} is due to OH groups symmetric-asymmetric

stretching of H_2O, small sharp band at 1628cm^{-1} is due to H-O-H bending, sharp broad band centered at 1045cm^{-1} is related to phosphate groups vibration.

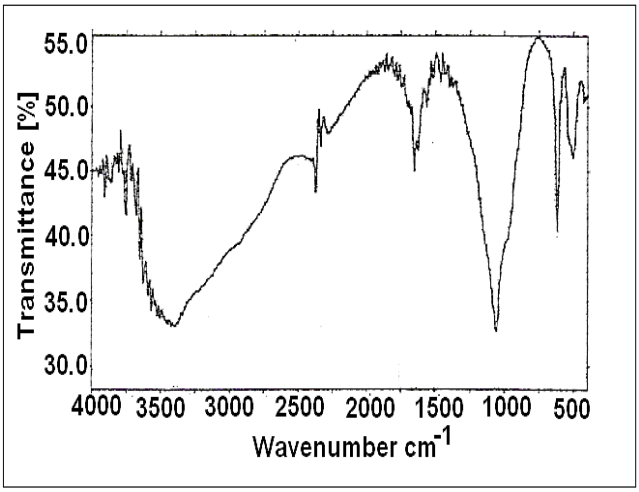

Figure 3. FT-IR spectrum of fibrous cerium Phosphate

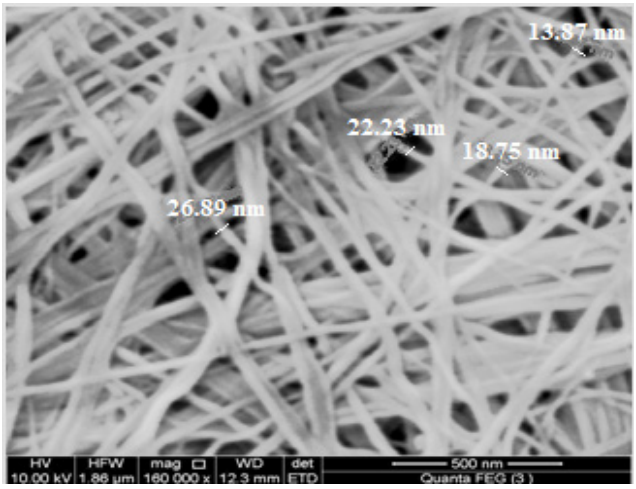

Figure 4. SEM image of fibrous cerium phosphate

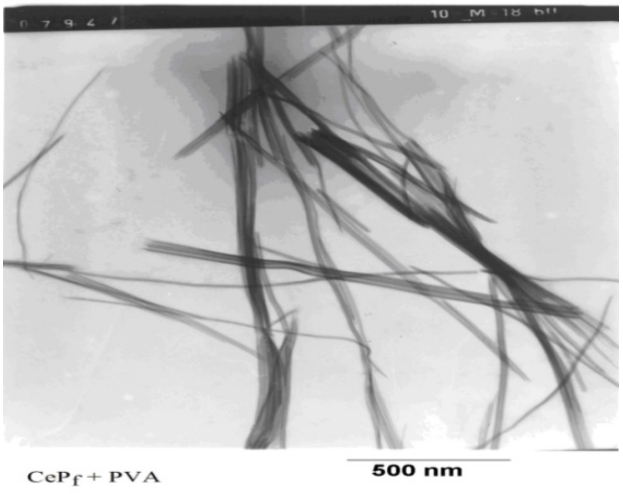

Figure 5. TEM image of fibrous cerium phosphate

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

TEM image of the nanosized fibro us cerium phosphate (in polyvinyl alcohol) is shown Figure 5. The photograph shows its average size is ~15nm.

The ion exchange capacity of fibrouscerium phosphate found to be equal to 5.21 meq/g.

Pellicular γ-zirconium phosphate membrane was prepared from protonation of monoammonium form of γ-zirconium phosphate with 1MHCl at 15°C.

Figure 6 shows the Its X-ray diffractogram (XRD), γ-$Zr.PO_4.H_2PO_4.2H_2O$, its d_{001}= 12.25Å.

Its thermogram is given in figure 7. The thermal decomposition found to occur in three steps. The loss of water of hydration, two moles of water of hydration are lost at ~100°C. At higher temperature a two stages condensation of POH groups occurs. The first is accompanied by loss of water at ~370°C and yield $Ze_3(HPO_4)_2(P_2O_7)_2$. The second loss occurs between 500-700°C resulting in formation of ZrP_2O_7 as final product. So the total loss are 3 molecules of water per unit formula.

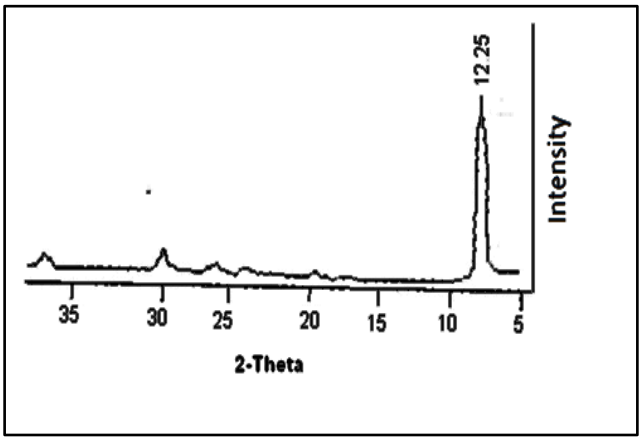

Figure 6. XRD of pellicular γ-zirconium phosphate, showsiso-oriented structure of its crystalline form

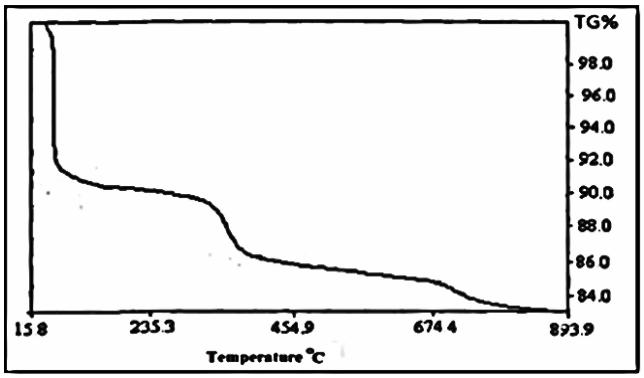

Figure 7. TG of γ-zirconium phosphate

Its FT-IR spectra is shown in Figure 8. Broad band at 3560cm^{-1} is due to symmetric-asymmetric stretching of OH groups, small sharp band at 1335cm^{-1} is related to H-O-H bending and broad sharp band centered at 1025cm^{-1} corresponds to phosphate groups vibration.

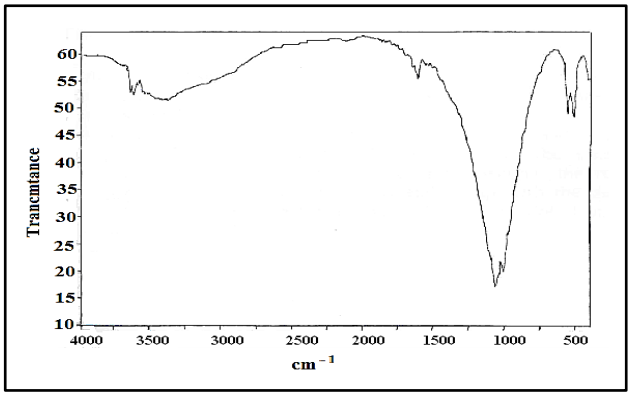

Figure 8. FT-IR spectrum of pellicular γ-zirconium phosphate

TEM image of pellicular γ-zirconium phosphate (dispersed in polyvinylalcohol in form of thin film) is shown in Figure 9. The photograph shows its average size is in the nanosized scale.

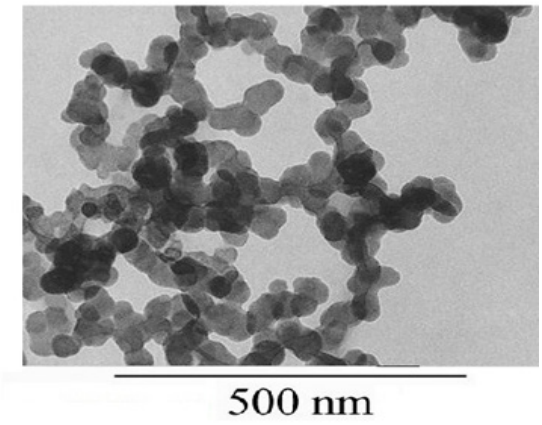

Figure 9. TEM image of γ-zirconium phosphate

Composites of pellicular γ-zirconium phosphate-fibrouscerium phosphate membranes

Mixing slurry aqueous solution of pellicular γ-zirconium phosphate with slurry aqueous solution of fibrous cerium phosphate in wt/wt% mixing ratios 60:40 , 50:50, 33:67 and 25:75% , results in the formation of composite membranes:

$[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.6}[Ce(HPO_4)_2]._{0.4}\ 2.68._{.}H_2O$, $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.51}[Ce(HPO_4)_2._{.}]_{0.49}.\ 2.\ 56H_2O$,

$[\gamma\text{-}Zr.PO_4.H_2PO_4]_{0.34}[Ce(HPO_4)_2]_{0.66}.4.4H_2O$ and $[\gamma\text{-}Zr.PO_4.H_2PO_4]_{0.27}[Ce(HPO_4)]_{0.73},3.47H_2O$, respectively, They were designated as composite compounds**(I-IV)**, 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 pγ-ZrP and $nCeP_{f.}$

Metal(IV)phosphate 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 $[\gamma\text{-}Zr.PO_4.H_2PO_4.nH_2O]_x$ $[Ce(HPO_4)_2.nH_2O]_{1-x}$ is $[Zr_xCe_{1-x}]P_2O_7$, where x, 1-x represents their original mixing of wt/wt% ratios, respectively.

Figure 10 shows the x-ray diffractogram of the composite compound**(I)** with dspacing reflections at11.85Å and 11.01Å which are characteristic of the composite, with higher intensity peak at 11.85Å, the predominate pγ-ZrP content of the composite material, as expected.

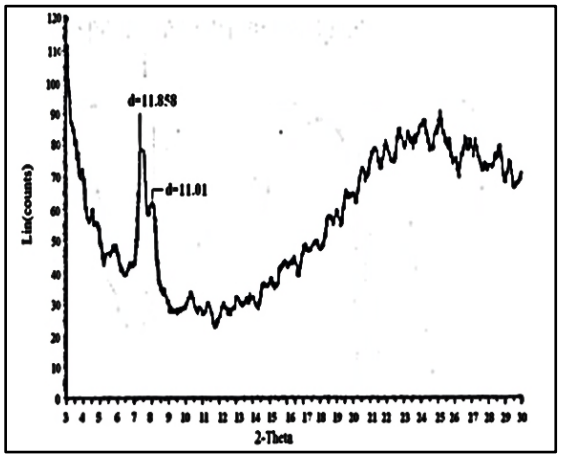

Figure 10. XRD of $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.6}[Ce(HPO_4)_2]._{0.4}2.68H_2O$

Thermal analysis of all the composite products were carried out between ~20-750°C. Thermogram of composite compound **(I)** is shown in Figure 11. The thermal decomposition occurs in two steps, loss of hydration water that occur between 70-220°C, followed by second stage, the POH groups condensation. The final product was $(Zr_{0.60}Ce_{0.40})P_2O_7$. The total weight loss is equal to 19.1%.

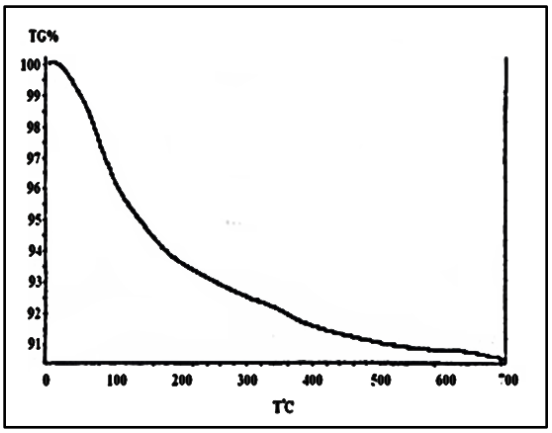

Figure 11. TG of $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.6}[Ce(HPO_4)_2]._{0.4}2.68H_2O$

The infrared spectra of every composite compounds **(I-IV)**, 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 $3425cm^{-1}$ due to OH groups symmetric-asymmetric stretching, small sharp band at $1665cm^{-1}$is related to H-O-H bending, sharp broad band centered at $1090cm^{-1}$ corresponds to phosphate groups vibration.

XRD pattern of the composite **(II)** is shown in Figure 13 with d spacing reflections at 12.1Å and 11.18 Å.

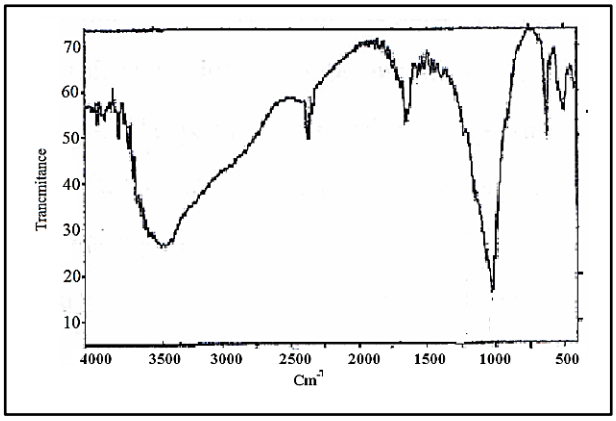

Figure 12. FT-IR spectra of $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.6}[Ce(HPO_4)_2]_{.\ 0.4,2.68}.H_2O$

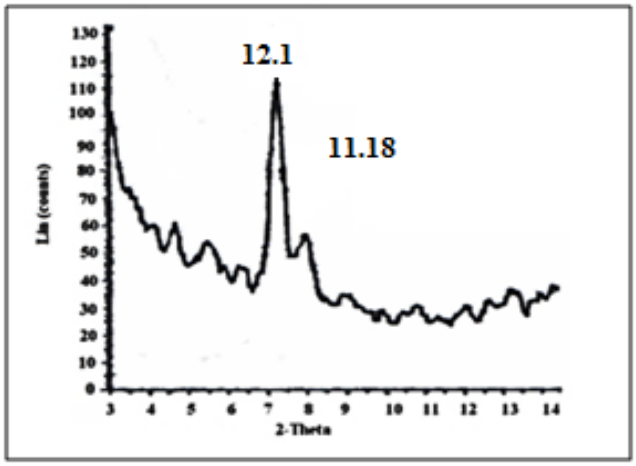

Figure 13. XRD of $[\gamma\text{-}Zr.PO_4.H_2PO_4.]_{0.51}[Ce(HPO_4)_2.]_{0.49}.\ 3.56H_2O$

Figure 14 shows the thermogram curve of the composite **(II)**, thermal decomposition occure in three steps, the loss of hydration water at temperature between ~70-230°C followed by POH groups condensation, with total weight loss equal to 22.12%. the final product was $[Zr_{0.51}Ce_{0.49}]P_2O_7$.

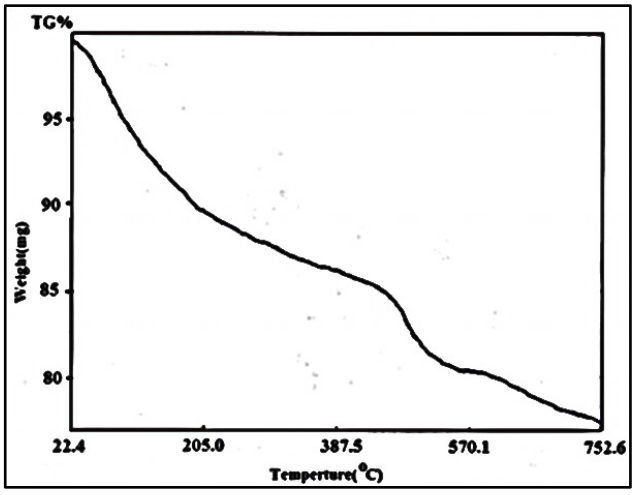

Figure 14. TG of $[\gamma\text{-}Zr.PO_4.H_2PO_4.\ ]_{0.51}[Ce(HPO_4)_2.\ ]_{0.49}.\ 3.56H_2O$

XRD pattern of the composite **(III)** is shown in figure (15) with d spacing reflections at 12.043Å and 10.858 Å, which corresponds x-ray pattern pellicular γ-zirconium phosphate and to that of fibrous cerium phosphate, repectively. Typical XRD pattern that expected for such types of composite membranes.

Its thermogram is shown in figure (16). 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 $[Zr_{0.34}Ce_{0.66}]P_2O_7$, the total weight loss found to be equal to 24.66%.

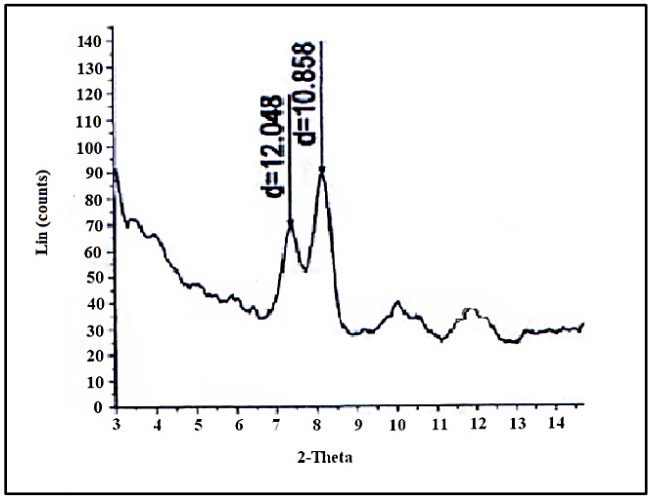

Figure 15. XRD of $[\gamma\text{-}Zr.PO_4.H_2PO_4.\ ]_{0.34}[Ce(HPO_4)_2\ ]_{0.66}.\ 4.4\ H_2O$

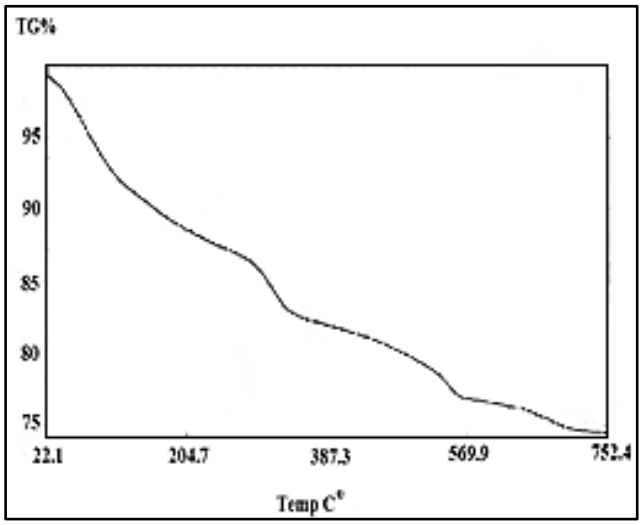

Figure 16. TG of $[\gamma\text{-}Zr.PO_4.H_2PO_4.1.4H_2O]_{0.34}\,[Ce(HPO_4)_2\ ]_{0.66}\ .\ 4.4\ H_2O$

XRD pattern of the composite **(IV)** is shown in Figure 17 with d spacing reflections at 12.20Åand 10.90Å. Which corresponds x-ray pattern pellicular γ-zirconium phosphate and to that of fibrous cerium phosphate, respectively.

Its thermogram curve is shown in Figure 18. 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 the total weight loss found to be equal to $[Zr_{0.27}Ce_{0.73}]P_2O_7$, 21.11%.

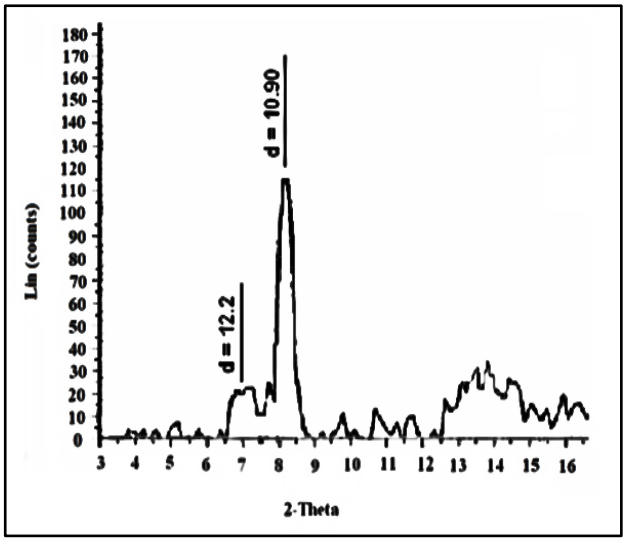

Figure17. XRD of $[\gamma\text{-}Zr.PO_4.H_2PO_4]_{0.27}[Ce(HPO_4)]_{0.73},3.47H_2O$

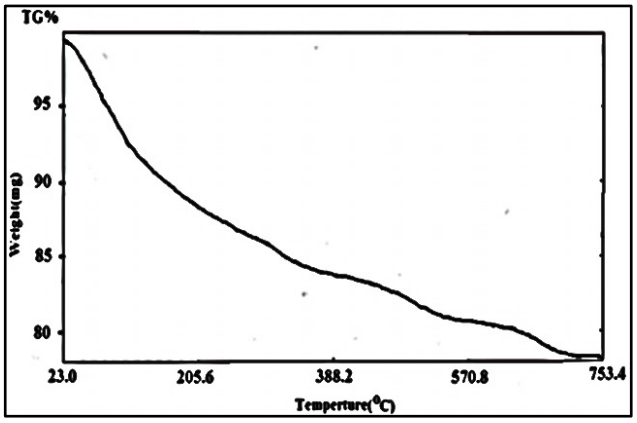

Figure 18. TG of $[\gamma\text{- }Zr.PO_4.H_2PO_4.\ ]_{0.27}[Ce(HPO_4)_2]_{0.73}3.47H_2O$

The information obtained from x-ray, thermal analysis and FT-IR spectra support the formulation of the resultant composite materials **(I-IV)**.

4. Conclusions

Pellicular γ-zirconium phosphate, and nanosized fibrous cerium phosphate, $\gamma\text{-}Zr.PO_4\ (HPO_4).2H_2O$ (pγ-ZrP), $Ce(HPO_4)_2.\ 3H_2O$ ($nCeP_f$), respectively, were prepared and characterized.

The study shows that metal(IV)phosphate nano composite 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 tailored made inorganic membrane-membrane composites, 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 spectra of their original materials. These novel composite membranes can be considered for potential applications as solid acid catalysts, inorganic ion exchangers intercalates and as proton conductance materials.

AKNOWLEGEMENTS

To Department of Chemistry, Faculty of Science, Tripoli University, for providing facilities for this research, and to Geol. Adel Bayuomi, Institute of Mineral Resources, Cairo, Egypt for providing facilities for TGA, SEM and TEM analysis.

REFERENCES

[1] Shakshooki S.K, Naqvi N, Kowaleczyk J.K, Khalil S, Rais M and Taris. F, 1988, Effect of composition of ion exchange properties of amorphous zirconium- titanium phosphates, Reactive Polymer, 7, 221.

[2] Clearfield, A., Inorganic Ion Exchange Materials, Bocca Raton, CRC Press, FL. USA,1982.

[3] Shakshooki, S.K., Azzabi, O.H., Khalil, S., Kowalczyk, J. and Naqvi, N., 1988, Crystalline mixed hafnium-titanium phosphates, Reactive Polymers, 17, 191-196.

[4] Alberti, G., Bernasconi, M.G., Costantino, U. and Gill, G.S.,1977, Ion exchange of trivalent cations on zirconium phosphate with large interlayer distance, J. Chromatog., 132, 177.

[5] Clearfield, A., 1993, Ion exchange and adsorption in layered phosphates, Mater, Chem. and Phys., 35, 257-263.

[6] Shakshook, S.K., Khalifa, M.M. and El-Mashri, S.M., 2001, Thermal behavior, FT-IR and ionic conductance of granular zirconium phosphate and mixed zirconium titanium phosphates, Sohag Bulletin of Pure and Applied Sci., 1, 15.

[7] Alberti, G., Casciola, M., Captani, D., Donnadio, A., Narducci, R., Pica, M. and Sganappa, M.N., 1977, Novel nafion-zirconium phosphate composite membranes with enhanced stability of proton conductivity, Electrochemica Acta, 52, 8125.

[8] Vecchio, S., Di-Rocco, R. and Ferragina,C., 2007, Intercalation compounds of γ-zirconium and γ-titanium phosphates 1,10- phenantroline copper complex materials, Themochimica acta, 453, 105-112.

[9] Diaz, A., Saxena, V., Gunzalez, J., David, A., Casanas, B., Carpenter, C., Batteas, J.D., Colon, J., Clearfield, A. and Hussain, M.D., 2012, Zirconium phosphate nano-platelets: a novel platform for drug delivery in cancer therapy , Chem Commun., 48,1754.

[10] Alberti, G. and Costantino, U., 1974, Recent progress in the field of synthetic inorganic exchanger having a layered and fibrous structure, J. Chromatogr., 102,5.

[11] Alberti .G, Costantino. U, and Casciola. M, 1985, Pellicular zirconium phosphate, J. Coll. Interface. Sci, 107, 256-260.

[12] Shakshooki. S. K, Preparation of pellicular hafnium

phosphate, PM-35-0,6thsymposium on ion exchange, Balaton lake, Hungry, September 1990.

[13] Shakahooki. S. K, El-Azzabi.O. H, Turki .F. M, El-Akari. F.A, Abodlal. R. S, and El-Tarhuni. S. R, 2012, FT-IR and thermal behavior of θ-typezirconium- and hafnium Phosphates and their pellicular membranes, Egypt J. Anal. Chem., 21, 45-56.

[14] Shakshooki .S.K, Mokthar. R, Idris. R, Morghom .L.O and Hanash. H. B, Preparation of pellicular γ-zirconium phosphate-phosphite, γ-hafnium phosphateand their phosphate-phosohites, Patenet Lb.95/94, Industrial Research Centre, Tripoli, Libya, 1994.

[15] Shakshooki S.K, El-Agaili H.B, Formation of pellicles membranes of mixed zirconium-titanium phosphate via exfoliation with flouro benzene on their parent crystalline layered materials, 1stConf. on Recent Developments in Chemistry, proceedings, pp 80-95,Sebha, Libya, November 2006.

[16] Oyama. S.T. and Williams.S.M..S, Edt(r), Inorganic polymeric and composite membranes, Elsevier vol.14, 2011.

[17] Lin. S.k. and Burggraaf. A.J., 1991, Preparation and characterizationof high temperature thermal stablealumina composite membrane S, J.A.Chem.Soc.,140, 361.

[18] Zhang. S.S, Xu. K. and Jow T.R., 2005, composite membrane as separator of Li-ion batteries, J.of Power Source, 140, 361.

[19] Shakshooki S.K., A. M. Elhamassi and N. M. Etorki, 2012, Novel composites of alpha-type zirconium phosphate-phosphite-fibrous cerium phosphate membranes, Sohag Bulletin of Pure and Applied Science, 14, 159.