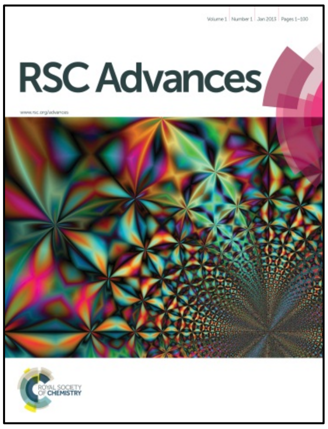
RSC Advances

A comparative study for the characterization of polyaniline based nanocomposites and membrane properties

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-02-2014-001040.R2
Article Type:	Paper
Date Submitted by the Author:	14-Mar-2014
Complete List of Authors:	Shahadat, md; A.M.U, Aligarh, Chemistry; universiti Sains Malaysia, School of Industrial Technology, U.S.M., malaysia Bushra, Rani; Aligarh Muslim University, Aligarh, Chemistry Khan, Md.; Aligarh Muslim University, Aligarh, Chemistry Rafatullah, Mohd; Division of Environmental Technology,, School of Industrial Technology,

RSC Advances

An international journal to further the chemical sciences



RSC Advances is an international, peer-reviewed, online journal covering all of the chemical sciences, including interdisciplinary fields.

The **criteria for publication** are that the experimental and/ or theoretical **work must be high quality, well conducted adding to the development of the field**.

RSC Advances* has a 2012 partial impact factor of 2.56

Thank you for your assistance in evaluating this manuscript.

Guidelines to the referees

Referees have the responsibility to treat the manuscript as confidential. Please be aware of our Ethical Guidelines, which contain full information on the responsibilities of referees and authors, and our Refereeing Procedure and Policy.

It is essential that all research work reported in *RSC Advances* is well-carried out and well-characterised. There should be enough supporting evidence for the claims made in the manuscript.

When preparing your report, please:

- comment on the originality and scientific reliability of the work;
- comment on the characterisation of the compounds/materials reported - has this has been accurately interpreted and does it support the conclusions of the work;
- state clearly whether you would like to see the article accepted or rejected and give detailed comments (with references, as appropriate) that will both help the Editor to make a decision on the article and the authors to improve it.

Please inform the Editor if:

- there is a conflict of interest
- there is a significant part of the work which you are not able to referee with confidence
- the work, or a significant part of the work, has previously been published
- you believe the work, or a significant part of the work, is currently submitted elsewhere
- the work represents part of an unduly fragmented investigation.

For further information about *RSC Advances*, please visit: www.rsc.org/advances or contact us by email: advances@rsc.org.

*Data based on 2012 Journal Citation Reports®, (Thomson Reuters, 2013).

Dear Dr Suzanne Howson MRSC
Publishing Editor,
Reply to reviewer's comments on the Manuscript ID RA-ART-02-2014-001040.R1

Dear Professor,

Thank you very much for your mail regarding above manuscript along with the reviewers comments, questions as well as suggestions. We are really appreciated for the insightful comments from anonymous reviewers, which are believed to improve the quality of the manuscript considerably. We have tried our best efforts to revise the manuscript as per their suggestions and guidelines. The changes done in the manuscript are marked by the green text. The replies to the referee comments are given below:

Referee: 2

Comments to the Author

In my opinion, the article has considerably improved its quality in the present form. I think it can be accepted for publication. I only have some minor comments:

1. Despite the fact that the procedure presented for the synthesis of composite membranes could imply an interesting advance in the field, I am not sure about the possibility of using the membranes to detect K+, since the difference in transport numbers and effective fixed charge densities between K+ and Na+ are very low. Moreover, could this slight difference has more to do with the mobilities of the ions itself rather than with the selectivity of the membranes?

Answer: We agreed with the comments. In future we will try to synthesize the materials that show large difference in transport numbers and effective fixed charge densities among different cations.

2. Line 141, page 6: In my opinion "That's why..." seems to informal for a scientific paper.

Answer: Modified sentence has been mentioned (Line 141-142, page 6)

With these clarifications I hope the present manuscript is now suitable for publication in your esteemed journal.

Yours Sincerely
Prof. Tjoon Tow Teng

Division of Environmental Technology,
School of Industrial Technology,
Universiti Sains Malaysia,
11800 Penang, Malaysia
Email address: mdshahadat93@gmail.com

A comparative study for the characterization of polyaniline based nanocomposites and membrane properties

Mohammad Shahadat[1], Rani Bushra[2], Md. Ramir Khan[2], Mohd. Rafatullah[1], Tjoon Tow Teng [*1]

[1]Division of Environmental Technology, School of Industrial Technology,
Universiti Sains Malaysia, 11800 Penang, Malaysia
[2]Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

Abstract

Polyaniline (PANI) based novel nanocomposites have been fabricated by using a simple sol-gel method. The experimental conditions including mixing volume ratio of reactants, pH and temperature were established for their synthesis. For the comparative studies, characterizations were performed by using FTIR, TGA, SEM, TEM and XRD analyses. The structural studies expose amorphous and semi-crystalline nature with the particle size in nano range. PANI supported nanocomposites exhibit improved conducting behavior, higher ion uptake capacity along with chemical and thermal stability. Membrane potentials of monovalent electrolytes namely KCl, NaCl and LiCl have been studied at different concentrations to examine the relationship between effective fixed charge density and transport properties of the membrane. Present study revealed that among Li^+, K^+ and Na^+ ions, PANI-Zr(IV)sulphosalicylate nanocomposite membrane shows more cation-selective behaviour towards K^+ ions. Effective fixed charge densities were found to follow the order $K^+ > Na^+ > Li^+$.

Key word: *Synthesis, characterization, nanocomposite, thermal and chemical stability, membrane properties.*

Corresponding authors; mdshahadat93@gmail.com, (T.T. Teng)

1.0 Introduction

Polyaniline (PANI) is one of the potential conducting polymers owing to its simple preparation, excellent environmental stability.[1-4] Recently PANI based nanostructures such as nanofibre, nanowire, nanotubes have established great interest because of their successful applications in diverse fields.[5-10] In addition, PANI nanoparticles can be synthesized either by chemically or electrochemically through the polymerization or self assemble process.[11, 12] However, there are some drawbacks associated with pure PANI due to its intractable nature as it is usually obtained as an insoluble powder and electrochemically thin brittle film.[13] To overcome limitations and improve the performance of the conducting polymer, organic-inorganic hybrid material was synthesized by the reaction of organic polymer (PANI) with inorganic precipitate. The conjugation of inorganic precipitate with organic polymer improves the performance of both the 'host' and the 'guest' thereby leads to interesting physical and chemical properties. In this regard, a number of investigations concerning the development of the techniques for the incorporating of nanoparticles into the matrix of PANI have been published.[14-19] These composite materials possess interesting physical and chemical properties and showed interesting applications in diverse fields.[20-26] PANI based organic-inorganic composites materials (PANI-Ti(IV)arsenate, PANI-Ti(IV)tungstate and PANI-Zr(IV)S) have been successfully used as ion exchangers, conducting materials and photocatalyst as reported earlier.[27-30] To apply these composite materials in diverse field work was continued and it was found that these materials can also be effectively used as an ion selective electrode membrane. A number of papers related to PANI based membrane electrodes have been published however, no work associated with membrane properties of PANI-Zr(IV)S nanocomposite has not been reported yet. The present work reports a comparative study for the characterizations of PANI based organic-inorganic composite materials and their ion selective membrane potential. The ion exchange and transport properties of composite materials in the form of membrane have also been explored. The electric potential of the composite membrane, in contact with different monovalent electrolyte solutions, has been measured to evaluate the thermodynamically effective fixed charge density by means of different proposed approaches.[31-34] The experimental values of potential have also been used to calculate the mobility ratio, transport numbers of counter-ions and permselectivity of the polystyrene blended hybrid membrane.

2.0. Experimental

2.1. Materials and Methods

All reagents and chemicals were of analytical grade and used without any treatment. The main reagents for the synthesis: aniline, potassium persulphate, sodium tungstateand, 5-Sulphosalicylic acid and zirconium(IV)oxychloride were procured from Loba Cheme Pvt. Ltd. Titanium tetrachloride, carbon tetrachloride and sodium arsenate were from CDH, India. For the characterization of all three nanocomposites the instruments such as pH meter, Fourier Transform-IR Spectrometer, Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA), X' Pert PRO analytical diffractometer, Scanning Electron Microscope (SEM; LEO, 435 VF), Transmission Electron Microscopy (TEM) Jeol H-7500 Microscope, temperature controlled shaker and Muffle furnace were used as described in previous paper.[35] A digital potentiometer model 118 (Electronics India) was employed for measuring the membrane potential.

2.2.0. Synthesis of PANI and inorganic precipitates

The synthesis of PANI and inorganic precipitates of Ti(IV)arsenate, Ti(IV)tungstate and Zr(IV)sulphosalicylate were carried out by using the sol gel method as described in previous reported paper.[27] An inorganic precipitate of Ti(IV)arsenate was prepared by the mixing solutions of titanium tetrachloride (0.1M) and sodium arsenate (0.25M) gradually with constant stirring at 25±2°C for 1h whereby gel type slurries were obtained. The pH of the solution was maintained by adding dilute solution of HCl or HNO_3. The resulting white precipitate so formed was kept overnight in the mother liquor for digestion. For the synthesis of Ti(IV)tungstate and Zr(IV)sulphosalicylate, the similar method was applied as mentioned above except the change in concentration of zirconium oxychloride (0.25M) and 5-sulphosalicylic acid (0.5 M). The resulting white precipitate (of each solution) was kept overnight in the mother liquor for digestion. After decanting off the supernatant liquid, the remaining precipitate was washed with demineralized water to remove any excess reagent.

2.2.1. Synthesis of PANI-Ti(IV)arsenate, PANI-Ti(IV)tungstate and PANI-Zr(IV)sulphosalicylate composite materials

Each composite material was prepared by adding gel of PANI individually to each inorganic precipitate in a volume ratio of 1:1, by mixing thoroughly with continuous stirring for 1 h at 25±2°C. The resultant green gel obtained was kept for 24 h at room temperature for digestion. The supernatant liquid was decanted and the gel was filtered under suction. The excess acid was removed by washing with DMW and each sample of material was dried in an oven at 50±2°C. The dried material was ground into small granules, sieved and converted into H^+ form by treating with 1M nitric acid solution for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess of acid was removed after several washings with DMW and finally the granules of composite materials were dried at 50±2°C. Thus, under varying conditions of mixing ratio, pH and temperature, various samples of each composite material were synthesized (as shown in supplementary Tables (S-1, S-2 and S-3)). Among the synthesized samples of composite materials, on the basis of optimum ion uptake capacity, physical appearance of the beads and percentage yield, three samples were selected (as shown in Table 1) that were used for exhaustive studies. The comparative studies of composite materials were carried out in terms of characterization, ion exchange capacity and electrical conductivity. The ion exchange capacity and electrical conductivity of selected samples were determine by using same method as described in reported paper.[36,37] Among all samples of Table 1, the sample that showed higher ion exchange capacity and electrical conductivity was chosen for the measurement of membrane potential in detail.

2.2.2. Fabrication of hybrid membranes

The composite precipitates were powdered and sieved through 200 meshes (Granule size < 0.07 mm). To improve the stability of the membrane, polystyrene has been used as a binder as its cross-linked rigid framework provides adequate adhesion to the molecules of composite which accounts for the high mechanical stability to the membrane over other binders like polyvinyl chloride (PVC), cellulose acetate, etc. Pure crystalline polystyrene was also ground to fine powder and sieved through 200 meshes. The precipitates were then mixed with granulated polystyrene with the help of a pestle and mortar to get ion-exchange membranes[38] having a varying percentage (by mass) of polystyrene (15-35%). The thicknesses of the membranes were found to be 0.08 cm when it is applied with a pressure of 146 M.Pa. The membranes having 25% polystyrene were only selected for electrochemical studies because the membranes containing less or more than 25% polystyrene was found to be mechanically less stable.

2.4. Measurement of potential

The freshly prepared inorganic-organic nanocomposite membrane was cemented in a Pyrex glass tube cell having two compartments in which a saturated calomel electrode was placed for measuring the membrane potential. The schematic diagram of the constructed electrochemical cell of the above type is shown in **Fig. 1**.[39] The monovalent electrolytes of concentrations c_1 and c_2 in both the compartments of the cell, where the ratio $\gamma (= c_2 / c_1)$ is fixed at 10, were vigorously stirred by a magnetic stirrer to minimize the effects of boundary layers on the membrane potential (mV ± 0.5). The experiment was conducted at room temperature and atmospheric pressure.

3. Results and Discussion

3.1 Synthesis

All nanocomposite materials were prepared by employing a very simple sol-gel chemical route. The optimum conditions for the synthesis of all three composite materials have been shown in supplementary Tables (S-1, -S2 and S-3). Among all three samples, PANI-Zr(IV)S (sample V_3) showed higher ion exchange capacity and electrical conductivity (Table 1). The higher ion uptake capacity and electrical conductivity of this material is due to the existence of more number of ionogenic groups as compared to PANI-Ti(IV)W and PANI-Ti(IV)As. On the basis of higher ion exchange capacity and electrical conductivity, PANI-Zr(IV)S nanocomposite was selected for the measurement of membrane potential.

3.2. Characterization

To identify the presence of functional groups in all materials FTIR studies were carried out at room temperature (25±2°C). The appended FTIR spectra of the composite materials are shown in **Fig. S-1**. In all the spectra a strong extensive band in the range 3550 to 3000 cm^{-1} corresponds to the presence of hydroxyl groups.[40] A broadband in the region (1600 to 1630) cm^{-1} is ascribed to aquo H–O–H bending and C–C in plane stretching. The peaks near 1442 cm^{-1} correspond to the presence of considerable amounts of polyaniline while the peaks at 1385, 1136 and 614 cm^{-1} are recognized as in plane bending vibration of the -CH bands.[41] In each spectrum, a band close to 500 cm^{-1} may be due to the presence of metal oxide stretching. In the spectrum of PANI Ti(IV)W, the peak at 1013 cm^{-1} is owing to vibration of O=W=O bond.[42] More intense bands at 811 cm^{-1} may be due to stretching vibration of Ti–O–W bond. The spectrum of PANI Ti(IV)As, show a medium intensity broad band at 871 cm^{-1} is assigned to □ (As–O–Ti) vibration.[43] In the spectrum of PANI Ti(IV)S two sharp bands at 1160 and 1030 cm^{-1} are attributed to the SO_3 asymmetric and symmetric stretching vibrations of sulphonic acid salts, respectively.[44]

In order to get an idea concerning thermal stability of all composite materials, the TGA analyses were performed **(Fig. S-2)**. All spectra show a continuous weight loss of mass (4, 25 and 10%, respectively) up to 100ºC.[45] The weight loss (4, 7 and 6%, respectively) from 100ºC to 200ºC is by the condensation of -OH groups. Further, weight loss (1, 1 and 6%, respectively 4.3%) from 300° to 500°C may be due to complete decomposition of the organic part of the materials. A gradual decrease in weight loss beyond 500°C may be due to the formation of metal oxide. TGA analysis studied shows that among all three materials, PANI-Ti(IV)W was found to be more thermally stable, due to the presence of tungsten metal which has a high melting point.

X-ray diffraction patterns of PANI-Ti(IV)W and PANI-Ti(IV)As **(Fig. S-3)** show no sharp peaks of high intensity which suggests amorphous nature while the spectra of PANI-Zr(IV)S demonstrate some weak intensity peaks which indicate slight crystalline character. SEM image **(Fig. S-4)** also confirms the amorphous nature of PANI-Ti(IV)W and PANI-Ti(IV)As and semicrystalline morphology of PANI-Zr(IV)S. TEM studies of each composite material **(Fig. S-5)** show particles size is in the range of 20-50 nm. To investigate the surface morphology, thickness, homogeneity, pore structure and cracks of nanocomposite PANI-Zr(IV)S membrane, SEM with EDEX studies were performed. SEM images **(Fig. 2A, B)** demonstrate the uniform distribution of organic and inorganic substrates on the surface without any cracks with 2 µm surface thickness. In addition, SEM images do not show translucent characteristics which indicate heterogeneous nature of the composite membrane.[46]

The existence of cavities on the surface of membrane (**Fig. 2A**) suggests the porous nature of membrane on which Li^+, Na^+ and K^+ ions can be easily adsorbed resulting ion selective nature of the membrane. The cross section photograph of nanocomposite membrane together with EDEX spectrum and weight percentage of membrane elements are shown in **Fig. 2** (**BCD**).

3.3 Measurements of membrane transport potential

For the transport properties of the composite membrane, membrane potential values have been measured. When electrolyte solutions (KCl, NaCl and LiCl) of different concentrations are separated by a membrane, an electrical potential difference develops across the membrane due to the development of charge on the membrane surface which is because of the diffusion of oppositely charged ions through it with different mobilities. This charge imparts some important electrochemical properties of the membrane, the most important being the differences in the permeabilities of co-ions, counter ions and neutral molecules. The quantity of charge required to generate the potential is small, especially when dilute solutions are used. Membrane potential has been measured for the composite membranes equilibrated with various monovalent electrolyte solutions of concentrations ranging between 1 and 0.007mol/dm^3. The membrane potential, ψ_m data obtained with the composite membrane using different electrolytes are plotted as a function of $1/c_1$ (**Fig. 3A**). The magnitude of the membrane potential is dependent on many factors such as the applied pressure at the membrane preparation stage, concentration of electrolyte solutions used, the counter-ion to co-ion mobility ratio, the exchange characteristics of the membrane material for various cations. It was observed that the hybrid membrane prepared at higher applied pressure exhibited higher membrane potential for a fixed c_2/c_1. The values of membrane potentials observed across the membrane in contact with various monovalent electrolytes show the potential order to be $K^+ > Na^+ > Li^+$.

It was observed that during the experiment, the membrane potential increased with time up to a maximum value and then decreased gradually. Such variation was also reported by other workers.[47] The time taken for the attainment of maximum potential is found to be concentration dependent, more time being required for concentrated solution, and it differs with different electrolytes. Membrane potential has been regarded as a measure of membrane selectivity for a long time. The measurement of ion activity by means of a membrane electrode is most successful in the concentration range over which the membrane behaves as ideally permselective and obeys the Nernst equation. An ideally permselective membrane is one in which the permeability for co-ions is negligible as compared to that for counter-ions.

The deviation from Nernstian behavior is due to the co-ion transference[48] and the dependence of the exchange of cations between the solution and the membrane phase and on the electrolyte concentration. The values in **Fig. 3A** show that the potential values increase with decrease in concentration of all the tested electrolyte solutions and are of the order of positive mV indicating that the membrane is negatively charged i.e. cation selective. The selectivity increases with a decrease in the concentration because of the structural changes occurring in the electrical double layer at the membrane-solution interface[49]. The increase in selectivity with dilution is also supported by the increasing value of the counter-ion transport numbers, t_+ **(Table 2)**.

When an ionic gradient is maintained by using two solutions of different concentrations of same electrolyte on both sides of the membrane, the mobile species infiltrate the membrane at different magnitudes inducing various transport phenomena into the system, including the development of potential across it. The influence is greater in case of counter-ions than in the co-ions. The ratio of the molar mobilities of the cation and anion

'u_+/u_-' is defined as the mobility ratio ($\overline{\omega}$) of the membrane. The values of the mobility ratio calculated for the composite membrane are also represented in **Table 2**. The values of $\overline{\omega}$ in the membrane phase were found increasing with decrease in concentration for all the monovalent electrolytes used (KCl, NaCl and LiCl). The high mobility is attributed to a higher transport number of comparatively free cations as compared to the anion of electrolytes.

When a negatively charged membrane is imposed between two solutions of a monovalent electrolyte of unequal concentrations c_1 and c_2 ($c_2>c_1$), the observed membrane potential, ψ_m is related with electrolyte concentration by the following equation:[31, 33]

$$-\psi_m = \frac{RT}{F}\left(\frac{\gamma}{\gamma-1}\right)\left(\frac{\phi X}{2}\right)\frac{1}{c_1} \qquad (1)$$

Here, ϕX is the effective fixed charge density of the negatively charged membrane. Eqn. (1) Indicates that the plot of ψ_m against $1/c_1$ will be linear **(Fig. 3A)** with a slope equal to $\frac{RT}{F}\left(\frac{\gamma}{\gamma-1}\right)\left(\frac{\phi X}{2}\right)$ from which the values of ϕX for different electrolytes have been evaluated. The calculated values are represented in **Table 3**.

Another widely accepted approach to calculate the fixed charge density was derived by Kobatake *et al.* [32,33] who suggested that when two solutions of an electrolyte of different concentrations c_1 and c_2 are separated by a membrane, the inverse of the apparent transport number of the anion, t_{-app} in a high salt concentration range could be expressed by the following equation:

$$\frac{1}{t_{-app}} = \frac{1}{1-\alpha} + \frac{\alpha(\gamma-1)}{(1-\alpha)\gamma\ln\gamma}\left(\frac{\theta\overline{X_c}}{c_1}\right) \qquad (2)$$

Here, α is the ratio of molar mobility of cation to the sum of molar mobilities of cation and anion, $\theta\overline{X_c}$ is the effective fixed charge density of the membranes under investigation and c_1 (in mol/dm^3) the concentration of the monovalent electrolyte in the lower concentration side of the cell.

The apparent transport number of the anion t_{-app} is defined by the Nernst equation:

$$\psi_m = (RT/F)(1-2t_{-app})\ln\frac{c_2}{c_1} \qquad (3)$$

Eqn. (2) indicates that the values of α and $\theta\overline{X_c}$ can be evaluated by using the values of intercept $(\frac{1}{1-\alpha})$ and slope $(\frac{\alpha(\gamma-1)}{(1-\alpha)\gamma\ln\gamma}\theta\overline{X_c})$ from the linear plot of $1/t_{-app}$ against $1/c_1$ **(Fig. 3B)**. The calculated values of the fixed charge densities $\theta\overline{X_c}$ of the polystyrene blended calcium tungstate composite membrane are also given in **Table 3**. The fixed charge density of the hybrid membrane under different electrolytic environments is found to be in the order KCl > NaCl > LiCl. The data in **Table 3** show that the fixed charge density is highest for KCl and lowest in the case of LiCl for the same electrolytic concentration, indicating that the composite membrane shows higher cation selectivity towards K^+ ions. The same result has also been explained in terms of counter-ion transport numbers.

4. Conclusions

PANI based nanocomposite materials have been successfully synthesized by using a simple sol-gel route. XRD and SEM analysis revealed that PANI-Ti(IV)W and PANI-Ti(IV)As showed amorphous while PANI-Zr(IV)S demonstrated semi crystalline nature. The particle size of each material was found to be in the range of 20-50 nm by TEM analysis. Thermally and chemically stable materials covered semiconductor range together with good ion uptake capacity and can be used as an ion exchanger as well as conducting materials. Among three materials, PANI-Zr(IV)S demonstrated higher ion exchange capacity together with electrical conductivity. The results of transport properties of the composite membrane indicate that the fixed charge density values were in the order KCl > NaCl > LiCl and the membrane was found to be selective for K^+ ions. Membrane transport results indicate that besides behaving as ion exchanger, conducting material, photocatalyst and antimicrobial agent, PANI-Zr(IV)sulphosalicylate can also be successfully used as an ion selective membrane for the detection of K^+ ions.

Acknowledgment

One of the authors (Mohammad Shahadat) is grateful to the Universiti Sains Malaysia, for providing assistance under the post doctoral scheme for this work

References

[1]S.K. Dhawan, D. Kumar, M.K. Ram, S. Chandra, D.C. Trivedi, Sens. Actuators B., 1997, 40, 99.

[2] A.G. MacDiarmid, Synth. Met., 1997, 84, 27.

[3] N. Gospodinova, L. Terlemezyan, Prog. Polym. Sci., 1998, 23, 1443.

[4] D. Xie, Y. Jing, W. Pan, D. Li, Z. Wu, Y. Li, Sens. Actuators B, 2002, 81, 158.

[5] J. Janata, M. Josowicz, Nat. Mater., 2003, 2, 19.

[6] X.P. Chen, C.A. Yuan, C.K.Y. Wong, H. Ye, S.Y.Y. Leung, G.Q. Zhang, Sens. Actuators B, 2012, 174, 210.

[7]X.P. Chen, C.K.Y. Wong, C.A. Yuan, G.Q. Zhang, Sens. Actuators B 175 (2012) 15.

[8]A. Olad, R. Nabavi, J. Hazard. Mater., 2007, 147, 845.

[9]D. Shao, C. Chen, X. Wang, Chem. Eng. J., 2012, 185-186, 144.

[10] D.S. Dhawale, D.P. Dubal, V.S. Jamadade, R.R. Salunkhe, C.D. Lokhande, Synth. Met., 2010, 160, 519.

[11] Z. Wei, Z. Zhang, M. Wan, Langmuir, 2002, 18, 917.

[12] L.M. Huang, Z.B, Wang, H.T, Wang, X.L. Cheng, A. Mitra, Y.X. Yan, J. Mater. Chem., 2002, 12, 388.

[13] H.S.O. Chan, S.C. Ng, W.S. Sim, K.L. Tan, B.T.G. Tan, Macromolecules, 1992, 25, 6029.

[14] Y. Yin, C. Liu, B. Wang, S. Yua, K. Chen, Dalton Trans., 2013, 42, 7233.

[15] M.R. Karim, K.T. Lim, M.S. Lee, K. Kim, J.H. Yeum, Synt. Met., 2009, 159, 209.

[16] L. Zhang, P. Liu, Z. Su, Polym. Degrad. Stabil., 2006, 91, 2213.

[17] Z. Liu, W. Guo, D. Fu, W. Chen, Synth. Met., 2006, 156, 414.

[18] J. Li, L. Zhu, Y. Wu, Y. Harima, A. Zhang, H. Tang, Polymer, 2006, 47, 7361.

[19] R. Bushra, Md. Shahadat, S.A. Nabi, A.S. Raeissi, M. Oves, K. Umar, M. Muneer, S.A. Nabi, A. Ahmad, J. Hazard. Mater., 2014, 264, 481.

[20] O.M. Vatutsina, V.S. Soldatov, V.I. Sokolova, J. Johann, M. Bissen, A. Weissenbacher, Funct. Polym., 2007, 67, 184.

[21] Y. Li, Y. Yu, L. Wu, J. Zhi, Appl. Surf. Sci., 2013, 273, 135.

[22] S.A. Nabi, Md. Shahadat, R. Bushra, A.H. Shalla, F. Ahmed, Chem. Eng. J., 2010, 165, 405.

[23] O. Arrad, Y. Sasson, J. Org. Chem., 1989, 54, 4993.

[24] A.A. Khan, Innamuddin, Sens. Actuators B, 2006, 120, 10.

[25] A.A. Khan, U. Baig, Sens. Actuators B, 2013, 177, 1089.

[26] N.K. Raman, M.T. Anderson, C.J. Brinker, Chem. Mater., 1996, 8, 1682.

[27] Md. Shahadat, S.A. Nabi, R.Bushra, A.S. Raeissi, K. Umar, M.O. Ansari, RSC Advances 2012, 2, 7207.

[28] S.A. Nabi, Md. Shahadat, Rani Bushra, M. Oves, F. Ahmed Chem. Eng. J., 2011, 173, 706.

[29] S.A. Nabi, Md. Shahadat, Rani Bushra, A.H. Shalla, A. Azam, Colloids Surf. B., 2011, 87, 122.

[30] S.A. Nabi, Md. Shahadat, Rani Bushra, A.H. Shalla, Chem. Eng., 2011, J. 175, 8.

[31] M. Tasaka, N. Aoki, Y. Kondo, and M. Nagasawa, J. Phys. Chem., 1975, 79, 1307.

[32] M. Nagasawa and Y. Kobatake, J. Phys. Chem., 1952, 56, 1017.

[33] Y. Kobatake, H. Fujita, J. Phys. Chem., 1968, 72, 2871.

[34] N. Kamo, M. Oikawa, and Y. Kobatake, J. Phys. Chem., 1993, 77, 92.

[35] S.A. Nabi, Md. Shahadat, R. Bushra, A.H. Shalla, F. Ahmed, Chem. Eng. J., 2010, 165, 405.

[36] S. A. Nabi, R. Bushra, Md. Shahadat, A.S. Raeissi, *Desalination*, 2012, 289, 1.

[37] M.C. Marti-Calatayud, M. Garcia-Gabaldon, V. Perez-Herranza, S. Sales, S. Mestre, Ceram. Int., 2013, 39, 4045.

[38] F. Jabeen, Rafiuddin, J. Porous Mater., 2009, 16, 257.

[39] J.H. Choi, S.H. Moon, J. Colloid Interface Sci., 265, 93.

[40] C.N.R. Rao, Chemical Application of Infrared spectroscopy, Academic Press. New York 1963, p. 355.

[41] R.M. Silverstein., G.C. Bassler., T.C. Morrill, Spectrometric identification of organic compounds, John Wiley and Sons. New York 1981 4th ed, Ch. 3, p.111.

[42] A. Medinaa, J.L. Solis, J. Rodriguez, W. Estrada, Sol. Energy Mater. Sol. Cells., 2003, 80, 473.

[43] M. Zhang, G. He, G. Pan, J. Colloid Interface Sci., 2009, 338, 284.

[44] G. Socretes, Infrared Characteristic Group Frequencies, John Wily & Sons, New York, 1980, p. 115.

[45] C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam 1963, p. 315.

[46] M.Y. Kariduraganavar, R.K. Nagarale, A.A. Kittur, S.S. Kulkarni, Desalination, 2006, 197, 225.

[47] M.J.D. Brand, G.A. Rechnitz, Anal. Chem., 1970, 42, 304.

[48] F.G. Helfferich, Ion Exchange, Dover Publication, New York, 1962.

[49] R.W. Baker, Membrane technology and Applications, John Wiley & Sons Ltd. Ch. 10.

Table 1: Selected samples of PANI based nanocomposite materials at 25±2ºC (pH= 1.0).

S.No	Composite materials	Colour	IEC (meq g^{-1}) for Na^+ ions	Conductivity (S cm^{-1})
V_1	PANI Ti(IV)W	Green granules	0.85	0.168
V_2	PANI Ti(IV)As	Green granules	1.37	0.178
V_3	PANI Zr(IV)S	Green granules	1.80	0.278

Ion exchange Capacity (IEC)

Table 2: Calculated values of transport number (t_+) and mobility ratio ($\overline{\omega}$) of the nanocomposite membrane from the measured membrane potential values with various monovalent electrolytes at different concentrations with $c_2/c_1 = 10$ at an applied pressure 146 MPa at 25 ± 1 °C.

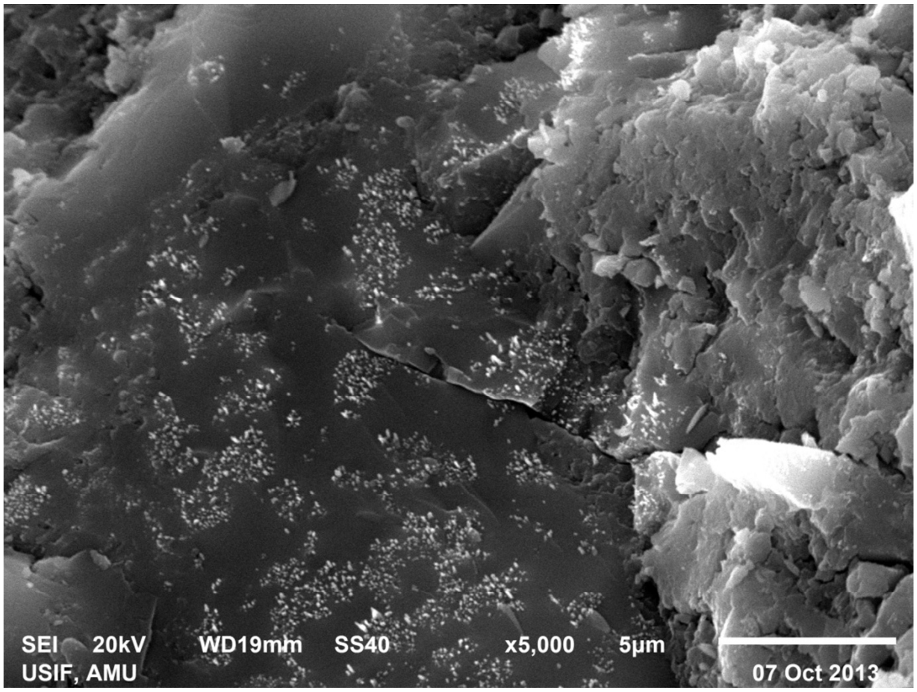
Electrolyte	c_2 (mol/dm^3)	t_+	$\overline{\omega}$
	1	0.628	1.6893
	0.7	0.641	1.7870
KCl	0.5	0.656	1.9103
	0.25	0.682	2.1492
	0.1	0.778	3.5050
	0.07	0.848	5.5588
	1	0.609	1.5550
	0.7	0.617	1.6130
NaCl	0.5	0.630	1.7051
	0.25	0.661	1.9475
	0.1	0.754	3.0672
	0.07	0.826	4.7409
	1	0.602	1.5131
	0.7	0.613	1.5836
LiCl	0.5	0.617	1.6130
	0.25	0.652	1.8739
	0.1	0.739	2.8304
	0.07	0.804	4.1044

Table 3: Comparison of the values of the effective fixed charge densities, calculated from different methods, of the nanocomposite membrane in contact with different electrolytes.

Electrolyte	**KCl**	**NaCl**	**LiCl**
ϕX ©	0.0126	0.0125	0.0108
$\theta \overline{X_c}$ @	0.0165	0.0161	0.0138

© from the slope of **Fig. 7A** with **Eqn. (1)**.

@ from the slope of **Fig. 7B** with **Eqn. (2)**.



SEM image of PANI-Zr(IV)S nanocomposite membrane

Figure captions:

Fig. 1 Schematic diagram for the measurement of membrane potential.

Fig. 2 SEM images of nanocomposite membrane. Surface image (A), cross sectional image (B), EDAX spectrum (C) and percentage content (D) of PANI-Zr(IV)S nanocomposite membrane.

Fig. 3 Plots of (A) potential values, ψ_m and (B) $1/t_{-app}$ against $1/c_1$ of polystyrene based composite membrane for different monovalent electrolytes.

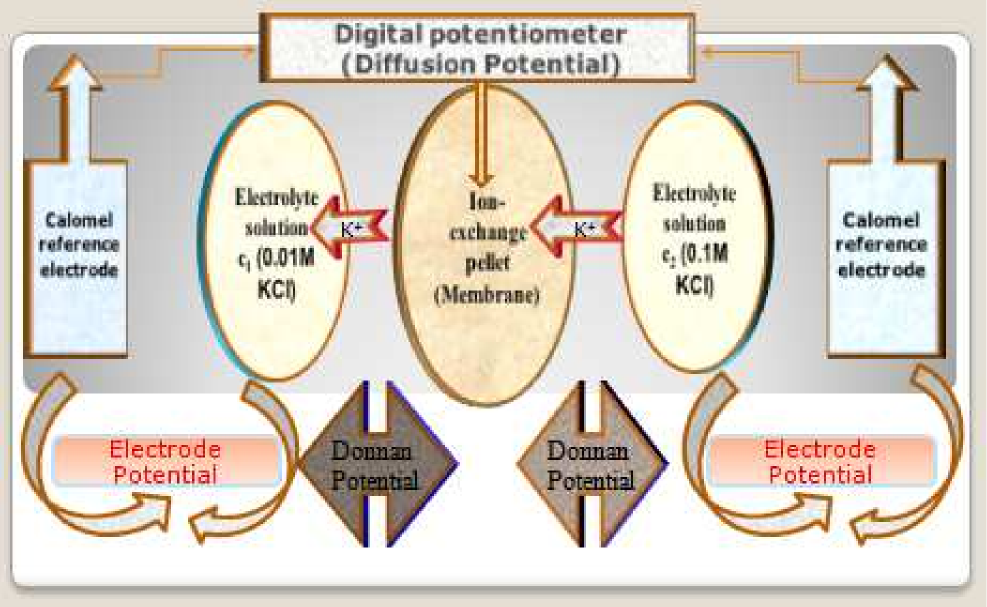


Fig. 1

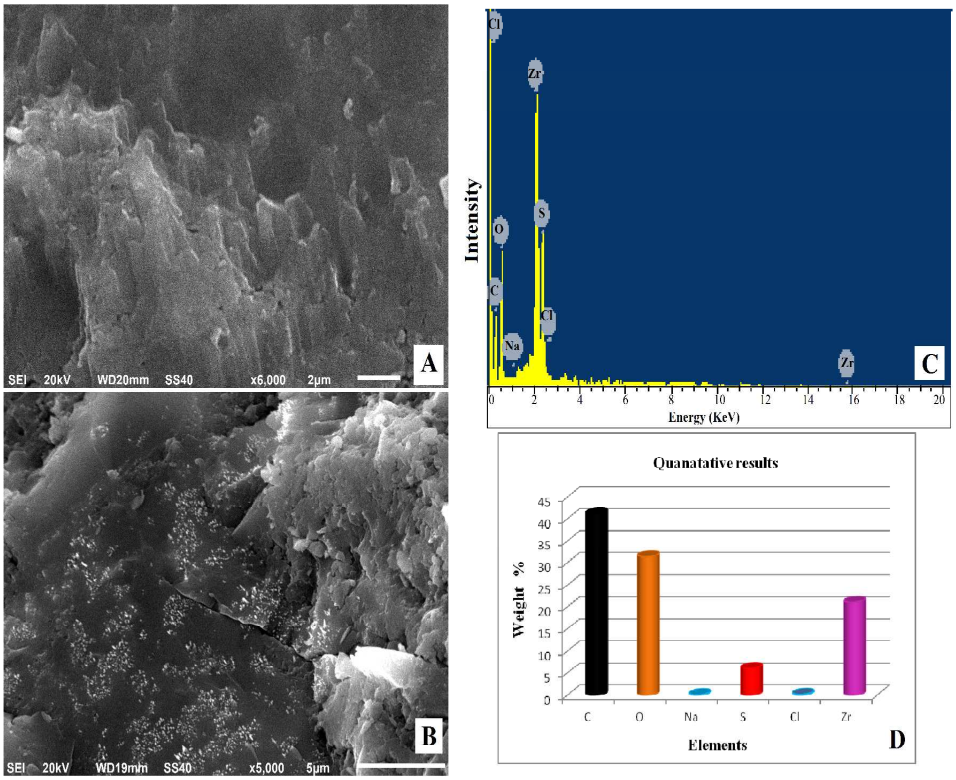

SEI 20kV WD20mm SS40 x6,000 2µm
A
SEI 20kV WD19mm SS40 x5,000 5µm
B
Cl
Zr
S
O
C
Cl
Na
Zr
C
Intensity
0
2
4
6
8
10
12
14
16
18
20
Energy (KeV)
Quanatative results
45
40
35
30
25
20
15
10
5
0
Weight %
C
O
Na
S
Cl
Zr
Elements
D

Fig. 2 (ABCD)

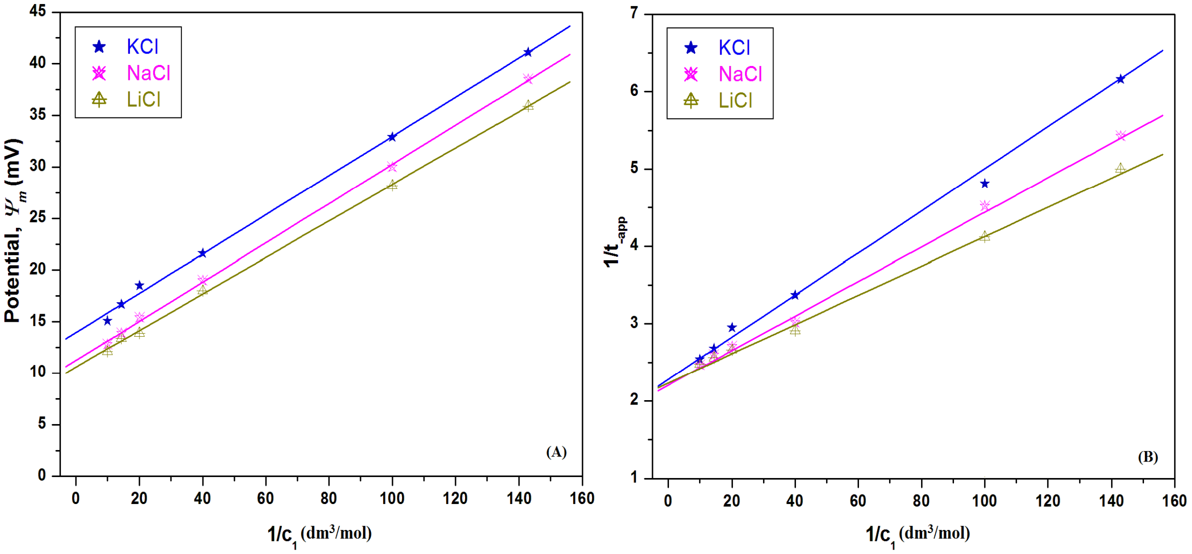

Potential, Ψ_m (mV)
1/c$_1$ (dm^3/mol)
KCl
NaCl
LiCl
(A)
0
5
10
15
20
25
30
35
40
45
0
20
40
60
80
100
120
140
160
1/t$_{-app}$
1/c$_1$ (dm^3/mol)
KCl
NaCl
LiCl
(B)
1
2
3
4
5
6
7
0
20
40
60
80
100
120
140
160

Fig. 3 (A, B)

Supporting Information

A comparative study for the characterization of polyaniline based nanocomposites and membrane properties

Mohammad Shahadat[1], Rani Bushra[2], Md. Ramir Khan[2], Mohd. Rafatullah[1], Tjoon Tow Teng *[1]

[1]Division of Environmental Technology, School of Industrial Technology,
Universiti Sains Malaysia, 11800 Penang, Malaysia

[2]Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

Table S-1 Conditions for the synthesis of PANI-Ti(IV)W cation exchanger.

S.No	A	B	C (%) v/v	Mixing ratio v/v/v	Temperature (°C)	pH	Appearance of bead	IEC for Na^+	Yield (g)
T-1	0.25	0.1	--	1:1	25±2	0.5	White granular	0.25	1.68
T-2	0.25	0.1	--	1:1	25±2	1.0	White granular	0.60	1.96
T-3	0.25	0.1	--	1:1	100±2	1.0	White granular	0.40	1.85
T-4	0.25	0.1	10	1:1	25±2	1.5	Green granular	0.35	2.95
T-5	0.25	0.1	10	1:1:1	25±2	0.5	Green granular	0.65	2.33
T-6	0.25	0.1	10	1:1:1	25±2	1.0	Green granular	0.85	2.99
T-7	0.25	0.1	10	1:1:1	100±2	1.0	Green granular	0.70	3.00
T-8	0.25	0.1	10	1:1:1	25±2	1.5	White granular	0.55	3.25

Sodium tungstate (Mol L-1), B. Titanium tetrachloride (Mol L-1), C. (stock solution of 10 % PANI), IEC. Ion Exchange Capacity (meq g–1)

TablesS-2 Conditions for the synthesis of PANI-Ti(IV)As cation exchanger.

S.No	A	B	C (%) v/v	Mixing ratio v/v/v	Temperature (ºC)	pH	Appearance of bead	IEC for Na^+ ions	Yield (g)
A-1	0.25	0.1	--	1:1	25±2	0.5	White granular	0.75	1.62
A-2	0.20	0.1	--	1:1	25±2	1.0	White granular	0.99	1.96
A-3	0.25	0.1	--	1:1	100	1.0	White granular	0.70	2.01
A-4	0.25	0.1	--	1:1	25±2	1.5	Green granular	1.00	2.90
A-5	0.25	0.1	10	1:1:1	25±2	0.5	Green granular	1.10	2.30
A-6	0.25	0.1	10	1:1:1	25±2	1.0	Green granular	1.37	3.99
A-7	0.25	0.1	10	1:1:1	100	1.0	Green granular	1.00	3.30
A-8	0.25	0.1	10	1:1:1	25±2	1.5	White granular	0.90	3.45

A. Sodium arsenate (Mol L-1), B. Titanium tetrachloride (Mol L-1), C. (stock solution of 10 % PANI), IEC. Ion Exchange Capacity (meq g–1)

Table S-3 Conditions for the synthesis of nanocomposite PANI-Zr(IV)sulphosalicylate cation exchanger at 25± 2 ºC.

S. No	A	B	C (%)	Mixing ratio v/v/v	pH	Appearance of bead	IEC for Na^+ ions	Yield (g)
S-1	0.25	0.5	--	1:1	0.5	White granular	---	----
S-2	0.25	0.5	--	1:1	1.0	White granular	1.05	2.46
S-3	0.25	0.5	--	1:1	1.5	White granular	0.70	2.50
S-4	0.25	0.5	10	1:1:1	0.5	Green granular	1.25	2.54
S-5	0.25	0.5	10	1:1:1	1.0	Green granular	1.80	3.54
S-6	0.25	0.5	10	1:1:1.5	1.0	Green granular	1.24	2.94
S-7	0.25	0.5	10	1:1:1	1.5	Green granular	1.20	3.90
S-8	0.25	0.5	12	1:1:1	1.0	Light green granular	1.54	2.90
S-9	0.25	0.5	15	1:1:1	1.0	Dark green granular	1.40	2.98

A. Zirconium oxychloride (Mol L-1), B. Sulphosalicylate (Mol L-1), C. (stock solution of 10 % PANI), IEC. Ion Exchange Capacity (meq g–1)

Figure captions:

Fig. S-1 FTIR spectra of nanocomposite materials.

Fig. S-2 TGA curves of nanocomposite materials.

Fig. S-3 Powder XRD patterns of nanocomposite materials.

Fig. S-4 SEM images of nanocomposite materials.

Fig. S-5 TEM images nanocomposite materials.

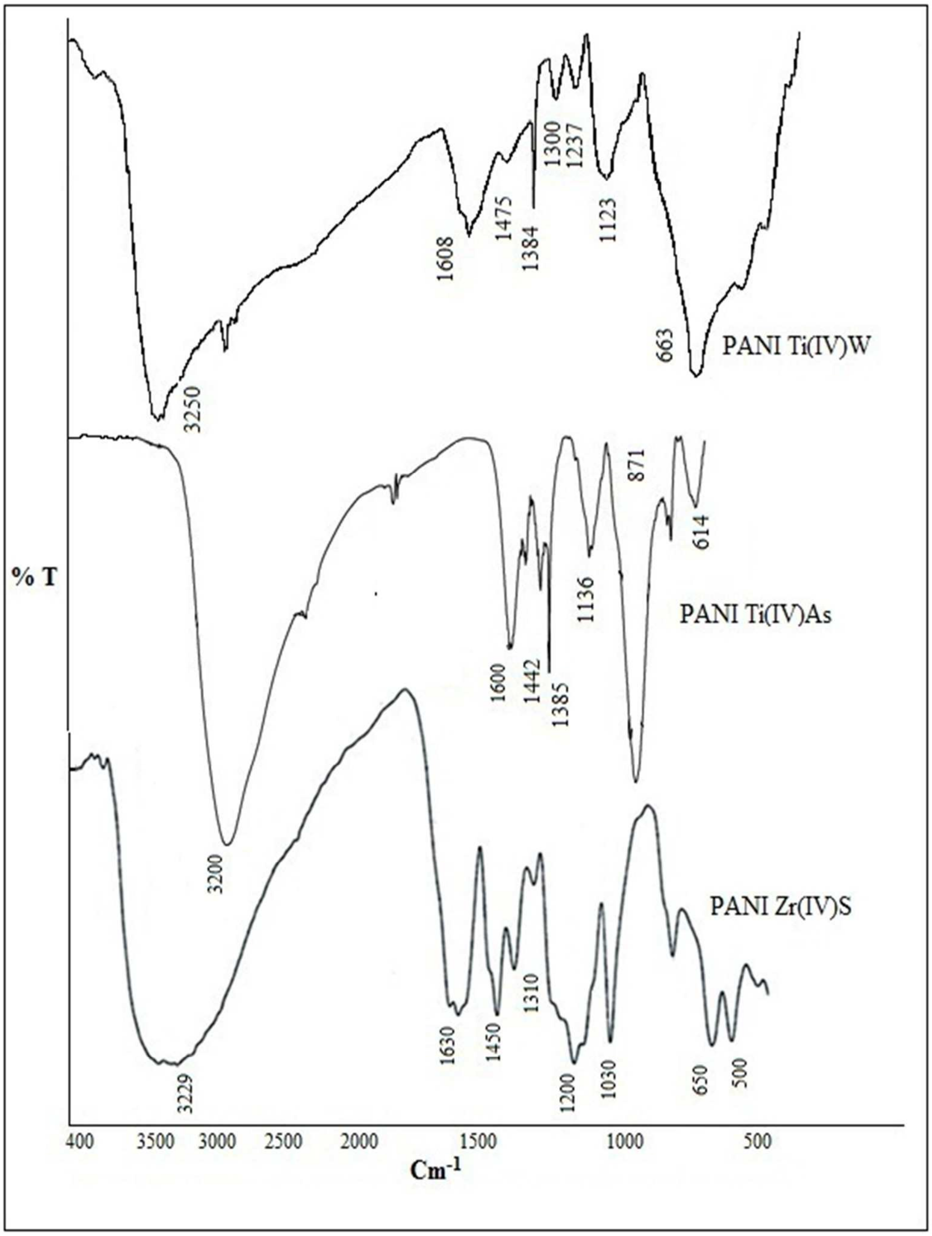

% T
PANI Ti(IV)W
3250
1608
1475
1384
1300
1237
1123
663
PANI Ti(IV)As
3200
1600
1442
1385
1136
871
614
PANI Zr(IV)S
3229
1630
1450
1310
1200
1030
650
500
400
3500
3000
2500
2000
1500
1000
500
Cm-1

Fig. S-1

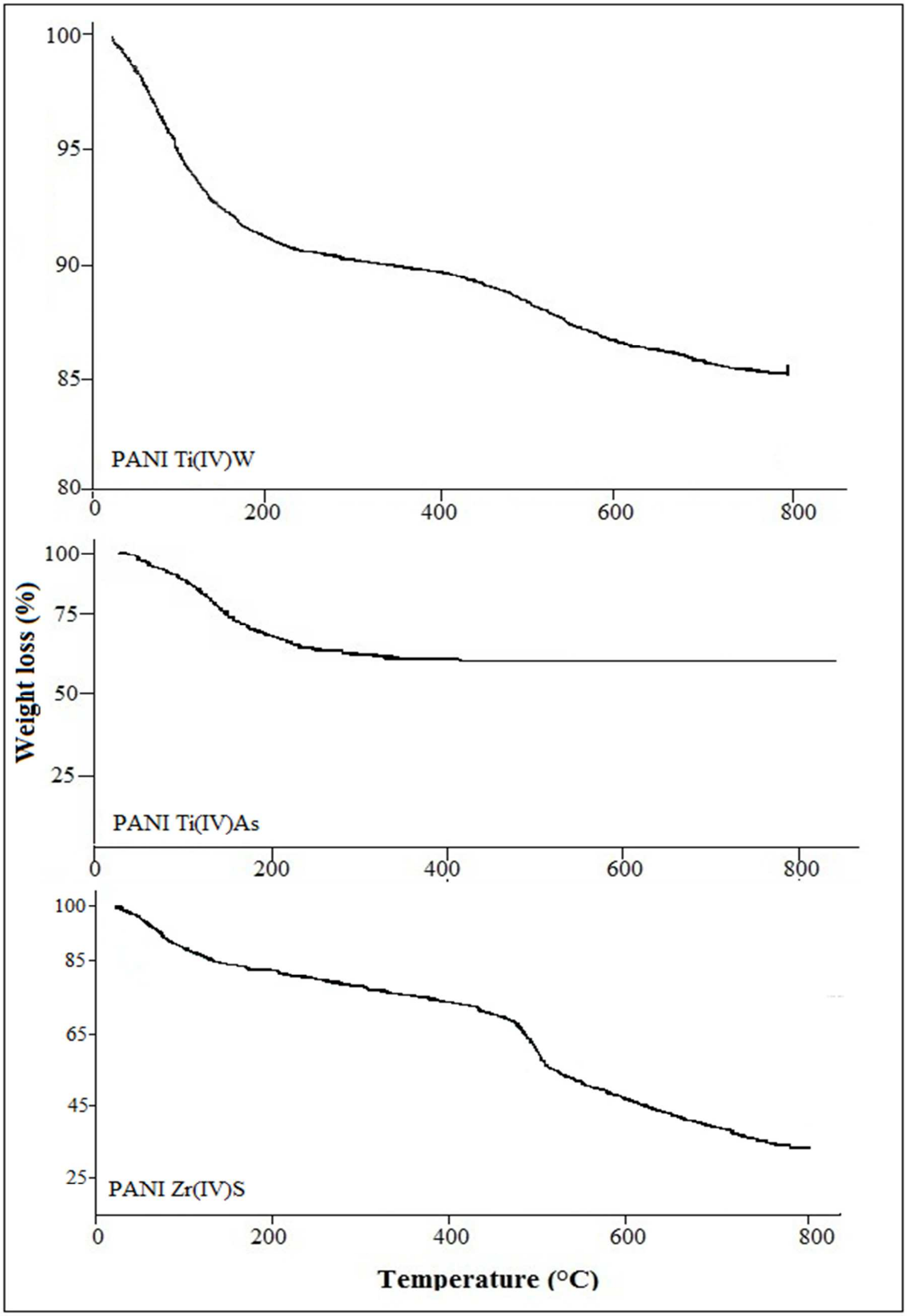

100
95
90
85
80
PANI Ti(IV)W
0
200
400
600
800
100
75
50
25
Weight loss (%)
PANI Ti(IV)As
0
200
400
600
800
100
85
65
45
25
PANI Zr(IV)S
0
200
400
600
800
Temperature (°C)

Fig. S-2

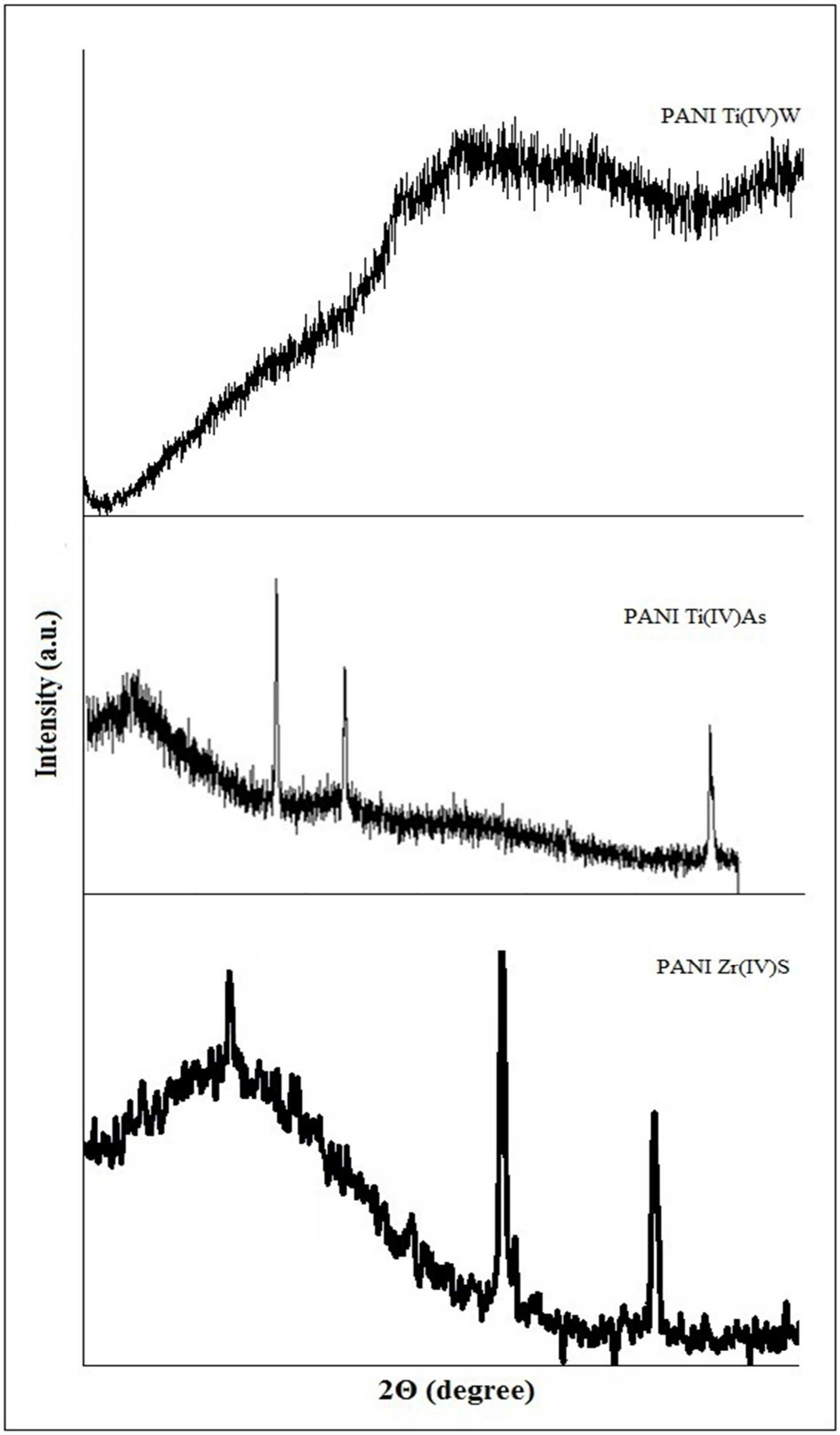


Fig. S-3

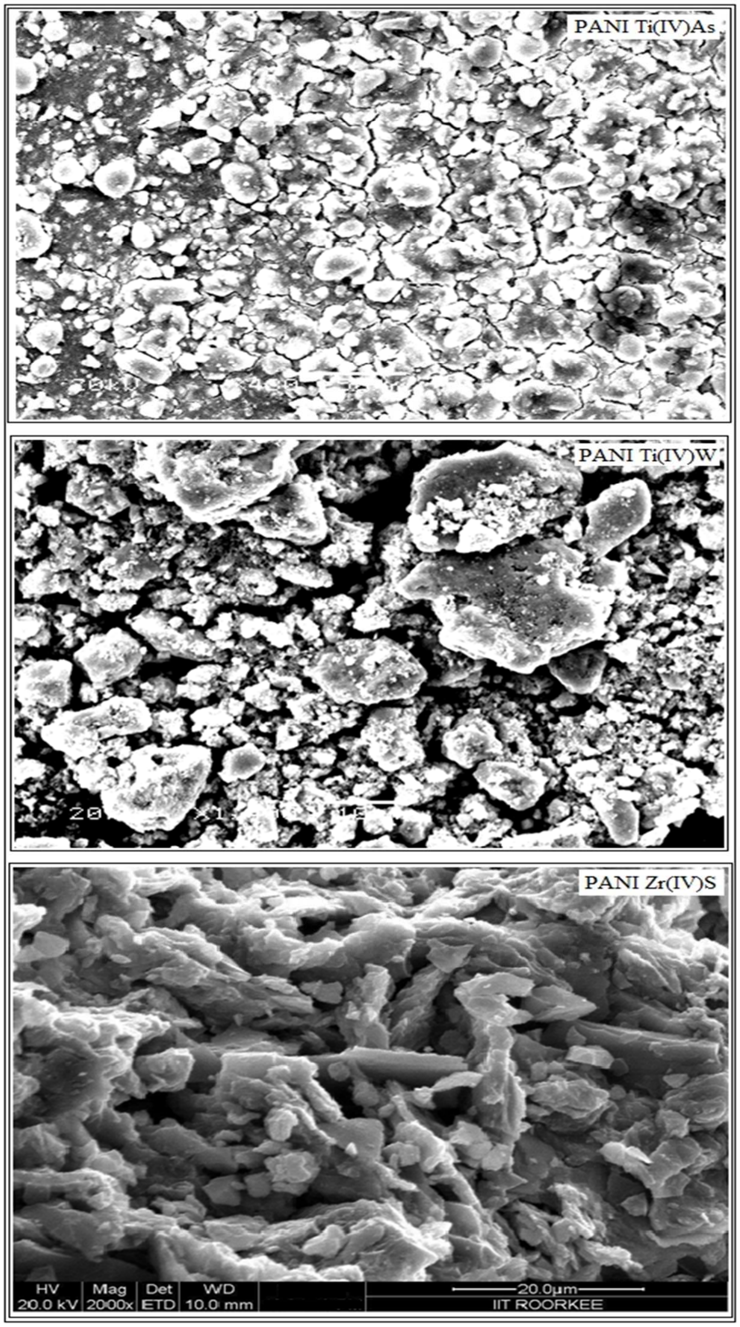

PANI Ti(IV)As
PANI Ti(IV)W
PANI Zr(IV)S
HV
Mag
Det
WD
20.0 kV
2000x
ETD
10.0 mm
20.0µm
IIT ROORKEE

Fig. S-4

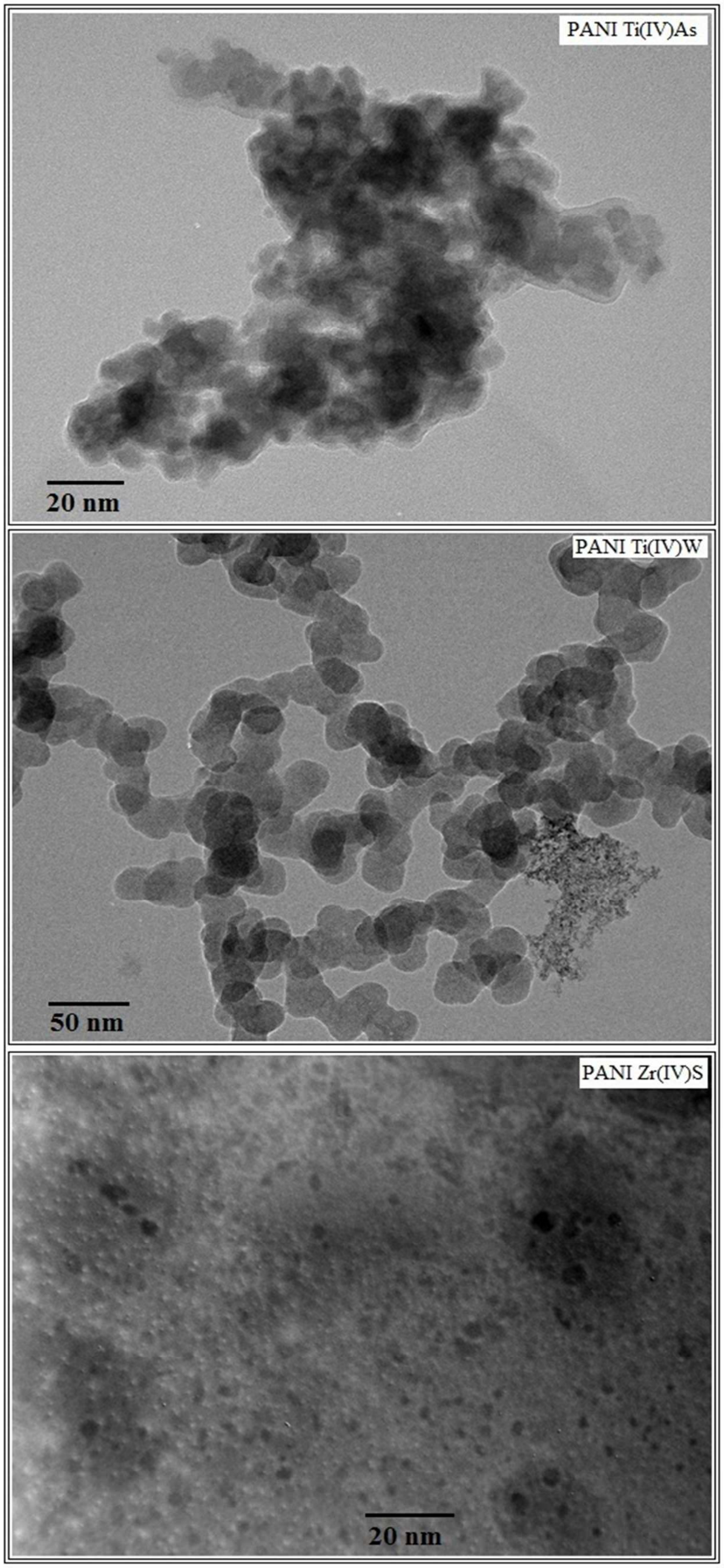


Fig. S-5