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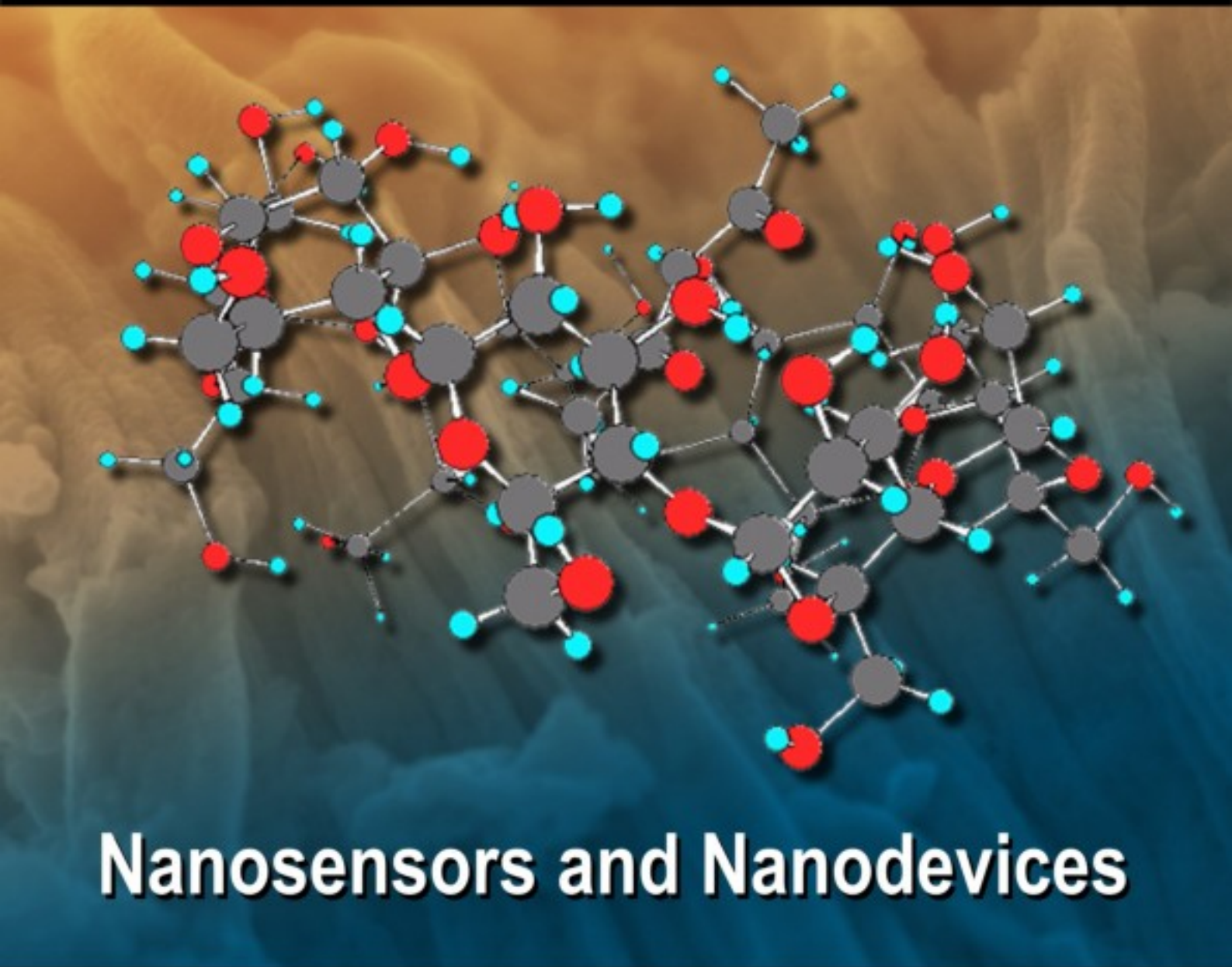

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Potentiometric Determination of Low Content of Water in Different Organic Solvents Using NASICON Based Probe

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Abstract: NASICON is a solid state ionic material which shows high ionic conductivity. NASICON based low cost, highly sensitive sensor probe for detection of very small content of the water nearly ppm level in organic solvents has been fabricated and characterized. The sensor utilizes the potentiometric method for detection of water content in solvents. The results indicate nearly linear variation of emf with increase in water content up to 10 % with a sensitivity of 0.0075 mV per ppm. Such a high value of sensitivity is extremely useful in detection of water in medical science and chemical industries. *Copyright © 2012 IFSA.*

Keywords: Ethanol, NASICON, Potentiometry, Sol-gel, Solid state electrolyte, Water sensor.

1. Introduction

NASICON type materials are potentially important in solid state ionic devices due to its application as solid electrolytes. High ionic conductivity and stability of phosphate units are advantages of NASICON over other electrolyte materials such as sodium beta alumina, cubic stabilized zirconia [1- 3]. Because of its high ionic conductivity, researchers are employing NASICON material (acronym for Na SuperIonic CONductors) for various applications such as gas sensing, Na^+ based batteries, ion selective electrodes, fuel cells, gas separation membranes, ionic switches etc. The high value of ionic conductivity of this group of compounds is because of high ion charge carrier concentration and high mobility of the charge carriers. Both of the above properties of the charge carriers of these solid electrolytes are due to the crystal structure of these compounds [2, 4, 5]. General formula of NASICON compounds is written as $A_mM_nP_3O_{12}$, where position A can be filled by alkali ion or by alkaline rare earth ions, M is one or more ions in tri-, tetra- or pentavalent state [6].A new type of

NASICON material is found in this series whose chemical formula is $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ and it has three dimensional framework for Na^+ migration [2, 4]. The mobile ions are generally small size cations, so such type of conductors are called cation conductors. The basic structure of NASICON material is rhombohedral in which two ZrO_6 octahedra are separated by three $(Si,P)O_4$ tetrahedra with which they share corner oxygen atoms and two types of Na sites (Na1 and Na2). The Na1 site is, surrounded by six oxygen atoms, located between two octahedra along the *c* axis and Na2 site is symmetrically distributed about three fold symmetry of the axis with ten-fold oxygen coordination and located at midway of two Na1 sites along the *a* axis [7- 9]. The two sodium sites, Na1 and Na2, inside the channels, are connected through triangular bottlenecks of oxygen atoms. The bottleneck between both sites for the rhombohedral symmetry is formed of three oxygen atoms whose centres make up an isosceles triangle (Fig. 1). For NASICON, bottleneck size of conduction channel is larger than the size of mobile sodium ions so cations which have size less than the sodium ion can easily move through the bottleneck.

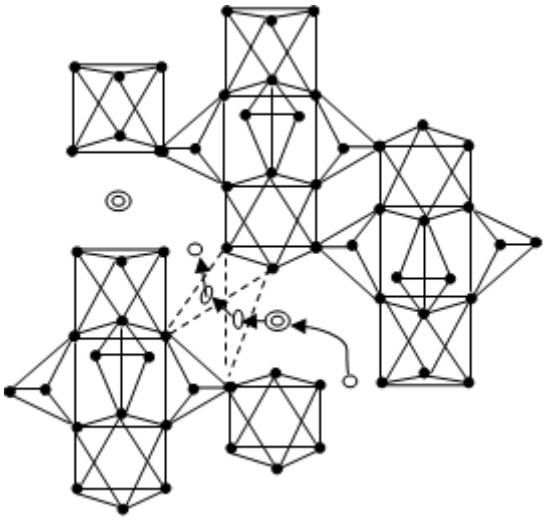

Fig. 1. Schematic representation of NASICON structure. Two sites for Na^+ ions are represented as follows: Na1 by double circles and Na2 by open circles. Oxygen atoms are represented by closed circles and the bottleneck is shown by dotted lines.

Detection of water contents in organic solvents has become very important as these are commonly used in laboratories, pharmaceutical industries, and in other applications as well. One of the organic solvent Ethanol, is a popular bio fuel which can be used as an alternative to fossil fuel such as gasoline or diesel and much attention has been made because of the limited quantity of fossil fuel, the pollution concern and the ever-increasing cost [10]. Water is completely soluble in some of the organic solvent such as ethanol, acetone and tetrahydrofuran so in the production process of these compounds it can come out as an impurity [11, 12]. A lot of well established methods have been reported for the analysis of water content in organic solvent systems, such as Karl Fischer titrations [13, 14], chromatography [15], and many other methods [16, 17]. Karl Fischer titration (KFT) is widely used for detection of the water content in liquids. However, this method is very slow and its detection limit is also very low. So convenient and simple methods are required for the determination of water content in the organic solvents. Although various optical methods have been successfully employed using fiber optic evanescent wave [18] and surface plasmon based sensors [19, 20]. One more method, which has successfully been employed in sensing for different purposes, is based on potentiometry [21, 22]. In this method electromotive force (emf) is measured between two electrodes, one of the electrodes is working electrode and other one is reference electrode. Working electrode consists of a metallic wire and a specific electrode material at its top. This electrode material should be selective for ion of interest.

In this paper we report the fabrication and characterization of a low cost NASICON based potentiometric sensor for the detection of very small content of water nearly ppm level in some organic solvents such as ethanol, acetone and tetrahydrofuran. The sensor utilizes electrochemical cell method. This sensor measures the change in concentration of H^+ ions with changing water content in the organic solvents and H^+ ions also modify the NASICON structure and generate EMF across the electrodes which vary linearly with water content in organic solvents up to 10 % with a sensitivity of 0.0075mV per ppm. To check the reproducibility of the response curve of the sensor, experiments have been repeated several times on different days.

2. Materials and Methods

2.1. Materials

For the preparation of NASICON nanograin powder, sodium hydroxide, silicon dioxide and ammonium dihydrogen phosphate were purchased from Merck. For testing purposes, ethanol (99.8 % pure), acetone and tetrahydrofuran were also purchased from Merck (India). For the preparation of sample, zirconium isopropoxide was purchased from Sigma Aldrich. The water used for making different samples of organic solvents–water solution was taken from a millipore system. All the chemicals were used in the same form as received, without any further change or purification.

2.2. Fabrication of NASICON Probe

NASICON powder has been prepared by sol-gel technique in which a measured volume of zirconium isopropoxide solution ($Zr(OC_3H_2)_4$) was mixed with distilled water. This solution was then mixed with aqueous solution of NaOH and SiO_2 powders in appropriate ratio and stirred for 30 minutes. The calculated amount of aqueous ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was added to previous solution and kept for precipitation. The final precipitate was dried at 150 ^{0}C and then sintered at 1000 ^{0}C for 2 h. Prepared sintered powder was uniaxially (11 MPa) pressed in the form of pellet and again sintered at 1000 ^{0}C for 3 h. Pellet prepared this way was attached at the bottom of hollow glass tube whose diameter was 0.9 cm.

A silver wire of diameter 1.5 mm was polished and fixed with silver conducting glue (EPOTECHNY) on one of the faces of the pellet. After 12 h of drying, the pellet was fixed with two component Araldite glue on the end side of a glass tube so that no water can penetrate into the tube. The surface area in contact with the liquid electrolyte was 2.54 cm^2. The external reference electrode was an Ag wire. Schematic of the probe is shown in Fig. 2. The electrochemical cell can be described by the following sequence:

$$Ag / Ag / Ag^+ // NASICON // solution\ under\ test / Ag$$

2.3. Sample Preparation

The organic solvents used in the present study are ethanol, acetone and tetrahydrofuran. Samples of organic solvents and water were prepared by adding different volume percentage of water in organic solvents. This mixture was then rigorously stirred. The total volume of each sample prepared was 50 ml. For preparing samples, a micropipette having an accuracy of 4 µl was used. The volume percentage of water in solvents was varied slowly from 0 to 10 % in steps of 0.005 % and then up to 80 % in steps of 20 %. Induced emf was measured by Keithley electrometer (6517A).

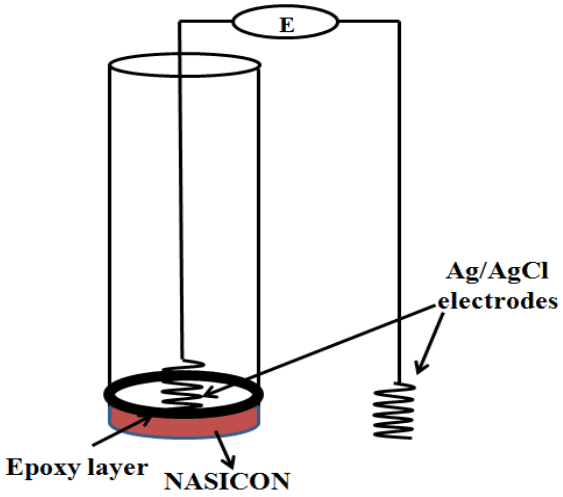

Fig. 2. Schematic of NASICON based probe.

3. Results and Discussion

Fig. 3 shows the XRD pattern of NASICON nanograin powders, prepared by sol-gel technique and sintered at 1000 ^{0}C. Peaks are well matched to the NASICON phase, reported elsewhere [23] which confirms the formation of NASICON phase.

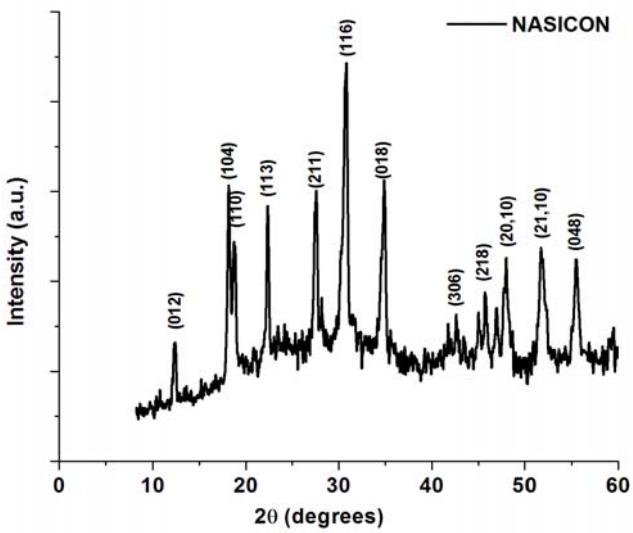

Fig. 3. XRD pattern of NASICON sintered at 1000 ^{0}C.

To study the response characteristics of the sensor, emf values were recorded for different percentages of water in different organic solvents. Fig. 4 shows the graph between emf and water percentage in ethanol for NASICON sensing probe with varying water percentages. In figure, symbols are the experimental data points. It is observed from the figure that corresponding to a particular water percentage in ethanol–water solution, a unique emf was generated. The emf measurements were carried out for ethanol containing 0.005 % (50 ppm) to 100 % water. From the figure it is clear that the emf increases linearly at the rate of 0.0075 mV per ppm with increase in water concentration in ethanol up to 10% but for higher concentration of water, the emf increases gradually at the rate of 0.0002 mV per ppm. From the figure we can see that line joining the experimental data is not passing through the

origin and cutting the x axis which confirms that some amount of water is already present in organic solvents as an impurity.

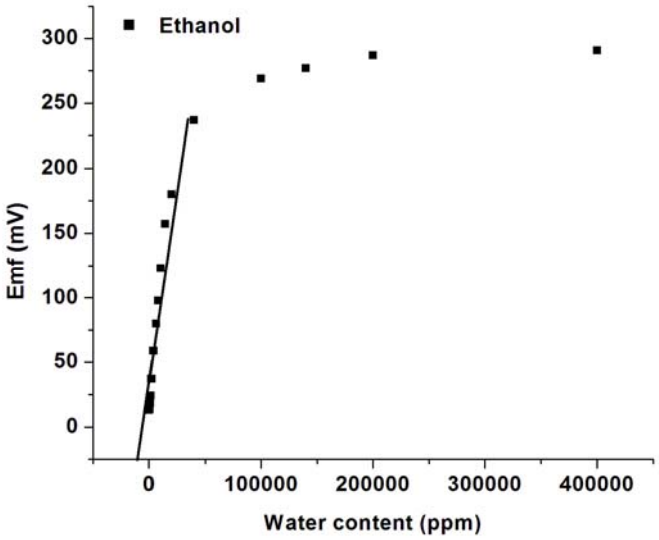

Fig. 4. Variation of EMF with water content (in ppm) in ethanol-water mixture.

Similar experiments were also carried out on other organic solvents such as acetone and tetrahydrofuran and results obtained are shown in Figs. 5 and 6. From these figures it is observed that for both of these cases rate of change of emf per ppm are nearly same as that of ethanol. Sensing mechanism of water by this sensing probe is as follows.

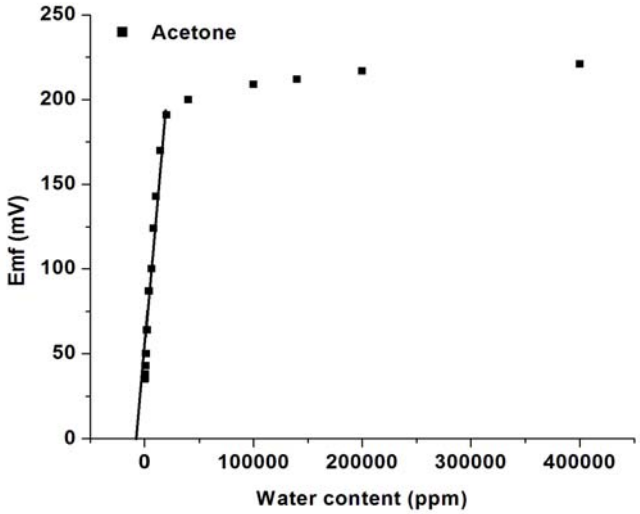

Fig. 5. Variation of EMF with water content (in ppm) in acetone-water mixture.

NASICON is an ionic conductor, and two types of conduction sites are available for sodium ion conduction. When water is added in the different organic solvents, it dissociates in the solution as H^+ and OH^- ions. These H^+ ions start going towards electrode by passing through the sodium sites present in NASICON and emf is generated across the electrodes. To understand whether these H^+ ions generate emf only or they also modify the NASICON structure we have carried out X Ray Diffraction (XRD) and absorption studies in ultra-violet region.

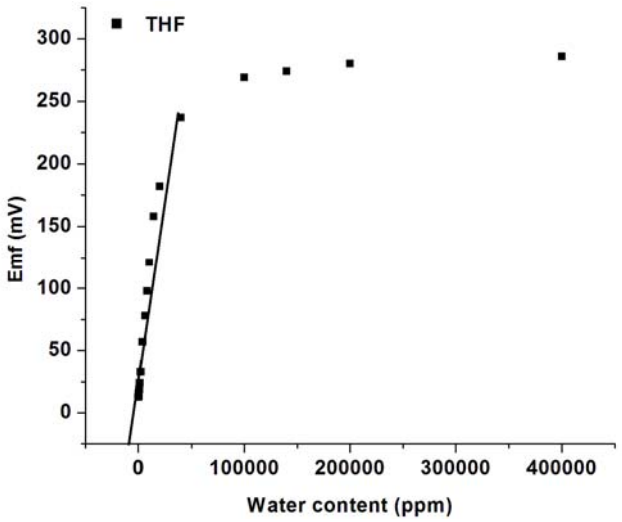

Fig. 6. Variation of EMF with water content (in ppm) in THF-water mixture.

Transmittance spectra of NASICON with only ethanol and ethanol with different concentration of water are shown in Fig. 7. From figure, it can be seen that when no water is added in the solution (Ethanol and NASICON only) a sharp dip is observed and when water is added in very small amount in the solution (20 ppm), dip intensity decreases continuously and with further increase in the water concentration up to 50000 ppm we observed that the dip nearly vanishes and at this ppm level we observed some modification in the structure that has been confirmed by XRD data which can be explained as follows.

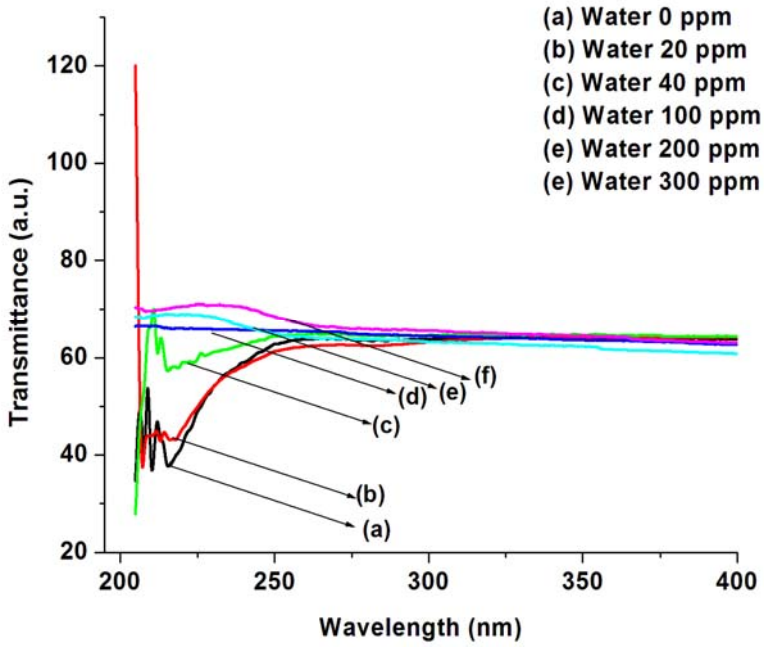

Fig. 7. Transmittance spectra for different water contents in ethanol-water mixture.

XRD was taken for three different samples (i) Fresh NASICON sample (ii) NASICON dipped in water (iii) After removing water from pellet by heating it at 50 ^{0}C. XRD Results corresponding to hkl planes [116] and [018] are shown in Fig. 8 (a, b and c). In Fig. 8(a) we observed single peak corresponding to

pure NASICON whereas in the water dipped pellets, we observed splitting of the peaks (Fig. 8(b)). While in the third case after heating the same sample at 50 ^{0}C for 10 min, it has been found that doublets of the peak have been removed and peaks regain its previous position as that of fresh NASICON sample (Fig. 8(c)). The possible reasons for splitting in XRD peaks may be due to hydration and dehydration of Na_3PO_4 (well known hygroscopic material in nature) which is the second phase, already present along with the NASICON. The other reason may be the ionic exchange between H_3O^+ ion from the solution and Na^+ ion from NASICON or due to dissolution of Na_3PO_4 in the solution [24].

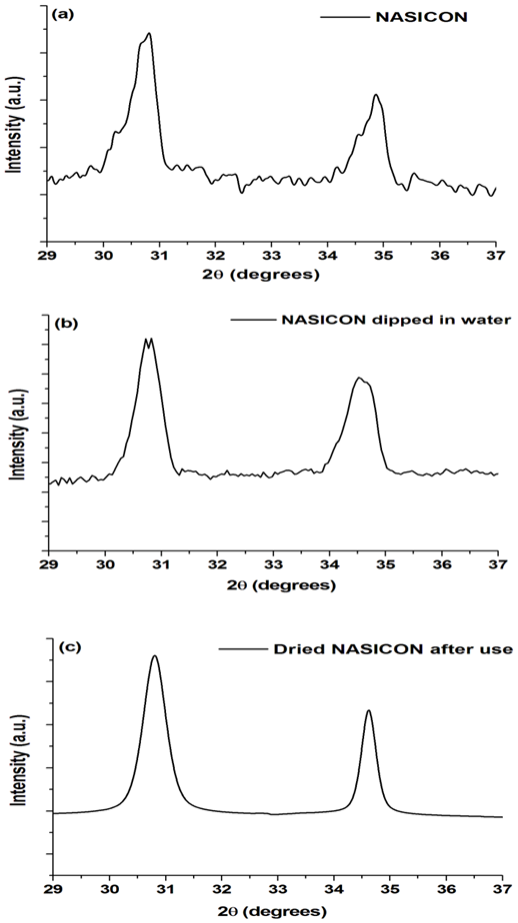

Fig. 8. XRD pattern of (a) standard NASICON, (b) when it is dipped in water, (c) when it is dried after use.

4. Conclusion

NASICON based low cost, highly sensitive sensor with fast response probe for detection of very small content of the water, nearly ppm level, in organic solvents has been fabricated and characterized. The sensor utilizes the electrochemical cell method for detection of water content in solvents. The measurements were carried out up to 50 ppm of water. The results indicate nearly linear variation of emf with increase in water content up to 10 % with a sensitivity of 0.0075 mV per ppm. The possible mechanism of detection has been discussed. This probe is extremely useful for detection of water in medical science and chemical industries.

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References

[1]. N. Miura, S. Yao, Y. Shimizu, N. Yamazoe, High performance solid electrolyte carbon dioxide sensor with a binary electrode, *Sensors and Actuators B*, Vol. 9, 1992, pp. 165-170.
[2]. Y. Sadaoka, Y. Sakai, M. Matsumoto, T. Manabe, Solid-state electrochemical CO2 gas sensors based on sodium ionic conductors, *Journal of Material Science*, Vol. 28, 1993, pp. 5783-5792.
[3]. A**.** Anantharamulu, K. K. Rao, G. Rambabu, B. V. Kumar, V. Radha, M. Vithal, A wide- ranging review on Nasicon type materials, *Journal of Material Science*, Vol. 46, 2011, pp. 2821-2837.
[4]. D. H. H. Quan, T. A. Wheat, W. Nesbitt, Synthesis characterization and fabrication of $Na_{1+x}Zr_2Si_x\ P_{3-x}O_{12}$, *Materials Research Bulletin*, Vol. 15, 1980, pp. 1533-1539.
[5]. H. Y. P. Hong, Crystal structure and crystal chemistry in the system $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, *Materials Research Bulletin*, Vol. 11, 1976, pp. 173-182.
[6]. K. C. Sobha, K. J. Rao, Investigation of phosphate glasses with the general formula $A_xB_yP_3O_{12}$ where A = Li, Na or K and B = Fe, Ga, Ti, Ge, V or Nb, *Journal of Non-Crystalline Solids*, Vol. 201, 1996, pp. 52-65.
[7]. J. B. Goodenough, H. P. Y. Hong, J. A. Kafalas, Fast Na^+ ion transport in skeleton structures, *Materials Research Bulletin*, Vol. 11, 1976, pp. 203-220.
[8]. J. P. Boilot, P. Salanie, G. Desplanches, D. L. Potier, Phase transformation in $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ compounds, *Materials Research Bulletin*, Vol. 14, 1979, pp. 1469-1477.
[9]. H. Kohler, H. Schulz, Na^+-diffusion path and its relation to the structure, *Materials Research Bulletin*, Vol. 20, 1985, pp. 1461-1471.
[10]. J. Beauchaine, J. Briggs, Measurement of water in ethanol using encoded photometric NIR spectroscopy, *Spectroscopy*, Vol. 22, 2007, pp. 40-44.
[11]. Q. Chang, Z. Murtaza, J. R Lakowicz, G. Rao, A fluorescence lifetime-based solid sensor for water, *Analytica Chimca Acta*, Vol. 350, 1997, pp. 97-104.
[12]. S. J. Glenn, B. M. Cullum, R. B. Nair, D. A. Nivens, C. J. Murphy, S. M. Angel, Lifetime-based fiber optic water sensor using a luminescent complex in a lithium-treated nafion membrane, *Analytica Chimica Acta*, Vol. 448, 2001, pp. 1-8.
[13]. Y. Y. Liang, Automation of Karl Flscher water titration by flow injection sampling, *Analytical Chemistry*, Vol. 62, 1990, pp. 2504-2506.
[14]. C. Oradd, A. Cedergren, Colulometric study of recovery rates for Karl Fischer titration of water in aldehydes and ketones using rapidly reacting methanolic and 2-methoxyethanolic reagents, *Analytical Chemistry*, Vol. 67, 1995, pp. 999-1004.
[15]. R. Oguchi, K. Yamaguchi, T. J. Shibamato, Determination of water content in common organic solvents by a gas chromatograph equipped with a megabore fused-silica column and a thermal conductivity detector, *Journal of Chromatographic Science*, Vol. 26, 1988, pp. 588-590.
[16]. W. Liu, Y. Wang, W. Jin, G. Shen, R. Yu, Solvatochromogenic flavones dyes for the detection of water in acetone, *Analytica Chimica Acta*, Vol. 383, 1999, pp. 299-307.
[17]. S. Cho, H. Chung, Y. A. Woo, H. J. Kim, Determination of water content in ethanol by miniaturized near-infrared (NIR) system, *Bull. Korean Chem. Soc.*, Vol. 26, 2005, pp. 115-118.
[18]. B. Xiong, D. Sisler, Determination of low-level water content in ethanol by fiber-optic evanescent absorption sensor, *Optics Communications*, Vol. 283, 2010, pp. 1326-1330.
[19]. K. Matsubara, S. Kawata, S. Minami, A compact surface plasmon resonance sensor for measurement of water in process, *Applied Spectroscopy*, Vol. 42, 1988, pp. 1375-1379.
[20]. S. K. Srivastava, R. Verma, B. D. Gupta, Surface plasmon resonance based fiber optic sensor for the detection of low water content in ethanol, *Sensors and Actuators B*, Vol. 153, 2011, pp.194-198.
[21]. X. Zheng, Z. Guo, Potentiometric determination of hydrogen peroxide at MnO2-doped carbon paste electrode, *Talanta*, Vol. 50, 2000, pp. 1157-1162.
[22]. Y. Wang, H. Xu, J. Zhang G. Li, Electrochemical sensors for clinic analysis, *Sensors*, Vol. 8, 2008, pp. 2043-2081.
[23]. P. Yadav, M. C. Bhatnagar, Structural studies of NASICON material of different compositions by sol–gel method, *Ceramic International*, Vol. 38, 2012, pp. 1731-1735.

[24].F. Mauvy, E. Siebert, P. Fabry, Reactivity of NASICON with water and interpretation of the detection limit of a NASICON based Na^+ ion selective electrode, *Talanta*, Vol. 48, 1998, pp. 293-303.

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- Sensor instrumentation;
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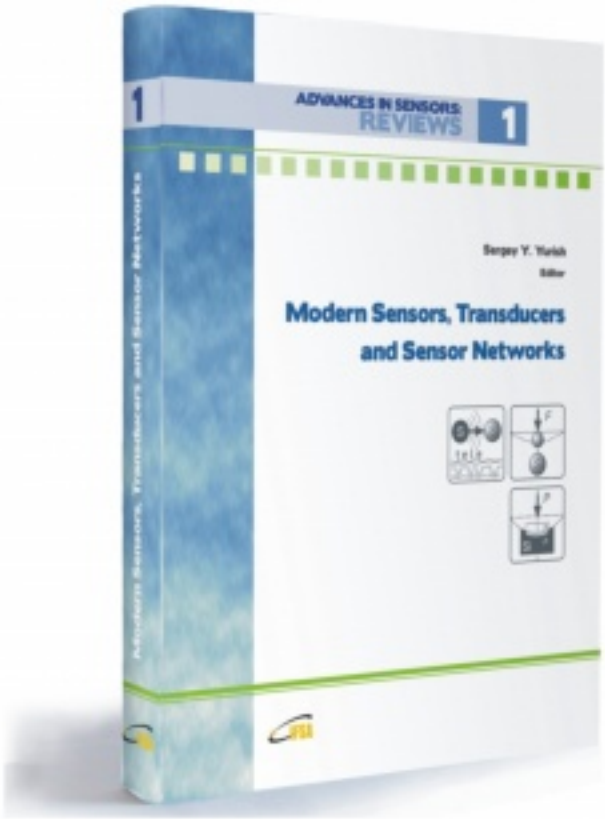
Modern Sensors, Transducers and Sensor Networks



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