

Studies on Structural and Electrical Properties of NaHCO₃ Doped PVA Films for Electrochemical Cell Applications

J. Ramesh Babu, K.Vijaya Kumar*

Department of Physics, K L University, Vaddeswarram – 522 502 Guntur Dt.,
Andhra Pradesh, India.

Abstract: Solid polymer electrolyte films using polyvinyl alcohol (PVA) as polymer and sodium bicarbonate (NaHCO₃) as dopant has been prepared at different wt% ratios by solution cast technique. The films have been characterized using analytical techniques such as X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The complex formation between PVA and NaHCO₃ has been inferred from the FTIR data while semi-crystalline nature of the polymer electrolytes and the increase of amorphous nature with increase in the wt% of NaHCO₃ in the films and also the homogenous distribution of NaHCO₃ in the host polymer PVA, have been revealed by XRD studies. The variation of film morphology has been examined by SEM and it indicates some uniformness of surfaces but with different degrees of roughness as the wt% of NaHCO₃ increases. The conductivity Vs temperature plots for the films have shown an increase in conductivity with increase in wt% of NaHCO₃ concentration and also increase with the temperature. The maximum ionic conductivity has been found to be 2.37×10^{-7} S/cm at 303K and 1.20×10^{-5} S/cm at 373K for 70:30 wt% film. Further, the activation energy is decreasing with the increase in the % of NaHCO₃ in the Polymeric films. It is proved from the transference number data that the conduction is predominantly due to Na⁺ ions. Using these doped polymeric films, a solid state electrochemical cell has been fabricated and the cell parameters such as open-circuit voltage (OCV), short-circuit current (SCC), energy density and power density has been calculated and compared with the data from the earlier reports.

Keywords: Solid polymeric electrolyte; Doped PVA; Ionic Conductivity; FTIR-XRD-SEM studies; Electrochemical Cell Applications.

1: Introduction

Recent research indicates that much effort is being envisaged in developing new energy storing devices in view of day by day increasing in demand for power but depletion in naturally existing resources to meet the required demand. In this aspect Energy storage devices are assuming importance.

As is known that in the energy storage devices, electrolyte which carries electrical charges are vital component and generally liquid or solid electrolytes are used. Solid electrolytes are preferable over liquid electrolytes as they are endowed with chemical as well as thermal stability, sustainability and longevity and non-leakage. In this concept, polymers or blends of polymers either complexed or doped with inorganic salts or alkalis are being probed for their utility in high performance energy storage devices such as batteries, fuel cells and super capacitors for enhancing their performance¹. These polymer electrolytes show ample high conductivity for an optimum amount of the dopant^{2,3}.

In this context, PVA complexed electrolytes are interesting as the polymer is easy to prepare and produce excellent films with high tensile strength, chemical stability, non/less-permeability for many solvents and more over it is non-toxic. These features are attributed to the availability of functions groups such as –OH, C=O, COOH on the surface of the film. There are reports in literature using PVA blended with other polymers or doped with some electrolytes of diverse nature⁴⁻³². When Alkali halides such as LiCl, NaF, NaCl, KCl, CsCl, KBr, and KI have been doped in PVA, there has been a marked increase in the crystallinity of the

polymeric layer by a factor of 1.3 to 1.6.^{4,5} Balaji Bhargav *et al*⁶ have found that when NaF doped in PVA, the conductivity has been found to be increasing with the increase of dopant concentration as well as temperature.

Several combinations of PVA with acids or salts such as phosphoric acid (H_3PO_4), hypophosphorous acid (H_3PO_2), heteropolyacid, dipotassium phosphate (K_2HPO_4), and sulfosuccinic acid have been studied so as to improve the proton conductivity of the PVA⁷⁻¹⁵. The addition of ceramic filler, TiO_2 , into the PVA polymer matrix, has been found to reduce the glass transition temperature (T_g) and the crystallinity of the polymer, and also allow the increase the amorphous phases of polymer matrix that results in the increase in the ionic conductivity.

There are various other ceramic fillers, such as Al_2O_3 ¹⁶⁻²², SiO_2 ²³⁻²⁵, ZnO ²⁶, TiO_2 ²⁷, MgO and $BaTiO_3$ ²⁸, and ZrO_2 ^{29, 30} have been also studied. When PVA is blended with another polymer Chitosan, the conductivity of the polymer electrolyte has been found to be improved³¹. When the blend of PVA and PVP (1:0.5 w/w) is doped with KOH (8 M), the maximum conductivity up to 0.53 S/cm at room temperature has been achieved³². Thus, by using the doped polymers as polymeric electrolytes, the conductivity properties of the polymer may be altered and this phenomenon is of immense use in developing electrochemical cell and this aspect of research is being actively being pursued throughout the Globe.

In the present work, thin-films have been prepared by doping $NaHCO_3$ in PVA and the resulting films are characterized using techniques like FTIR, XRD and SEM. Further, their conducting properties have been investigated to find their suitability in developing an efficient electrochemical cell.

2: Materials And Method

A.R. Grade LOBA chemicals of PVA (molecular weight 85,000) and $NaHCO_3$ were used in this work.

There are many techniques available for making films such as Sputtering, hot pressing method, flash evaporation method and Solution casting technique³³. Of these, Solution casting technique is the best and easiest technique to get a good electrolyte homogeneous film. Hence we adopted this technique in this work.

Films of various compositions of PVA and $NaHCO_3$ as detailed in the Table 1, were prepared by dissolving the requisite amounts of the said chemicals in the triple distilled water and then the solution was stirred for 48 hours to get homogeneous solution. The resulting homogeneous solution then was cast onto polypropylene dishes and dried slowly at room temperature for 48 hrs and then the resulting films were vacuum dried.

The dried thin-films formed were peeled and characterized with FTIR, XRD and SEM. The FTIR Spectra were recorded with the help of Perkin Elmer FTIR Spectrophotometer in range 4000 to 500 cm^{-1} using KBr pellet method. The spectra obtained was depicted in the Fig 1.

XRD Bruker D8 instrument with Cu $K\alpha$ radiation for 2θ angles between 10^0 to 80^0 C was used to record spectra of the films and the obtained spectra was presented in Fig 2.

The Scanning Electron microscope (SEM) is one of the most versatile instruments used for the examination and analysis of the microstructure morphology. In this work, the microphotographs of the samples were recorded using FE-SEM, Carl Zeiss, Ultra 55 model and were presented in the Fig. 3.

The conductivities of the films were measured using Lab made conductivity set up³⁴ in the temperature range 303-373 K. The effect of temperature and salt percentage on the conductivity of PVA as well as blends was studied and presented in the Fig. 4 and 5 respectively.

The transference number measurements were made using Wagner's polarization technique³⁵ and Watanbe technique³⁶. Electrochemical cells were fabricated with the configuration of "Na (anode)/polymer electrolyte/($I_2 + C +$ electrolyte) (cathode)". The discharge characteristics like open circuit voltage (OCV), short circuit current (SCC), power density etc. were monitored under a constant load of 100 K Ω .

3: Results and Discussion

A: FTIR Analysis:

FTIR is a promising instrument which is useful to find the nature of functional groups and also the formation of any new bonds on the surface of the polymeric blends. In the present study the pure PVA and its blends with NaHCO_3 at varying concentrations, were probed for FTIR spectra and they were presented in Fig.1.

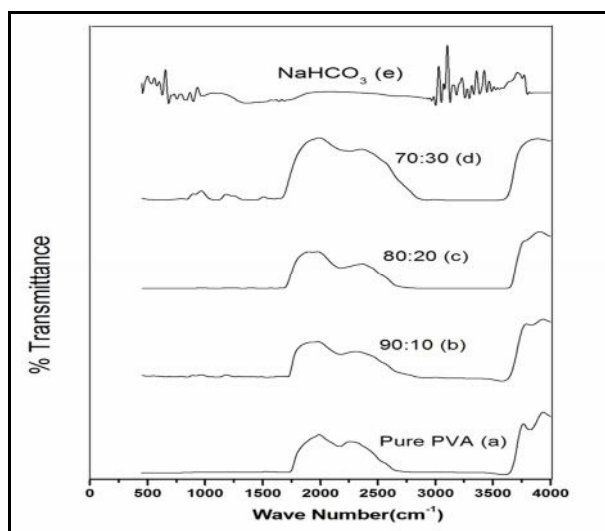


Fig. 1: FTIR Spectroscopic graphs (a) Pure PVA (b) PVA+ NaHCO_3 (90:10) (c) PVA+ NaHCO_3 (80:20) (d)PVA+ NaHCO_3 (70:30) (e) NaHCO_3 .

It is observed from the spectra that the wide band in the region $3596\text{--}2854\text{ cm}^{-1}$ of pure PVA spectra is pertaining to the intermolecular hydrogen bonded O-H stretchings in pure PVA. This band was found to be shifted to $3578\text{--}2843\text{ cm}^{-1}$, $3630\text{--}2936\text{ cm}^{-1}$ and $3778\text{--}2984\text{ cm}^{-1}$ in the blends respectively of 10%, 20% and 30% of NaHCO_3 and PVA. Further, the C-H stretching frequency at 2787 cm^{-1} in the pure PVA was shifted to 2718 , 2821 and 2993 cm^{-1} in the blends as the concentration of NaHCO_3 was increasing progressively to 10%, 20% and 30% respectively. These shifts in the bands may be attributed to the complex formation between PVA and NaHCO_3 .

B: X-Ray diffraction analysis:

The structural characteristics of pure PVA and blends of NaHCO_3 and PVA were evaluated using X-ray diffraction studies and were shown in Fig. 2.

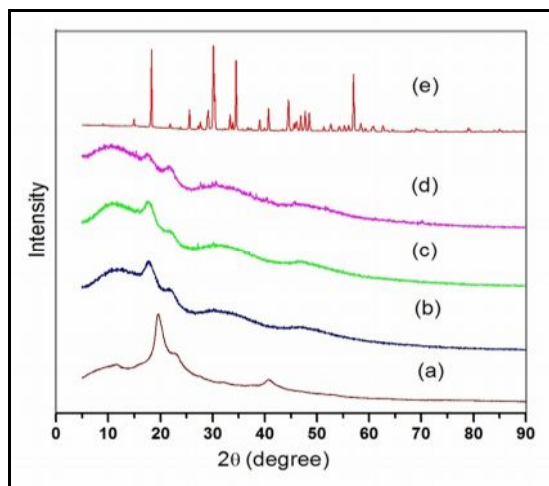


Fig.2: XRD plots of (a) Pure PVA (b) PVA+ NaHCO_3 (90:10) (c) PVA+ NaHCO_3 (80:20) (d) PVA+ NaHCO_3 (70:30) (e) NaHCO_3 .

It can be noted from the Figure that the diffraction peaks for pure PVA appeared at 19.41, 22.88' and 40.87°. The peak at 19.41 is the characteristic peak for orthorhombic lattice centered structure indicating the semi-crystalline nature³⁷. This peak intensity is found to be decreasing as the concentration of NaHCO₃ is increased progressively in the blends. This indicates the decrease of crystalline with simultaneous increase in amorphous nature with the increase in the % of NaHCO₃ in the blends. These observations are in tandem with the observations of Hodge et al.³⁸ who established a correlation between the intensity of the peak and the degree of crystallinity. Moreover, the absence of any sharp peak in the blends is suggesting the dominance of amorphous phase in the blends³⁹. This decrease in the degree of Crystallinity of the polymers of PVA complexed with NaHCO₃, imparts a good ionic diffusivity in the polymers that results in the enhanced ionic conductivity as is being generally found in amorphous polymers having flexible backbone².

Further, the absence of peaks pertaining to NaHCO₃ at 18.34, 30.17, 34.92 and 57.17° in the blends indicate the complete dissolution and homogenous distribution of NaHCO₃ in the PVA.

C: SEM Analysis::

Scanning electron microscopy (SEM) is frequently used to understand the compatibility between dissimilar components of the polymer electrolytes through the perception of phase separations and interfaces^{40,41}. The compatibility between the polymer matrix and inorganic dopants has great influence on the ionic conductivity, transport and mechanical properties of the polymeric electrolyte systems. The morphology of pure PVA, NaHCO₃ complexed PVA polymeric electrolyte systems were studied using SEM technique and these SEM photographs were shown Fig 3 .

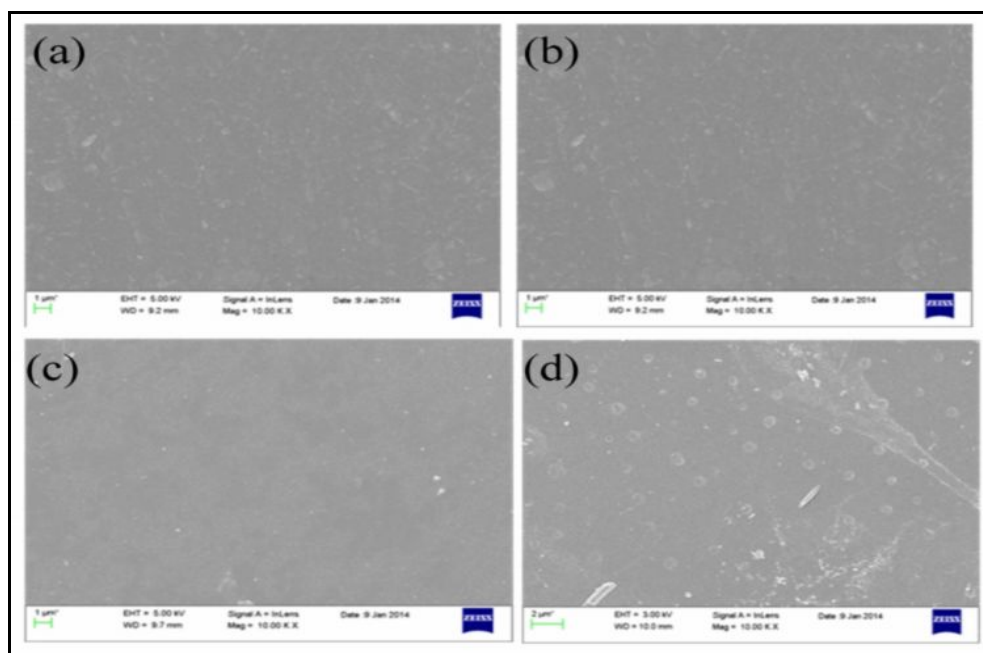


Fig.3: SEM photographs of (a) Pure PVA (b) PVA+NaHCO₃ (90:10) (c) PVA+NaHCO₃ (80:20) (d)PVA+NaHCO₃ (70:30).

They were characterized with some uniformness in surfaces and with different degrees of roughness and further, the roughness was found to be increasing with increase salt concentration. This reveals the phase segregation phenomenon.

D: Conductivity Analysis:

The conductivity of pure PVA and its blends with NaHCO₃ was found to be increasing with the increase in Temp. and wt% of salt Fig No. 4 & 5

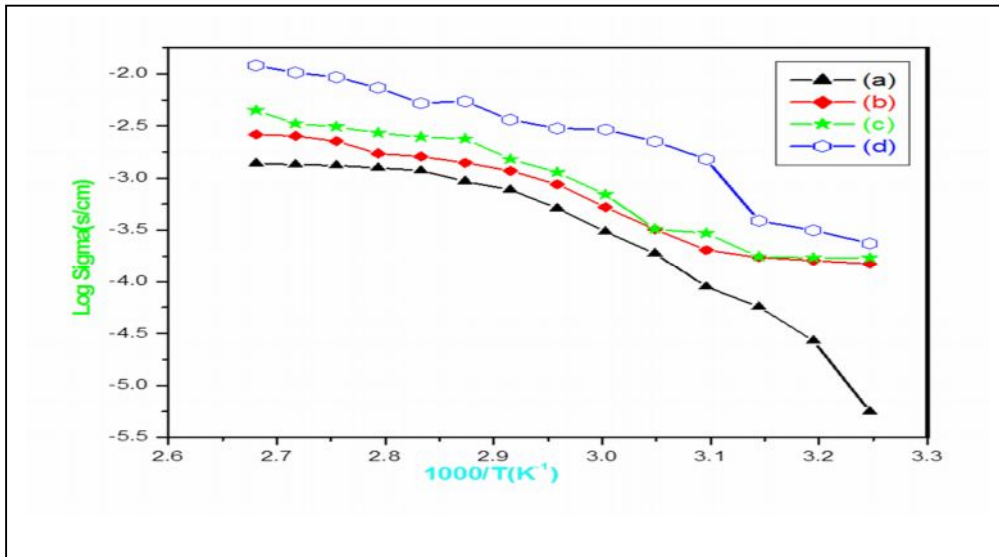


Fig.4: The temperature dependence of dc conductivity of (a) Pure PVA (b) PVA+NaHCO₃ (90:10) (c) VA+NaHCO₃ (80:20)(d)PVA+NaHCO₃(70:30)

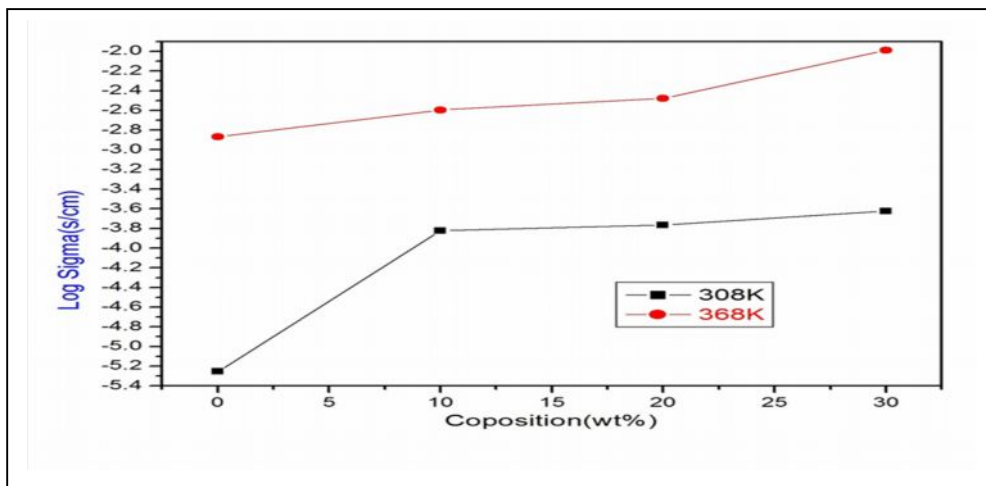


Fig.5: Composition dependence of conductivity in PVA+NaHCO₃ Polymer electrolyte systems at different temperatures

In the case of pure PVA the conductivity was increased from 5.59×10^{-10} s/cm at 303 K to 1.38×10^{-8} s/cm at 373 K while its blends with NaHCO₃, the increase was found to be from 1.49×10^{-7} to 2.62×10^{-6} , 1.71×10^{-7} to 4.46×10^{-6} and 2.37×10^{-7} to 1.20×10^{-5} s/cm with 10%, 20% and 30% of NaHCO₃ in the blends respectively. It is interesting to note that the increase is 2 orders in the case of pure PVA and 30% blend PVA and NaHCO₃ while in the case of other blends, the increase is in between 1 and 2 orders.

Activation energies for PVA and its blends were calculated from Arrhenius plots drawn between the Conductivity Vs Temperature ($\log \sigma$ Vs $1000/K$) and were presented in Table No.1. In the Fig.6 the variation of activation energy with NaHCO₃ salt concentration was illustrated. It was observed that (PVA+NaHCO₃) (70:30) had highest conductivity and lowest activation energy when compared to the other samples.

Further, the ionic transference numbers of PVA and its blends had been measured using Wagner’s polarization method. In this method, the D.C. current was altered as a function of the time on application of a constant dc voltage (1.5V) across the cell: Anode(Na)/polymer electrolyte/Cathode. Graphs were plotted between the Polarization Current and Time using equation: $t_{ion} = (i_i - i_f) / i_i$ where i_i is the initial current and i_f is the final residual current as shown in Fig.7.

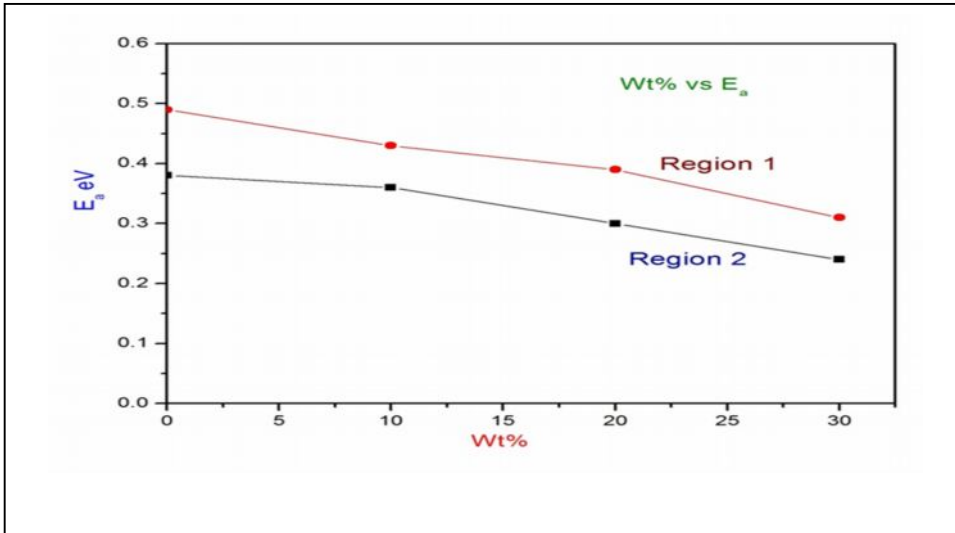


Fig.6: Variation of activation energy with NaHCO₃ weight percentage

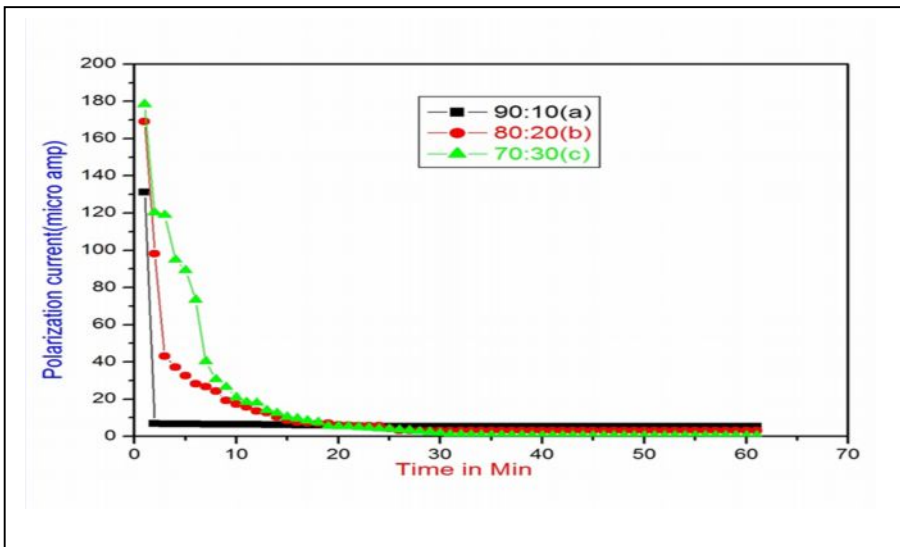


Fig. 7: (a) PVA+NaHCO₃ (90:10) (b) PVA+NaHCO₃ (80:20) (c) PVA+NaHCO₃ (70:30).

Table-1: D.C. Conductivity, Activation Energies and Transference number of (PVA+NaHCO₃) Electrolyte Systems.

Sl.No	Polymer Electrolyte	Conductivity at 303K(R _T)(S/Cm)	Conductivity at 73K(S/Cm)	Activation Energies(eV)		Transference number	
				Region-1	Region-2	t _{ion}	t _{ele}
1	Pure PVA	5.59x10 ⁻¹⁰	1.38 x 10 ⁻⁸	0.49	0.38	-	-
2	PVA+NaHCO ₃ (90:10)	1.49x10 ⁻⁷	2.62x10 ⁻⁶	0.43	0.36	0.96	0.04
3	PVA+NaHCO ₃ (80:20)	1.71x10 ⁻⁷	4.46x10 ⁻⁶	0.39	0.30	0.98	0.02
4	PVA+NaHCO ₃ (70:30)	2.37x10 ⁻⁷	1.20x10 ⁻⁵	0.31	0.24	0.99	0.01

The calculated transference numbers, t_{ion} and t_{ele} were given in Table1. Here, it was observed that the transference number values for all the samples were close to unity indicating that the charge transport was predominantly due to sodium ions while the electronic contribution to the charge transport was very small.

E: Discharge Studies:

The solid-state electrochemical cell was fabricated with the configuration “anode (Na)/ (PVA + NaHCO₃)/cathode (I₂ + C + electrolyte)”. The thickness of both the electrodes is 1mm. The surface area and thicknesses of the ‘PVA+ NaHCO₃’ electrolyte were 1.34cm² and 150 μm respectively. The discharge Characteristics of the cell for a constant load of 100KΩ were evaluated at room temperature and were shown in Fig.8.

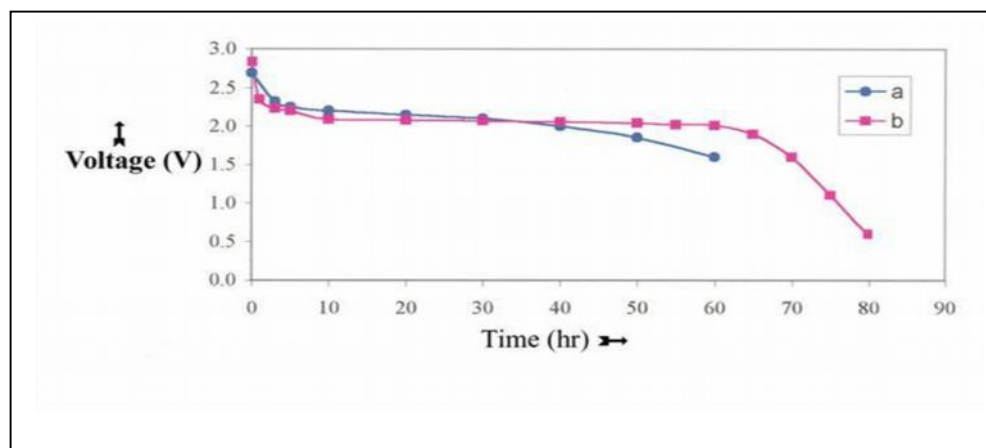


Fig.8: Discharge Characteristics of an Electrochemical cell for a constant load of 1KΩ

The initial sharp decrease in the voltage in these cells may be due to polarization and the formation of thin layer of sodium salt at the electrode-electrolyte interface. The open circuit voltage, short circuit current values and some cell parameters like current density, energy density and discharge time, were calculated and were presented in the Table 2.

Table- 2: Cell Parameters of Na/PVA+NaHCO₃/(I₂+C+electrolyte) polymer electrolytes

Sl. No.	Cell parameters	PVA+NaHCO ₃ (90:10)	PVA+NaHCO ₃ (80:20)	PVA+NaHCO ₃ (70:30)
1	Open Circuit Voltage(V)	2.90	2.96	2.99
2	Short Circuit Current (μA)	230	304	365
3	Area of the Cell (cm ²)	1.34	1.34	1.34
4	Weight of the Cell (gm)	1.29	1.32	1.36
5	Discharge Time(h)	46	63	81
6	Current Density(μA cm ⁻²)	170	204	234
7	Power Density(W kg ⁻¹)	0.268	0.491	0.637
8	Energy density(Wh kg ⁻¹)	28	46	70
9	Discharge capacity(μAh ⁻¹)	1.5	2.52	3.16

From these cell parameters it may be concluded that the developed solid state electrochemical cell is simple, economical and environment friendly and it may find applications in cost effective electrolyte in high density solid state electrochemical cells.

4: Conclusions

A solid polymer electrolyte has been developed by blending varying concentration of NaHCO₃ with pure PVA using Solution Cast Technique. The polymer as well as its blends has been characterized by adopting techniques like FTIR XRD and SEM.

FTIR studies proved that there is a complex formation between PVA and NaHCO₃ while XRD studies indicated the decrease of crystalline nature with simultaneous increase in amorphous nature with the increase in the % of the dopant (NaHCO₃) in the polymeric blends and further, it proved the homogenous distribution of

the dopant in the polymer. Thus semi-crystalline nature of the polymeric blends has been revealed. Further, the doping has been found to enhance ionic conductivity as is being generally found in amorphous polymers having flexible backbone.

The conductivity has been found to be increasing with the increase in temperature for the polymer as well as the blends of the polymer with the dopant. Activation energy has been found to be decreasing with the increase in the % of dopant in the Polymer. The Transference Number data indicates that the conduction in these polymer electrolyte systems is predominantly due to Na⁺ ions and not due to electrons.

Table-3: Cell parameters of polymer electrolyte batteries

Sl. No	Polymer battery configuration- Anode/electrolyte/cathode	Open circuit Voltage (V)	Short circuit current (μ A)	Discharge time (h)	References
1	Ag/(PEO+AgNO ₃)/ (I ₂ +C+Electrolyte)	0.61	4.4	4.4	[15]
2	Na/(PEO+NaClO ₃)/ (I ₂ +C+Electrolyte)	2.44	240	51	[16]
3	Na/(PVA+NaHCO ₃) (70:30)/ (I ₂ +C+Electrolyte)	2.99	365	81	Present work

Finally, with these PVA+NAHCO₃ developed solid polymer electrolyte systems, a Solid State Polymer Electro-chemical Cell has been developed with the configuration “Na/(PVA + NaHCO₃)/(I₂ + C + electrolyte)” and the discharge characteristics have been studied. The Cell parameters such as Open Circuit Voltage (OCV) and Short Circuit Current (SCC) are found to be 2.99 V and 365 μ A respectively. The Cell parameters acquired on this polymer electrolyte system are given in Table 3 along with the parameters reported for other cells^{42, 43}. From Table 3, it is confirmed that the present solid state cell parameters are better than the earlier reported sodium based polymer electrolyte cell systems.

Acknowledgements:

The authors thank the Er. Koneru Satyanarayana, President, Er. Koneru Raja Hareen Vice president, Dr. A. Anand Kumar Principal, Dr. K. L. Narayana, Dean R&D of K L University for providing the necessary facilities to carry out our research work and financial support and Prof.K.Ravindhranath for his suggestions in compiling this work..

5: References

1. Shriver D.F. Papke B.L. Ratner M.A. Brodwin M. Duppon R. and Wong T., Structure and ion transport in polymer-salt complexes, *Solid State Ionics.*, 1981, 5, 83-88.
2. Mohammad A.A. Mohamad N.S. Yahya M.Z.A. Othman R. Ramesh S. Alias Y. and Arof A.K., Ionic conductivity studies of poly(vinyl alcohol) alkaline solid polymer electrolyte and its use in nickel-zinc cells, *Solid State Ionics.*, 2003, 156, 171-177.
3. Subba Reddy Ch.V. Sharma A.K. and Narasimha Rao V.V.R., Effect of plasticizer on electrical conductivity and cell parameters of PVP+PVA+KClO₃ blend polymer electrolyte system, *J. Power Sources.*, 2002, 111, 357-360.
4. Tretinnikov O. N. and Zagorskaya S. A., Effect of Alkali Halide Salt Additives on the Structure of Poly(vinyl alcohol) Films Cast from Aqueous Solutions, *Polymer Science.*, 2013, 55, 463-470.
5. Tretinnikov O. N. and Zagorskaya S. A., Effect of inorganic salts on the crystallinity of polyvinyl alcohol, *Journal of Applied Spectroscopy.*, 2014, 78, 904-908.
6. Balaji Bhargav P. Madhu Mohan V. Sharma A.K. and Rao V.V.R.N., Investigations on electrical properties of (PVA:NaF) polymer electrolytes for electrochemical cell applications, *Current Applied Physics.*, 2009, 9, 165-171.
7. Gupta P.N. and Singh K.P., Characterization of H₃PO₄ based PVA complex system. *Solid State Ionics.*, 1996, 86, 319-323.

8. Vargas M.A. Vargas R.A. and Mellander B.E., New proton Conducting membranes based on PVAL/H₃PO₂/H₂O, *Electrochim Acta.*,1999, 44,4227–4232.
9. Vargas M.A. Vargas R.A. and Mellander B.E., More studies on the PVAI + H₃PO₂ + H₂O proton conductor gels, *Electrochim Acta.*,2000, 459,1399–1403.
10. Li L. Xu L. and Wang Y.X., Novel proton conducting composite membranes for direct methanol fuel cell, *Mater Lett.*,2003, 57,1406–1410.
11. Xu W.L. Lin C.P. Xue X.Z. Su Y. Lu Y.Z. Xing W. and Lu TH., New proton exchange membranes based on poly(vinyl alcohol) for DMFCs, *Solid State Ionics.*, 2004,171,121–127.
12. Suzuki M. Yoshida T. Koyama T. Kobayashi S. Kimura M. Hanabusa K. and Shirai H., Ionic conduction in partially phosphorylated poly(vinyl alcohol) as polymer electrolytes, *Polymer.*,2000, 41,4531–4536.
13. Rhim J.W. Park H.B. Lee C.S. Jun J.H. Kim D.S. and Lee Y.M., Crosslinked poly(vinyl alcohol) membranes containing sulfonic acid group:proton and methanol transport through membranes, *J Membr Sci.*, 2004,238,143–151.
14. Kim D.S. Park H.B. Rhim J.W. and Lee Y.M. , Preparation and characterization of crosslinked PVA/SiO₂ hybrid membranes containing sulfonic acid groups for direct methanol fuel cell applications, *J Membr Sci.*,2004, 240,37–48.
15. Li G.H. Li C.H. Li Y.M. and Cho C.G., Preparation of poly(vinyl phosphate-b-styrene) copolymers and its blend with PPO as proton exchange membrane for DMFC applications, *Solid State Ionics.*,2006, 177,1083–1090.
16. Croce F. Persi L. Scrosati B. Serraino-Fiory F. and Hendrickson H.A., Role of the ceramic fillers in enhancing the transport properties of composite polymer electrolytes, *Electrochimica Acta.*,2001, 46 , 2457-2461.
17. Li Z. Su G. Gao D. Wang X. and Li X., Effect of Al₂O₃ nanoparticles on the electrochemical characteristics of P(VDF-HFP)-based polymer electrolyte, *Electrochim. Acta.*,2004, 49, 4633-4639.
18. Tambelli C.C. Bloise A.C. Rosario A.V. Pereira E.C. Magon C.J.and Donoso J.P., Characterisation of PEO-Al₂O₃ composite polymer electrolytes, *Electrochimica Acta.*,2002, 47, 1677-1682.
19. Jayathilaka P.A.R.D. Dissanayake M.A.K.L. Albinsson I. and Mellander B.E., Effect of nano-porous Al₂O₃ on thermal, dielectric and transport properties of the (PEO)₉LiTFSI polymer electrolyte system, *Electrochimica Acta.*,2002,47, 3257–3268.
20. Dissanayake M.A.K.L. Jayathilaka P.A.R.D. Bokalawala R.S.P. Albinsson I. and Mellander B.E, Effect of concentration and grain size of alumina filler on the ionic conductivity enhancement of the (PEO)₉LiCF₃SO₃:Al₂O₃ composite polymer electrolyte, *Journal of Power Sources.*,2003,119,409-414.
21. Park C.H. Kim D.W. Prakash J. and Sun Y K., Electrochemical stability and conductivity enhancement of composite polymer electrolytes, *Solid State Ionics.*,2003, 159,111-119.
22. Kumar B. Rodrigues S.J. and Koka S., The crystalline to amorphous transition in PEO-based composite electrolytes: Role of lithium salts, *Electrochimica Acta.*,2002, 47, 4125-4131.
23. Y Liu Y. Lee J.Y. and Hong L., Functionalized SiO₂ in poly(ethylene oxide)-based polymer electrolytes, *Journal of Power Sources.*,2002,109,507-514.
24. Fan L. Nan C.W. and Zhao S., Effect of modified SiO₂ on the properties of PEO-based polymer electrolytes, *Solid State Ionics.*,2003, 164,81-86.
25. Xiong H.M. Zhao K.K. Zhao X. Wang Y.W. and Chen J.S., Elucidating the conductivity enhancement effect of nano sized SnO₂ fillers in hybrid polymer electrolyte PEO-SnO₂-LiClO₄, *Solid State Ionics.*,2003, 159,89-95.
26. Fan L. Dang Z. Wei G. Nan C.W. and Li M., Effect of nanosized ZnO on the electrical properties of (PEO)₁₆LiClO₄ electrolytes, *Materials Science and Engineering: B.*,2003,99, 340–343.
27. Adebahr J. Byrne N. Forsyth M. MacFarlane D. R. and Jacobsson P., Enhancement of ion dynamics in PMMA-based gels with addition of TiO₂ nano-particles *Electrochim. Acta.*,2003, 48, 2099-2103.
28. Kumar B. Rodrigues S.J. and Scanlon L.G., Ionic conductivity of polymer-ceramic composites, *J. Electrochem. Soc.*,2001, 148, A 1191- A1195.
29. Kim J.D. and Honma I., Proton conducting polydimethylsiloxane/zirconium oxide hybrid membranes added with phosphotungstic acid, *Electrochim. Acta.*,2003, 48, 3633-3638.
30. D'epifanio A. Fiory F.S. Licocchia S. Traversa E. and Scrosati B., Metallic-lithium, LiFePO₄-based polymer battery using PEO-ZrO₂ nanocomposite polymer electrolyte, *J. Appl. Electrochem.*,2004, 34, 40-46.
31. Kim D.W. Park J.R. and Rhee H.W., Conductivity and Thermal studies of solid polymer electrolytes prepared by blending poly(ethylene oxide)poly(oligo[oxyethylene]oxysebacoyl) and lithium perchlorate, *solid state ionics.*,1996,83,49-59.

32. Jinli Qiao. Jing Fu. Rui Lin. Jianxin Mac. and Jianshe Liu., Alkaline solid polymer electrolyte membranes based on structurally modified PVA/PVP with improved alkali stability, *Polymer.*,2010, 51, 4850-4859.
33. White M., Thin polymer films, *Thin Solid Films.*,1973, 18, 157–172.
34. Vijaya Kumar K. and Sunita sundari G., Conductivity Studies of (PEO+KHCO₃) Solid Electrolyte system and its application as an Electrochemical Cell, *International Journal of Engineering Science and Technology.*,2010, 5, 130-139.
35. Wagner J.B. and Wagner C.J., Wagners Polarization method, *Chem.Rev.*,1957,20,1597-1602.
36. watanabe M. Nagano S. Sanui K. and Ogata N., Estimation of Li⁺ transport number in polymer electrolytes by the combination of complex impedance and potentiostatic polarization measurements, *Solid State Ionics.*,1988,28,911-917.
37. Kurumova M. Lopez D. Benaventa R. Mijangos C. and Perena J.M., Effect of cross linking on the mechanical and thermal properties of poly(vinyl alcohol), *Polymer.*,2000, 41, 9265-9272.
38. Hodge R.M. Edward G.H. and Simon G.P, Water absorption and states of water in semi-crystalline poly(vinyl alcohol) films, *Polymer.*,1996, 37, 1371-1376.
39. Madhu Mohan V. Raja V. Sharma A.K. and Narasimha Rao V.V.R., Ionic conductivity and discharge characteristics of solid-state battery based on novel polymer electrolyte (PEO + NaBiF₄), *Mater Chem Phys.*,2005, 94, 177-181.
40. Zang S. Lee J.Y. and Hong L., Visualization of particle distribution in composite polymer electrolyte systems, *Journal of Power Sources.*,2004,126,125-133.
41. Peter P. Chu. and Jaipal Reddy M., Sm₂O₃ composite PEO solid polymer electrolyte, *Journal of Power Sources.*,2003, 115,288-294.
42. Sreepathi Rao S. Rao K.V.S. Shareefuddin Md. U.V.Subba Rao. and S.Chandra., Ionic conductivity and battery characteristic studies on PEO+AgNO₃ polymer electrolyte, *Solid State Ionics.*,1994, 67, 331-334.
43. Jaipal Reddy M. Sreekanth T. Chandrasekhar M. and Subba Rao U. V., Ion transport and electro chemical cell characteristic studies of a new (PVP 1 NaNO₃) polymer electrolyte system, *J.Mater.Sci.*,2000,35, 2841-2845.
