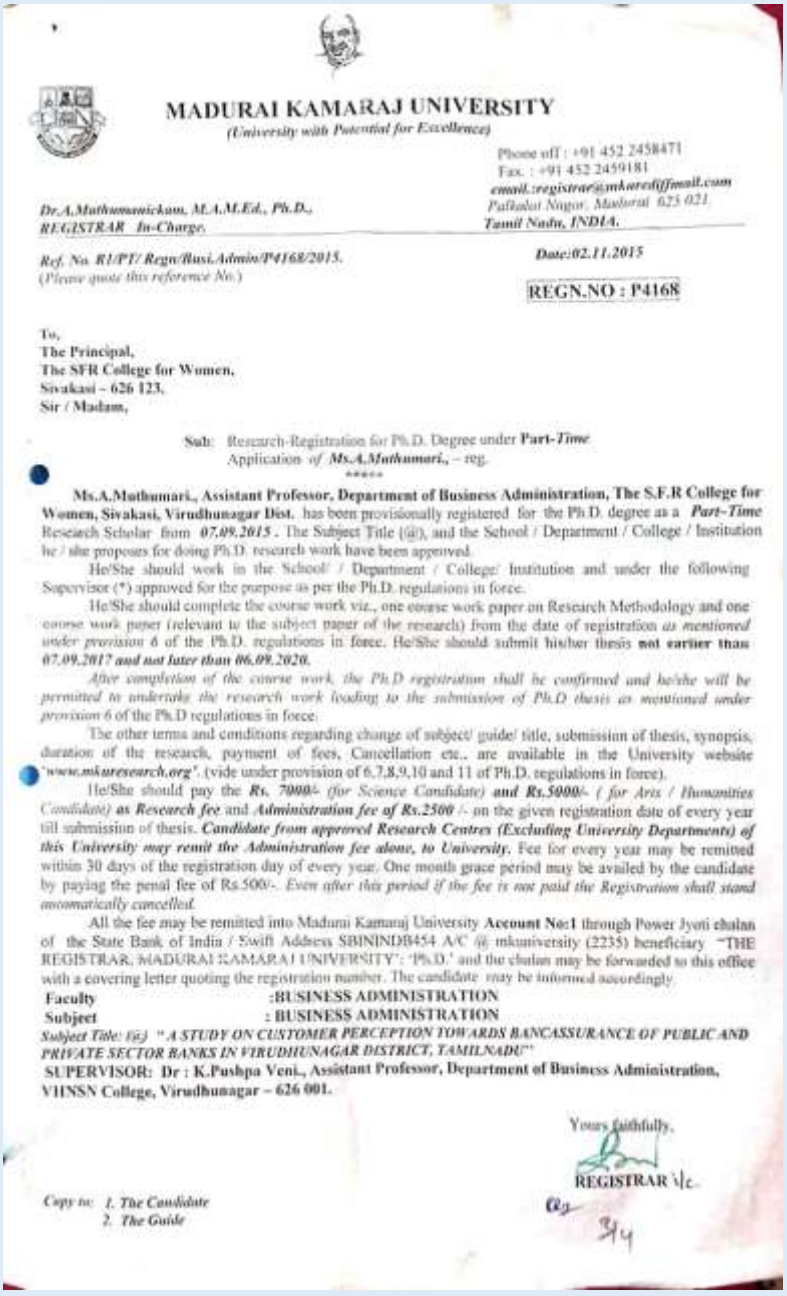
RESEARCH

2015-2016

THE STANDARD FIREWORKS RAJARATNAM COLLEGE FOR WOMEN (AUTONOMOUS), SIVAKASI – 626 123.

(Affiliated to Madurai Kamaraj University, Re-accredited with A Grade by NAAC,
College with Potential for Excellence by UGC and Mentor Institution under UGC PARAMARSH)

Title of the Collaborative Activity : Pursing Ph.D.,



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Dr.A.Muthumanickam, M.A.,M.Ed., Ph.D.,
REGISTRAR In-Charge.

Ref. No. R1/PT/ Regn/Busi.Admin/P4168/2015.
(Please quote this reference No.)

Date:02.11.2015

REGN.NO : P4168

To,
The Principal,
The SFR College for Women,
Sivakasi – 626 123.
Sir / Madam,

Sub: Research-Registration for Ph.D. Degree under **Part-*Time***
Application of ***Ms.A.Muthumari.,*** – reg.

*****

Ms.A.Muthumari., Assistant Professor, Department of Business Administration, The S.F.R College for Women, Sivakasi, Virudhunagar Dist. has been provisionally registered for the Ph.D. degree as a ***Part-Time*** Research Scholar from ***07.09.2015***. The Subject Title (@), and the School / Department / College / Institution he / she proposes for doing Ph.D. research work have been approved.

He/She should work in the School/ / Department / College/ Institution and under the following Supervisor (*) approved for the purpose as per the Ph.D. regulations in force.

He/She should complete the course work viz., one course work paper on Research Methodology and one course work paper (relevant to the subject paper of the research) from the date of registration *as mentioned under provision 6* of the Ph.D. regulations in force. He/She should submit his/her thesis **not earlier than *07.09.2017 and not later than 06.09.2020.***

After completion of the course work, the Ph.D registration shall be confirmed and he/she will be permitted to undertake the research work leading to the submission of Ph.D thesis as mentioned under provision 6 of the Ph.D regulations in force.

The other terms and conditions regarding change of subject/ guide/ title, submission of thesis, synopsis, duration of the research, payment of fees, Cancellation etc., are available in the University website "***www.mkuresearch.org***". (vide under provision of 6,7,8,9,10 and 11 of Ph.D. regulations in force).

He/She should pay the ***Rs. 7000/-*** *(for Science Candidate)* ***and Rs.5000/-*** *(for Arts / Humanities Candidate)* ***as Research fee*** and ***Administration fee of Rs.2500*** /- on the given registration date of every year till submission of thesis. ***Candidate from approved Research Centres (Excluding University Departments) of this University may remit the Administration fee alone, to University.*** Fee for every year may be remitted within 30 days of the registration day of every year. One month grace period may be availed by the candidate by paying the penal fee of Rs.500/-. *Even after this period if the fee is not paid the Registration shall stand automatically cancelled.*

All the fee may be remitted into Madurai Kamaraj University **Account No:1** through Power Jyoti chalan of the State Bank of India / Swift Address SBININBB454 A/C @ mkuniversity (2235) beneficiary "THE REGISTRAR, MADURAI KAMARAJ UNIVERSITY': 'Ph.D.' and the chalan may be forwarded to this office with a covering letter quoting the registration number. The candidate may be informed accordingly.

Faculty :**BUSINESS ADMINISTRATION**
Subject : **BUSINESS ADMINISTRATION**

Subject Title: (@) "A STUDY ON CUSTOMER PERCEPTION TOWARDS BANCASSURANCE OF PUBLIC AND PRIVATE SECTOR BANKS IN VIRUDHUNAGAR DISTRICT, TAMILNADU"

SUPERVISOR: Dr : K.Pushpa Veni., Assistant Professor, Department of Business Administration, VHNSN College, Virudhunagar – 626 001.

Yours faithfully,

REGISTRAR i/c

Copy to: 1. The Candidate
2. The Guide

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Title of the Collaborative Activity : Paper Publication

Ionics
DOI 10.1007/s11581-016-1672-7

ORIGINAL PAPER

Characterization of blend polymer PVA-PVP complexed with ammonium thiocyanate

M. Premalatha[1,2] · N. Vijaya[1] · S. Selvasekarapandian[2,3] · S. Selvalakshmi[1]

Received: 21 November 2015 / Revised: 27 January 2016 / Accepted: 13 February 2016

Abstract Thin films of blend polymer electrolytes comprising poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) complexed with ammonium thiocyanate (NH_4SCN) salt in different compositions have been prepared by solution casting technique using distilled water as solvent. The prepared films have been investigated by different experimental techniques. The complexation of these films has been studied by FTIR spectroscopy. The increase in amorphousness of the films with increase in NH_4SCN content has been confirmed by XRD analysis. The addition of ammonium thiocyanate salt to PVA-PVP polymer blend shows a shift in T_g of the blend. The effect of salt concentration and temperature on the ionic conductivity of the polymer blend films has been analyzed using AC impedance spectroscopy. The maximum conductivity of 6.85×10^{-6} S cm^{-1} at room temperature has been observed for the blend with 50 mol% PVA-50 mol% PVP complexed with 40 mol% NH_4SCN. The activation energy has been found to be minimum (0.24 eV) for this sample. Wagner's polarization technique shows that the charge transport in these blend films is predominantly due to ions. Using the highest conductivity blend polymer electrolyte, a proton battery has been fabricated and its discharge characteristics have been studied.

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Published online: 14 March 2016

Keywords Blend polymer · XRD · FTIR · AC impedance spectroscopy · Ionic conductivity · Transference number

Introduction

The amorphous polymeric materials especially proton-conducting polymer electrolytes play a vital role in the ionic devices such as fuel cells, supercapacitors, batteries, and electrochemical devices because of their high conductivity, thermal stability, life time, and mechanical strength properties [1–3]. Nafion is a standard proton conducting membrane used in fuel cells [4]. The researchers are now developing a new polymer membrane to replace Nafion because of its high cost. For developing a new proton-conducting polymer electrolytes, high ambient temperature conductivity, flexibility, durability, and mechanical strength are considered as important factors. Various efforts such as adding plasticizers and inorganic inert fillers to polymer electrolytes, use of copolymers, and blending two polymers [5–10] have been made to enhance the electrical, mechanical, and electrochemical properties of polymer electrolytes. Among the various approaches that have been employed for the preparation of polymer electrolytes with high ionic conductivity and appreciable thermal stability at ambient temperature, blending of polymers is an important method. Polymer blends are polymer systems originated from the physical mixture of two or more polymers and/or copolymers, without a high degree of chemical reactions between them. The advantages of polymer blends lie in the ability to combine existing polymers into new compositions obtaining in this way, materials with specific properties for desired applications. This strategy allows for savings in research and development of new materials with equivalent properties, as well as versatility, simplicity, relatively low cost and faster development time of new materials [11]. The most

Characterization of proton conducting blend polymer electrolyte using PVA-PAN doped with NH_4SCN

M. Premalatha, T. Mathavan' , S. Selvasekarapandian, F. Kingslin Mary Genova' , and R. Umamaheswari

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Characterization of proton conducting blend polymer electrolyte using PVA-PAN doped with NH_4SCN

M.Premalatha[1,2], T. Mathavan[1,*], S.Selvasekarapandian[2], F.Kingslin Mary Genova[3,*], R.Umamaheswari[3]

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Abstract. Polymer electrolytes with proton conductivity based on blend polymer using polyvinyl alcohol (PVA) and poly acrylo nitrile (PAN) doped with ammonium thiocyanate have been prepared by solution casting method using DMF as solvent. The complex formation between the blend polymer and the salt has been confirmed by FTIR Spectroscopy. The amorphous nature of the blend polymer electrolytes have been confirmed by XRD analysis. The highest conductivity at 303 K has been found to be 3.25×10^{-3} S cm^{-1} for 20 mol % NH_4SCN doped 92.5PVA:7.5PAN system. The increase in conductivity of the doped blend polymer electrolytes with increasing temperature suggests the Arrhenius type thermally activated process. The activation energy is found to be low (0.066 eV) for the highest conductivity sample.

Keywords: FTIR, XRD, AC impedance, activation energy

INTRODUCTION

In the field of electrochromic energy devices such as batteries, fuel cells etc., proton conducting polymer electrolytes play a essential role because of its mechanical and electrical properties **[1]**.Various methods have been adopted to improve the electrical, mechanical and electrochemical properties of polymer electrolytes. Among the various methods, Polymer blending is the most promising way to improve these properties which is a mixture of structurally different polymers. There are many reports available based on PVA-PVP **[2]**, P[VdF-HEP]- PVAc**[3]**, PVAc-PMMA**[4]**, PVdF-PMMA**[5]** and so on. PVA is a semi crystalline polymer containing hydroxyl group attached to methane carbons which can be a source of hydrogen bonding. PAN is a synthetic, semi crystalline organic polymer resin which is a common substitute for wool in clothing and home furnishings. It is already reported that the molecular weight of 92.5%PVA: 7.5% PAN exhibits the conductivity of 1.13×10^{-7} S cm^{-1} at room temperature **[6]**. In this work, proton conducting polymer blend electrolyte based on PVA-PAN doped with ammonium thiocyanate (NH_4SCN) is synthesized and characterized. Ammonium salts have already been reported as a good proton donors to the polymer matrix **[7]**.

EXPERIMENTAL TECHNIQUE

Blend polymer electrolytes are prepared with optimized compositions of 92.5% PVA(MW 1,25,000): 7.5 % PAN (MW 1,40,000) and various compositions of ammonium thiocyanate using di-methyl formamide (DMF) as solvent by solution casting technique. 92.5% weight of PVA is stirred in DMF at 60°C for 3 hours and after its complete dissolution, 7.5 % weight of PAN is added and stirred for 2 hours after which the ammonium salt is added. The mixture is stirred till it becomes homogeneous. Then it is poured in the petri dish and evaporated at 60°C in vacuum oven. Free standing film is obtained after 48 hours. Films obtained with 5 mol%, 10mol %, 15 mol%, 20mol% and 25mol % by weight of ammonium thiocyanate. Then the film is carefully removed from the petridish and sealed in an airtight cover. Then the prepared films were subjected to Fourier transform infrared spectroscopy (FTIR) using SHIMADZU-IR Affinity-1 spectrophotometer. The XRD patterns were recorded at room temperature using a XPERT-PRO Diffractometer with Cuka radiation at 40 KV and 30 mA in the 2θ range of 10 - 80°. The electrical properties of the films were

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Lithium Ion-Conducting Blend Polymer Electrolyte Based on PVA-PAN Doped with Lithium Nitrate

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Title of the Collaborative Activity : Paper Publication

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COMPOSITES

Study on Blend Polymer (PVA-PAN) Doped with Lithium Bromide[1]

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Abstract—Blend polymer electrolyte membranes that consist of poly(vinyl alcohol) (PVA), poly (acrylonitrile) (PAN) and different concentrations of lithium bromide (LiBr) have been prepared by solution casting technique using dimethylformamide (DMF) as solvent. The amorphous nature of the blend polymer (92.5 PVA : 7.5 PAN)—salt complexes has been confirmed by X-ray diffraction analysis. The formation of blend polymer (92.5 PVA : 7.5 PAN)—salt complexes has been confirmed by Fourier transform infrared spectral studies. The decrease in glass transition temperature (T_g) with the salt reveals the increase in segmental motion. Conductivity studies have been carried out using ac impedance spectroscopy and it has been found that, the maximum ionic conductivity is 3.0×10^{-4} S cm^{-1} for 30 wt % LiBr doped—92.5 PVA : 7.5 PAN electrolyte. The temperature dependence of conductivity of the blend polymer electrolyte has been discussed. The activation energy is calculated for all compositions of blend polymer doped with LiBr using Arrchenius plot. The dielectric spectra show low frequency dispersion. Ionic transference number (t_+) has been found to be 0.98 for the blend polymer (92.5 PVA : 7.5 PAN) with 30 wt % LiBr. This result reveals that the conducting species are predominantly ions. Primary battery has been constructed with the configuration $Zn + ZnSO_4 \cdot 7H_2O$/92.5 PVA : 7.5 PAN : 30 wt % LiBr/$PbO_2 + V_2O_5$ using the maximum conducting blend polymer, and its discharge characteristics has been discussed.

DOI: 10.1134/S0965545X15070052

INTRODUCTION

Polymer electrolytes are of technological interest due to their possible applications in rechargeable batteries, chemical sensors, fuel cells and electrochromic display devices [1, 2]. High ionic conductivity at ambient temperature, good mechanical strength, appreciable transference number, good thermal and electrochemical stabilities and better compatibility with electrodes are the pre-requisites for a polymer electrolyte for solid state battery applications. Various approaches have been made to modify the structure of polymer electrolytes in order to improve their electrical, electrochemical and mechanical properties. These approaches include: synthesizing new polymers [3]; cross linking two polymers [4]; blending of two polymers [5]; adding plasticizers to polymer electrolytes [6]; adding inorganic inert fillers [7] to make composite polymer electrolytes. Out of these methods blending of two polymers is easy for preparation, as well as polymer blends are physical mixtures of structurally different polymers that interact through secondary forces and that are miscible to the molecular level and control the physical properties within the compositional regime. The significant advantages of polymer blends are that the properties of the final product can be tailored to the requirement of applications, which cannot be achieved alone by one polymer. However, the film properties depend on the miscibility of blend. The polymer-polymer miscibility may arise from any one of the interactions such as hydrogen bonding, dipole-dipole forces and charge transfer complexes for homopolymer mixtures [8–13]. A lot of blend polymer electrolytes based on PEO-PAN [14], P(VdF-HFP)-PVAc [15], PVC-PMMA [16], etc. have been reported.

Poly (vinyl alcohol) (PVA) is a semicrystalline polymer, having high dielectric strength, good charge storage capacity and dopant dependent electrical properties. It has carbon chain back bone with hydroxyl groups attached to methane carbons. These O–H groups can be a source of hydrogen bonding and therefore, assist the formation of polymer complexes [17]. It has excellent mechanical properties and shows both ionic and electronic conduction [18]. Polyacrylonitrile (PAN) polymer has been extensively studied due to its good chemical and flame resistance and electrochemical stability [19]. PAN is a semicrystalline, synthetic resin prepared by the polymerization of

[1] The article is published in the original.