Final Report of the work done on the Major Research Project.

1. Project report No. **Final report**


3. Period of report: from **01/07/2015** to **30/06/2018**

4. Title of research project: **Preparation and Characterization of Nano-composite Polymer Electrolytes for device applications**

5. (a) Name of the Principal Investigator: **Prof. P. N. Gupta**
   
   (b) **Department of Physics, Institute of Science, Banaras Hindu University, Varanasi–221005, (U.P.) INDIA**
   
   (c) **University/College where work has progressed: Department of Physics, Institute of Science, Banaras Hindu University, Varanasi–221005, (U.P.) INDIA**

6. Effective date of starting of the project: **01/7/2015**

7. Grant approved and expenditure incurred during the period of the report:

   a. Total amount approved **Rs. 9, 33, 800/-**
   
   b. Total grant received **Rs. 5, 54, 800/-**
   
   c. **Final Expenditure Rs. 5, 53, 835/-**
   
   c. Report of the work done: **Please see the attached sheet**

   i. Brief objective of the project **Preparation and Characterization of Nano-composite Polymer Electrolytes**

   ii. Work done so far and results achieved and publications, if any, resulting from the work (Give details of the papers and names of the journals in which it has been published or accepted for publication: **4 (Please see the Annexure A)**

   iii. Has the progress been according to original plan of work and towards achieving the objective. if not, state reasons : **YES**

   iv. Please indicate the difficulties, if any, experienced in implementing the project: **NIL**

   v. If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet. **NA**
vi. If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants Commission. (Please see Annexure B)

vii. Any other information, which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any

(a) Manpower trained: 08 (M.Sc Dissertation) (Please see Annexure B): 02 (Ph. D. awarded) (Please see Annexure B)
(b) Publication of results: 4 (Published) (Please see Annexure B)

SIGNATURE OF THE P.I.

Dr. P.N. Gupta, (P.I.)
UGC Proj. P-01/718
Physics Department
B.H.U., Varanasi

SIGNATURE OF THE CO-P.I.

Co-Investigator
Physics Department
B.H.U., Varanasi

REGISTRAR/PRINCIPAL
(Seal)

Expenditure verified

V/HEAD
Department of Physics
Institute of Science
Banaras Hindu University, Varanasi.
Preparation and Characterization of Nano-composite Polymer Electrolytes for device applications

Final Report
(From July 1, 2015 to June 30, 2018)

UGC Reference No.:
F. No. 43-528/2014, MRP-Major-Phys-2013-31824,
Dated 30/9/2015

Funded by

University Grants Commission
(Ministry of Human Resource Development, Govt. of India)
Bahadurshah Zafar Marg, New Delhi – 110002

Principal Investigator

Prof. Prem Narain Gupta

Department of Physics,
Institute of Science,
Banaras Hindu University
Varanasi-221005
Work done so far and results achieved and publications

Project code: F. No. 43-528/2014, MRP-Major-Phys-2013-31824, Dated 30/9/2015

The main objectives of the project:

2. Characterization of polymeric thin films using various experimental techniques.
3. Study of ion transport properties
4. Mechanism of ion conduction in solid polymeric materials
5. Structure and dynamics of condensed matter in the form of membranes
6. Dielectric relaxation properties of conducting polymers

Important Results:

Different series of new Polymer electrolytes have been prepared using solution casting technique. Investigation of prepared films have been made using various experimental techniques like X-ray diffraction (XRD), Attenuated total reflection–fourier transform infrared (ATR-FTIR), Thermo-gravimetric analysis (TGA), Differential scanning calorimetric (DSC), AC impedance spectroscopy. AC conductivity spectra, temperature dependent dc conductivity, dielectric properties, electrical modulus and mobility, total number of charge carrier density has been studied. The details are given below:

1. Gupta et al., International J of Polymeric materials and polymeric biomaterials, 2018, VOL. 67, NO. 4, 258–265. In this paper we have prepare the following series of samples:
   PA-1/P-1 – PVA film with 10 wt% of AgI salt content
   PA-2/P-2 - PVA film with 20 wt% of AgI salt content
   PA-3/P-3 - PVA film with 30 wt% of AgI salt content

   The film with AgI salt shows good antibacterial activity against three of the bacteria A. hydrophila, S. boydii and S. typhii. The activity against the bacteria E. coli is observed in PA-2
film at higher concentration. SEM micrographs show aggregates formed in PA-1, PA-2 and PA-3 film having the dimension of about 2-4 µm. Correlation of dielectric property with antibacterial activity indicates the existence of Ag⁺ ions. The value of exponent n greater than 1 indicates the caged movement of ions in the polymer matrix. The antibacterial study reveals that the synthesized film may be used as potential material in food packaging.

2. Saroj et al., Journal of Non-Crystalline Solids, 473 (2017) 87–95: A series of polymer electrolyte films based on Poly(vinyl alcohol) (PVA) and ionic liquid, 1-Butyl-2, 3-dimethylimidazolium tetrafluoroborate [BDMITFB], PVA-BDMITFB-1 to PVA-BDMITFB-5, has been prepared by varying the concentration of BDMITFB viz. 5, 10, 15, 20, 25 wt%, respectively using solution cast technique.

The change in vibrational band frequencies from ATR-FTIR results, showed the interaction of cationic BDMITFB with hydroxyl group of PVA. XRD result showed that the % degree of crystallinity decreased with BDMITFB loading in PVA except at 15 wt% of BDMITFB due to aggregation of PVA and BDMITFB. The DSC analysis showed that the glass transition temperature, T_g and melting temperature, T_m were found to decrease with BDMITFB content in PVA due to plasticization effect of BDMITFB. T_m was found to be increased in PVA-BDMITFB-3, due to enhancement in crystallinity. SEM results showed that higher aggregation of BDMITFB/PVA was found in PVA-BDMITFB-3. TGA analysis showed two step decomposition of BDMITFB, multi step decomposition of PVA and PVA-BDMITFB complexes and T_d, onset was found to decrease with BDMITFB loading. Temperature dependent conductivity and dielectric relaxation frequency followed the Arrhenius type thermally activated process below and above T_g. The activation energy E_a1 below & E_a2 above T_g decreased with higher BDMITFB loading at higher temperature. The conductivity (σ) and dielectric relaxation frequency (f_r) increased with BDMITFB content in PVA at higher temperature (140°C).

3. Pankaj Singh et al., Journal of Non-Crystalline Solids, 494 (2018) 21–30]: The polymeric films have been prepared using conventional solution casting method. In this method we have taken 50PVA-50PVP-10PEG with x wt%MeSO4Na (x=0, 10, 15, 20) viz. PVA-PVP-PEG, PVA-PVP-PEG-10MeSO4Na, PVA-PVP-PEG-15MeSO4Na and PVA-PVPPEG-20MeSO4Na, respectively. All the materials were dissolved in DMSO and then
kept this mixture in oven at 50 °C for 24 h for swelling. The solution is stirred for 5 h in order to obtain the homogeneous viscous slurry and slurry was poured into poly propylene Petri-dishes. These Petri-dishes containing slurry were kept in oven to dry for the evaporation of solvent at 40 °C for 10 days, after that we select free standing films having uniform thickness of ~50 μm the films were stored in dried silica gel containing evacuated desiccators for further measurements.

The FTIR results show the Interaction/complexation of MeSO$_4$Na with PVA-PVP blend. TGA supported by DTGA analysis gives the evidence of formation of PVA-PVP miscible blend with two step decomposition. Temperature depended conductivity follows the Arrhenius type behavior. The activation energy for PVA-PVP-PEG-20MeSO$_4$Na based blend electrolyte has ~0.25eV with dc conductivity ~1.67 x 10$^{-5}$ S cm$^{-1}$ at 303K. Dielectric studies suggest that the relaxation is activated thermally and charge carrier hopping is taking place. AC conductivity curves follow the JPL with the exponent n<1 (support the dc free hopping) for PVA-PVP-PEG-20MeSO$_4$Na based blend while for lower concentration of MeSO$_4$Na has the value of exponent n>1 support the caged type movement of ions. The scaled conductivity spectra of 20MeSO$_4$Na based polymer blend electrolyte with temperature collapsed into a single master curve which indicates that all these ion dynamics have the same origin and only the number of charge carriers and mobility are being affected by the temperature. ESW is found to be greater than ±3.0V for higher loading of PVA-PVP-PEG-20MeSO$_4$Na at different scan rate.

4. Satyendra Kumar et al. Physica B: Condensed Matter 554 (2019) 158-164: The nano-composite polymer electrolyte films designated as [((70-x)PVA:xPVP):30 wt%NaI]:1 wt%SiO$_2$ where x=0 (a), x=10 (b), x=20 (c), x=30 (d), x=40 (e) and x=50 (f), respectively has been prepared using solution casting technique.

The increase of amorphous behaviour in polymer electrolytes and their complexation were confirmed by XRD along with the compatibility between the PVA and PVP polymers. ATR-FTIR studies show the possible interactions of their constituents into blend electrolytes. DSC thermograms show a single glass transition temperature which confirms the miscibility of PVA and PVP together. The $dc$ conductivity of the polymer electrolyte enhances approximately one order of magnitude for the sample [30PVA-40PVP-30NaI-SiO$_2$] with minimum activation energy ~ 0.17eV. The temperature dependent conductivity shows two distinct Arrhenius regions one before glass transition and another after it. It has been found that the $ac$ conductivity has a
better correlation with the JPL i.e. ion hopping type mechanism takes place (n<1). Further, electric modulus formalism suggests that the ionic conductivity and polymer segmental motion of blend electrolytes are coupled together and governed by a single relaxation peak only. Low frequency dispersion of dielectric permittivity reveals the electrode polarization phenomena and the loss tangent curve shows two relaxation behaviours for each samples namely $\beta$ and $\alpha$ relaxation. The observed decreased long tail at low frequency in electric modulus spectra is due to large capacitance associated with electrodes.

**List of Publications**


## Summary of the findings in the form of published work

**Project code:** F. No. 43-528/2014, MRP-Major-Phys-2013-31824, Dated 30/9/2015

<table>
<thead>
<tr>
<th>Objectives of the Project</th>
<th>Published /communicated work against the objectives</th>
</tr>
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Important findings:

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**List of Publications**


**Manpower trained under the Project**

**(A) M.Sc. Dissertation**

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Name</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Design of digital electronics circuit for wide range of capacitance measurement</td>
<td>Mr. Jeetendra Kumar</td>
<td>2015-2016</td>
</tr>
<tr>
<td>3.</td>
<td>Study of ion transport electrical conducting and dielectric constant of solid polymeric electrolyte film</td>
<td>Km. Shobha Gandhi</td>
<td>2015-2016</td>
</tr>
<tr>
<td>4.</td>
<td>Synthesis and characterization of ion conducting glasses based on ionic liquids.</td>
<td>Mr. Vineet kumar panday</td>
<td>2014-2015</td>
</tr>
<tr>
<td>5.</td>
<td>Study on electrical transport properties of Biopolymer electrolyte</td>
<td>Mr. Ramanivas yadav</td>
<td>2016-2018</td>
</tr>
<tr>
<td>6.</td>
<td>Investigation on Structural, Thermal, and AC conductivity of chitosan-NaI based Biopolymer electrolyte</td>
<td>Mr. Suhel ahmad khan</td>
<td>2017-2018</td>
</tr>
</tbody>
</table>
(B) Ph. D. awarded

1. Title of the thesis: “Preparation and characterization of PVA based composite, blend and nano-composite solid polymer electrolyte films”
   Research scholar: Ms. Niharika Kulshrestha
   Degree awarded: 2016
   Supervisor: Prof. P. N. Gupta, P. I. of the project.

2. Title of the thesis: “Study of polymer blend and polymer blend nano-composite solid polymer electrolytes based on PVA, PVP and starch”
   Research scholar: Mr. Bhasker Bhattacharya
   Degree awarded: 2015
   Supervisor: Prof. P. N. Gupta, P. I. of the project
Contribution to the Society

Nano-composite polymer electrolytes are emerging as a noble group of materials for electrochemical applications using various types of polymers as well as copolymers, and salts like LiClO₄, NaClO₄, MgClO₄, in different weight percent ratio dispersed with nano size SiO₂, TiO₂ etc has been synthesized and characterized using various characterization techniques. The present report has the interest for scientists/ researchers /technologists working in the field of Physics, Chemistry and material science. Therefore the present work is of wide interdisciplinary interest very useful to the society.