University of Delhi

RC/2015/9435 31 August, 2015

The Principal,
Shivaji College
Ring Road, Raja Garden,
New Delhi-27

Subject: - **Innovation Projects 2015-16**

Dear Principal,

The University of Delhi is pleased to announce the third round of the undergraduate research initiative in colleges, Innovation Projects 2015-16. You will be glad to know that the following project submitted by your college has been selected for award

Project Code: SHC 304
Project Title: Investigation Of Polymer Based Electrodes For All Solid State High Performance Super-Capacitor

The distribution of grant under different budget heads as below:

Sr. No.	Budget Head	Amount
1.	Equipment/Consumables	Rs 2,25,000/-
2.	Stipends	Rs. 1,20,000/- (1000x10x12)
3.	Travel	Rs 55,000/-
4.	Honorarium	Rs 25,000/-
5.	Stationery/Printing	Rs 20,000/
6.	Contingency	Rs 55,000/-
	Total	Rs 500,000/-
Rs 5 lakhs (Rupees five lakhs only)		
Amount to be released in first phase by Finance Branch- Rs 3,50,000/		

Budget head No. 1 and half of the remaining grant will be released as the first instalment. The second and final instalment will be released after submission of half-yearly report (by 15 February 2016), satisfactory review and recommendation of release of the second instalment.
Please refer to the detailed guidelines for implementation of the project. Any queries may be addressed to- innovationprojects1516@gmail.com.

With best wishes,

Yours sincerely,

Prof. Malashri Lal

UNVERSITY OF DELHI

INNOVATION PROJECTS 2015-16

FINAL REPORT

1. PROJECT CODE: - SHC - 304

2. PROJECT TITLE: - **Investigation of polymer based electrodes for all solid state high performance Supercapacitors**

3. NAME OF COLLEGE/INSTITUTION: - Shivaji College

4. PRINCIPAL INVESTIGATOR: - Dr. Rajni Kanojia
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5. MENTOR: - Dr. Priyanka Heda Maheshwari
   Scientist
   Physics and Engineering of Carbon
   Division of Materials Physics & Engineering
   CSIR - NATIONAL PHYSICAL LABORATORY
   MINISTRY OF SCIENCE & TECHNOLOGY
   (Govt. of India)

6. STUDENTS INVOLVED IN THE PROJECT

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Final Report

1. **Project Title: - Investigation of polymer based electrodes for all solid state high performance Supercapacitors**

2. **Project Code: - SHC 304**

3. **Abstract**

The conducting polymer- metal oxide composite electrode materials such as polyaniline (PANI) and PANI-ZnO have been prepared with different w/w ratios of ZnO (i.e. 10%, 20%, 30%) by chemical oxidative polymerisation method for application in flexible super capacitor devices and characterized using technique such as X- ray diffraction. Gel polymer electrolyte (GPE) based on Poly (vinylidinefluoride-co-hexafluoropropyline) P(VDF-HFP) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) ionic liquid (IL) at the mass ratio of 1:4 was prepared. The electrical conductivity of gel polymer electrolyte was measured at different temperature. The faradic electrode material ZnO in polymer based metal composite shows the advantages of both the double layer capacitance and the pseudocapacitance, thereby offering potential applications for supercapacitors.

4. **Introduction**

Due to the increasing demand of energy in modern society, and decreasing stock of non-regenerative fossil fuels, there is a global attention to find low cost, environmental-friendly, renewable sources of energy, and to develop technologies for the energy conversion and storage. The effective and useful energy conversion/storage devices include rechargeable batteries, fuel cells and electrochemical supercapacitors. Of these devices, the supercapacitor (also referred as ultracapacitor or electrochemical capacitor) is one of the most promising candidates, which possesses high specific capacitance, higher specific energy than electrolytic capacitors, higher power density and longer cycle life than rechargeable batteries. Conducting polymers (CPs) are among the most potential pseudocapacitor materials for the foundation of flexible supercapacitors due to their high flexibility and ease in fabrication and motivating the existing energy storage devices toward the future advanced flexible electronic applications due to their high redox active-specific capacitance and inherent elastic polymeric nature. CPs are organic polymers that conduct electricity through a conjugated bond system along the polymer chain. Among all kinds of CPs, polyaniline, polypyrrole, and derivatives of polythiophene have been widely studied as active electrode materials for Electrochemical Supercapacitors (ES) due to the high electrical conductivity, high pseudocapacitance, and low cost. Polyaniline (PANI) is found to be the most promising because of its ease of synthesis, low cost monomer, tunable properties, and better stability compared to other conducting polymers.

Metal oxides (MO_x) are considered as most promising materials for the next generation of ES providing higher pseudocapacitance through bulk redox reactions, but due to the poor electrical conductivity, MO_x also suffers from low capacitive behaviors. On the contrary, CPs provides the good electrical conductivity with additional flexible polymeric nature. Therefore, significant synergistic effects are expected between MO_x and CPs when combined at the molecular scale, and these may lead to novel flexible supercapacitors with improved capacitive properties superior to those of each individual material. The aim is to maximize the practical use of the combined advantages of both CPs and MO_x as active ES materials to improve the electrochemical energy storage and solve the current ES electrode problems experienced by those of pure CPs or MO_x as active materials. In a composite, CPs provide polymeric flexibility and high electrical conductivity to allow easy processing of MO_x in the composite for high performance and improved cycle stability of flexible supercapacitors application.

According to the electrode designing aspects, besides the proper choice of active electrode materials, appropriate choice of electrolytes is also important to improve the ES performance. our need is to achieve a high specific power and energy density taking advantage of the higher working potential window in the eco-friendly ionic liquid electrolyte system [6].

5. Research problem/hypothesis/objectives

The main objectives of this research are to develop nano-structured conducting polymer electrodes for high specific energy and power solid state supercapacitors. Towards realization of this, broad objects of this project are:

- Nano-structured conducting polymers based electrodes will be synthesized and characterized using various experimental techniques. Strategies will be developed to overcome the restrictions during charge transfer kinetic & provide high surface area for construction of efficient electrodes.
- Fabricate all solid state supercapacitor utilizing polymer based electrodes and gel polymer

electrolyte. Study and optimize performance of supercapacitors and obtain enhance energy density and stability.

This innovative project will enable the students of Delhi University to deepen the basic knowledge of "Solid State charge transfer kinetics" and its potential applications in various electrochemical energy storage devices say rechargeable batteries, supercapacitors and fuel cells.

6. Methodology Techniques/Sampling /Tools/Materials

Electrochemical performance of the device is thoroughly analyzed followed by construction of electrode materials. Systematic investigation broadly involves the following:

- ➢ Synthesis of the polymeric electrode material and doping of metal oxide
- ➢ Modelling the novel materials/structures

6.1 Chemical

Poly (vinylidenefluoride hexafluoropropylene) P[VDF-HFP], and 1-butyl-3-methyl-imidazolium tetrafluoroborate [BMIM][BF_4] and Perfluorinated ion exchange resin (Nafion) were purchased from Sigma-Aldrich. Zinc Oxide (ZnO), Aniline, Ammonium per sulphate (APS), Hydrochloric Acid (HCl), Sodium sulphate (Na_2SO_4), isopropyl alcohol (IPA), acetone, ethanol were purchased from Merck.

6.2 Synthesis of Polyaniline (PANI)

Aniline added dropwise to HCl solution on stirring and kept the solution in ice bath to attain temperature 0°C to 5°C. Ammonium per sulphate added to above solution. Stir overnight the solution @ 500 rpm at 0°C to complete polymerization, Filtered it using 0.45 μm whatmann filter paper and wash with Deionised water several times and then with ethanol. Dried under vacuum for 4 hrs at 60°C to form PANI powder.

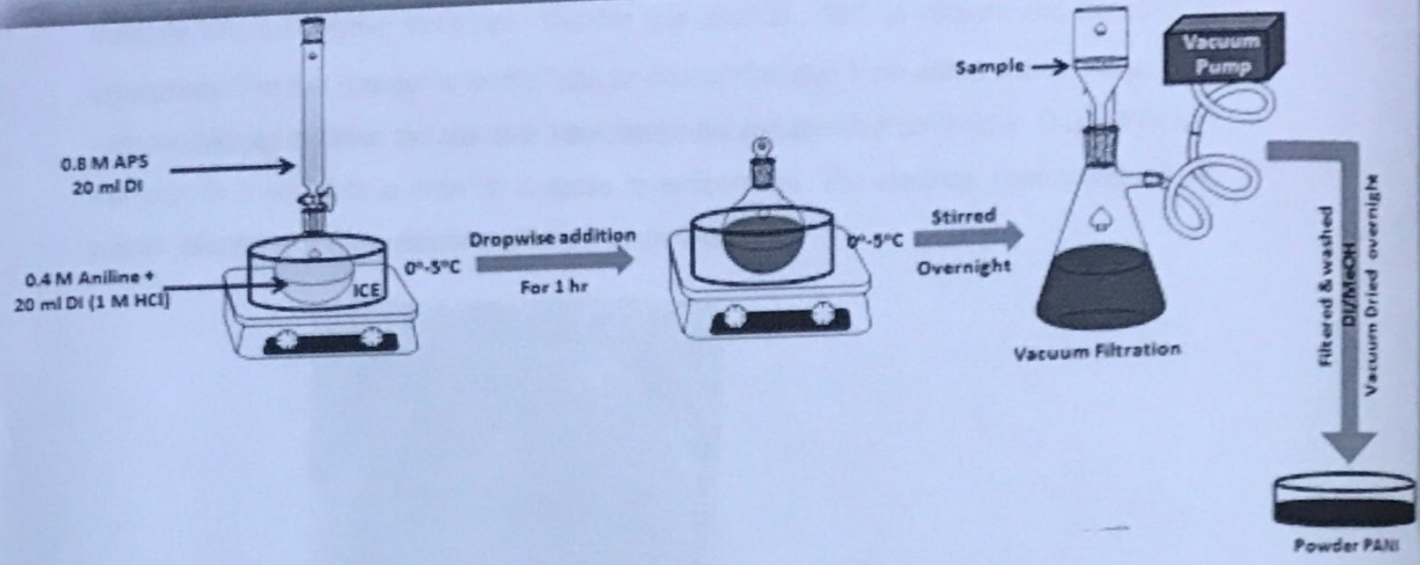

Fig. 1. Schematic representation of Polymer preparation

6.3 Synthesis of PANI - ZnO (metal oxide (Zno) doping into polyaniline)

PANI- 10 % ZnO, PANI- 20 % ZnO, PANI- 30 % ZnO were synthesized by chemical oxidative polymerisation. To prepare PANI–ZnO composites of different w/w ratios, the following steps were followed. 0.568, 1.137 and 1.705 g of ZnO were mixed to aniline. The experiment procedure was the same as described above section. XRD is used to characterize the structure.

6.4 Characterisation

The X-ray diffraction system (BRUKER, D8 Advance - difractometer using nickel filter) was used for the X-ray analysis with Cu-Kα radiation (λ = 1. 540 Å). Step scanning was used with 2θ intervals from 5° to 70°.

6.5 Synthesis of Ion Gel Polymer Electrolyte

Host polymer Poly (vinylidinefluoride-co-hexafluoropropyline) P(VDF-HFP):ionic liquid [BMIM(BF4)], 1:4 ratio was used to form free standing gel polymer electrolyte. slurry product formed and was casted in glass petri-dishes and allowed to evaporate the solvent (acetone) slowly to form gel polymer electrolyte. The film was dried at ~50°C in vacuum and stored in Ar atmosphere. The film was cut in form of circular disk of diameter 1 cm with a cutter. These films were sandwiched between two stainless steel electrodes and kept in a cell holder. This cell holder was kept on a hot plate in order to increase its temperature. The electrical conductivity of gel polymer electrolyte was measured at different temperature.

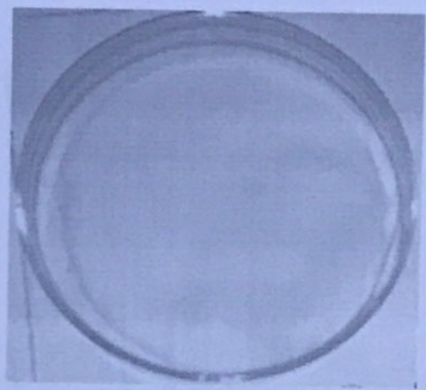

Fig. 2. Gel Polymer Electrolyte film

7. Result and Discussion

X-ray diffraction (XRD analysis or XRPD analysis) is a unique method in determination of crystallinity of a compound. The Scherrer formula for the calculation of crystallite size (grain diameter), D, of the sample is

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where, D is the crystallite size, K is a constant varies with crystallite shape, λ is the wavelength of source radiation and β is full-width at half maximum (FWHM) of the peak, in radians and θ is the Bragg's angle.

The XRD pattern of PANI and PANI - ZnO composites is shown in Fig. 3. The inset picture showed the XRD pattern of PANI and the peak was observed at 2θ = 17° suggesting that the perfect oxidative Polymerisation. The observed XRD patterns (prominent peak) of sample PANI - ZnO (20%) and PANI - ZnO (30%) represented that the material is homogeneous. XRD patterns for PANI - ZnO (20%) show strong diffraction peaks at 22.4, 32.3 respectively and for PANI - ZnO (30%) show strong diffraction peaks at 24.9, 30.2 respectively. The patterns show sharp and well defined peaks, indicating the crystallinity of the synthesized materials. Intensity of diffraction peaks for the composite PANI - ZnO (20%) is lower than that of composite PANI - ZnO (30%). This implies that the intensity depends on the composition of the material.

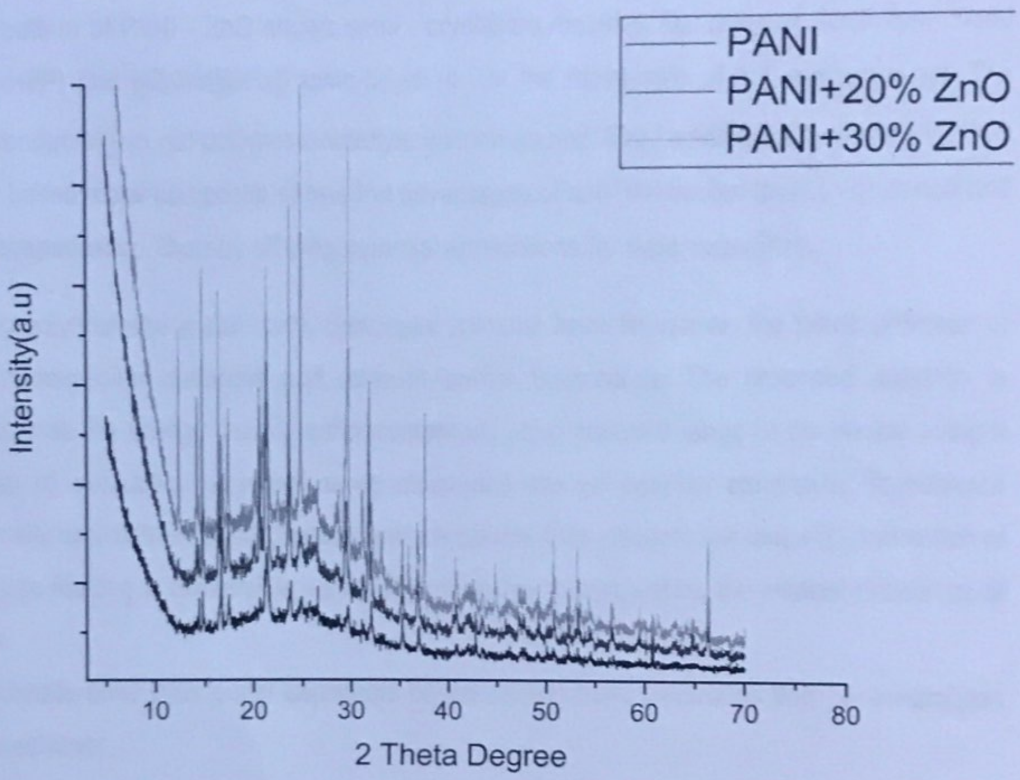

Fig. 3. XRD pattern of PANI & PANI -ZnO composite with different mass ratio

8. Innovations shown by the project

- Polymer based all solid state supercapacitor has attracted considerable interest worldwide as an excellent substitute for liquid electrolytes based device as it encompasses the safety concerns which are associated with the liquid electrolytes.
- The most advantageous feature is their wide potential range and flexibility which will not only enhance the energy density of the device but make it efficient for applications in portable electronics of modern era.
- Innovative ideas will be incorporated for the development and tailoring of electrode properties towards realization of high performance devices.

9. Conclusion and Future Direction

PANI-ZnO composite have been prepared with different mass ratios for application in flexible super capacitor devices and characterized using technique such as X- ray diffraction. X - ray diffraction pattern of PANI - ZnO shows semi - crystalline material. Gel polymer electrolyte based on P(VDF-HFP) and ([BMIM][BF_4]) ionic liquid (IL) at the mass ratio of 1:4 was prepared. The electrical conductivity of gel polymer electrolyte was measured. The faradic electrode material ZnO in polymer based metal composite shows the advantages of both the double layer capacitance and the pseudocapacitance, thereby offering potential applications for supercapacitors.

Conducting polymer and metal oxide composite material have impact on the future direction of flexible supercapacitor materials and relevant device fabrications. The proposed research is directed towards the energy density enhancement via large potential range of the device using a combination of conducting polymers based electrodes and gel polymer electrolyte. To enhance energy density and stability of solid state super capacitors This research will focus on prevention of self discharge leading to irreversible loss of stored charge by decreasing the internal resistance of the device.

We will fabricate solid state super capacitors based on polymeric electrodes and gel electrolytes and aim to achieve:

- High conductivity with improved charge transfer characteristics for power density super capacitors
- High endurance for high energy super capacitors operating in large voltage range.
- The use of solid electrolyte will further enhance the portability of the device and will attract the worldwide attention for wearable electronics.

10. References

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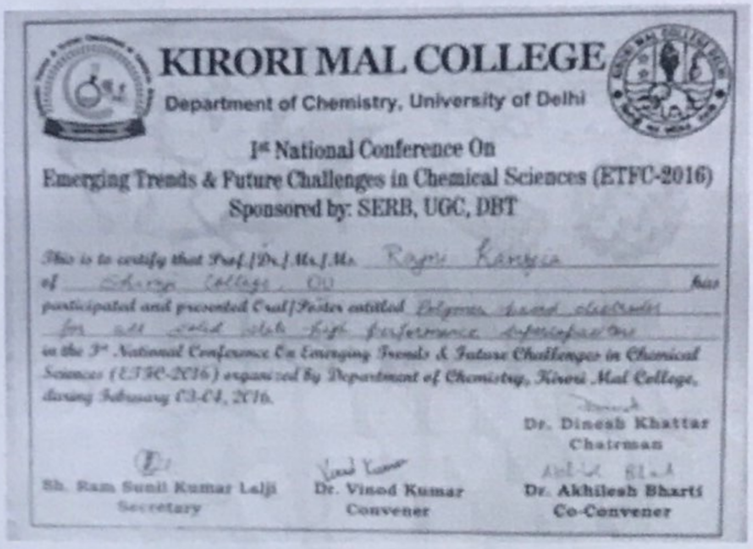
11. **Publication/s from the work. (attach copies)** - N.A.

12. **Conference Presentation/s (attach copies)**

Poster presented in National Seminar emerging and future challenges in chemical science organised by Kirori Mal College, University of Delhi,was held on 3-4 feb' 2016.



KIRORI MAL COLLEGE

Department of Chemistry, University of Delhi

1st National Conference On

Emerging Trends & Future Challenges in Chemical Sciences (ETFC-2016)

Sponsored by: SERB, UGC, DBT

This is to certify that Prof./Dr./Mr./Ms. Rajni Kanojia of Shivaji College, DU has participated and presented Oral/Poster entitled Polymer based electrodes for all solid state high performance supercapacitor in the 3rd National Conference On Emerging Trends & Future Challenges in Chemical Sciences (ETFC-2016) organized by Department of Chemistry, Kirori Mal College, during February 03-04, 2016.

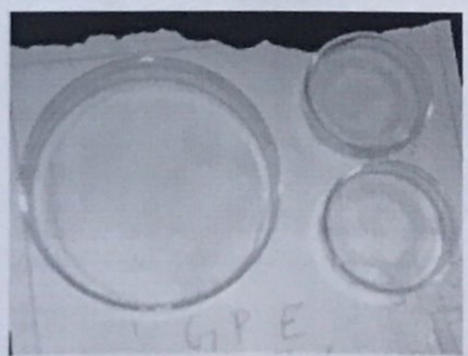
Dr. Dinesh Khattar
Chairman

Sh. Ram Sunil Kumar Lalji
Secretary

Dr. Vinod Kumar
Convener

Dr. Akhilesh Bharti
Co-Convener

13. **Patent/s and Technology Transfer (attach copies)** - N.A.
14. **Media Coverage (attach copies)** - N.A.
15. **Pictures related to the project.**



16. **Annexure/Any other information** - N.A.